

Eliminating the Occurrence and Consequences of Toxic Release in Petrochemical Industry through Intervention of Safety Engineering Tools

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Abstract: *The aim in this project is to analyze the risk associated with different toxic releases which is occurring in the chemical industry and to minimize its release using safety engineering tool in order to make the working environment safer. The sector of petrochemical industries is very important and have specific place in our country. Since the beginning, the Indian petrochemical industry has shown an enviable growth rate. This industry also contributes largely to the economy of the country and the growth and development of manufacturing industry as well. Petrochemical industry has a high risk of toxic release. The main causes of accidents are the chemical splashes which can occur for instance when a pipe or a tank burst under pressure or during disassembling operations of pipes or valves. There are a number of ways of toxic release at each and every process of petrochemical industry. We have identified the way in each process of the petrochemical industry. We have taken H₂S as toxic gas and performed analysis, with the help of Bowtie methodology. Result obtained by evaluating various processes in petrochemical industry, we found that H₂S can be released in three major sections i.e. transportation, storage and processing units. Using bowtie method, resolutions has been done to decrease or eliminate the possibilities of leakage of H₂S.*

Keywords: H₂S toxic gas, Bowtie methodology, Petrochemical, Accident, Risk, Safety Health, Hazards etc

I. INTRODUCTION

1.1 Toxic chemicals

Substances that can cause severe illness, poisoning, birth defects, disease, or death when ingested, inhaled, or absorbed by living organisms. A "release" refers to different ways that toxic chemicals from industrial facilities enter the air, water and land. We are aware with the fact that chemical industries greatly contribute to climate change by producing chemicals that are themselves potent greenhouse gasses. Each and every second 310 Kg of toxic chemicals are released into our air, land, and water by industrial facilities around the world. This amounts to approximately 10 million tons of toxic chemicals released into our environment by industries each year. Of these, over 2 million tons per year are recognized carcinogens. This amounts to about 65 Kg each second. Toxicology is traditionally divided between human and eco-toxicology. The various harmful toxic releases from different chemical industries are:

- Fertilizer industries: oxides of nitrogen & sulphur
- Pesticides industries: PM, chlorine, arsenic, mercury, phenol
- Electroplating industries: effluents with heavy metals ions like of: nickel, chromium, zinc, lead, mercury
- Petrochemical industries: SO_x, NO_x, PM, metal traces, sludge, hydrogen sulfide, CO, etc.

1.2 Background and motivation:

The aim of industrial emissions control is to protect human health and minimize environmental impact by reducing air pollution from industrial emissions. Pollution has been discussed ever since the industrial revolution has brought the bonuses and onuses of industrial and technological development. Today we all observe the changes in our surrounding

and environment due to the rapid civilization, this made the importance of controlling emissions very important. The aim of industrial emissions control is to protect human health and minimize environmental impact by reducing air pollution from industrial emissions. Today, wishing to experience the surroundings in pure form is what motivates us to bring control and reduction to the emission from the wide spectrum of chemical industries existing. This force drives towards introducing new techniques to reduce harmful emissions. Controlling the emission of greenhouse gasses has been a great challenge today. Reducing greenhouse gas emissions can improve air quality and save lives. Reducing global greenhouse gas emissions to slow climate change could prevent millions of premature deaths due to air pollution over the next century. Industrial process emits huge amounts of organic compounds carbon monoxide, hydrocarbons, and chemicals into the air. A high quantity of carbon dioxide is the reason for the greenhouse effect in the air. Air pollutants are responsible for a number of adverse environmental effects, such as photochemical smog, acid rain, death of forests, or reduced atmospheric visibility.

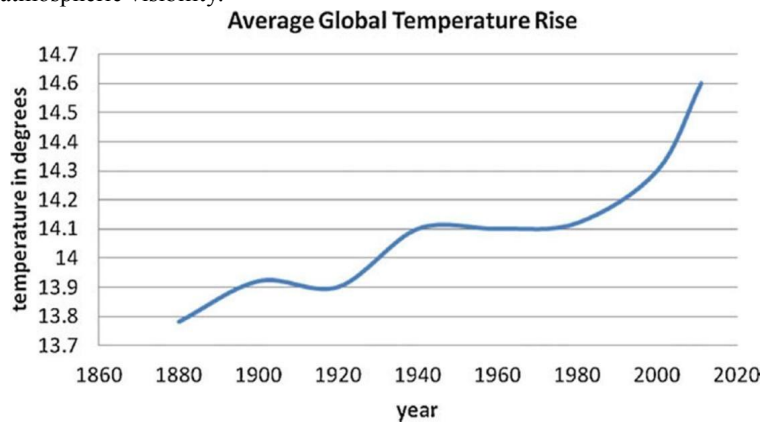


Figure1.2 (A) Average Temperature rise graph

The graph above shows how the temperature is rising globally within decades. This is a global concern and hence a major driving force to introduce effective safety engineering tools to control the toxic releases from industries. These releases didn't only deteriorate our surroundings but also deteriorated our human health, reduced mortality rate. And if we see the global surveys, India got highest health losses due to the pollution as stated in the graph below. Hence it's immensely important for us to work on the pollution and emission control for both nationwide health and environmental gain instead of fast moving toward deteriorating point

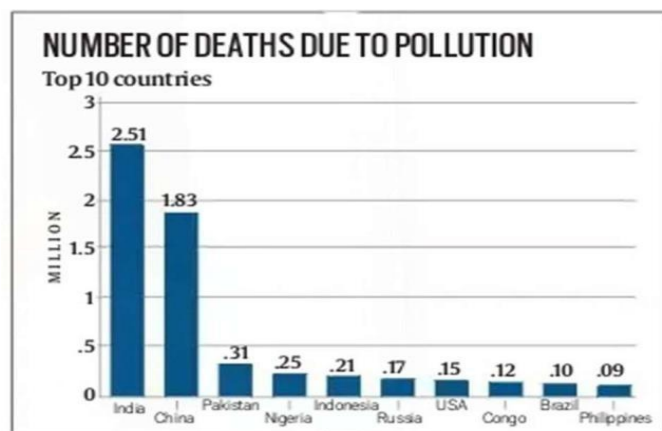


Figure1.2 (B) Number of death due to pollution graph

The motivation drive was heated also because of our practical visits in petrochemical industry during our internship. The drive through the issues with toxic releases there was a big motivation. The uneasiness due to releases in atmosphere of the premises is a big ban to the workers and employees there, especially when there is maintenance, cleaning and scrapping work going on there

1.3. Objective of the Project

One of the greatest challenges faced by our society is the environmental hazard. Petroleum and refinery gases are complex combinations of petroleum hydrocarbons produced by petroleum refineries, upgraders and natural gas processing facilities. The main objective of the project is to eliminate the occurrence of toxic releases in petrochemical industry during its process in various units using a safety engineering tool. Various gases released in petrochemical industries are hydrogen sulfide, carbon monoxide, carbon dioxide, ammonia, benzene, sulfur dioxide, nitrogen dioxide, methyl bromide etc. Toxic releases damage life of living beings and cause prolonged illness and even death. The air composition getting spoiled day by day causing many respiratory ailments as well as skin diseases once inhaled or absorbed by skin or eyes. It may lead to nausea, headache, bronchitis, asthma and other respiratory and neurological problems. This project mainly will be an aid to reduce the exposure to the toxic gases for the people working in the premises. This project describes the release of toxic gases: chlorine (Cl), hydrogen sulfide (H₂S), benzene (C₆H₆), ammonia (NH₃).

This 1st identifies the nodes in the refining process in a petrochemical industry i.e. the unit where chlorine, hydrogen sulfide, benzene and ammonia are releases that can affect the Environment and the health of the workers in the premises and then using safety engineering tool we control its release in effort to reduce the exposure from it to the workers in the premises.

1.4. Scope of the Project

In petrochemical industry, there are chances of occurrence of different hazards due to toxic releases that results in health hazards in workers and others present in the premises. The scope of this project is to minimize the toxic releases in different units of the petrochemical industry by using some engineering tools.

II. LITERATURE REVIEW

2.1 Introduction:

The literature review is one of the most important processes in documenting a project, it helps in analyzing various kinds of research which are already carried out beforehand and it gives out the required data needed for project to undergo. Research and evaluation of the available literature based on Toxic releases in Petrochemical industries. It provides an overview of current knowledge, allowing you to identify relevant theories, methods, and gaps in the existing research.

A literature review has 4 main objectives: -

- It surveys the literature in your chosen area of study.
- It also synthesizes the information in that literature into a summary.
- With help of it we can critically analyze the information gathered by identifying gaps in current knowledge.
- It presents the literature in an organized way.

In this First Phase of our project, we have read 20 Research Papers related to the Toxic releases in Petrochemical industries. From these research papers we got to know about different techniques and different methods used to minimize and control toxic releases. We also got to know about different consequences related to toxic releases.

2.2 Literature Contribution to Project Work:

1. A computational analysis of go sheet in environment of toxic gases for potential sensing platform.
2. Numerical modelling for effect of water curtain in mitigating toxic gas release.
3. Toxic releases from power plants.
4. human and organizational failures analysis in process industries using FBN-HFACS model: learning from a toxic gas leakage accident
5. synergistic effects on the physical effects of explosions in multi- hazard coupling accidents in chemical industries
6. fuzzy fault tree analysis of chlorine gas release hazard in chlor-alkali industry using α -cut interval-based similarity aggregation method
7. toxicity by descent: a comparative approach for chemical hazard assessment

8. toxic chemicals and persistent organic pollutants associated with micro-and Nano plastics pollution
9. Air quality and management in petroleum refining industry

III. AREA OF STUDY

3.1 Industry Introduction:

Petrochemical Industries: Petrochemicals are the chemical products obtained from petroleum by refining. Some chemical compounds made from petroleum are also obtained from other fossil fuels, such as coal or natural gas, or renewable sources such as maize, palm fruit or sugar cane. The two most common petrochemical classes are olefins (including ethylene and propylene) and aromatics (including benzene, toluene and xylene isomers).

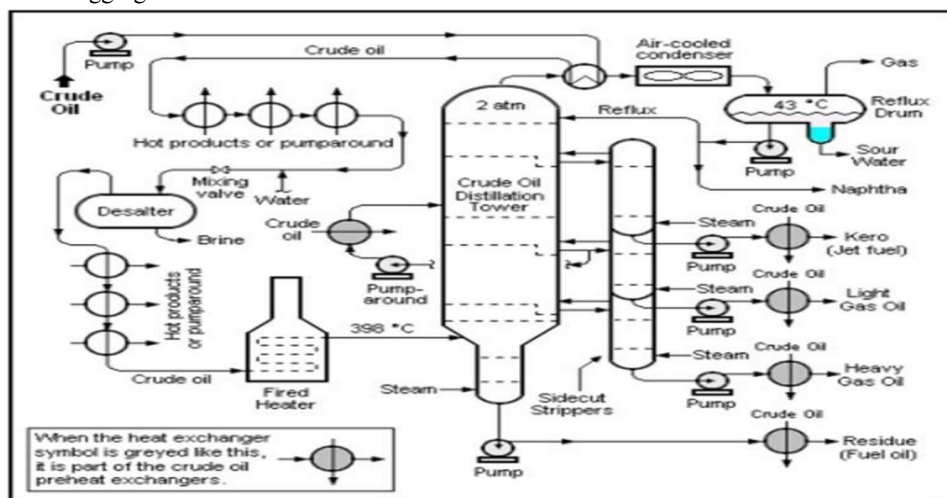
Petrochemicals are derived from various chemical compounds, mainly from hydrocarbons. These hydrocarbons are derived from crude oil and natural gas. Among the various fractions produced by distillation of crude oil, petroleum gases, naphtha, kerosene and gas oil are the main feed stocks for petrochemical industry.

Petrochemical are important organic chemicals derived from petroleum products, LPG and coal. The industry produces:

- i) Fertilizers and insecticides.
- ii) Resins, adhesives for industries
- iii) Plastic sheets, bowls, paints.

Petrochemical Industry, this industry and the products it makes play an enormous role in our daily lives. Imagine life without gasoline, cosmetics, fertilizers, detergents, synthetic fabrics, asphalt, and plastics. All of these products and many more are made from petrochemicals chemicals derived from petroleum or natural gas. The Characteristics of Indian Petrochemical Industry.

The Petrochemical Industry in India is cyclical. This industry, not only in India but also across the world, is dominated by volatile feedstock prices and sulky demand. India has one of the lowest per capita consumptions of petrochemical products in the world. For example, the per capita consumption of polyester in India lies at 1.4 kg only compared to 6.6 kg for China and In recent years, India is emerging as one of the competitive and high-quality manufacturing destinations in the global market, attracting foreign investments. Presently, India's chemical and petrochemical (CPC) industry holds a significant position in the world market, worth 178 billion USD, and it is expected to grow to about 300 billion USD by 2025. The pandemic has compelled the global chemical and petrochemical industry to diversify its supply chain base to regions which offer a more lucrative business ecosystem with favourable investment policies. India appears as one of the major potential investment regions with Asia's growing contribution to the production and sales of the CPC industry. The report aims to understand the chemical and petrochemical industry's landscape, especially at the disaggregated level of the states and union territories



TYPICAL PETROLEUM REFINERY

Figure 3.1 Petroleum Refinery layout

3.3 kg for the whole world. Similarly, the per capita consumption of polymers is 4 kg in India, whereas the per capita consumption is around 20 kg for the entire world. Presently, India has three gas-based and three naphtha-based cracker complexes with a combined annual capacity of 2.9 MMT of ethylene. Besides this, there are also four aromatic complexes with a total of 2.9 MMT of Xylenes

3.2 The refining process:

Every refinery begins with the separation of crude oil into different fractions by distillation. The fractions are further treated to convert them into mixtures of more useful saleable products by various methods such as cracking, reforming, alkylation, polymerization and isomerization. These mixtures of new compounds are then separated using methods such as fractionation and solvent extraction. Impurities are removed by various methods, e.g. dehydration, desalting, sulphur removal and hydro treating. Refinery processes have developed in response to changing market demands for certain products. With the advent of the internal combustion engine the main task of refineries became the production of petrol. The quantities of petrol available from distillation alone was insufficient to satisfy consumer demand. Refineries began to look for ways to produce more and better quality petrol. Two types of processes have been developed:

- breaking down large, heavy hydrocarbon molecules
- Reshaping or rebuilding hydrocarbon molecules

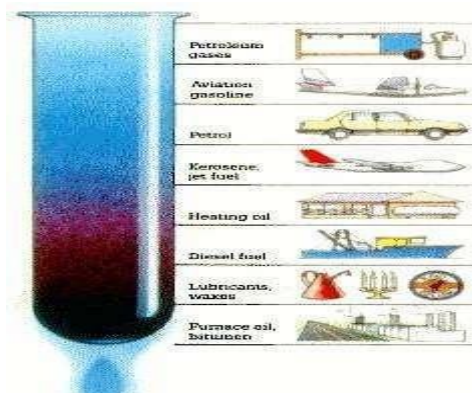


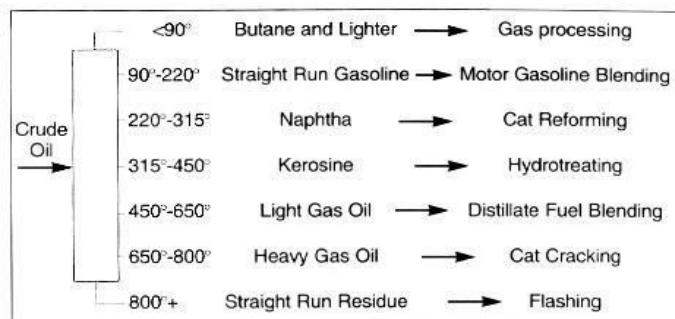
Figure 3.2 (E) the Refinery process

3.3 Distillation (Fractionation):

Because crude oil is a mixture of hydrocarbons with different boiling temperatures, it can be separated by distillation into groups of hydrocarbons that boil between two specified boiling points. Two types of distillation are performed: atmospheric and vacuum. Atmospheric distillation takes place in a distilling column at or near atmospheric pressure. The crude oil is heated to 350 - 400°C and the vapour and liquid are piped into the distilling column. The liquid falls to the bottom and the vapour rises, passing through a series of perforated trays (sieve trays). Heavier hydrocarbons condense more quickly and settle on lower trays and lighter hydrocarbons remain as a vapour longer and condense on higher trays. Liquid fractions are drawn from the trays and removed. In this way the light gases, methane, ethane, propane and butane pass out the top of the column, petrol is formed in the top trays, kerosene and gas oils in the middle, and fuel oils at the bottom. Residue drawn off the bottom may be burned as fuel, processed into lubricating oils, waxes and bitumen or used as feedstock for cracking units

To recover additional heavy distillates from this residue, it may be piped to a second distillation column where the process is repeated under vacuum, called vacuum distillation. This allows heavy hydrocarbons with boiling points of 450°C and higher to be separated without them partly cracking into unwanted products such as coke and gas. The heavy distillates recovered by vacuum distillation can be converted into lubricating oils by a variety of processes. The most common of these is called solvent extraction. In one version of this process the heavy distillate is washed with a liquid which does not dissolve in it but which dissolves (and so extracts) the non-lubricating oil components out of it. Another version uses a liquid which does not dissolve in it but which causes the non-lubricating oil components to

precipitate (as an extract) from it. Other processes exist which remove impurities by adsorption onto a highly porous solid or which remove any waxes that may be present by causing them to crystallize and precipitate out.



Distilling crude and product disposition

Figure 3.2 (F) Distillation products

3.4 Refineries and the environment:

Air, water and land can all be affected by refinery operations. Refineries are well aware of their responsibility to the community and employ a variety of processes to safeguard the environment.

The processes described below are those used by the Shell refinery at Geelong in Victoria, but all refineries employ similar techniques in managing the environmental aspects of refining.

3.5. Description on Project Area:

Petrochemicals refer to all those compounds that can be derived from the petroleum refinery products. Petrochemical industries impart vital role in the national economy. Environmental issues have now become important considerations due to the potential harmful impacts produced by chemical releases. Unsafe emissions may be due to improper production process, poor maintenance practices and internal operational process problems. Petrochemicals cause acute and chronic health diseases such as ulcer, allergy, cancer, and liver and kidney problems to the living beings. This review article discusses some of the chemical releases in petrochemical industries.

Chlorine gas:

Chlorine (Cl₂) is among the ten highest volume chemicals manufactured in the United States. It is produced commercially by electrolysis of sodium chloride brine. Chlorine is used in industry and in household cleaning products. Chlorine was also the first poison gas to be used as a weapon during World War I.

Benzene:

Benzene is accepted to be a human carcinogen with no safe level of exposure. Epidemiology studies have demonstrated an association between high exposure and the development of leukemia. No threshold for carcinogenicity has been demonstrated and it is not possible to establish a level below which risk to health cease to exist. Benzene works by causing cells not to work correctly. For example, it can cause bone marrow not to produce enough red blood cells, which can lead to anemia. Also, it can damage the immune system by changing blood levels of antibodies and causing the loss of white blood cells

Hydrogen sulfide:

H₂S does occur naturally, primarily as the result of organic material decomposition at the hands of bacteria. Areas in nature where this can occur are within low oxygen environments such as swamps and polluted water. H₂S also forms as a part of natural gas, petroleum, sour crude oil (oil with more than 0.05% sulfur content), sulfur deposits, volcanic gases, and sulfur springs. But H₂S may also be produced during industrial processes. Depending on your job within the industry, you need to know all the possibilities of H₂S exposure while performing your duties. H₂S exposure is a major concern in the petroleum industry, especially at oil and natural gas wells, refineries, natural gas plants, and pipelines

IV. PROBLEM STATEMENT

Petrochemical industries have several undesired environmental effects in terms of toxic and carcinogenic chemical species, harmful gaseous emission, effluent release and hazardous chemical content in petroleum products. The aim of our review study is to divide an overview of various forms of toxic and hazardous content coming from the petrochemical industries with particular reference industries in India.

Toxic releases are the major source of industrial hazard in case of petrochemical industries, and preventing the toxic releases would be first and foremost choice.

We have selected this one of the problems from the major hazardous industry, because industry has everlasting number of hazards at its different stages of processing. Its releases many toxic substances which can affect worker in petrochemical industry as well as environment

V. PROBLEM FORMULATION

5.1 Legal Parameters:

This project is mainly directed by legal parameters that specifies the limit of exposure from toxic gases to a worker under the work hours in the premises. The legal drafts with such specifications that helps to estimate the safe permitted exposure to toxic substances are

1. Factories act
2. Manufacture storage and import of hazardous chemical rule 1989
3. Occupational safety, health and working condition rules 2022

5.1.1 Factories act 1948

The main objectives of the Indian Factories Act, 1948 are to regulate the working conditions in factories, to regulate health, safety welfare, and annual leave and enact special provision in respect of young persons, women and children who work in the factories. In factories act 1948, 2nd schedule, we see the permissible levels of certain chemical substances in the work environment. The table shown below shows the permissible limits of chlorine, benzene, hydrogen sulphide and nitrogen dioxide

Table 5.1: Schedule II: Permissible Levels of Certain Chemical Substances in Work Environment [Section 41F]

S. No	Substance	Permissible limits of exposure			
		Time-weighted average Concentration (8hrs) M		Short-term exposure limit (15min)*	
		ppm	mg/m ^{3**}	ppm	mg/m ^{3**}
1	2	3	4	5	6
1.	Acetaldehyde	100	180	150	270
2.	Acetic acid	10	25	15	37
3.	Acetone	750	1780	1000	2375
4.	Acrolein	0.1	0.25	0.3	0.8
5.	Acrylo nitrile -Skin	2	4.5	-	-
6.	Aldrin -skin	-	0.25	-	-
7.	Allylchloride	1	3	2	6
8.	Ammonia	25	18	35	27
9.	Aniline-Skin	2	10	-	-

10.	Anisidine (o-p-isomers) Skin	0.1	0.5	-	-
11.	Arsenic and Soluble com- pounds (as)	-	0.2	-	-
12.	Benzene(S.C.)	10	30	-	-
13.	Beryllium and Compound (as Be) (S.C.)	-	0.002	-	-
14.	Boron trifluoride -C	1	3	-	-
15.	Bromine	0.1	0.7	0.3	2
16.	Butane	800	1900	-	-
17.	2-Butane (methylethyl Ketone -MEK)	200	590	300	835
18.	n-Butyl acetate	150	710	200	950
19.	n-Butyl alcohol-Skin-C	50	150	-	-
20.	Sec./ tert.Butyl acetate	200	950	-	-
21.	Butyl mercaptan	0.5	1.5	-	-
22.	Cadmium dusts and salts (as Cd)	-	0.05	-	-
23.	Calcium oxide	-	2	-	-
24.	Carbaryl (Sevin)	-	5	-	-
25.	Carbofuran (Furadan)	-	0.1	-	-
26.	Carbon disulphide-Skin	10	30	-	-
27.	Carbon monoxide	50	55	400	440
28.	Carbon tetrachloride – Skin (S.C)	5	30	-	-
29.	Chlordene -Skin	-	0.5	-	2
30.	Chlorine	1	3	3	9
31.	Chlorobenzene (Monochloro benzene)	75	350	-	-
32.	Chloroform (S.C.)	10	50	-	-
33.	bis (Chloromethyl) ether (H.C.)	0.001	0.005	-	-
34.	Chromic acid and chromates (as Cr.)	-	0.05	-	-
35.	Chromous salts (as Cr)	-	0.5	-	-
36.	Copper Fume	-	0.2	-	-
37.	Cotton dust, raw*	-	0.2*	-	-
38.	Creosol, all isomers - Skin	5	22	-	-
39.	Cyanides (as CN)-Skin	-	5	-	-
40.	Cyanogen	-	10	20	-
41.	DDT (Dichlorodi phenyl trichloroethane)	-	1	-	-
42.	Demeton -Skin	0.01	0.1	-	-

43.	Diazinon-Skin	-	0.1	-	-
44.	Dibutyl phthalate	-	5	-	-
45.	Dichlorvos (DDVP)-Skin	0.1	1	-	-
46.	Dieldrin-Skin	-	0.25	-	-
47.	Dinitrobenzene (all isomers)-Skin	0.15	1	-	-
48.	Dinitrotoluene-Skin	-	1.5	-	-
49.	Diphenyl-(Biphenyl)	0.2	1.5	-	-
50.	Endosulfan (Thiodan)-Skin	-	0.1	-	-
51.	Endrin -Skin	-	0.1	-	-
52.	Ethylacetate	400	1400	-	-
53.	Ethyl alcohol	1000	1900	-	-
54.	Ethylamine	10	18	-	-
55.	Fluorides (as F)	-	2.5	-	-
56.	Fluorine	1	2	2	4
57.	Formaldehyde (S.C.)	1.0	1.5	2	3
58.	Formic acid	5	9	-	-
59.	Gasoline	300	900	500	1500
60.	Hydrazine-Skin (S.C.)	0.1	0.1	-	-
61.	Hydrogen Chloride-C	5	7	-	-
62.	Hydrogen Cyanide-Skin-C	10	10	-	-
63.	Hydrogen flouride (as F)-C	3	2.5	-	-
64.	Hydrogen peroxide	1	1.5	-	-
65.	Hydrogen sulphide	10	14	15	21
66.	Iodine -C	0.1	1	-	-
67.	Iron oxide fume (Fe ₂ O ₃)(as Fe)	-	5	-	-
68.	Isoamyl acetate	100	525	-	-
69.	Isomyl alcohol	100	360	125	4500
70.	Isobutyl alcohol	50	150	-	-
71.	Lead, inorg Dusts, dusts and fumes (as Pb).	-	0.15	-	-
72.	Lindane -Skin	-	0.5	-	-
73.	Malathion Skin	-	10	-	-
74.	Manganese (as Mn) dust and compounds-C	-	5	-	-
75.	Manganese fume (as Mn)	-	1	-	3

76.	Mercury (as Hg)-Skin- (i) Alkyl compounds (ii) All forms except alkyl vapor	- -	0.01 0.05	- -	0.03 -
77.	Aryl and inorganic compounds	-	0.1	-	-
78.	Methyl alcohol (Methanol)-Skin	200	260	250	310
79.	Methyl Cellosolve (2-Methoxy ethanol)-Skin	5	16	-	-
80.	Methyl isobutyl ketone	50	205	75	300
81.	Methyl isocyanate ketone	0.02	0.05	-	-
82.	Naphthalene	10	50	15	75
83.	Nickel carbonyl (as Ni)	0.05	0.35	-	-
84.	Nitric acid	2	5	4	10
85.	Nitric oxide	25	30	-	-
86.	Nitrobenzene-Skin	1	5	-	-
87.	Nitrogen dioxide	3	6	5	10
88.	Oil mist-mineral	-	5	-	10
89.	Ozone	0.1	0.2	0.3	0.6
90.	Parathion-Skin	-	0.1	-	-
91.	Phenol-Skin	5	19	-	-
92.	Phorate (Thimet)-Skin	-	0.05	-	0.2
93.	Phosgene (Carbonyl chloride)	0.1	0.4	-	-
94.	Phosphine	0.3	0.4	1	1
95.	Phosphoric acid	-	1	-	3
96.	Phosphorus (yellow)	-	0.1	-	-
97.	Phosphorus pentachloride	0.1	1	-	-
98.	Phosphorus trichloride	0.2	1.5	0.5	3
99.	Picric acid - Skin	-	0.1	-	0.3
100.	Pyridine	5	15	-	-
101.	Silane (Silicon tetrahydride)	5	7	-	-
102.	Sodium Hydroxide-C	-	2	-	-
103.	Styrene, monomer (Phenyl-ethylene)	50	215	100	425
104.	Sulphur dioxide	2	5	5	10
105.	Sulphur hexaflouride	1000	6000	-	-
106.	Sulphuric acid	-	1	-	-

107	Tetraethyl lead (as Pb)-Skin	-	0.1	-	-
108	Toluene (Toluol)	100	375	150	560
109	o- Toluidine -Skin(S.C)	2	9	-	-
110	Tributyl phosphate	0.2	2.5	-	-
111	Trichloro -ethylene	50	270	200	1080
112	Uranium, natural (as U)	-	0.2	-	0.6
113	Vinyl chloride (H.C.)	5	10	-	-
114	Welding fumes	-	5	-	-
115	Xylene (o,m,p -isomers)	100	435	150	655
116	Zinc oxide (i) Fume	-	5	-	10
	(ii) Dust (Total dust)	-	10	-	-
117	Zirconium compounds (as Zr)	-	5	-	10

5.1.2 Manufacture storage and import of hazardous chemical rules 1989:

Govt. of India has promulgated “Manufacture, Storage, and Import of Hazardous Chemicals (MSIHC) Rules, 1989” under the Environment (Protection) Act, 1986. It enlists 684 hazardous chemicals on the basis of toxicity, flammability and explosives. It classifies toxic chemicals into 3 levels in its schedule 1 part 1, as shown below:

Serial no.	toxicity	Oral toxicity LD50 (mg/kg)	Der LD50 LD50 (mg/kg)	Inhalationtoxicity LC50 (mg/kg)
1	Extremely toxic	>5	<40	<0.5
2	Highly toxic	>5-50	>40-200	<0.5-2
3	Toxic	>50-200	>200-1000	>2-10

Table 5.2 Classification of toxicity

5.1.3 Occupational safety, health and working condition rules 2022

The permissible limits expressed in this rule for gases of our interest i.e. chlorine, benzene, hydrogen sulfide, nitrogen dioxide are as shown below: It defines chlorine as oxidizing agent and also as a corrosive material.

S. no	Substances	Time weightedaverage concentration (TWA) (8 hrs)		Short term maximum concentration (STEL) 15min).	
		Ppm	mg/m ³	ppm	mg/m ³
1	Benzene	0.5	1.5	25	7.5
2	Chlorine	1	3	3	9
3	Hydrogen sulfide	10	14	15	21
4	Nitrogen dioxide	3	6	5	10

Table 5.3 TWA and STEL of toxic substances

VI. METHODOLOGY

6.1 Introduction:

This project is focused on the evaluation of detection of toxic releases in petrochemical industries with the use of Bowtie methodology. The present work reports detection of H₂S gas during transportation, operation and storage.

6.2 Description on Engineering Tool:

6.2.1 Bow Tie Method

Bow Tie methodology is a graphical risk assessment tool that helps organizations identify, assess and manage potential risks in their operations. It is commonly used in industries such as aviation, healthcare, oil and gas, and chemical manufacturing.

The bow tie diagram is a visual representation of the potential causes and consequences of a specific hazard, and the controls that are in place to manage the risk. The diagram consists of a central knot, which represents the hazard, with two branches extending outwards representing the potential causes and consequences of the hazard. The left-hand side of the diagram represents the preventive controls that are in place to stop the hazard from occurring, while the right-hand side represents the mitigating controls that are in place to reduce the impact of the hazard if it does occur.

The bow tie methodology can be used for both qualitative and quantitative risk assessments. It is a useful tool for identifying potential hazards, analyzing the likelihood and consequences of those hazards, and determining the most effective controls to manage the risks

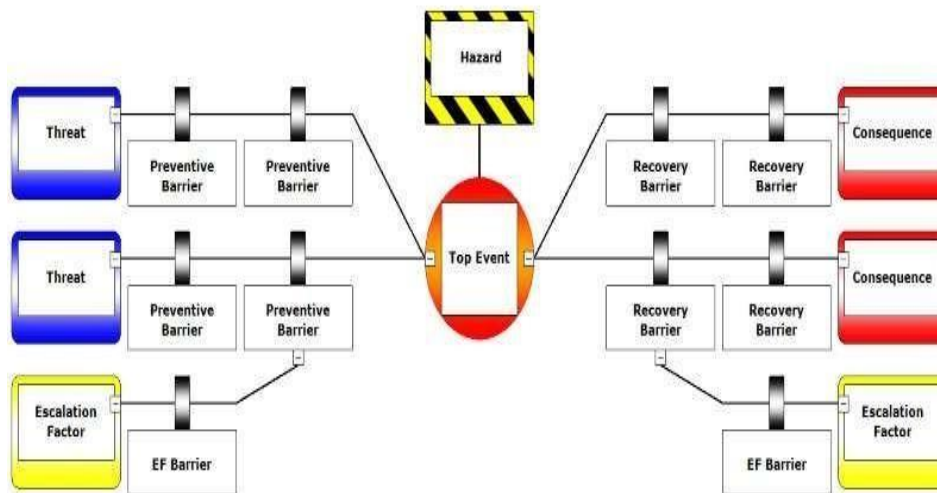


Figure 5.1 Typical bowtie diagram

Some benefits of using the bow tie methodology include:

1. It provides a visual representation of the risk management process, which is easy to understand and communicate to stakeholders.
2. It helps to identify potential causes and consequences of a hazard, which can aid in the development of effective controls.
3. It allows for a systematic and structured approach to risk management.
4. It facilitates the identification of gaps in control measures and areas for improvement.

However, it is important to note that the bow tie methodology should not be used in isolation and should be complemented with other risk management tools and techniques. Additionally, the quality of the analysis depends on the quality of the information used to develop the bow tie diagram. Therefore, it is important to ensure that the information used is accurate and up-to-date. Bowties are diagrams representing the relationship between an unwanted event, its potential causes, its consequences and the controls in place, as shown below in Figure 5.2(B).

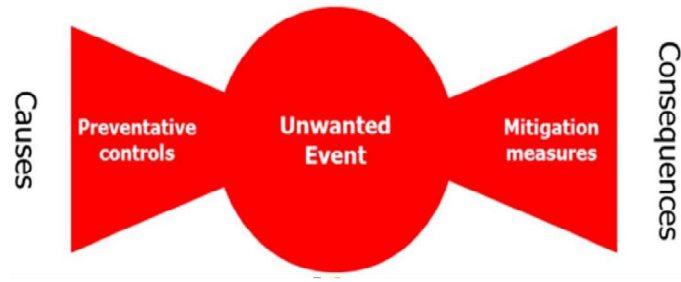


Figure 5.2 Basic bowtie diagram

Bowties are thought to have originated in the late 1970s in ICI (Imperial Chemical Industries). However it was not until the early 1990s, that Shell became the first company to incorporate bowties into its operations. Following Shell, the bowtie method started to be widely used throughout the oil and gas industry, as bowties became known as a powerful visual tool to aid risk management. In the last decade the bowtie method has also spread to other industries including aviation, mining, maritime, chemical and healthcare.

to a failure or degradation of a control, for example a floating level indicator on a tank (the barrier being claimed) seizes and does not register a change in level. This could be mitigated by installing an additional instrument to provide level manual checks on the level reading (this would be the barrier on the escalation factor).

6.2.2 Advantages of Bowties in Process Safety Management:

There are numerous advantages to using bowties as a tool for effective process safety management. These are discussed below:

Effective communication: The simple representation of the safety processes makes them ideal to use in Safety Cases and Reports. The popularity of bowties is due to their ability to simply and effectively communicate how risks associated with Major Accident Hazards are managed on a particular facility or during a particular operation. This is an approach that has gained traction with regulators such as the UK HSE (Health and Safety Executive), and many safety cases and COMAH cases are now developed with bowties at their core.

ALARP reviews: They are an effective and visual way of representing the risk management process and provide a strong starting point for ALARP reviews.

Identification of Safety Critical Elements: Bowties offer a systematic way to identify safety critical elements (SCEs) and activities and then to use this information to develop the SCEs and associated performance standards.

Workforce engagement: Bowties are powerful in engaging the workforce. The development and refining of bowties should include the workforce who then take ownership of the bowties. Bowties are a great basis for training and explaining the importance of safety critical equipment/activities.

Communication with management: Bowties provide a framework for process safety conversations with senior management whose main focus is an overview rather than detailed analysis of processes. They may also be used as part of the safety induction process for new managers.

6.2.3 Industrial Application:

Hydrogen sulfide is a hazardous gas that is commonly encountered in the chemical industry. The bowtie methodology can be used to identify potential sources of hydrogen sulfide and develop effective controls to prevent its release and mitigate its consequences. Here are the steps to implementing the bowtie methodology to eliminate hydrogen sulfide in the chemical industry.

- Identify the Hazard
- Determine the Causes
- Identify the Consequences
- Develop Preventive Controls
- Develop Mitigating Controls
- Develop Monitoring and Review Processes

By implementing the bowtie methodology to eliminate hydrogen sulfide in the chemical industry, companies can identify potential hazards and develop effective controls to prevent accidents and mitigate their consequences. This can help to improve safety performance, reduce the risk of regulatory penalties and legal liabilities, and enhance the company's reputation as a responsible corporate citizen.

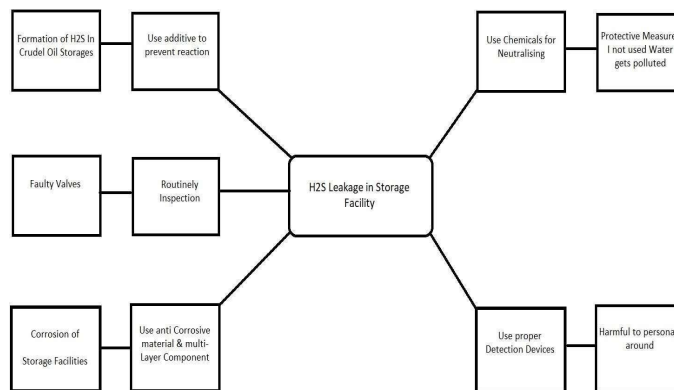
Implementing Bowtie methodology to eliminate H₂S leak in chemical industry:

Hydrogen sulfide (H₂S) can leak from various areas in a petrochemical industry, depending on the specific process and equipment used. Some common areas from which H₂S can leak include:

1. Leakage from storage unit.
2. Leakage from processing equipment.
3. Leakage during transportation.

H₂S leakage from storage unit:

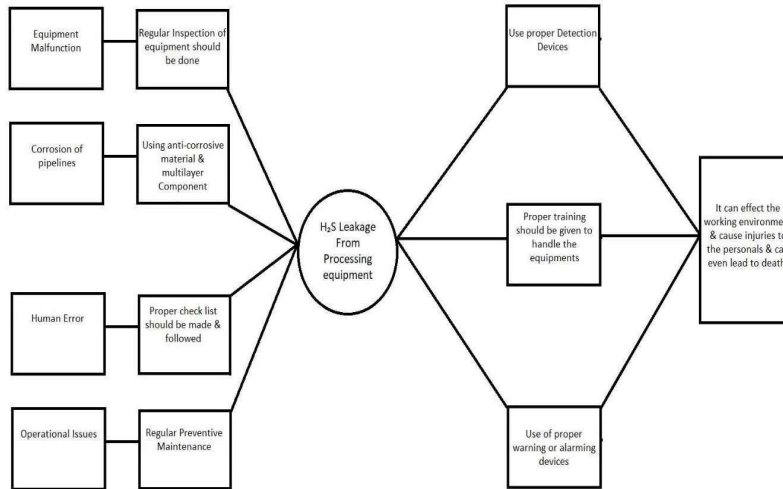
H₂S is commonly stored in tanks within petrochemical facilities. Leaks can occur due to damage or corrosion to the tank, faulty valves or fittings, or overfilling, formation of H₂S in crude oil storages. To prevent these leaks we use different preventive measures like routine inspections, use of anti-corrosive materials and multi-layer components and also we can use additives to prevent H₂S formation reactions. Also we have analyzed protection measures through bowtie method for controlling H₂S release like use chemicals for neutralizing H₂S gas, and also we can proper detection devices



6.1 Flow Chart: H₂S Leakage in Storage Facility

H₂S leakage from processing equipment:

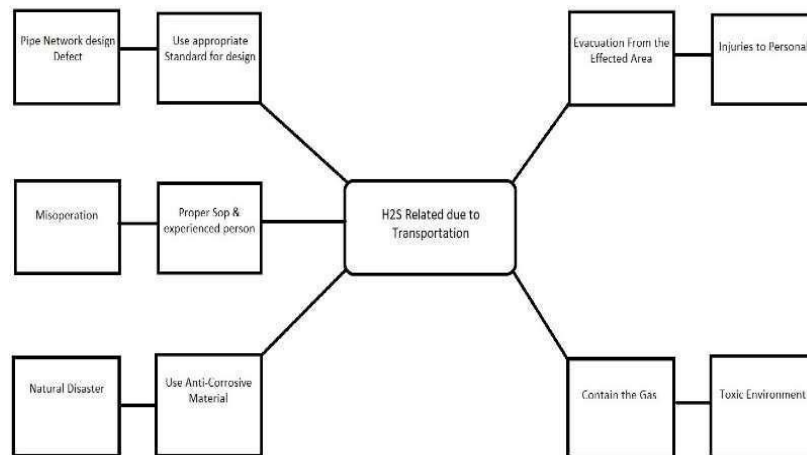
H₂S is often produced or used in various processing equipment within petrochemical facilities, such as reactors or distillation columns. Leaks can occur due to equipment failure, damage, or inadequate maintenance, corrosion of pipelines, operational issues (due to lack of knowledge), and also leaks can occur due to human errors. Routine inspections, use of anti-corrosive materials, by preparing and following proper checklist can prevent these leaks. Also we have analyzed protection measures through bowtie method for controlling H₂S release like use of proper detection devices, providing proper training, etc.



Flow Chart: H2S Leakage from Processing Equipment

H2S leakage from transportation:

H2S leakage can occur during any stage of transportation, leading to serious safety and environmental concerns. The severity of the risk depends on the concentration and duration of exposure. To prevent H2S leakage during transportation, various measures can be taken. For instance, pipelines can be fitted with H2S sensors that trigger alarms when the gas is detected. Tankers and trucks can be equipped with H2S detection systems to monitor the air quality inside the vehicle.



6.3 Flow Chart: H2S Leakage from Transportation

Additionally, training and education programs can be implemented to teach workers about the hazards of H2S and how to respond in case of a leakage. In case of a H2S leakage, emergency response procedures should be in place to ensure the safety of workers and the surrounding environment. The affected area should be evacuated immediately, and the source of the leakage should be identified and contained. H2S is highly reactive with many materials, so only trained personnel equipped with appropriate personal protective equipment should be allowed to respond to the leakage. If proper precautionary measures are not taken, this could lead to consequences like it can lead to water pollution, effect working environment, can cause injuries to personals, and sometimes it can even lead to death.

VII. RESULTS, SUMMARY AND DISCUSSION

7.1 Result Obtained and Interpretation

The result obtained by evaluating various processes in petrochemical industry, it has been found that H2S can be released in three major sections:

1. Transportation

2. Storage

3. Processing

- While H₂S being in storage facilities can leak from faulty valves and due to corrosion of storage facilities.
- In transportation, leakage can happen due to fire network design defects, disoperations, natural disaster etc.
- In processing, the H₂S can leak because of equipment malfunction, corrosion of pipelines, human error and operational issues.

Using bowtie method, resolutions has been done to decrease or eliminate the possibilities of leakage of H₂S in the above mentioned processes. The resolutions that has been done are:

Resolutions for leakage issues of H₂S in storage:

1. Resolution for formation of H₂S in crude oil storages: Use additive to prevent reaction
2. for leakage due to faulty valves: Routinely inspection
3. Leakage due to corrosion of storage facilities: Use anti corrosive material and multi- layer components

Resolutions for leakage issues of H₂S in transportation:

1. Resolution of leakage due to pipe network design defect: Use appropriate standard for design
2. Leakage due to disoperation: Use proper SOP and experienced person
3. Leakage due to natural disasters: Feasible for any environmental condition
4. Leakage due to corrosion of transportation medium: Use anticorrosive material

Resolution for leakage issues of H₂S in processing:

1. Leakage due to equipment malfunction: Regular inspection of equipment's
2. Leakage due to corrosion of pipelines: Using anticorrosive material in multi-layer components
3. Leakage due to human error: Proper checklist should be made and followed
4. Leakage due to operational issues: Regular preventive maintenance.

7.2 Important Findings and Conclusion

The important findings and Conclusions of this project can be described as the following major points:

1. It is found that the petrochemical industries having crude oil as their raw material has a high potential to catch Fire, thus it is required to be handled carefully by skilled professionals;
2. With the use of Bow Tie Method that are mentioned in the previous sheet, the risk and hazards can be drastically reduced.
3. It provides all the critical information of risk such as threats, critical events, consequences, barriers.
4. Bowties can highlight area where organizational control is weak, enabling proactive, sustainable strategies to reduce the risk to be targeted on these areas.
5. Bow Ties have also been used to ensure that critical controls do not fall through the cracks after a company reorganization. Bow tie can be used during incident investigation to identify organizational weakness that allowed risk control to fail.
6. It is concluded that the risk and hazards can be identified and eliminated by the Bow Tie Method along with any processes, or transportation activities, or storage facilities that gives us the preventive and protective measures to eliminated or reduce the risk.

It is evident that the identification of hazards and risk through Bow Tie Method and recommended safety measures shall reduce the risk for each hazards and reduce the chances of incidents, accidents, and fatalities.

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