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The Strategy for Process Safety during the Initial Stages of R &D reactions – Toxicity and Flammability Hazard Evolution Techniques

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Abstract - *Process safety studies play a crucial role in the specialty chemicals, agrochemicals, pharmaceuticals, and petrochemicals industries, spanning from the development phase of new molecules to their commercial implementation. The process safety team conducted a literature review on explosive materials and processes during the initial stages of molecular development. Process safety personnel initially identify and comprehend potential hazards by analyzing historical incident data. This involves a systematic review of relevant literature, including scientific papers and professional articles, focusing on various types of hazards such as chemical process and reaction risks, health hazards, explosion risks, dust hazards, and the flammability of combustible gases and vapors, as well as environmental hazards.*

This review paper outlines the initial identification of hazards conducted through a literature survey, data from Bretherick's handbook, and an analysis of previous accident history. Outlined the hazards associated with toxicity and flammability, along with a risk assessment of these hazards. Assessed the toxicity risks of both single components and multicomponent mixtures utilizing the LD50, LC50, and TLV equations. Analyzed the flam ability risks of mixtures through the application of LFL and LOC equations. A process safety strategy during the R&D phase of reactions is essential for attaining operational excellence. This approach enables businesses in process industries to identify and mitigate risks throughout their production lifecycle, effectively managing or eliminating hazards within their facilities while adhering to the highest safety standards.

Key Words: **Process safety, Process Safety Incident, Literature review, Toxicity hazard, Flammability hazard etc**

1. INTRODUCTION

Number of products of the chemical, pharmaceutical, agrochemicals & petrochemicals industry is produced using potentially hazardous reactions. The toxic and flammable hazardous substance involved in the industry process. A flammable hazard refers to a material or substance that can easily catch fire and burn when exposed to an ignition source, such as heat, sparks, or opens flames. These substances are typically volatile and have low flash points, meaning they can ignite at relatively low temperatures. New materials, chemicals, and processes are often tested, and many of these may involve substances that are flammable or pose other combustion-related hazards. Toxicity hazards are a significant concern in many industrial, scientific, and research environments. Early identification, a robust risk assessment process, and implementation of appropriate control measures are essential to preventing harm to people, animals, and the environment. The initial stage of research and development for new products involves assessing the potential hazards and evaluating the feasibility of these hazards through experimental investigations of all reactions occurring in the production processes, which can be quite costly. Early phase of research & development work, to identify reagents are acceptable to use in a scale process requires the practical assessment of specific hazardous properties. Energetic materials like nitro compound, diazo compound, propellants and pyrotechnic compositions are high explosive hazards, resulting from the high quantities of heat and gas that can be released upon rapid decomposition. These can be identified in early phase and categories risk assessment to determining the likelihood or severity of unwanted hazards.[3] Initiated the process safety study in early phase of the research & development work which helped to identify hazardous material properties like explosive, flammable, toxic etc. Eliminated the hazardous materials from the process, substituted the hazardous material with non-hazardous materials for the design of the inherently safe process at R&D stage. Based on the hazardous materials risk like explosive, toxic, flammable used the appropriate PPEs, provided appropriate administrative controls and appropriate engineering controls for the inherently safe design process for commercial scale

2. PROCESS SAFETY INCIDENTS:

Many process safety incidents occurred due to hazardous, explosive materials and reaction process in chemical, pharmaceutical, agrochemicals & petrochemicals industries and chemical operations, such fires, explosions and leaks etc. Most incidents were due to hazard awareness & identification, design, controls, safeguards, operating procedures and layers of protection, safety culture, and preventative maintenance. List of few contributing factors for

the process safety incidents like safety culture missing, PHA data not available, mechanical integrity etc. [3]

2.1 Aarti chemical plant explosion

On March 13, 2013, disastrous explosion occurred at Aarti Drugs, Boisar, Maharashtra, India, which led five fatalities and 18 injuries. It was reported that the explosion happened during a nitration reaction, as brownish fumes were seen prior to the blast then some additional minor blasts continued after the fire started. Manufactured methyl nitro imidazole, a chemical used in the production of pharmaceuticals. The administrative office where the victims were seated was too close to the 2000 kg of chemical tank which exploded. Seven people were charged with culpable homicide for negligence related to this event, including some senior authorities.

The unnoticed increase in temperature within the chemical tank was one of the contributing factors. The causes for this incident include a poor safety culture, facility siting, hazard awareness and design based on press reports of the incident. [3]

2.2 Yibin Hengda explosion

On July 12, 2018, a series of seven disastrous explosion occurred within 10 minutes at Yibin Hengda Technology Co., Yibin, Sichuan Province, China which led 19 fatalities and 12 injuries. Three buildings were reduced to steel frames and windows of nearby buildings were shattered due to the explosions. The company manufactures 300 TPA of benzoic acid, and 2000 TPA of 5-nitroisophthalic acid, for medicines and dyes. After the incident occurred, 15 people, including the legal representative, were arrested.

The workers lacked basic knowledge of safe operating practices in the chemical industry. A deputy chief reportedly had only studied for three years in an elementary school. The contributing cause of the accident was a worker misplacing unlabeled chemicals into a dehydration pool, causing a fire and explosion. The causes of the incident include a poor safety culture, lack of personnel training and certification, hazard awareness, negligence of law, illegal production and regulatory oversight. [4]

2.3 Tianjiayi Chemical explosion -

On March 21, 2019, a catastrophic explosion occurred at Tianjiayi Chemical Co., Ltd., Xiangshui county, China, that caused 78 deaths and injured more than 617 individuals, with a property loss of as much as US$ 100 million. An explosion crater with a diameter of 98 m was generated. According to an on-site survivor, a warehouse used for storing dinitrobenzene (DNB) and recovering off-spec or substandard nitro compounds was believed to be the explosion site, which caught fire. Based on the results of the consequence analysis performed by three methodologies, it can be concluded that the Tianjiayi Chemical Co. warehouse not only stored a substantially large quantity of dinitrobenzene but was also located too close to adjacent structures without an adequate separation distance. Judging by the effect of explosive blast on personnel, a fatality radius was determined to be about 400 m from the explosion center. [5]

3. PROCESS SAFETY LITERATURE:

Process safety extensive literature review has been carried out about process safety education. Process safety literature model preliminary identifies and understands potential hazards, chemical process and reaction hazards, health hazards, explosion hazards and dust hazards, and combustible gas and vapor flammability, environmental hazards and past incidents data through the systematize the literature review and investigated scientific papers as well as professional articles and so-called grey literature.

3.1 Research Methodology –

The hazardous materials information was extracted from both scientific and professional literature. Google Scholar, Science Direct, and Web of Science (WOS) were used to search on the internet for scientific literature. Bretherick's handbook data, conference papers, articles and records from reputed organizations were used to search for professional literature. Few reputed professional process safety organizations such as Identification Board (CSB), the Loss Prevention and Safety Promotion Symposium series, the Center of Chemical Process Safety (CCPS), UK Health and Safety Executive (HSE), Dutch National Institute for Public Health and the Environment (RIVM) and American Institute of Chemical Engineers (AICHE). [6]

Table 1 - List of Journals with corresponding review articles (January 2017–April 2017)

Sr. No.	Name of Journal	No. of Articles
1	Process Safety Process	19
2	Journal of Loss Prevention in the Process Industries	13
3	Process Safety and Environmental Protection	6
4	Education for Chemical Engineers	5
5	Chemical Engineering Transaction, The Publication of AIDIC	3
6	Safety Science	3
7	Journal of Safety Research	3
8	Chemical Engineering Progress	2
9	Chemical Engineering Technology	2
10	Chemical Health and Safety	2

11	Journal of Hazardous Material	2
12	Institution of Chemical Engineers (IChemE)	2
13	Current Opinion in Chemical Engineering	1
14	International Symposium on Advances in Technology Education	1
15	Journal of European Industrial Training	1
16	Occupational Health and Safety	1
17	Journal of Professional Issues on Engineering Education and Practice	1
18	Procedia Engineering	1
19	Science and Engineering Ethics	1
20	IIE Transactions on Occupational Ergonomics and Human Factor	1
21	AICHE Journal	1
22	Chemical Engineering Education	1
23	Computers Chemical Engineering	1
24	Proceedings of the Canadian Engineering Education Association	1
25	Cognition, Technology and Work	1
26	Journal of Integrated Security Science	1
27	Reliability Engineering and System Safety	1
28	Q Science Proceedings	1
29	Procedia Computer Science	30
30	Computers and Industrial Engineering	1

3.2 Process safety research found in scientific literature

Research in the literature on process safety is a crucial strategy for encouraging the advancement of cutting-edge technology and scientific understanding in the process industry. Process safety research contributes to the development of solutions for existing industrial problems, which advances the process industry. The study of process safety research includes equipment design, chemistry, human factors, hazard identification and risk analysis, and asset integrity and reliability. According to Gibson (1999), Schmidt (2013), and Meyer (2015), these research areas foster process safety competencies, which are essential for prevent major & minor accidents in the process industry. [6]

Table 2 - Process safety research domain found in scientific literature

Scientific research	Reference
Fire and explosion studies, Design	Gibson, 1999
Chemistry related courses and Process control	Mannan et al., 1999
Safety performance and sustainability	Willey, 1999. Knegtering and Pasman, 2009, Pfeil et al.,2013, Schonbucher et al., 2013
Risk analysis and Management	Lundin and Jonsson, 2002
Process safety education	McKay et al., 2011, Schonbucher et al., 2013
Asset integrity and reliability, Chemistry related courses, Design, Hazard identification and risk analysis, Human factor, Incident management, Risk management, Safety culture, Process safety management knowledge	Mannan,2012, Amyotte, 2013, Pasman et al., 2014
Chemistry related courses, Design, Fire and explosion studies, Hazard identification and risk analysis, Risk decision making, Security, Safety performance indictor	Mannan, et al., 2012
Asset integrity and reliability, Chemistry related courses, Design, Fire and explosion studies, Hazard identification and risk analysis, Human factor, Incident management, Risk management, Safety culture, Safety management	Pasman et al., 2014
Safety management	Nesheim and Gressgard, 2014, Krause, 2016
Hazard identification and risk analysis, Incident management	Vechot et al., 2014
Design, Hazard identification and risk analysis	Dee et al., 2015, Meyer, 2015

Bretherick's Handbook of Reactive Chemical Hazards (6th edition), which covers the full spectrum of relevant published literature up to 1999, is by no means a replacement for this succinct synopsis. Bretherick's Handbook is extensive and may be perceived as unwieldy, potentially deterring individuals who ought to be acquainted with its significant material. An overview of some typical organic and inorganic explosion dangers is provided, including those involving the nitro, hydrazide, and azido groups, the perchlorate ion, peroxides, acetylides, and fulminates. [7]

4. TOXICITY HAZARDS:

The potential risks that materials or chemicals may pose to the environment, wildlife, or human health because of their toxic qualities are known as toxicity hazards. These risks can

result from coming into touch with chemicals, biological agents, or physical agents that can have negative consequences when consumed, inhaled, or come into contact with the skin, among other exposures. The material, concentration, exposure time, and the particular vulnerabilities of the organism impacted can all effect toxicity.

Common categories of toxicity hazards:

1. Chemical Toxicity
2. Physical Toxicity
3. Biological Toxicity
4. Environmental Toxicity

Routes of Exposure:

- Inhalation: Breathing in toxic gases, dust, fumes, or vapors can affect the respiratory system and the body's ability to function.
- Ingestion: Swallowing toxic substances can damage the gastrointestinal tract or be absorbed into the bloodstream.
- Dermal Contact: Skin contact with hazardous chemicals can lead to burns, rashes, or absorption of toxins into the bloodstream.
- Injection: Less common, but some hazardous substances can enter the body through puncture wounds or other means.

4.1 Toxicity Severity:

Toxicity severity calculation involves determining the potential harm a substance can cause based on its concentration, exposure route, and the duration of exposure. This process typically uses standardized measures and models to estimate the severity of a toxic substance's effects on health or the environment.

Following key factors in toxicity severity:

1. Dose: The amount of the toxic substance that an organism is exposed to.

The dose units depend on the method of delivery. The dosage for drugs that are injected or consumed directly into the body is expressed in milligrams of the agent per kilogram of body weight. This makes it possible for researchers to extrapolate findings from little animals, like mice, who have body weight fractions of a kilogram to people, who weigh roughly 70 kg for men and 60 kg for women. The dosage for gaseous airborne chemical is expressed in milligrams of agent per cubic meter of air (mg/m3) or parts per million (ppm).

2. Exposure Route: The way the substance enters the body through inhalation, ingestion, injection and dermal.

3. Exposure Duration: The length of time an organism is exposed to the toxic substance.

Acute exposure - Short-term exposure, typically less than 24 hours.

Chronic exposure - Long-term, often repeated exposure over months or years.

Sub-chronic exposure: Intermediate-term exposure, typically 1 to 90 days.

4.2 Lethal Dose (LD50):

LD is known as Lethal Dose is the amount of substance that is tested and can result in the death of a test animal. Most often available in safety data sheets provided by chemical supplier. LD50 is the single dose of a material which on the basis of laboratory tests is expected to kill 50% of a group of test animal. LD50 is expressed in terms of mg or g of material per kg of animal body weight (mg/kg or g/kg)

Table 3 – Packaging group and hazard assignments of liquid

Sr. No.	Packing Group	Oral Toxicity LD_{50} (mg/kg)	Dermal Toxicity LD_{50} (mg/kg)	Inhalation toxicity by dusts and mists LC_{50} (mg/L)
1	I	≤5.0	≤50	≤0.2
2	II	>5.0 and ≤50	>50 and ≤200	>0.2 and ≤2.0
3	III	>50 and ≤300	>200 and ≤1000	>2.0 and ≤4.0

Example- 1: Omkar is exposed to phenol when opening a flange and it splashed all over his body. A source model determined that 0.5 kg was released and assumed that all of it splashed on the person. Calculate the LD50 dose based on the omkar weight of 105 kgs.

Solution: The LD50 value reported in the Fisher scientific SDS is 630 mg/kg.

LD50 = 630mg/kg * 105 kg = 66150 mg = 0.066 kg

LD50 value is 0.066 kg and personnel were exposed to 0.5 kg. i.e Phenol is a highly toxic dermal hazard.

4.3 Lethal Concentration (LC50)

LC is known as Lethal Concentration of a gas, vapor, mist that is tested and can result in the death of a test animal. The LC50 is expressed as parts of material per million parts of air, by volume (ppm) for gases and vapors or as micrograms of material per liter of air (micro-g/L) or milligrams of material per cubic meter of air (mg/m3) for dusts and mists as well as for gases and vapors.

Inhalation toxicity refers to the potential for a substance to cause harm when inhaled, which can result in various acute or chronic health effects depending on the chemical properties, exposure levels, and the duration of exposure. When assessing the risk of inhalation toxicity for hazardous materials, packing groups and hazardous zones are used as part of classification systems to ensure proper handling, transportation, and safety precautions.

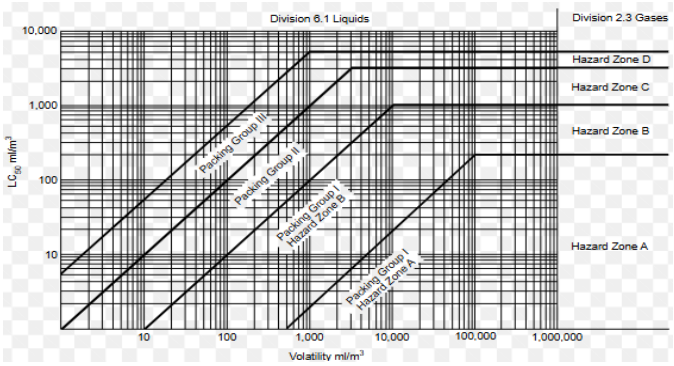

Figure 1 – Inhalation toxicity: Packing Group and hazard zones

Sr. No.	Hazard Zone	Inhalation Toxicity
1	Hazard Zone A	LC_{50} less than or equal to 200 ppm
2	Hazard Zone B	LC_{50} greater than 200 ppm and less than or equal to 1000 ppm.
3	Hazard Zone C	LC_{50} greater than 1000 ppm and less than or equal to 3000 ppm.
4	Hazard Zone D	LC_{50} greater than 3000 ppm or less than or equal to 5000 ppm.

Table 4 – Packaging group and hazard assignments of liquid

Example-2: Determine the toxicity of Methyl Isocyanate?

Solution: Toxicity is also function of vapor pressure

Vapor pressure @ 25°C = 61.5 kPa

Boiling point = 39°C

Volatility (ml/m3) (vol%) = (Pvap * 10^6) / 101.325

_____(01)

V = 606,958 ml/m3

By referring figure 1,

LC50 = 40 ppm (Hazard Zone A, based on the packaging group and hazard assignment)

4.4 Threshold Limit Values (TLV)

The minimum value on the response versus dose curve is referred to as the threshold dose. The American Conference of Governmental Industrial Hygienists (ACGIH) has set threshold doses known as threshold limit values (TLVs) for numerous chemical substances. These TLVs represent airborne concentration levels that are considered safe, indicating that no significant adverse health effects are anticipated over a worker's lifetime. This exposure is limited to standard working hours, specifically eight hours a day, five days a week. Previously, the TLV was referred to as the maximum allowable concentration (MAC). Occupational Safety and Health Administration (OSHA) has established a specific threshold dose known as a permissible exposure level (PEL). A commonly referenced quantity is the level that poses an immediately dangerous to life and health (IDLH). It is essential to avoid any exposure to this level or higher under all circumstances.

There are three different types of TLV –

4.4.1 Threshold Limit Value – Time weighted average (TLV-TWA) - The time-weighted average for a standard 8-hour workday or a 40-hour work week is designed to ensure that most workers can be exposed to it consistently, day after day, without experiencing negative effects. Temporary exceedances of this limit are permissible as long as they are balanced by periods of exposure below the limit.

4.4.2 Threshold Limit Value - Short-term exposure limit (TLV-STEL) - Short-term exposure limit refers to the highest concentration of a substance that workers may be exposed to for a continuous duration of up to 15 minutes without experiencing severe irritation, long-term or irreversible damage to tissues, or a level of narcosis that significantly raises the risk of accidents, hinders self-rescue efforts, or substantially decreases work efficiency. It is important to note that no more than four exposure instances are allowed in a single day, with a minimum interval of 60 minutes between each exposure, and the daily time-weighted average (TLV-TWA) must not be surpassed.

4.4.3 Threshold Limit Value-Ceiling - The concentration that should not be exceeded, even instantaneously.

Threshold limit value determined by using below equation, TLVs are expressed for vapors in ppm (parts per million by volume), mg/m3 (milligrams of vapor per cubic meter of air) and for dusts, mg/m3 or mppcf (millions of particles per cubic foot of air).

Concentration in ppm = Cppm = (22.4 / M) (T / 273) (1 / P)

(mg/m3) _____(02)

= 0.08205 (T / P M) (mg/m3)

_____(03)

Where, T is the temperature in degrees kelvin,

P is the absolute pressure in atm,

M is the molecular weight in g/mol

Table 5 – TLVs and PELS for a few of Chemical Substances

Sr. No.	Chemical Name	TLV – TWA		OSHA PEL	
		ppm	mg/m3 @ 25°C	ppm	mg/m3 @ 25°C
1	Acetaldehyde	100	180	200	360
2	Benzene	10	30	1	3
3	Chlorine	0.5	1.5	1	3
4	Dioxane	25	90	100	360
5	Ethylamine	5	9.2	10	18
6	Fluorine	1	2	0.1	0.2

4.4.4 Evaluating exposure to single toxicants substance by monitoring

A straightforward approach to assess worker exposures involves the continuous monitoring of air concentrations of toxic substances in the workplace. To calculate the time-weighted average (TWA) concentration from the continuous concentration data C(t), the following equation is utilized.

$$TWA = (1/8) \int C(t)\, dt \quad \text{_____(4)}$$

$$TWA = \frac{C_1T_1 + C_2T_2 + \cdots + C_nT_n}{8\ \text{hr}}. \quad \text{_____(5)}$$

Where, T is the exposure time in hour

C is the concentration in ppm

Example-3: Determine the 8-hr TWA worker exposure if the worker is exposed to benzene vapors as follows:

Duration of exposure (hr) (T)	Measured concentration (ppm) (C)
2	110
2	330
4	90

Solution:

TWA = ((110*2) + (330*2) + (90*4))/ 8 = 155 ppm

Because the TLV-TWA for benzene is 10 ppm, the worker is overexposed. Additional control measures need to be developed.

4.4.5 Evaluating exposure to multiple toxicants substance by monitoring

In situations where multiple chemicals are present in the workplace, a common approach is to consider the effects of these toxic substances as cumulative. The overall exposure from various toxicants, each with distinct TLV-TWAs, can be calculated using a following equation.

$$\sum_{i=1}^{n} \frac{C_i}{(\text{TLV-TWA})_i}, \quad \text{_____(6)}$$

Where, n is the total number of toxicants,

Ci is the concentration of chemical i with respect to the other toxicants,

(TLV-TWA) is the TLV-TWA for chemical species i.

If the sum in equation 06 exceeds 1, then the workers are overexposed.

$$(\text{TLV-TWA})_{\text{mix}} = \frac{\sum_{i=1}^{n} C_i}{\sum_{i=1}^{n} \frac{C_i}{(\text{TLV-TWA})_i}}. \quad \text{_____(7)}$$

Where, n is the total number of toxicants,

Ci is the concentration of chemical i with respect to the other toxicants,

(TLV-TWA) is the TLV-TWA for chemical species i.

If the sum of the concentrations of the toxicants in the mixture exceeds this amount, then the workers are overexposed.

Example-4: Air contains 5 ppm of benzene (TLV-TWA of 10 ppm), 20 ppm of dioxane (TLV-TWA of 25 ppm), and 10 ppm of ethylamine (TLV-TWA of 5 ppm). What is the mixture TLV-TWA and has this level been exceeded?

Solution: By using equation 06,

(TLV-TWA) mix = (5/10) + (20/25) + (10/5)

= 3.3 ppm

Because this quantity is greater than 1, The workers are overexposed under these circumstances.

By using equation 07,

(TLV-TWA) mix = (5+20+10) / ((5/10) + (20/25) + (10/5))

= 10.6 ppm

The total mixture concentration is 5 + 20 + 10 = 35 ppm. The workers are overexposed under these circumstances

4.4.6 Evaluating exposure to multiple toxic dust substance by monitoring

Toxicological theory indicates that the dust particles posing the highest risk to lung health typically fall within the respirable size range of 0.2 to 0.5 micrometers. Particles exceeding 0.5 micrometers generally do not reach the lungs, while those smaller than 0.2 micrometers tend to settle too slowly and are predominantly exhaled.

Dust evaluation calculations are conducted in the same way as those for volatile vapors. However, rather than employing ppm as the unit of concentration, it is more practical to use mg/m3 or mppcf (millions of particles per cubic foot).

$$\text{TLV of mixture} = \frac{1}{\frac{C_1}{\text{TLV}_1} + \frac{C_2}{\text{TLV}_2}} \quad \text{_____(8)}$$

Where, Ci is the concentration of chemical i with respect to the other toxicants,

TLV is the for chemical species i.

Example-5: Determine the TLV for a uniform mixture of dusts containing the following particles?

Sr. No.	Type of dust	Concentration (Wt %)	TLV (mppcf)
1	Nonasbestiform talc	70	20
2	Quartz	30	2.7

Solution: By using equation 08,

(TLV-TWA) mix = 1 / ((0.70/20) + (0.30/2.7))

= 6.8 mppcf

Special control measures will be required when the actual particle count exceeds 6.8 mppcf.

4.5 Toxic Risk Screening Criteria

The following acute toxic screening criteria is typically used for safety screening:

- Emergency Response Planning Guidelines (ERPG) for all air contaminants.
- Immediately Dangerous to Life and Health levels (IDLH) established by NIOSH
- Emergency Exposure Guidance Levels (EEGLs) and short-term public emergency guidance levels (SPEGLs) issued by the National Academy of Sciences/National Research Council
- Acute Exposure Guideline Level (AEGL) – a toxic endpoint promulgated by the US EPA as part of the Risk Management Process (RMP)
- Protective Action Criteria (PAC) – a database published by the US Department of Energy containing ERPG, AEGL and Temporary Emergency Explosion Guideline (TEEL) values for hazardous chemicals.

4.6 Emergency Response Planning Guidelines (ERPG)

- The American Industrial Hygiene Association listed down a set of concentration values for ERPG that has been accepted with industry and government.
- ERPG 1: This indicates the maximum airborne concentration below which all the individuals can be exposed up to 1 hour without experiencing any effects other than mild health effects.
- ERPG 2: This indicates the maximum airborne concentration below which all the individuals can be exposed up to 1 hour without any serious health effects that can reduce or decrease their ability to take protective action.
- ERPG 3: This indicates the maximum airborne concentration below which all the individuals can be exposed up to 1 hour without developing any life-threatening health effects.

Determine the ERPG toxicity value of the mixture by using below equation, ERPG are expressed for vapors in ppm (parts per million by volume)

ERPG mixture = $1 / \Sigma (y_i / \text{ERPG } i)$ _____(9)

Where, yi is the vapor fraction (Relative volatility) of individual components

ERPG values of individual components.

Example-6: Calculate the equivalent ERPG -3 toxicity value for 50/50% ammonia (ERPG-3 = 1500 ppm) and chlorine (ERPG-3 = 20 ppm) mixture stored at 25°C.

Sr. No.	Chemical Name	Mixture Fraction	Vapor Fraction (Relative Volatility)
1.	Ammonia	0.5	0.85
2.	Chlorine	0.5	0.15

Solution:

By using equation no. 09,

ERPG -3 mixture = 1 / ((0.85 / 1500) + (0.15 / 20))

= 124 ppm

5. FLAMMABILITY HAZARDS:

Chemical industry used number of flammable materials with large quantity of the flammable substance in the manufacturing process. Flammable materials can easily ignite and cause fires. They can be solids, liquids, or gases, and are commonly found in chemical process industry. Flammable materials can be dangerous, if not handled properly. Ignition, explosion, vapors cloud explosion, oxidizing hazards associated with flammable materials. Initially phase of research and development stage of any manufacturing

process identifies the flammable hazards in the process and handle the process with appropriate design system [14]

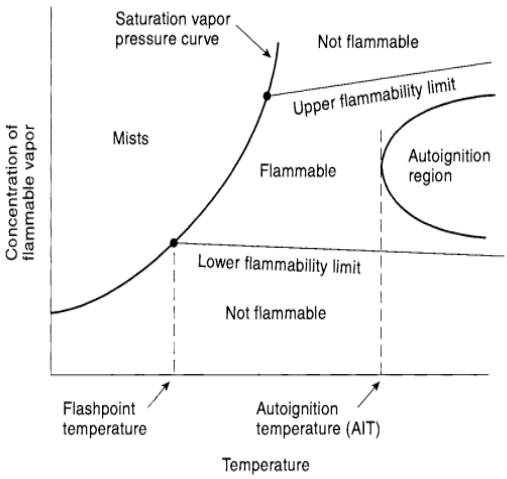

Figure 2 - Relationships between various flammability properties

Autoignition temperature: Auto-ignition temperature is the lowest temperature at which the fuel will spontaneously ignite in a normal atmosphere without an external source of ignition such as a flame or spark.

5.1 Flash point criteria for evaluating flammable risk –

The flash point temperature is one of the major quantities used to characterize the fire and explosion hazard of liquids. The flash point of a liquid is the lowest temperature at which it gives off enough vapor to form an ignitable mixture with air. The flash point generally increases with increasing pressure. The two most commonly used methods are open cup and closed cup, depending on the physical configuration of the experimental equipment. Early phase of research and development work, experimental cost of flash point determination is high for all flammable components and all mixture present in the process.

Fire point: The fire point is the lowest temperature at which a vapor above a liquid will continue to burn once ignited; the fire point temperature is higher than the flash point.

Table 6 – Hazard classification based on the flash point data

HAZARD CLASSIFICATION FOR FLAMMABLE LIQUIDS				
Sr. No.	**Class**	**Flash Point**	**Boiling Point**	**Examples**
1.	I – A	Below 73°F (23°C)	Below 100°F (38°C)	Diethyl ether, pentane, ligroin, petroleum ether
2.	I – B	Below 73°F (23°C)	at or above 100°F (38°C)	Acetone, benzene, cyclohexane, ethanol
3.	I – C	73-100°F (24-38°C)	--	p-xylene
HAZARD CLASSIFICATION FOR COMBUSTIBLE LIQUIDS				
4.	II	101-140°F (39-60°C)	--	Diesel fuel, motor oil, kerosene, cleaning solvents
5.	III - A	141-199°F (61-93°C)	--	Paints (oil base), linseed oil, mineral oil
6.	III - B	200°F (93°C) or above	--	Paints (oil base), neatsfoot oil

Satyanarayana and Rao showed that the flash point temperatures for pure materials correlate well with the boiling point of the liquid. [15]

$$T_f = a + \frac{b(c/T_b)^2 e^{-c/T_b}}{(1 - e^{-c/T_b})^2},$$

_____(10)

Where Tf, is the flash point temperature (K),

a, b, and c are constants provided in Table-7 (K)

Tb, is the boiling point temperature of the material (K).

Table 7 – Constant used for the predicting the flash point

Sr. No.	Chemical group	A	B	C
1.	Hydrocarbons	225.1	537.6	2217
2.	Alcohols	230.8	390.5	1780
3.	Amines	222.4	390.5	1900
4.	Acids	323.2	416.6	2970
5.	Ethers	275.9	600.1	2879
6.	Sulfur	238.0	577.9	2297
7.	Esters	260.8	449.2	2217
8.	Ketones	260.5	296.0	1908
9.	Halogens	262.1	414.0	2154
10.	Aldehydes	264.5	293.0	1970
11.	Phosphorus-containing	201.7	416.1	1666

12.	Nitrogen-containing	185.7	432.0	1645
13.	Petroleum fractions	237.9	334.4	1807

5.2 Flash point of mixtures –

Flash points of the mixture is also important component for identify the flammability hazards in the process. If only one of the components is combustible and flash point is known in a two components mixture then flash points of mixtures can be approximated. Flash point of mixture temperature is calculated by determining the temperature at which the vapor pressure of the flammable component in the mixture is equal to the pure component vapor pressure at its flash point. If multicomponent mixtures with more than one flammable component then recommended to determine the experimentally flash point of the mixture. [14]

Example-7 – Methanol has a flash point of 54°F, and its vapor pressure at this temperature is 62 mm Hg. What is the flash point of a solution containing 75% methanol and 25% water by weight?

Solution:

Sr. No.	Compound Name	M.W. (g/mol)	Weight (%)	Moles	Mole fraction
1	Water	18	25	1.39	0.37
2	Methanol	32	75	2.34	0.63
			Total	**3.73**	**1.00**

By using Raoult's Law, calculate vapour pressure of methanol,

P = X * P vap. _____(11)

P vap = X / P = 62/0.63 = 98.4 mm Hg

Where, X = Mole fraction of pure components

P = Partial pressure of component

P vap = Partial vapour pressure of pure component

By using graph of vapor pressure vs temperature shown flash point of the solution is 20.5°C.

5.3 Flammability Limits

Flammability limits are the main properties that represent flammability characteristics of specific fuels. Vapor-air mixtures will ignite and burn only over a well-specified range of compositions. The mixture will not burn when the composition is lower than the lower flammable limit (LFL); the mixture is too lean for combustion. The mixture is also not combustible when the composition is too rich; that is, when it is above the upper flammable limit (UFL). A mixture is flammable only when the composition is between the LFL and the UFL. Commonly used units are volume percent fuel.

20-L spherical apparatus used for experimentally determine the flammability data by using the American standard ASTM E-681 test method. Early phase of research and development work, experimental flammability data determination cost is high as well as time taken activity. Theoretical determine the flammability limit of the chemicals to identify the preliminary flammability hazards.

5.3.1 Flammability Limit of single component -

Flammability limit of well-known solvents and chemicals data easily available in MSDS and literature, but few chemical data not available in any literature. Theoretical determine the flammability limit of the chemicals to identify the flammability hazards. [21]

Following few methods for determine the theoretical flammability limits -

Stoichiometric concentration –

LFL = 0.55 Cs _____(12)

UFL = 3 Cs _____(13)

UFL = 3.5 Cs _____(14)

Where, Cs is stoichiometric concentration.

Example - 8, Ethanol's stoichiometric reactions are:

1 C2H5OH + 3 O2 + 11.28 N2 →2 CO2 + 3 H2O + 11.28 N2.

For this reaction, Cs = 6.54%. Using Eq. (12) and (13), LFL = 3.59% and UFL = 19.62%.

Alternative,

The stoichiometric concentration for most organic compounds is determined using the general combustion reaction

$$C_mH_xO_y + zO_2 \rightarrow mCO_2 + \frac{x}{2}H_2O$$

$$LFL = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1} \quad \text{_____(15)}$$

$$UFL = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1} \quad \text{_____(16)}$$

Combustion enthalpy -

LFL = – 4354 /ΔHc _____(17)

Where, ΔHc is combustion enthalpy (kJ/mol)

Example-9, ethanol has a combustion enthalpy of –1281 kJ/mol, LFL is 3.39%.

Alternative,

$$LFL = \frac{-3.42}{\Delta H_c} + 0.569\Delta H_c + 0.0538\Delta H_c^2 + 1.80, \quad \text{_____(18)}$$

$$UFL = 6.30\Delta H_c + 0.567\Delta H_c^2 + 23.5, \quad \text{_____(19)}$$

Vapor pressure –

LFL = (Pf / P0)× 100 _____(20)

Where, Pf is the fuel vapor pressure at flashpoint

P0 is standard atmospheric pressure.

Example-10, The flash point of ethanol is 13°C. At this temperature, it has a vapor pressure of 28 mmHg with P0 = 760 mmHg, LFL = 3.68%.

Algebraic method -

LFL = 100 / (1 + Na) _____(21)

Where, Na is the number of moles of air per mole of fuel in the mixture at LFL.

Example-11, for ethanol, the reactants are

1 C2H5OH + 3 O2 + 11.28 N2. LFL obtained is 3.29%.

5.3.2 Flammability Limit Dependence on Temperature -

The flammability range increases with temperature. If the temperature increases, the lower flammability limits should decrease, while the upper flammability limits should increase. [18,19]

The following empirically derived equations are available for vapors:

$$LFL_T = LFL_{25} - \frac{0.75}{\Delta H_c}(T - 25) \quad \text{_____(22)}$$

$$UFL_T = UFL_{25} + \frac{0.75}{\Delta H_c}(T - 25), \quad \text{_____(23)}$$

Where, /ΔHc is the net heat of combustion (kcal/mole) and T is the temperature ("C).

5.3.3 Flammability Limit Dependence on Pressure –

Pressure has little effect on the LFL except at very low pressures (< 50 mm Hg absolute), where flames do not propagate. [20]

The UFL increases significantly as the pressure is increased, broadening the flammability range. An empirical expression for the UFL for vapors as a function of pressure is available.

UFL, = UFL + 20.6(log P + I), _____(24)

Where, P is the pressure (megapascals absolute) and UFL is the upper flammable limit (volume % of fuel plus air at 1 atm).

5.3.4 Flammability Limits of Mixture –

Flammability of the mixture is also important component for identify the flammability hazards in the process. These mixture limits are computed using the Le Chatelier equation [14]

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}}, \quad \text{_____(25)}$$

Where, LFLi is the lower flammable limit for component i (in volume %) of component i in fuel and air, yi is the mole fraction of component i on a combustible basis, and n is the number of combustible species.

$$UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}}, \quad \text{_____(26)}$$

Where, UFLi is the upper flammable limit for component i (in volume %) in fuel and air,

yi is the mole fraction of component i on a combustible basis, and

n is the number of combustible species.

5.3.4 Limiting Oxygen Concentration (LOC) –

Oxygen is the key components and there is a minimum oxygen concentration required to propagate a flame. This is an especially useful result, because explosions and fires can be prevented by reducing the oxygen concentration regardless of the concentration of the fuel.

The LOC has units of % of moles of oxygen in total moles. If experimental data are not available, the LOC is estimated using the stoichiometry of the combustion reaction and the LFL.[14]

$$LOC = \left(\frac{\text{moles fuel}}{\text{total moles}}\right)\left(\frac{\text{moles } O_2}{\text{moles fuel}}\right) = LFL\left(\frac{\text{moles } O_2}{\text{moles fuel}}\right) \quad \text{_____(27)}$$

Example - 12

$$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O.$$

Moles of O2 = 6.55, Moles of Butane = 1

LFL – 1.9% by volume

LOC = 12.4 vol % Oxygen

5.3.5 Limiting Oxygen Concentration of Mixture –

LOC of the mixture is also important component for identify the flammability hazards in the process. [17]

$$(\mathrm{LOC})_{\mathrm{mixt.}} = \sum x_i R_i / \sum x_i / L_i^* = \sum x_i R_i / \sum x_i R_i / (\mathrm{LOC})_i \quad \text{_____(28)}$$

$$(\mathrm{LOC})_{\mathrm{mixt.}} = (x_a R_a + x_b R_b) / \left[(x_a R_a / (\mathrm{LOC})_a) + (x_b R_b / (\mathrm{LOC})_b) \right] \quad \text{_____(29)}$$

Where, Ri is stoichiometric molar ratio of oxygen to fuel of component i and Xi is mole fraction of component i and LOCi is limiting oxygen concentration of component i.

6. CONCLUSION:

Preliminarily identify the hazards of the substance and process by conducting the literature review and past process safety incidents. Evaluating the risk assessment based on the availability of process safety literature data and learning from the past catastrophic incidents. This review article highlights the critical nature of nitro compounds and the nitration reaction in the incidents involving Yibin Hengda explosion, Aarti chemical plant explosion, and Tianjiayi Chemical explosion. For literature on process safety, consult articles and conference papers from reputable professional organizations, as well as data from Bretherick's handbook. In this review article, we assess the toxicity and flammability risks associated with both single-component and multi-component mixtures. This evaluation involves the theoretical calculation of LC50, TLV, and ERPG values to determine the toxic hazards present. The objective is to ascertain the theoretical flammability parameters, including flash point, flammability limits, and LOC values, in order to recognize potential flammability hazards. Based on this theoretical data, removed hazardous materials from the process and replaced them with non-hazardous alternatives during the design phase of the inherently safe process at the R&D stage. Considering the risks associated with hazardous materials, such as explosiveness, toxicity, and flammability, suitable personal protective equipment (PPE) was utilized, along with effective administrative and engineering controls to ensure a safe design for commercial implementation.

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