

SAFETY IN CHEMICAL AND PROCESS INDUSTRIES: A COMPREHENSIVE ASSESSMENT

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Safety in Chemical and Process Industries: A Comprehensive Assessment

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CONTENTS

PREFACE	i
CHAPTER 1 INTRODUCTION TO CHEMICAL SAFETY IN CHEMICAL AND PROCESS INDUSTRIES	1
INTRODUCTION	1
RISK IN CHEMICAL AND PROCESS INDUSTRIES	2
SAFETY MEASURES IN CHEMICAL AND PROCESS INDUSTRIES	9
PRIMARY AND SECONDARY REACTIONS	9
BATCH AND CSTR SYSTEMS	11
EXPLOSOPOHORE GROUPS	17
CHETAH METHOD	18
First Criterium	19
Second Criterium	25
Third Criterium	25
Fourth Criterium	26
ACKNOWLEDGEMENT	27
REFERENCES	27
CHAPTER 2 THEORY OF THERMAL EXPLOSIONS	28
INTRODUCTION	28
RUNAWAY PHENOMENON	28
SEMENOV THEORY	30
Adiabatic Case.....	30
<i>Autocatalysis</i>	36
<i>Non-Adiabatic Case</i>	37
THERMAL INERTIA	45
ACKNOWLEDGEMENT	49
REFERENCES	49
CHAPTER 3 CALORIMETRIC TECHNIQUES FOR THERMOKINETIC CHARACTERIZATION	50
INTRODUCTION	50
Adiabatic Calorimetry	50
US SADT TEST	59
SCANNING CALORIMETRY	63
ACKNOWLEDGEMENT	72
REFERENCES	72
CHAPTER 4 HOMOGENEOUS EXPLOSIONS	73
INTRODUCTION	73
STUDY OF EXPLOSIONS IN GAS AND VAPOUR SYSTEMS	74
AUTOIGNITION TEMPERATURE	78
Low-Temperature Oxidation Mechanism (250°C-300°C)	80
Intermediate Temperature Oxidation Mechanism (350°C-450°C).....	82
High Temperature Oxidation Mechanism (T>450°C).....	83
ACKNOWLEDGEMENT	89
REFERENCES	90
CHAPTER 5 HETEROGENEOUS EXPLOSIONS I	91
INTRODUCTION	91
THE FIRE TRIANGLE	91
Flammability Test	92
Flammability Limits in Air	97
ACKNOWLEDGEMENT	101
REFERENCES	101

CHAPTER 6 HETEROGENEOUS EXPLOSIONS II	102
INTRODUCTION	102
FLAMMABILITY LIMITS	102
LE CHATELIER'S EQUATIONS	107
FLASH POINT AND UPPER TEMPERATURE	111
FLASH POINT OF A MIXTURE OF LIQUID FUELS	115
MINIMUM OXYGEN CONTENT	119
ACKNOWLEDGEMENT	124
REFERENCES	125
CHAPTER 7 HETEROGENEOUS EXPLOSIONS III	126
INTRODUCTION	126
TRIANGULAR FLAMMABILITY DIAGRAM	126
Nose-type Flammability Diagrams	128
MINIMUM IGNITION ENERGY	129
QUENCHING DIAMETER	133
ACKNOWLEDGEMENT	136
REFERENCE	136
CHAPTER 8 CONSEQUENCES OF HETEROGENEOUS EXPLOSIONS AND FIRES	137
INTRODUCTION	137
CONFINED EXPLOSIONS	137
MECHANICAL EXPLOSIONS	145
EXPLOSIONS SUPPORTED BY CHEMICAL REACTIONS	147
VAPOUR CLOUD EXPLOSION	148
TNT-EQUIVALENCY METHOD	150
POOL FIRE AND DOMINO EFFECT	160
Pool Fire	160
BLEVE	165
ACKNOWLEDGEMENT	169
REFERENCES	169
CHAPTER 9 TOXICOLOGY AND INDUSTRIAL HYGIENE	170
INTRODUCTION	170
Toxicology	170
NUMERICAL SIMULATIONS	172
N-OCTANOL /WATER PARTITION COEFFICIENT	176
ANIMAL TESTING	177
Dose-Response Curve and Probit Model	179
Threshold Limit Values	182
INDUSTRIAL HYGIENE	184
MATERIAL SAFETY DATA SHEETS	184
ACKNOWLEDGEMENT	188
REFERENCE	188
CHAPTER 10 PREVENTIVE AND PROTECTIVE MEASURES	189
INTRODUCTION	189
INERTIZATION PROCEDURES	189
Vacuum Purging	190
Pressure Purging	192
Sweep-Through Purging	193
Siphon Purging	194
VENTILATION	195
Source Models	197
PROTECTIVE MEASURES	205
GENERAL APPROACH FOR DIMENSIONING THE VENT AREA	213
PRACTICAL METHOD FOR DIMENSIONING VENTING SYSTEM	219
FIRE CLASSES	219
ACKNOWLEDGEMENT	222

REFERENCES	222
CHAPTER 11 THE RISK ASSESSMENT APPLIED TO INDUSTRIALLY CONTAMINATED SITES	223
INTRODUCTION	223
CONTAMINANTS AND TRANSPORT MECHANISMS	225
THE RISK ANALYSIS FOR CONTAMINATED SITES	226
Management Steps	266
The Risk Assessment	228
Individual and Cumulative Risk	234
EXERCISE	238
RISK ASSESSMENT SOFTWARE	241
REMEDICATION TECHNOLOGIES	241
ACKNOWLEDGEMENT	243
REFERENCES	243
CHAPTER 12 THE HEALTH IMPACT ASSESSMENT WITHIN ENVIRONMENTAL IMPACT ASSESSMENT STUDIES	245
INTRODUCTION	245
THE ENVIRONMENTAL IMPACT ASSESSMENT (EIA)	246
The Legislative Framework at European Level	248
The EIA Report	248
THE HEALTH IMPACT ASSESSMENT (HIA)	251
Human Health and its Determinants	251
HIA Main Features	255
Health Impact Assessment within EIA Studies	257
<i>The HIA Procedure in Italy: a Case Study</i>	258
CONCLUSIVE REMARKS	261
ACKNOWLEDGEMENT	262
REFERENCES	262
SUBJECT INDEX	286



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PREFACE

Nowadays, huge amounts of chemicals are commercialized, shipped, stored, and converted to ensure the commercial availability of goods for daily use. Different hazards are involved in the use of these chemicals due to their intrinsic physicochemical properties, such as flammability, explosibility, and toxicity. Several accidents such as explosions, fires, and toxic exposure occurred in the past due to these hazards in chemical and process industries and serious consequences for people, buildings, and the environment resulted from these accidental events.

The present e-book has been developed in the framework of the European project “Erasmus+ Programme – Strategic Partnership SAFENGINE (Project Nr: 2020-1-RO01-KA203-080085)”. The book has been designed for Bachelors and Masters’ students in chemical, materials, and environmental engineering, chemistry, environmental science, and related disciplines. The possible audience of this book also includes PhD students and experts with a background in chemical and/or environmental engineering. It provides basic knowledge of safety procedures and experimental techniques for evaluating risks related to the storage, transport, and transformation of hazardous materials. To regard safety issues within industrial plants from a broader perspective, the e-book discusses the management of contaminated industrial sites, focusing on risk assessment to set remediation goals. Moreover, as the design and realization of most of these industrial plants undergo the Environmental Impact Assessment (EIA) procedure, their operation may turn out to be a relevant scenario for the preventive evaluation of the wider health implications. To this end, the course will also approach the Health Impact Assessment within EIA studies.

The book is organized as follows. Fundamentals of thermal explosions and calorimetric techniques are presented in Chapters 1-3. Homogeneous and heterogeneous explosions are described in detail in Chapters 4-7. Consequences of fires and heterogeneous explosions are introduced in Chapter 8, along with selected approaches to properly estimate damages related to these accidents in chemical and process industries. Basic knowledge of industrial hygiene and toxicology in the chemical industry is provided in Chapter 9. Preventive safety measures (*i.e.*, inertization and ventilation of working environments) and protective measures (*i.e.*, venting and use of extinguishing agents) are presented in Chapter 10 as an approach to reduce the risk related to potentially dangerous

chemicals in chemical and environmental processes. The risk assessment applied to industrially contaminated sites is fully presented in Chapter 11. Finally, the health impact assessment within environmental impact assessment studies is described in Chapter 12.

The chemical and environmental safety procedures thoroughly discussed in the present book aim at addressing many of the Sustainable Development Goals (SDGs) formulated in 2015 by the United Nations General Assembly.

More in detail, theoretical principles and practical examples of safety approaches are provided to meet the following targets:

- Goal 3 (*i.e.*, “Good health and well-being”). A reduction in illnesses and deaths from hazardous chemicals and pollution may arise by adopting the safety procedures and assessments reported in Chapter 10, 11, and 12.
- Goal 6 (*i.e.*, “Clean water and sanitation”). An improvement in water quality, wastewater treatment and safe reuse, along with increased protection of water-related ecosystems may result from the application of the chemical and environmental approaches described in Chapter 9, 10, 11, and 12.
- Goal 7 (*i.e.*, “Affordable and clean energy”). An expansion and upgrade of energy services may arise from the safe management of energy companies. In this regard, the basic principles of explosions and fires reported in Chapters 1-8 should be known to properly design and control industrial work environments.
- Goal 8 (*i.e.*, “Decent work and economic growth”). The overall content of the present book aims at improving resource efficiency in consumption and production (*i.e.*, Chapters 1÷8) and promoting safe working environments (Chapters 9÷12).
- Goal 9 (*i.e.*, “Industry, Innovation, and Infrastructure”). The overall book content seeks to promote inclusive and sustainable industrialization.
- Goal 12 (*i.e.*, “Responsible consumption and production”) The following specific targets are covered in the present book: i) achieving the environmentally sound management of chemicals and waste throughout their life cycle; ii) reducing waste generation through prevention, reduction, recycling, and reuse; iii) encouraging companies to adopt sustainable practices.
- Goal 14 (*i.e.*, “Life below water”) and Goal 15 (*i.e.*, “Life on land”). The safe practices regarding the proper management of thermally unstable substances and toxic chemicals reported in this book aim at protecting terrestrial and marine ecosystems.

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CHAPTER 1**Introduction to Chemical Safety in Chemical and Process Industries**

Abstract: Accidental events in chemical and process industries may have catastrophic consequences. The present chapter aims at discussing the hazards and risks in chemical and process industries, where chemical species are used and/or transformed. After defining the concept of chemical risk, the possible accidental events in the process industry are presented based on their probability of occurrence. Some examples of relevant chemical accidents that occurred in the past are thoroughly discussed further. Safety measures (*i.e.*, preventive and protective procedures) in safety and process industries and primary and secondary reactions are also described. Finally, a screening method capable of providing a hazard evaluation by calculating the power released during the thermal decomposition of a substance (*i.e.*, the CHETAH method) is presented.

Keywords: Accidents, Risk, Probability, Primary and Secondary Reactions, Chetah Method.

INTRODUCTION

Although not frequently, even at the beginning of the third millennium, accidents still happen in the process industry. Governmental agencies (*e.g.*, the US Chemical Safety Board) and private associations provide up-to-date databases reporting accidents in chemical and process industries in different countries and their consequences. In 2012, the European Parliament approved the **European directive 2012/18** to reduce the frequency of occurrence and mitigate the consequences of chemical accidents. An in-depth knowledge of the specific site, the properties of the substances used, the equipment and the safety measures to be adopted are needed to comply with the **European Directive 2012/18**. More in detail, this directive applies to all sites where **dangerous substances** are employed in quantities greater than a fixed threshold value [1]. As a chemical plant consists of hundreds of devices, it is necessary to understand on what equipment the attention should be focused on to carry out a detailed and appropriate safety analysis [2].

This approach can be implemented by means of the so-called **index methods** in which, based on the values assumed by certain indices, the equipment to be submitted to a more detailed analysis is selected.

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Once the equipment is identified, suited procedures should be applied to evaluate in what incidental scenarios the system may be involved (see the examples below).

All incidents in process and chemical industries evolve in three phases:

1. Initiation: it represents the event that initiates the accidental event.
2. Propagation: it represents the phase allowing the accidental event to evolve.
3. Termination: it represents the event that stops the accident.

The intrinsic properties of the substances are as follows:

- Flammability.
- Explosivity.
- Toxicity.

The intrinsic properties cannot be eliminated. However, their manifestation can be prevented.

RISK IN CHEMICAL AND PROCESS INDUSTRIES

In order to properly define accidental scenarios, it is necessary to know the consequences of accidents and the probabilities of their occurrence. This approach is part of the risk analysis [1, 2].

The risk of accidental events is the product between the impact of likelihood (*i.e.*, P, probability) and the impact of magnitude (*i.e.*, M, consequence):

$$R = P \cdot M^{\alpha} \quad (1)$$

where α is an amplification superscript value (>1) accounting for the impact of the accidental event on public opinion.

To decrease the risk, the probability or the magnitude (or both) has to be reduced.

Example 1

A jacketed reactor, in which an exothermic reaction is carried out and cooling water flows to remove the heat generated, is considered in Fig. (1).

The reactor is batch-type with respect to A and continuous with respect to B (*i.e.*, fed-batch reactor).

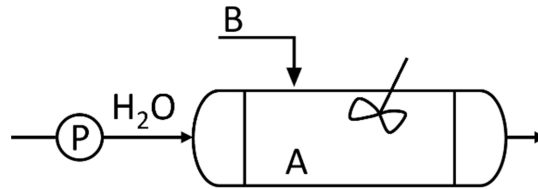


Fig. (1). Example of chemical reactor: batch mode with respect to A; continuous mode with respect to B.

The following procedures to identify and analyze incidental scenarios can be employed:

1. Hazop.
2. “What if” analysis.

According to the “What if” analysis, the following questions are considered: what happens if the cooling pump breaks? What happens if the actual supply flow rate of B is greater than its project flow rate?

The result of this analysis is the identification of possible accidental scenarios and safety measures to reduce the frequency of occurrence and/or the consequences of accidents in chemical and process industries.

For example, a temperature sensor could be inserted for the previous reactor (see Fig. (2)) so that, as soon as the temperature exceeds a certain value, the alarm sound starts up and a technician activates an auxiliary cooling circuit or closes a valve that interrupts the supply of B:

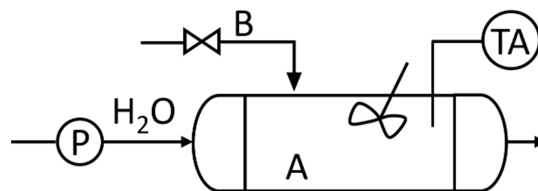


Fig. (2). Example of reactor endowed with temperature sensor.

By means of logical procedures (*i.e.*, the “event tree” and the “fault tree”, see Fig. (3)) an initiating event, such as the rupture of the pump, is set. Subsequently, a chain of events that can lead to an explosion is generated:

Theory of Thermal Explosions

Abstract: The theory on thermal explosions according to Semenov's approach is thoroughly described in this chapter. The main calorimetric tests to be carried out for a safe thermal analysis are also reported. The thermal inertia is defined and its effects on the characterization of reactive chemical systems is evaluated.

Keywords: Adiabatic Condition, Non-Adiabatic Case, Runaway Phenomenon, Semenov Theory, Thermal Inertia.

INTRODUCTION

Thermal explosions occur in chemical systems due to the presence of thermally unstable substances that decompose at certain temperatures, releasing high amounts of energy and gas [1].

The following conditions are needed for a thermal explosion to occur:

- An exothermic reaction that is capable of developing heat during its evolution.
- A runaway phenomenon (*i.e.*, a system overheating) since the power generated is greater than the power exchanged with the surroundings.
- A pressure increase due to the generation of gases by the reaction and/or the increase in vapour pressure of the liquid mixture.

RUNAWAY PHENOMENON

As shown in Fig. (1), an anomaly causing an incomplete heat removal occurs in the cooling system at t_0 time.

Subsequently, the rate of the heat released by the reaction and the temperature increase resulting in a further increase of the reaction rate. This dependence can be easily predicted based on the kinetic constant dependence on the temperature [2].

The reaction rate may be expressed by the following law:

$$v = k_0 \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(C) \quad (1)$$

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Where:

k_0 = Pre-exponential factor.

E = Activation energy of the reaction.

$f(C)$ = Function of the reagent concentration.

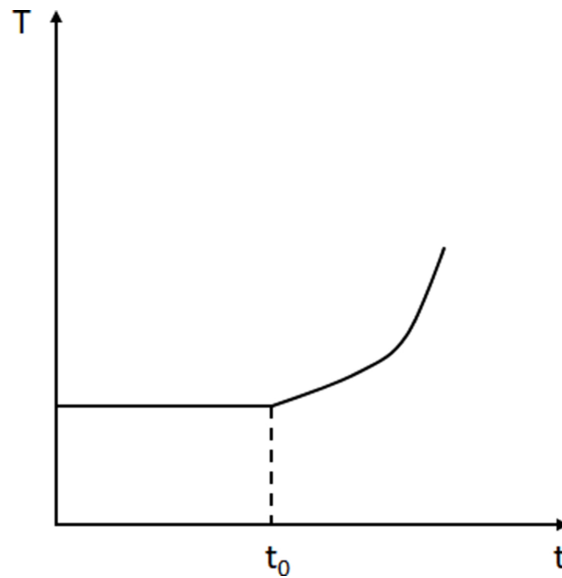


Fig. (1). At $t = t_0$ a runaway phenomenon occurs.

If no significant pressure increases happen during this event, no explosions occur.

However, the production of gaseous species is often associated to a runaway phenomenon, resulting into a pressure increase.

The following exothermic reaction can be considered:



The thermal power generated by this reaction can be evaluated by using the following equation:

$$P_G = V \cdot v \cdot Q \quad (2)$$

Where:

V = Volume of the reacting mass.

v = Reaction rate (moles/ volume·time).

Q = Heat developed by the reaction (energy/moles).

SEMENOV THEORY

The Semenov theory [1] has been developed in the following two parts:

1. Under adiabatic conditions.
2. When heat exchange is allowed.

Adiabatic Case

A substance defined as potentially hazardous based on preliminary screenings (*i.e.*, by using the CHETAH method) should be submitted to further experimental assessment *via* calorimetric tests under adiabatic conditions.

This theory considers a generic exothermic reaction A (reagent) \rightarrow P (product) occurring under adiabatic conditions.

If this is the case, the (T, t) diagram reported in Fig. (2) can be considered:

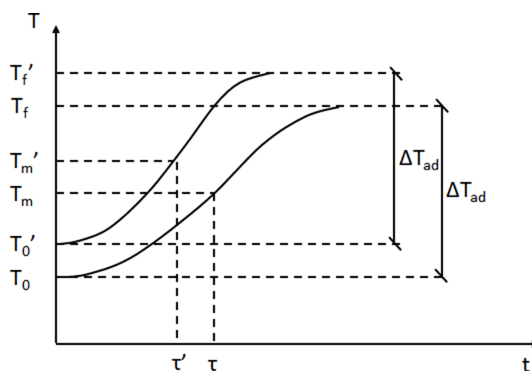


Fig. (2). Thermogram for identifying the time to maximum rate.

where:

T_0 = Starting temperature.

T_f = Final temperature achieved when all the reagent is consumed.

Calorimetric Techniques for Thermokinetic Characterization

Abstract: Calorimetric techniques allow us to evaluate the kinetics and heat developed during a reaction. In this chapter, adiabatic and scanning calorimeters are presented. An application of adiabatic calorimetry to evaluate Self Accelerating Decomposition Temperature (SADT) is also presented.

Keywords: Adiabatic Calorimetry, Scanning Calorimetry, Sadt Determination, Dta, Dsc.

INTRODUCTION

Calorimetric studies enable complete kinetic and thermodynamic analyses of thermal decomposition reactions [1].

Two different approaches may be employed to characterize the thermal behavior of a chemical system:

- Adiabatic calorimetry;
- Scanning calorimetry.

Adiabatic Calorimetry

Adiabatic calorimeters are used to observe the behaviour of the investigated systems in the worst conditions. Until a few decades ago, in order to achieve adiabatic conditions, heat exchange was prevented by using materials with low exchange coefficients and increasing their thickness.

Indeed, the exchanged power P_S can be estimated as follows:

$$P_S = U \cdot a \cdot (T - T_E) \quad (1)$$

Where:

U is the global heat transfer coefficient.

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a is the surface area through which the heat transfer takes place.

$T - T_E$ is the driving force.

Modern adiabatic calorimeters (*i.e.*, **Accelerating Rate Calorimeters, ARC**) try to reduce the $T - T_E$ driving force [1].

ARC calorimeters try to keep the driving force nearly zero during the run. The layout of an ARC calorimeter is reported in Fig. (1).

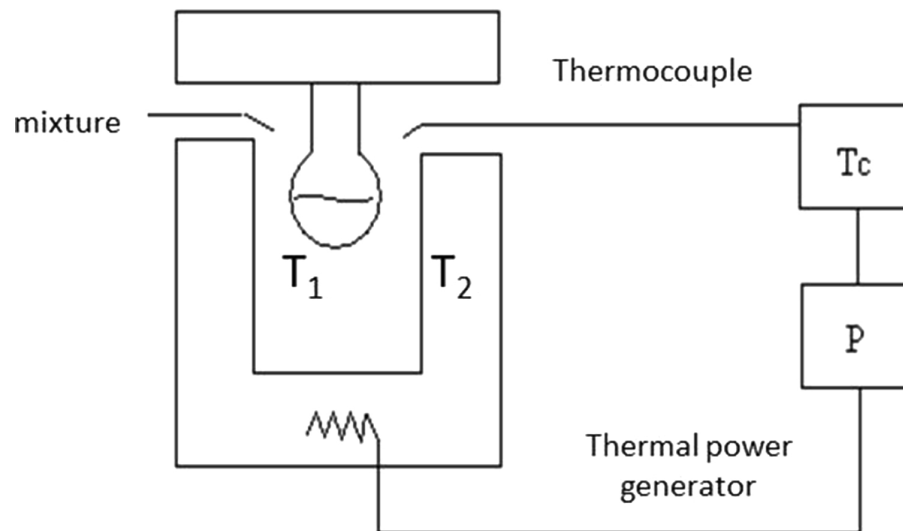


Fig. (1). ARC calorimeter scheme.

In the area where the chemical system is inserted, heat is developed so that T rises.

A thermocouple reads the T_1 temperature of the reacting mixture container and compares its value with the T_2 temperature of the surrounding walls.

If $T_1 > T_2$, a heat exchange occurs.

If $T_1 \approx T_2$, no heat exchange occurs.

The walls of the calorimeter contain electric resistances connected to an electric power generator.

A controller measures and compares T_1 and T_2 . As T_1 increases, it activates the power generator to ensure that T_2 increases accordingly.

An interesting feature of the instrument is that it is equipped with a pressure transducer. Consequently, it is possible to obtain a pressure-time diagram, in addition to the temperature-time trace (Fig. 2).

On the other hand, ARC calorimeters present the following drawbacks:

- ARC devices are not suitable for quick thermal decomposition reactions ($\frac{dT}{dt} > 10^\circ\text{C}/\text{min}$): In this case, instrument electronics cannot immediately ensure that $\Delta T \approx 0$;
- Reacting mixture containers are metallic (steel or titanium). They are very small (volume of about 5 millilitres). Possible catalytic effects may be observed during calorimetric tests.

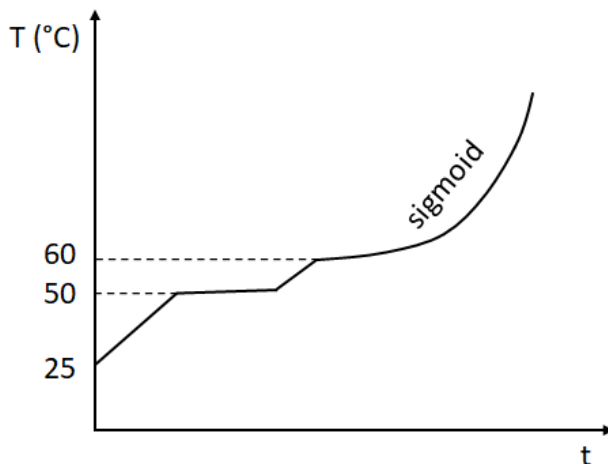


Fig. (2) Thermogram obtained during an ARC test.

To carry out calorimetric tests correctly, it is necessary to know (at least approximately) the temperature at which the system shows reactivity. The system is initially provided with a certain amount of heat which can cause a temperature increase from ambient value to one which has been chosen on the basis of literature indications. Once this temperature is reached, the system waits a certain time so that everything is balanced, switching off the generator. $\frac{dT}{dt}$ value is calculated in a certain time interval and it is compared with a threshold value, which is typically about $0.02^\circ\text{C}/\text{min}$:

Homogeneous Explosions

Abstract: Gas and vapour explosions can be classified as homogeneous and heterogeneous. Homogeneous explosions are characterized by an autoignition temperature and a delay time to ignition.

Keywords: Homogeneous Explosion, Heterogeneous Explosion, Autoignition Temperature, Delay to Ignition.

INTRODUCTION

The classification of possible explosions in process industry is reported in Fig. (1).

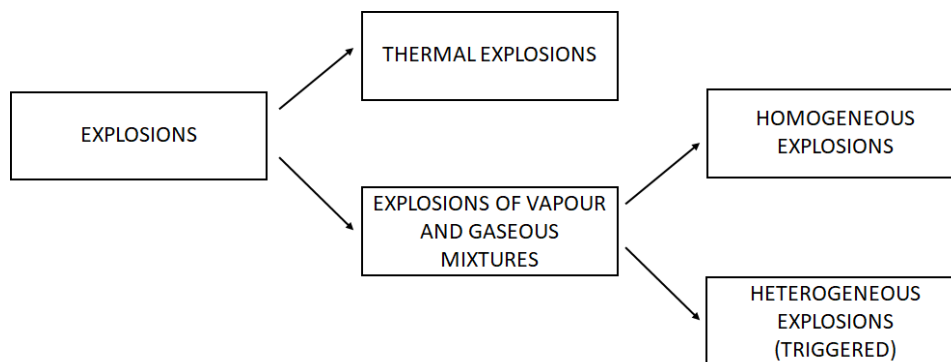


Fig. (1). Classification of possible explosions in process industry.

Thermal explosions affect liquids and solids, and their occurrence does not require the presence of an ignition source.

Triggered explosions concern mixtures of gases and vapors and require the presence of a mixture of fuel and oxidizer. In this case, a luminous zone appears and spreads by supplying energy at a certain point of the mixture containing a flammable species. As a result, over time, the mixture is increasingly affected by a flame propagation phenomenon.

If the same mixture is brought to a temperature higher than the surroundings in the absence of a conventional triggering (for example, spark, little flame, *etc.*), a luminous phenomenon always occurs instantly affecting the whole gaseous volume.

STUDY OF EXPLOSIONS IN GAS AND VAPOUR SYSTEMS

Therefore, gas and vapour explosions are divided into two categories [4]:

- Homogeneous explosions in which the flame instantly affects the entire volume;
- Heterogeneous explosions in which the flame first appears in a certain zone of the mixture and then extends to the whole volume (flame propagation phenomenon).

Homogeneous explosions are nominally classified as not triggered. However, high temperatures could be considered as the trigger of the gas/vapour mixture.

In case of homogeneous explosions, there is a common general trend of the pressure against the temperature as reported in Fig. (2).

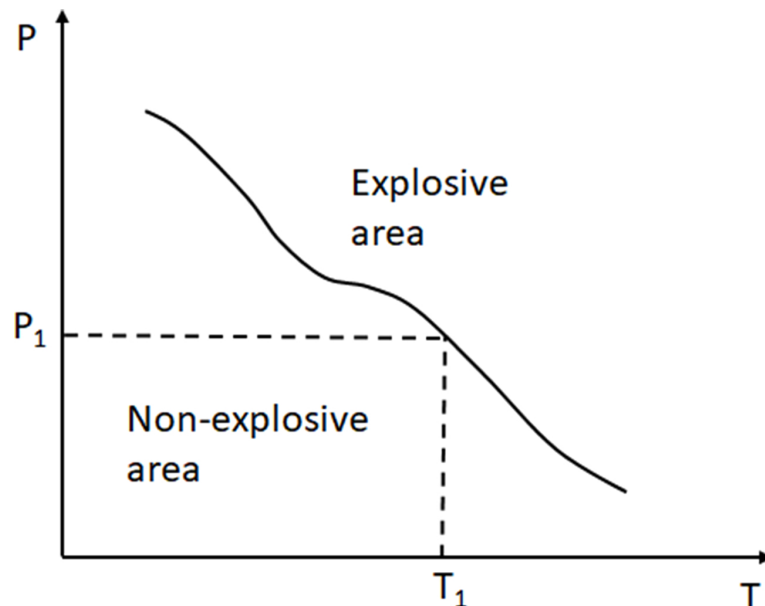


Fig. (2). Explosive and non-explosive areas.

The plane is divided into two areas by the curve: an explosive zone and a non-explosive zone, in which the curve is the geometric locus of the points representing boundary values of temperature and pressure.

At a fixed pressure P_1 , the system produces a homogeneous explosion only if the corresponding temperature reaches a value a little higher than T_1 .

T_1 is defined as **autoignition temperature** T_{Ai} [4].

However, it is noteworthy that for temperature values lower than T_{Ai} , the system is reactive, but the rates of the reaction are rather contained so that no explosive phenomena occur.

Some examples of common substances such as benzene, ethylbenzene and toluene showing this behaviour are reported in Fig. (3).

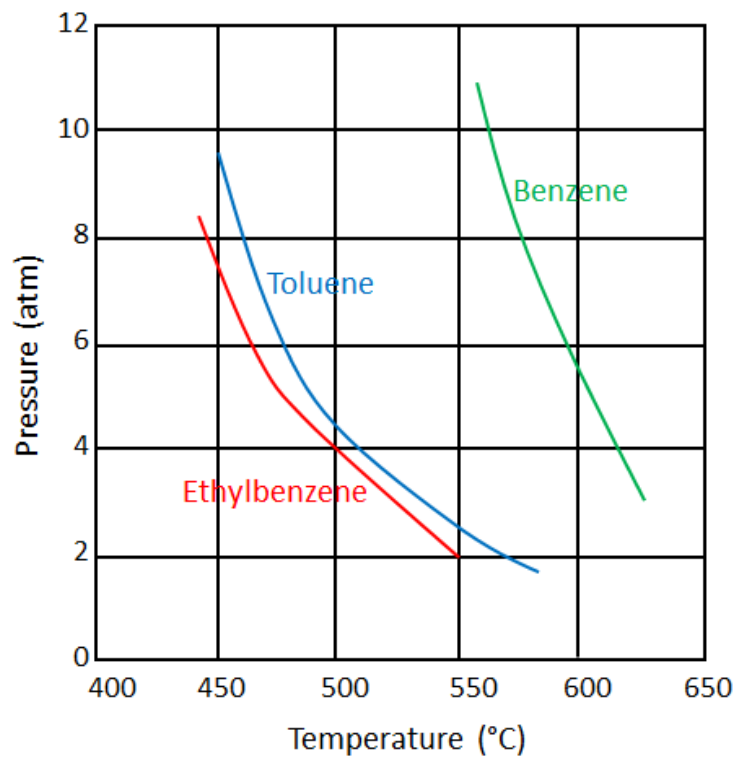


Fig. (3). Diagram Pressure-temperature for Benzene, toluene and ethylbenzene.

It is necessary to underline that when a system is not explosive, it doesn't mean that it is not reactive: there is a zone called slow oxidation where the systems can also be reactive, but reaction rates are rather contained to not lead to an explosive phenomenon.

CHAPTER 5**Heterogeneous Explosions I**

Abstract: Heterogeneous explosions are very common accidental typologies in chemical and process industries. The lower and upper flammability limits are presented in the present chapter. These threshold values differ depending on the mixture composition, as reported in detail.

Keywords: Heterogeneous Explosion, Fire Triangle, Flammability Test, Lower Flammability Limit, Upper Flammability Limit.

INTRODUCTION

Heterogeneous explosions are very common in the chemical industry.

Their typical phenomenology involves a luminous phenomenon that appears at a certain point of the mixture and then expands in the whole volume.

An ignition source located in the surroundings of this primary point provides the energy required to trigger the explosion.

Heterogeneous explosions are very different from autoignition phenomena and occur only if the local ignition source is present.

A complete prevention of explosive phenomena by eliminating all possible ignition sources cannot be ensured, as undisclosed ignition sources may be present.

THE FIRE TRIANGLE

As shown in Fig. (1), three conditions are necessary, but not sufficient, to have heterogeneous explosions [2]:

1. A fuel should be present;
2. An oxidizing agent or air should be present;
3. An ignition source should trigger the combustion reaction.
4. The fuel must be present in a certain concentration under the **flammability range**.

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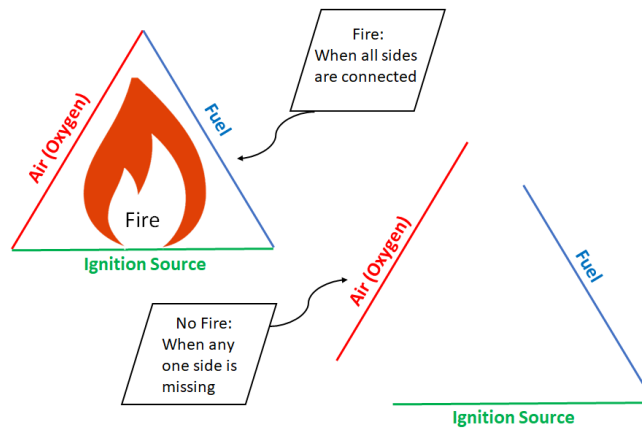


Fig. (1). The fire triangle.

In some cases no explosions occur even if all those three conditions are verified since a further condition should be satisfied:

Flammability Test

The following testing tube is commonly employed to evaluate phenomena related to heterogeneous explosions:

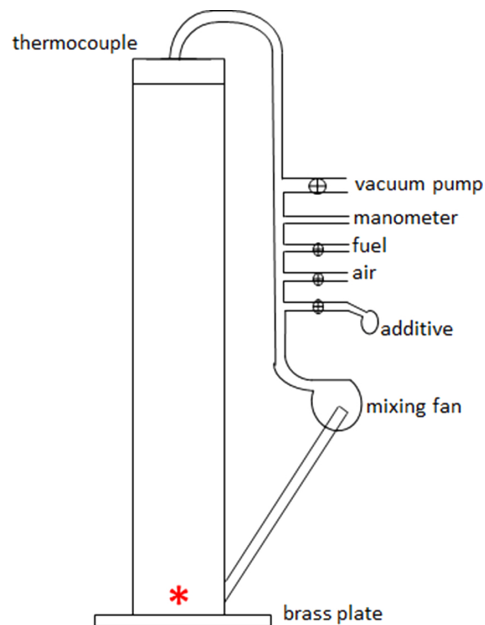


Fig. (2). Glass tube for flammability test.

The use of a glass tube allows an accurate cleaning after each test and lets the operator check the phenomenon progression inside the tube.

The glass tube has a length of about 150 centimeters and a diameter of about 10 centimeters.

At the beginning of the test, the tube is totally closed and is put in connection with a vacuum pump. Vacuum conditions are necessary to guarantee the complete elimination of air and the regulation of oxygen concentration to a fixed value.

Thanks to the small taps reported in Fig. (2), air and fuel are fed in a specific ratio. A small fan is used to homogenize the mixture in the tube and obtain the same concentration of fuel and air at each point of the vessel.

The system should be open during the explosion in order to avoid the tube rupture by increasing the pressure inside it.

As an example, the behaviour of a methane-air mixture can be considered.

After creating vacuum conditions, methane is fed and the fan homogenizes the mixture to obtain a fuel concentration of about 1 vol.%.

An ignition source is needed to trigger the reaction. The trigger should be located near the tube side that has been opened to avoid vessel rupture.

This outlet let all gases produced by the combustion out of the vessel. The trigger can be represented by the ignition candle of a combustion engine (*i.e.*, a small electrical circuit emitting a spark with a certain quantity of energy).

With a methane concentration in air of about 1 vol.%, no explosions occur.

The experiment can be repeated several times by using the following procedure:

1. Creating vacuum conditions;
2. Preparing the mixture at a fixed fuel concentration;
3. Homogenizing the mixture in the vessel;
4. Opening the tube on one side before triggering.

By fixing a methane concentration in air of 5 vol.%, a bright area (*i.e.*, the flame) appears in the surroundings of the ignition point:

Heterogeneous Explosions II

Abstract: Flammability limits depend on different parameters, such as pressure and flame propagation direction. In the present Chapter, Le Chatelier's equations and the Flash Point and Upper temperature are presented. The Minimum Oxygen Content is also defined.

Keywords: Flammability limits, Le Chatelier's equations, Flash Point temperature, Upper temperature, Minimum Oxygen Content.

INTRODUCTION

As reported in Chapter 5, heterogeneous explosions may occur only if the three required components of the fire triangle (*i.e.*, combustible, comburent, and ignition source) are present. Moreover, each component should have specific values for the heterogeneous explosion to happen. More in detail, the volume percentage of combustible should belong to a flammability range and the oxygen content should exceed a minimum value. The flammability of the vapours in equilibrium with a liquid combustible stored in a tank can also be evaluated by estimating the Flash Point and Upper temperature, as reported below.

FLAMMABILITY LIMITS

Flammability limits also depend on pressure. Indeed, different values of LFL and UFL may be observed at a pressure higher than the atmospheric pressure. Table 1 reports literature data on the effect of the starting pressure of a mixture on the flammability range.

The lower flammability limits do not depend on the starting pressure. On the other hand, an increase in the upper flammability limits is observed with increasing pressure, thus extending the flammability range. A remarkable increase in the upper flammability limit is observed for methane-air mixtures with increasing starting pressure.

For practical purposes, it is noteworthy to remember that increasing values of temperature and pressure result in a lower level of safety. Indeed, wider flammability ranges and higher likelihoods of explosive phenomena occur with

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rising temperature and pressure conditions. Preventing the formation of flammable mixtures is the best approach to avoid irreversible explosive phenomena [1].

Table 1. Variation in flammability limits as a function of pressure.

GAS PAIR	PRESSURE		
	10 atm	50 atm	124 atm
Hydrogen - air	10.1 - 68.7	10.0 - 73.3	9.9 - 75.0
Methane - air	5.9 - 17.2	5.7 - 29.5	5.7 - 45.5

By considering a testing tube in which the ignition source is located close to the outlet, three different flame propagation directions may be adopted (Fig. 1):

1. Upward: the flame moves from the bottom to the upper part of the tube.
2. Downward: the flame moves from the upper part to the bottom of the tube.
3. Horizontal: the tube's direction is parallel to the ground plane.

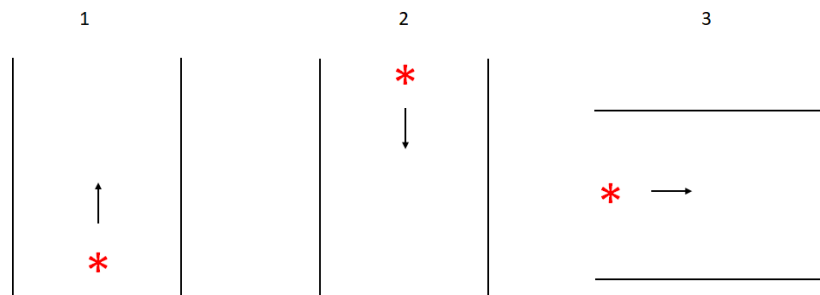


Fig. (1). Different propagation directions to the flame in a testing tube.

Table 2 reports the data obtained in experiments on the flammability limits of a methane-air mixture at ambient temperature and atmospheric pressure depending on the flame propagation direction. Small differences in the flammability limits may be observed in three cases.

Table 2. Flammability limits of methane in air depending on the flame propagation direction.

TUBE DIAMETER (cm)	PROPAGATION		
	UPWARD	HORIZONTAL	DOWNWARD
2.5	5.80 - 13.20	6.20 - 12.90	6.30 - 12.80
5.0	5.40 - 14.25	5.65 - 13.95	6.12 - 13.25
7.5	5.35 - 14.85	5.40 - 13.95	5.95 - 13.35

It is necessary to show dependence of the flammability limits on the starting temperature of the mixture. In particular, the following expressions may be employed:

$$\text{LFL}_T = \text{LFL}_{25} - \frac{0.75}{|\Delta H_C|} (T - 25) \quad (1)$$

$$\text{UFL}_T = \text{UFL}_{25} + \frac{0.75}{|\Delta H_C|} (T - 25) \quad (2)$$

Where T is the temperature expressed in °C and ΔH_C is the combustion enthalpy given in Kcal/mol.

$$\text{If } T > 25 \Rightarrow -\frac{0.75}{|\Delta H_C|} (T - 25) \text{ has negative values} \Rightarrow \text{LFL}_T < \text{LFL}_{25}.$$

Fig. (2) shows an example of diagrams regarding the flammability limits that can be easily found in the literature survey [1]. It reports on the effect of the starting temperature on the flammability limits of ammonia in the air at atmospheric pressure (the different symbols indicate measurements performed by different researchers). As the starting temperature increases, the flammability range extends.

Heterogeneous Explosions III

Abstract: Triangular flammability diagrams are herein presented as useful tools to evaluate the flammability of air-combustible mixtures. The nose-type diagrams and the Minimum Ignition Energy are also described in the following chapter.

Keywords: Triangular Flammability Diagram, Nose-Type Diagrams, Minimum Ignition Energy, Quenching Diameter, Flame Arrester.

INTRODUCTION

By referring once again to the fire triangle presented in Chapter 6, heterogeneous explosions may occur only if an ignition source is present. Moreover, a minimum ignition energy is required for the explosion to take place. Besides the fire triangle, another complex and more detailed tool (*i.e.*, the triangular flammability diagram) maybe employed to evaluate the flammability of all possible ternary mixtures made of air and comburent. In addition, the NOSE-type diagrams are used to evaluate the volume percentage of inert gas to be employed in order to inhibit the flame propagation phenomenon.

TRIANGULAR FLAMMABILITY DIAGRAM

To have a complete picture of the behavior of a ternary mixture formed by fuel, oxygen, and an inert, triangular flammability diagrams may be used (Fig. 1):

Triangular flammability diagrams provide several information on the flammability of the infinite possible ternary mixtures made of a comburent, a combustible, and an inert gas at $T=25^{\circ}\text{C}$ and $P=1$ atm. Indeed, data on MOC and flammability limits are available in the literature survey only for a limited number of mixtures.

As shown in Fig. (1), the three vertexes of the triangle refer to the pure elements (*i.e.*, fuel, inert species, and comburent). The sides represent the binary mixtures of the two pure components at the corresponding vertexes. The internal points of the triangle represent ternary mixtures.

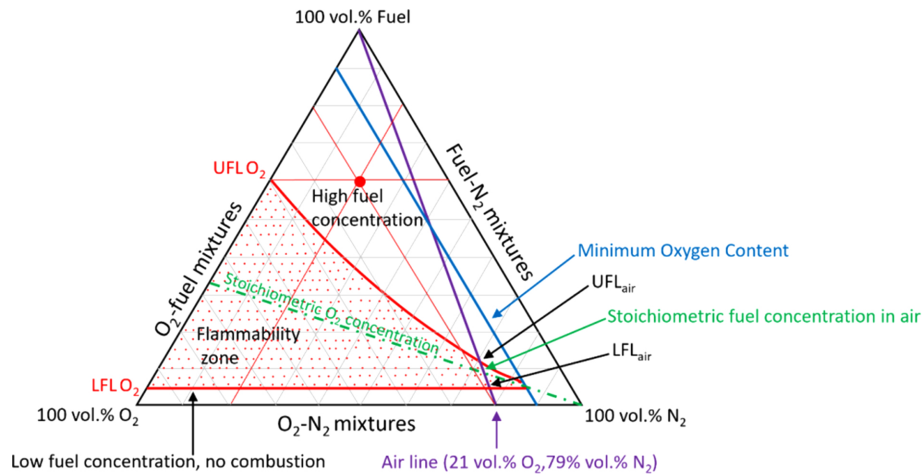


Fig. (1). Triangular flammability diagram of different possible fuel O_2 - N_2 mixtures ($T=25^\circ\text{C}$ and $P=1$ atm).

In order to evaluate the composition of ternary mixtures represented by the red point in Fig. (1), a simple procedure may be employed. By drawing three lines intersecting the red point and parallel to the triangle sides, the volume concentration of each pure component opposite to the parallel line can be evaluated. As an example, by drawing a line intersecting the red point and parallel to the side "O₂-fuel mixtures", a constant concentration of N₂ may be obtained, that is the N₂ concentration of the considered mixture.

The area filled with green dotted lines represents the flammability zone. On the oxygen-nitrogen side, the point representing the air composition is indicated in Fig. (1). The flammability zone may be obtained *via* experimental investigations.

By connecting the air point and the fuel vertex, the air line (purple) representing all possible air-fuel mixtures is obtained. Where the air line intersects the flammability zone, the flammability limits (*i.e.*, LFL and UFL) of the fuel in the air may be identified.

On the O₂-fuel side, that is where the N₂ concentration is zero, the LFL and UFL values in O₂ may be distinguished. By connecting the stoichiometric O₂ concentration with the N₂ vertex, the green dotted segment may be obtained. The intersection of this segment with the MOC line represents the vertex of the flammability zone.

By simply connecting the point representing a mixture with the air point, it can be concluded that an explosion in the air may occur if this segment crosses the flammability zone.

In conclusion, the triangular flammability diagram allows us to directly estimate the flammability risk of a gaseous mixture [1].

Nose-type Flammability Diagrams

By adding a certain quantity of inert species to a fuel-air mixture whose composition belongs to the flammability range, the flame propagation phenomenon may be inhibited. To this aim, the number of inert species to be added depends on the starting volumetric percentage of the fuel and the inert substance considered. The "**Nose-type diagrams**" are obtained by plotting the volume percentage of inert gas versus the volume percentage of fuel in air. An example of a nose-type diagram for methane-air mixtures in the presence of different inert gases is reported in Fig. (2). In the absence of additional inert gases (*i.e.*, when $x=0$), an LFL value of 5% and a UFL value of 15% may be obtained for the methane-air mixture, as previously reported. By increasing the inert gas percentage on the x-axis, the flammability range progressively narrows until no propagation phenomena may occur.

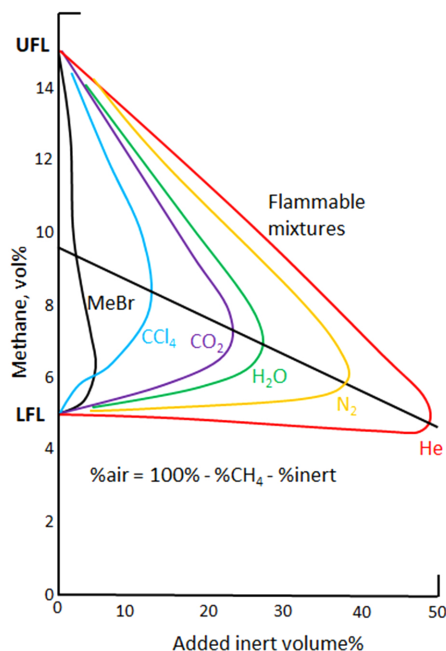


Fig. (2). Flammability limits of various methane-inert gas-air mixtures at $T=25^{\circ}\text{C}$ and $P=1\text{atm}$.

CHAPTER 8**Consequences of Heterogeneous Explosions and Fires**

Abstract: Heterogeneous explosions may occur in confined systems, thus leading to confined explosions. In the present chapter, mechanical and chemical explosions in confined and unconfined systems are considered, focusing the attention on their consequences by adopting the TNT-Equivalency method. Additional incidental typologies, such as Pool fire and BLEVE, are also described.

Keywords: Bleve, Chemical Explosion, Confined Explosions, Mechanical Explosion, Multi-Energy Method, Pool Fire, Tnt-Equivalency Method.

INTRODUCTION

The possibility of a heterogeneous explosion to occur in confined or unconfined environments leads to different possible accidental scenarios with potentially dangerous consequences for people and industrial facilities. Heterogeneous explosions may be classified in chemical explosions (*i.e.*, where a combustible is triggered in the presence of a comburent and an ignition source) and mechanical explosions (*e.g.*, explosions caused by the rupture of a tank containing a compressed inert gas). Several methods to evaluate the consequences of these accidental events are reported. Herein, the TNT-equivalency method is described in detail. Moreover, further incidental typologies, such as Pool fire and BLEVE, are presented.

CONFINED EXPLOSIONS

A heterogeneous explosion in a completely confined system is considered, that is, in a system in which the mixture is contained in a non-adiabatic vessel capable of withstanding the final pressure (*i.e.*, no vessel breakage occurs) [1].

The spherical vessel shown in Fig. (1) is considered.

Where r is the radius of the container and r_B is the radius of the sphere containing burnt gases at a time t after ignition.

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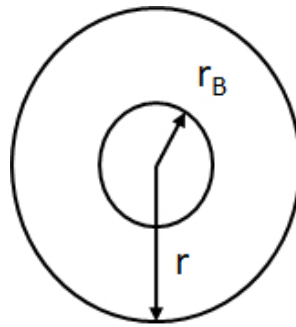


Fig. (1). Schematization of the flame propagation in a closed spherical vessel.

Vacuum is preventively created inside the vessel and then the flammable mixture is loaded at a fuel concentration in air within the flammable range. Initially, atmospheric pressure and ambient temperature conditions are adopted. The mixture is triggered from the center of the vessel by giving the mixture an amount of energy enough for the ignition of a deflagration phenomenon for the fuel adopted. In the case of a spherical container, gradually, a spherical reaction front expands at a speed lower than that of the sound in the same medium and its radius grows up r which is reached when the mixture is completely consumed.

From the phenomenological point of view, starting from the atmospheric initial pressure, the pressure trend *versus* time reported in Fig. (2) is observed, (P_M is the maximum pressure observed).

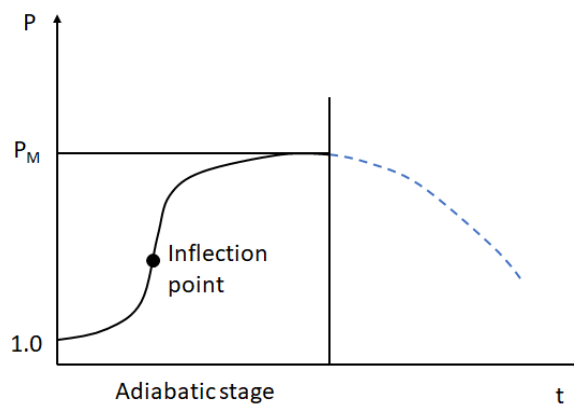


Fig. (2). Trend of pressure *versus* time measured inside a vessel during a confined explosion.

In the first stage, a sigmoid is observed, that is, a curve with an inflection point at which the derivative $\frac{dP}{dt}$ reaches a maximum. For longer reaction times, since the container is not adiabatic, the pressure trend is described by the blue dotted curve in Fig. (2).

Even for vessels with good heat exchange capacities, if the phenomenon is fast (*e.g.*, in the case of a combustion) the first stage until P_M can be considered as adiabatic because the time scale is very small.

An empirical law, known as cubic law, is associated to this phenomenon:

$$\frac{dP}{dt}(\max)V^{1/3} = K_G \quad (1)$$

With K_G being a constant. It is possible to use an approximate model to explain the cubic law.

It can be assumed that the relationship of Lewis-Von Elbe is valid:

$$\frac{P-P_I}{P_M-P_I} = \frac{m_B}{m_0} \quad (2)$$

Where:

- P is a generic pressure at time t ;
- P_I is the initial pressure;
- P_M is the maximum pressure;
- m_B is the mass of burnt gases;
- m_0 is the total initial mass.

P and m_B vary over time.

The relationship of Lewis-Von Elbe intuitively shows how, as the mass of burnt gases increases, P also increases. Therefore:

$$m_B = 0 \rightarrow P = P_I \text{ and } m_B \uparrow \rightarrow P \uparrow \quad (3)$$

The ratio between the masses can be assumed to be proportional to the ratio of the volume of the burnt gases and the volume of the sphere through a proportionality coefficient $\alpha = \frac{\rho_B}{\rho_0}$:

Toxicology and Industrial Hygiene

Abstract: In this chapter, the main routes of exposure to toxic chemicals and methods of eliminating them by the human body are presented. In particular, both defense and biotransformation mechanisms are described. The threshold limit values (TLV) and Material Safety Data Sheets are also introduced.

Keywords: Biotransformation, Industrial Hygiene, Material Safety Data Sheets, N-Octanol-Water Partition Coefficient, Toxicology, Threshold Limit Values.

INTRODUCTION

Toxic substances are chemicals capable of exerting adverse effects on biological organisms. Toxicity is thus an important property of substances that may cause damage to the human body.

Toxicology

Toxicology examines the way the uptake of toxic substances may occur in living organisms (*e.g.*, contact, stomach, and inhalation). The toxic effect of hazardous chemicals on both ecosystems and human health is also considered, along with the possible defense mechanisms (*i.e.*, excretion or accumulation) [1].

As reported in Fig. (1), four different routes of exposure to toxic chemicals may be distinguished:

1. Ingestion: eating and drinking may allow the chemicals to enter the body.
2. Inhalation: chemical species may be deposited in the alveoli of human lungs, potentially interfering with respiratory and cardiovascular functions.
3. Skin absorption: in this case, the uptake depends on skin permeability and chemical species.
4. Injection: injection of chemicals may occur through syringes or wounds already present on the skin.

In the presence of toxic substances, the following preventive and protective measures are commonly adopted:

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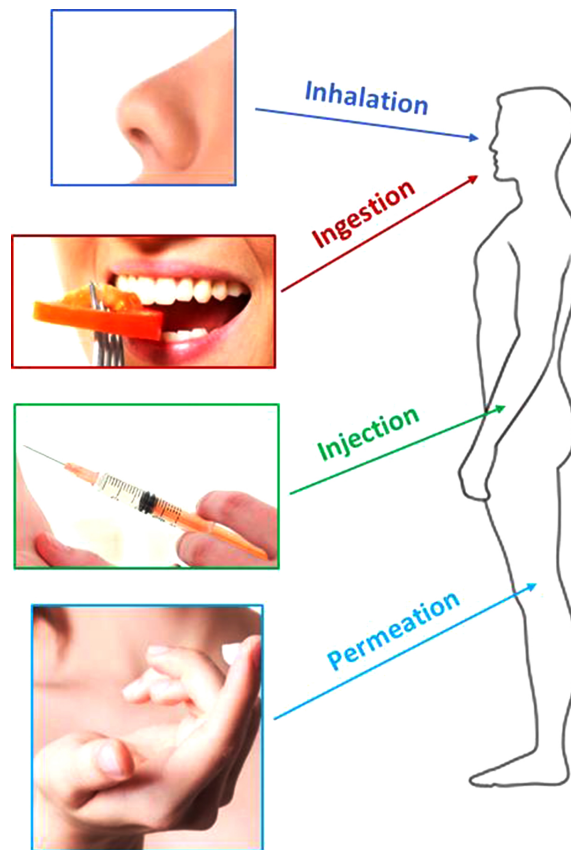


Fig. (1). Routes of exposure to toxic chemicals in human body.

- Prohibition of eating and drinking in working environment.
- Use of proper masks and respirators. Moreover, the operators must manipulate chemicals inside fume hoods.
- Use of suitable gloves and coats. Non-flammable and chemical resistant materials should be selected for these **personal protective equipments (PPE)**.

Fig. (2) plots the concentration of the substance in the blood against the time elapsed since its administration for the possible routes of exposure.

The maximum concentration in the blood is reached at different times and has different values, depending on the route of contact: injection exhibits the most dangerous effect, as high concentration of the toxic substance can be reached in the blood after a short time from its administration.

After approaching a maximum value, each curve shows a decreasing trend, thus proving the presence of defense mechanisms lowering the toxic species concentration in the blood.

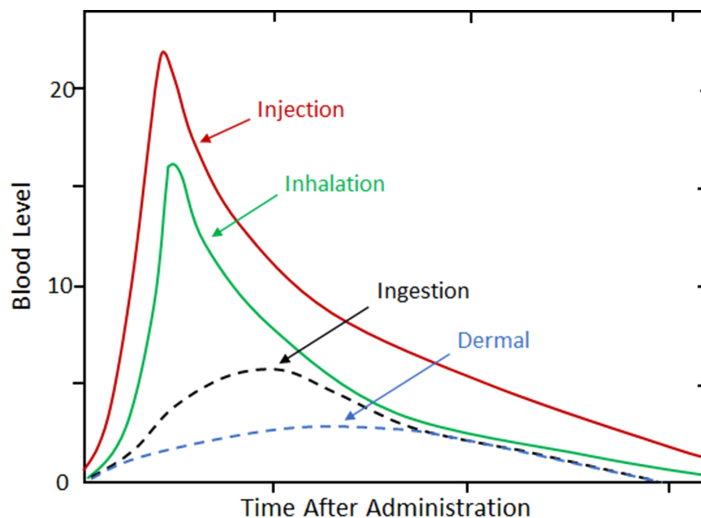


Fig. (2). Toxic blood level concentration as a function of route of exposure.

BIOTRANSFORMATION

Human body can rely on the following **defense mechanisms** to decrease the concentration of toxic species:

- Excretion: the body releases substances independently of their effects.
- Accumulation in adipose tissues: to understand this aspect, the example related to drugs is useful. Commercial drugs are substances that have a very low tendency to accumulate in the adipose tissues, otherwise, during pharmacological therapies, they would accumulate and could continue to exert their effects even when the human body does not need them anymore.

The first defense mechanism (*e.g.*, excretion) relies, in turn, on two different mechanisms allowing the human body to release some chemical species:

1. Biotransformation 1.
2. Biotransformation 2.

CHAPTER 10**Preventive and Protective Measures**

Abstract: Preventive measures are used to prevent explosive phenomena. In particular, inertization and ventilation procedures are discussed. Despite the adoption of these measures, explosive phenomena may still occur. Therefore, protective measures are necessary to reduce damages. Fire classes are also presented in this chapter.

Keywords: Fire Classes, Pressure Purging, Rupture Discs, Sweep-Through Purging, Siphon Purging, Ventilation, Vacuum Purging.

INTRODUCTION

Whenever a flammable substance is fed in an industrial container, oxygen concentration may be reduced below the MOC value to prevent explosive phenomena. To this aim, inertization procedures are used. On the other hand, whenever the presence of workers is required in an industrial environment, the concentration of flammable or toxic species may be reduced by adopting ventilation procedures [1].

As soon as an explosive phenomenon occurs, protective measures (*i.e.*, valves and rupture discs) are taken to contain the related damages. The technical bases to properly dimension the above mentioned preventive and protective measures are herein discussed.

INERTIZATION PROCEDURES

In order to prevent explosive phenomena, the most suitable inertization technique should be applied by considering the type of container, costs due to the consumption of inert gas, and the time required for inertization.

To this aim, the following four inertization procedures may be employed:

1. Vacuum purging;
2. Pressure purging;
3. Sweep-through purging;
4. Siphon purging.

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Vacuum Purging

Vacuum purging can be performed only if the tank is able to withstand vacuum. To decrease the risk, the probability or the magnitude (or both) has to be reduced. Evolution of pressure over time during Vacuum Purging is reported in Fig. (1).

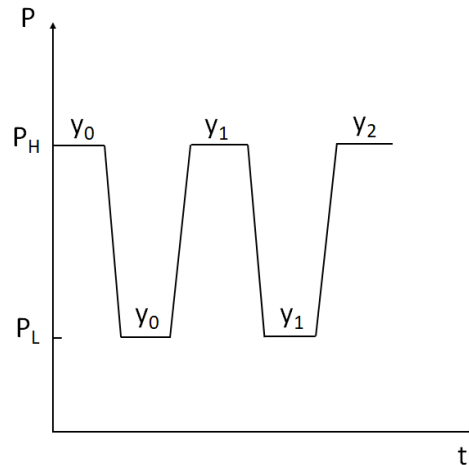


Fig. (1). Evolution of pressure over time during Vacuum Purging.

In the starting conditions, the container to be inertized has a high-pressure value P_H equal to 1 atm and a mole fraction of oxygen y_0 equal to 0.21. Indeed, air is initially present inside the container.

In order to obtain vacuum-pressure conditions, air is sucked out of the system until reaching a low-pressure P_L (e.g., 20-30 mmHg). In this first part of the cycle, oxygen concentration y_0 has a constant value of 0.21. Indeed, oxygen and nitrogen are simultaneously drawn out in their starting ratio. In the second part of the cycle, an inert gas restoring the atmospheric pressure and lowering the molar fraction of oxygen to the y_1 value is introduced into the system.

For this system, the following equations can be obtained:

$$n_H = \frac{P_H V}{RT} = \text{total moles at high pressure } P_H \quad (1)$$

$$n_L = \frac{P_L V}{RT} = \text{total moles at low pressure } P_L \quad (2)$$

Where V and T are the system volume and the ambient temperature, respectively, and they are constant during the operation.

By performing a mass balance on the oxygen moles after creating vacuum conditions during the first cycle of the procedure, the following equations can be obtained:

$$y_0 n_L = y_1 n_H \quad (3)$$

$$y_1 = y_0 \frac{n_L}{n_H} = y_0 \frac{P_L}{P_H} \quad (4)$$

$$n_L < n_H \Rightarrow y_1 < y_0 \quad (5)$$

Hence, the molar fraction of oxygen is reduced by performing a single inertization cycle. However, y_1 could still be higher than MOC. Therefore, an additional cycle should be repeated until obtaining the following values.

$$y_2 = y_1 \frac{n_L}{n_H} = y_0 \left(\frac{n_L}{n_H} \right)^2 \quad (6)$$

After performing j cycles:

$$y_j = y_0 \left(\frac{n_L}{n_H} \right)^j = y_0 \left(\frac{P_L}{P_H} \right)^j \quad (7)$$

Where $y_0 = 0.21$ and y_j is the final molar fraction of oxygen to be obtained.

In order to evaluate the number of cycles j :

$$\frac{y_j}{y_0} = \left(\frac{P_L}{P_H} \right)^j \quad (8)$$

$$\ln \frac{y_j}{y_0} = j \ln \frac{P_L}{P_H} \quad (9)$$

$$j = \frac{\ln \frac{y_j}{y_0}}{\ln \frac{P_L}{P_H}} \quad (10)$$

By knowing the number of cycles, the molar consumption of inert gas may be also evaluated:

CHAPTER 11**The Risk Assessment Applied to Industrially Contaminated Sites**

Abstract: Emissions of dangerous substances from ordinary industrial activities or industrial accidents may compromise the quality of soil and water. Indeed, industrial sites can be contaminated by a wide range of compounds, which represent a risk to the health of workers. To individuate whether the presence of contaminants represent a risk and how it is possible to remediate contaminated sites, it is necessary to apply the Risk Assessment technique. Risk assessment allows evaluation of the risk associated with the presence of contaminants, as well as remediation goals. The present chapter provides fundamentals on the risk assessment procedure applied to industrial contaminated sites. The main object is to provide a methodology to individuate contaminated sites and evaluate the remediation goals. To this aim, the main contents of the chapter are: basic concepts on contaminated sites, a description of the risk assessment method, an overview of the possible remediation techniques. Moreover, a practical exercise as well as a list of the most used software are provided.

Keywords: Contaminated sites, Industrial contamination, Remediation techniques, Remediation goals, Risk assessment, and Workers' safety.

INTRODUCTION

Potentially harmful chemical compounds are being added to soils since humans started mining. However, the phenomena that started speeding up the contamination of soils were the Industrial Revolution in the 19th century and the technological development in the 20th century. These events determined more than a proportional increase in the emissions of contaminants. Moreover, soils have been often intentionally used as a dump.

In the early 1970s, several countries introduced a few policies to protect soils from contamination. Nevertheless, only in the late 1970s did several notorious environmental events, such as the Love Canal disaster, led to a sudden awareness among the general public and decision-makers [1].

Nowadays, the presence of contaminated sites is a common issue in industrialized countries. Industrial activities can cause local and diffuse contamination, to such an extent that it might threaten the health of workers [2]. Moreover, when an industrial accident - such as the explosion or the fire of a chemical facility - occurs, soil contamination can easily occur and a subsequent risk mitigation is needed [3].

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Currently, there is no official definition of industrially contaminated sites agreed at European level. However, a common definition is:

“Areas hosting or having hosted industrial human activities which have produced or might produce, directly or indirectly (waste disposals), chemical contamination of soil, surface or ground-water, air, food-chain, resulting or being able to result in human health impacts”. In Europe, the industrialization process and poor environmental management practices have left a *legacy* of thousands of contaminated sites.

In August 2007, the European Environment Agency (EEA) published the first report titled “*Progress in management of contaminated sites in Europe*” [4], describing the state of the actual knowledge about contaminated sites in Europe. Successively (2011), the EEA urged member countries to identify contaminated sites in their territories and to formulate national remediation strategies.

Subsequently, the responsibility for the identification and management of contaminated sites in Europe passed to the Joint Research Center of the European Commission, which published an updated report in 2014.

According to the mentioned report, about 1,170,000 Potentially Contaminated Sites have been identified, to date. However, this number is estimated to be about the 45 % of the number of total possible potentially contaminated sites. Among them, one third of the estimated total of 342,000 have been confirmed to be identified Contaminated Sites for the EEA-39 and about 15 % of the estimated total have been remediated. However, there are still substantial differences in the underlying site definitions and interpretations used in different countries.

Some examples of industrially contaminated sites in Europe are:

- In the Swansea valley in the UK, where metal processing industries generated a major human health risk due to exposure to heavy metals;
- At a Norwegian Fjord near Bergen, where fish exploitation has been inhibited on a long-term basis due to PCB contaminated fjord sediments generated by industrial waste water discharges;
- In the Apulia region in Italy, where steel plants and refineries caused an environmental and public health disaster due to environmental emissions which have concerned national and European authorities for many years.

In Europe, waste disposal and treatment (37%), together with industrial and commercial activities (33%), have caused almost two thirds of the contamination. Considering that municipal and industrial waste contributes with similar shares, it can be concluded that Industrial and commercial activities are the main cause of soil contamination.

Regarding the type of industrial activities, of course, each country has its own specific industrial and commercial focuses. On average, at European level, the production sector has contributed to the contamination of about the 60% of sites, whilst the second polluting sector is that of service (32% of sites). To a lesser extent, mining activities are also important contributors to soil contamination (*i.e.* in Cyprus, Slovakia, FYROM). Concerning the production sector, textiles, leather, wood and paper industries are of minor importance (5%), while metal industries are most frequently reported (13%), followed by chemical industry (8%), oil industry (7%), and energy production (7%) that sum up around 35% of the production sector. Regarding service sector, gasoline stations are the most frequently reported (15%), followed by car service stations (>6%) [3].

CONTAMINANTS AND TRANSPORT MECHANISMS

The main categories of compounds that can contaminate a site are: Chlorinated Hydrocarbons (CHC), mineral oil, polycyclic Aromatic Hydrocarbons (PAH), heavy metals, phenols, cyanides and aromatic hydrocarbons (BTEX). The EEA also reported the distribution of these categories of contaminants in Europe, affecting the solid and the liquid (ground and surface water, leachate) matrix respectively. The distribution of the different contaminants is similar in the liquid and the solid matrix. The main contaminant categories are mineral oils and heavy metals. Moreover, the data suggests that phenols and cyanides make a negligible contribution to the total contaminant loading [3]. Depending on their properties, each contaminant can harm workers' health through different exposure mechanisms and cause different health effects. Concerning the possible health effects, which can be caused by the exposition to contaminants, some examples include: geohelminth infection and potentially harmful elements *Via* soil ingestion, cancers caused by the inhalation of fibrous minerals, hookworm disease, and podoconiosis caused by skin contact with soils. Nonetheless, human health can also be influenced in more indirect ways, as soils interact with the atmosphere, biosphere and hydrosphere [5].

The properties of contaminants influence the mechanisms through which they are transferred from the source of the contamination to the environmental

CHAPTER 12**The Health Impact Assessment within Environmental Impact Assessment Studies**

Abstract: Sustainability and sustainable development play a central role in addressing strategies and policies at the national and international level. Both these concepts have been largely discussed and different approaches have been proposed over time to promote their practical implementation, including the preventive one. In this context, Environmental Impact Assessment (EIA) has been built and developed to prevent or mitigate the negative impacts of a variety of anthropogenic activities on several environmental factors, including human health. Among the activities undergoing EIA, the building and operation of various chemical industrial plants may represent relevant scenarios to assess their wider health implications from a preventive perspective. The evaluation of these impacts on human health has been recently approached following a formally identified procedure, namely the Health Impact Assessment (HIA).

This chapter aims at providing an overview on HIA, with particular reference to its integration within the EIA procedures: the legislative framework is thus figured out and the main features of HIA are discussed to point out its strengths and weaknesses as a decision supporting tool during the assessment of the environmental impacts of projects.

Keywords: Environmental Impact, Hazard, Health, Precaution and Prevention Principles, Risk Assessment.

INTRODUCTION

Over the past decades, population growth, rapid technological development, industrialization, and agricultural expansion have developed rapidly, determining severe pressures on the natural environment. The depletion of natural resources, the release of waste streams and gaseous emissions have affected the features of natural ecosystems, raising the issue of the environmental effects of industrialization.

As reported by Bruhn Tysk and Eklund [1], the global concern on this issue was firstly approached at the Stockholm Conference in 1972, but it was only in 1987 that the need to bring together environmental and developmental problems was claimed in the report *Our Common Future*, also known as the Brundtland Report, published by the United Nations' World Commission on Environment and Development. This document clearly pointed out that many of the natural systems on which we depend were under increasing stress and addressed the synthesis between the need to protect the environment and that of ensuring the socio-

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economic development. Since then, the concepts of “*sustainability*” and “*sustainable development*” have been largely debated and different definitions have been presented, but the most widely known is that provided in the Brundtland report: “... *development that meets the needs of the present without compromising the ability of future generations to meet their own needs*”. The ability of present and future generations to meet their needs depends strongly on the environmental functions supporting life, so that the concern for the environmental health became inherent in the definition of sustainable development [2].

Later, the concept of “sustainable development” was further developed and the Rio Declaration that came after the Rio Conference in 1992 showed the main achievements in this field, which included an address towards a preventive approach to ensure the sustainability of development [1]. The 17th principle of the Rio Declaration calls for environmental impact assessment (EIA) to be undertaken as a national instrument “*for proposed activities that are likely to have a significant adverse impact on the environment and are subject to a decision of a competent national authority*”. Nowadays EIA is a well-established approach to prevent or mitigate the negative impacts from a variety of anthropogenic activities, including those related to the realization and operation of different kinds of industrial plants, including those susceptible to chemical accidents, as described in the previous chapters.

Within EIA, the assessment of the effects of these activities on human health has also been carried out and, over the past two decades, it has gained great importance, maturing as a form of impact assessment [3]. For the projects undergoing EIA, their building and operation stages may represent, indeed, relevant scenarios to assess their wider health implications from a preventive perspective.

This chapter aims at providing an overview on the health impact assessment, with particular reference to its integration within the environmental impact assessment procedures. To this end, EIA features and legislative frameworks are introduced; the main objectives and steps of the health impact assessment are then figured out, to approach its application to describe and assess the direct and indirect significant effects of a project on ‘*population and human health*’ in accordance with the Directive 2014/52/EU.

THE ENVIRONMENTAL IMPACT ASSESSMENT (EIA)

The Environmental Impact Assessment (EIA) was initiated in the United States in 1969, when the National Environmental Policy Act (NEPA) introduced the so-

called Environmental Impact Statement (EIS). The EIS was expected to become, among others, a tool to assess the environmental effects of plans and projects.

The introduction of such a procedure in Europe goes back to 1976, in France, with the enforcement of the Law n. 76-629 of the 10th of July *Relative à la protection de la nature*, dealing with environmental protection. This law laid the groundwork for the Directive 85/337CEE, approved on the 27th of June 1985 by the Council of the European Community, introducing the EIA for defined categories of projects. Since then, both the Directive and the corresponding laws transposed by the Member States developed. One of the major aspects to be updated over time was the list of works whose project had to undergo the EIA process.

This list was first split into two groups, depending on the extent of the potential impacts of the project: for those characterized by great impacts, Member States were in charge of the EIA process; in case of minor impacts, local Authorities carried out the process. Over time, due to an extension of the existing knowledge, the kind of works to be considered under the EIA legislation varied as well.

The rationale of EIA is that some projects can produce relevant effects on both environmental and human health. Therefore, it is important to properly evaluate these effects, due to the need to:

- **Protect human health and enhance the quality of life by safeguarding the environment;**
- **Contribute to maintain the biodiversity;**
- **Keep the generation capacity of natural ecosystems.**

Over time, this process has evolved and in the European Union, the last Directive 2014/52/EU has greatly emphasised the assessment of population and human health.

Nowadays, EIA is a well-established procedure that aims to provide a high level of protection to the environment and to promote the sustainable development of the territory, in accordance with the principles of prevention and precaution.

EIA is inspired indeed by the prevention principle, since it aims to either eliminate or reduce the adverse environmental effects before the project of a work comes to life. Similarly, it is based on the precaution principle, whereby projects likely to significantly affect the environmental health are made subject to an environmental assessment, prior to their approval or authorisation. In this regard, the assessment

SUBJECT INDEX

A

- Acid 6, 10, 76, 144, 175, 176
 acetylsalicylic 175
 glucuronic 176
 hydrocyanic 76
 picric 10
 stearic 144
 sulfuric 6
- Activities 225, 226, 227, 245, 246
 anthropogenic 245, 246
 mining 225
 polluting 226, 227
- Adiabatic 50, 59, 63
 calorimeters 50
 calorimetry 50, 59, 63
- Adipose tissues 172, 176, 177
- Air 127, 234
 composition 127
 inhaled 234
- American society for testing and materials (ASTM) 88
- ARC calorimeter reactor 58
- Aromatic rings 22, 24
- Assessment 245, 246, 247, 251, 256, 257, 259, 260, 261
 ecotoxicological 261
 environmental 247, 257
 epidemiological 259
 health effect 259
- ASTM organization 18
- Atmospheric pressure 76, 102, 103, 104, 105, 106, 111, 112, 113, 124, 145, 146, 192, 193, 216
- ### C
- Calorimetric 30, 50, 52
 techniques 50
 tests 30, 52
- Carbaryl pesticide 8
- Carbon 53, 76, 85, 122, 124, 129, 130, 221
 dioxide 53, 85, 124, 129, 221
 disulfide 76, 122, 130
 monoxide 76, 122
- Carcinogens 227
- Chatelier's equations 102, 107, 110
- Chemical 1, 2, 9, 18, 91, 137, 160, 173, 225, 246
 accidents 1, 246
 explosion 137
 industry 2, 91, 160, 225
 inhibitors 9
 reactions of biotransformation 173
 thermodynamic 18
- Chemical system 28, 42, 50, 51, 57, 58, 59, 60, 61, 95, 105, 209
 corrosive 209
 reactive 28
- CHETAH method 1, 18, 19, 25, 26, 30
- Chlorinated hydrocarbons (CHC) 225
- Cloud, gaseous 149, 150
- Coefficient 38, 40, 50, 78, 119, 139, 176, 177, 201
 global heat transfer 38, 40, 50, 78
 proportionality 139
 stoichiometric 119
- Combustion 91, 94, 104, 110, 129, 156, 161, 163, 164
 enthalpy 104
 heat 110, 156, 163, 164
 process 94
 reaction 91, 94, 129, 161
- Compounds 175, 226
 inorganic 226
 organic 226
 water-soluble 175
- Concentration 95, 148, 196, 197, 205
 hydrocarbon 95, 148
 pollutant 196, 197, 205
- Conditions 45, 83, 85, 91, 92, 112, 132, 160, 184, 187, 200, 238, 242
 acceptable cumulative risk 238
 occupational 184
 oxidative 85

Massimiliano Fabbriano, Roberto Andreozzi, Laura Clarizia, Alessandra Cesaro, Grazia Policastro & Concetta di Giovanni

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Consequences 1, 59, 137
 catastrophic 1
 economic 59
Consumption, molar 191
Contaminants 223, 225, 226, 228, 229, 230,
 231, 232, 233, 234, 235, 238, 239, 240,
 242, 243
 carcinogenic 229, 234
 degrading 242
 free 231
 influence 225
 migration of 230, 233, 242
 toxic 234
Contaminated 223, 226, 241
 food 226
 sites, industrial 223, 241
Contamination 223, 224, 225, 230, 231, 232,
 234, 241, 242
 chemical 224
 diffuse 223
Cooling 9, 11, 28, 40, 61, 162, 166, 210, 220,
 221
 circuit 210
 preventive 166
 system 11, 28, 40
CSTR reactor 11, 12
Cyclopropane 130

D

Damages 5, 9, 149, 150, 153, 154, 155, 157,
 160, 161, 162, 165, 166, 181, 189, 205
 heat irradiation 166
 irreversible 149, 150, 153, 155, 165
 to valves and pumps 5
Decomposition 11, 19, 26, 54, 56, 67, 81, 83,
 88, 151, 156, 186, 222
 heat 156
 process 67
 reaction 151
 temperature 186
Defense mechanisms 172
Dehalogenation 173
Dehydrogenates 6
Diseases 225, 251, 252
 hookworm 225
 vectors 251
DSC 68, 69
 calorimeters 68
 calorimetry 69

E

Effects 10, 31, 53, 170, 182, 187
 catalytic 53
 chronic 187
 reversible 182
 thermal 10, 31
 toxic 170
EIA 245, 247, 248, 249, 250, 257
 legislation 247
 procedures 245
 process 247, 248, 249, 250, 257
Electric 51, 131, 133
 circuits 131
 conductivity 133
 resistances 51
Energy balances 31, 32, 45, 107, 167
 integral 31, 32
 internal 167
Environment 148, 162, 186, 187, 189, 196,
 199, 245, 246, 247, 248, 249, 251, 253,
 257, 259
 industrial 162, 189, 196
 natural 245, 253
Environmental health 184, 254
 challenges 254
 hazards 184
Environmental matrices 231, 232, 237, 242
 sensitive 242
Environmental protection legislations 255
Exothermic 2, 8, 28, 45, 53, 65, 210
 decomposition process 53
 reaction 2, 28, 45
Explosions, adiabatic 107

F

Facilities, industrial 137
Factors 156, 187, 226, 233, 234, 245, 248,
 250, 251, 252, 257, 258
 air dispersion 234
 bioconcentration 187, 226
 biological 252
 environmental 245, 248
 outdoor air volatilization 233
Flame propagation 73, 74, 94, 95, 96, 97, 101,
 108, 119, 120, 121, 123, 126, 128, 129,
 134, 135, 136, 138, 149, 155, 213
 phenomena 73, 74, 94, 97, 101, 108, 119,
 120, 123, 126, 128, 129, 135

rate 213
speeds 155
Flammability 2, 102, 126
Fuel 7, 73, 76, 78, 91, 93, 94, 95, 108, 109,
110, 119, 121, 122, 126, 127, 128, 219,
220
diesel 7
gaseous 220
liquefiable solid 219
molar fraction 108
Fuel concentration 93, 106, 111, 119, 129, 138
stoichiometric 129
Function 14, 15, 16, 29, 33, 34, 103, 106, 129,
170, 172, 177, 211, 218
cardiovascular 170
thermal flywheel 129
Functional genomics 177

G

Gas(s) 8, 11, 28, 53, 74, 93, 100, 143, 145,
149, 162, 164, 201, 202, 226
burning 8
compressed 145
flue 149
nitrogen 164
toxic 8
vapour 8
volatilization 226
Geohelminth infection 225
Groundwater 187, 227, 228, 230, 231, 232,
233, 242, 243
contaminated 231, 243
geometry 232

H

Halogenated hydrocarbons 221, 222
Hazard index 230, 234, 238
Hazardous 17, 26, 30, 170, 176, 184, 185,
188, 227, 248
chemicals 170, 176
molecules 176
waste 248
Health 230, 246, 247, 255
environmental 246, 247, 255
risk analysis 230
Heat 10, 11, 25, 28, 30, 38, 39, 50, 51, 53, 64,
65, 68, 69, 71, 117, 121, 145, 146, 161,
163, 164, 165

and oxygen transports 161
exchange 30, 38, 50, 51, 117, 145, 146
ovens 68
radiated 164
radiation 165
transfer 39, 51, 161
vaporization 163
Heating powers 68, 69
Heavy machines 154
Henry's 118
constant 118
law 118
Hydraulic stabilization systems 242
Hydrocarbons 80, 85, 119, 123, 136, 155, 156,
161, 163, 219
Hydrogen 76, 80, 81, 82, 84, 122, 129
atom 80, 81, 82, 84
sulfide 76, 122, 129

I

Industrial 123, 124, 184, 205, 223, 224, 225
activities 223, 225
and commercial activities 225
applications 123, 124
hygienists 184
revolution 223
tanks and reactors 205
waste water discharges 224
Industrial plants 5, 158, 161, 162, 165, 245,
246, 258, 259, 261, 262
chemical 245
Industries, metal processing 224
Inert gas 124, 126, 128, 129, 137, 157, 189,
190, 191, 192, 193, 194, 221
compressed 137, 157
large consumption of 193, 194
pressurized 192
Inhalation 170, 225, 226, 235
indoor 235
outdoor 235
Integration 245, 246, 257
comprehensive 257
Interface 38, 198
liquid-gas 198
reactor-cooling system 38
Isentropic 145, 146, 147, 158, 168, 202, 214
expansion 146, 214
transformation 145, 146, 158, 168
Isotherm transformation 145

Subject Index

Isothermal 36, 146, 148
transformation 146

K

Kinetic 31, 82
law 31
order 82

L

Law, cubic 139, 140, 143
Liquid vaporization 161

M

Margules' equation 119
Mass fraction 43, 79, 168
vaporized liquid 168
Mechanisms, biotransformation 170
Microsomal 173
oxidations 173
reductions 173
Migration pathways 231, 238
Minimum 102, 119, 121, 122, 123, 124, 126,
129, 130, 143, 191, 192
ignition energy (MIE) 126, 129, 130, 143
oxygen content (MOC) 102, 119, 121, 122,
123, 124, 126, 191, 192

N

National environmental policy act (NEPA)
246
Nepero's constant 42
Nitrogen injection 210
Nonmicrosomal reductions 174
Nonnegligible infrared absorption 164

O

Oil(s) 220, 225
industry 225
mineral 225
Oxygen 25, 76, 78, 80, 82, 85, 93, 100, 101,
119, 120, 121, 123, 124, 161, 165, 189,
190, 191, 192, 193, 195
concentration 93, 119, 121, 123, 189, 190,
195

Safety in Chemical and Process Industries 267

molar fraction of 190, 191, 192
stoichiometric 25, 120
therapeutic 165

P

Phenomena 9, 28, 29, 74, 91, 128, 131, 166,
233
luminous 74, 91
migration 233
propagation 128
runaway 9, 28, 29
static electricity 131
vaporization 166
Podoconiosis 225
Pollutants immobilization systems 242
Polycyclic aromatic hydrocarbons (PAH) 225
Power 51, 64
electric 64
generator, electric 51
Pressure 7, 28, 113, 139, 254
anthropogenic 254
generic 139
vapour 7, 28, 113
Process 6, 10, 83, 84, 101, 224, 226, 262
environmental 262
industrial 101
industrialization 224
migration 226
nitration 10
oxidation 6
oxidative 83, 84
Protective venting systems 206
Pulmonary hemorrhage 182

R

Raoult's law 118
Reaction 8, 9, 10, 11, 19, 28, 29, 31, 36, 50,
52, 53, 54, 55, 81, 82, 83, 87, 151, 174,
175, 221
autocatalytic 36
biotransformation 175
generic 19
thermal decomposition 50, 52, 54, 55
Reductive dehalogenation 174
Relationship 46, 62, 80, 109, 254
Reynolds' number 199
Risk 223, 241
based corrective action 241

- mitigation 223
- Risk assessment 223, 227, 228, 229, 230, 232, 241, 245, 259
 - sanitary 259
 - method 223
 - procedure 223, 227, 228, 229, 232
 - software 241
 - technique 223
- Roult's law 118

S

- Salicylic acid nitration 10
- SEA reports 258
- Self-ignition 88, 97, 106
 - phenomenon 88, 106
 - temperatures 88, 97
- Semenov's 28, 34, 35, 37, 42, 47, 60, 78, 88
 - approach 28, 35
 - explosion theory 34
 - hypothesis 35, 47, 78
 - theory 37, 42, 60, 78, 88
- Social 252, 253
 - and community networks 252
 - determinants of health (SDH) 253
- Soil 225, 226
 - conditions 226
 - contaminant 226
 - ingestion 225
- Strategic environmental assessment (SEA) 257, 258
- Surface soil, contaminated 231
- System 11, 31, 39, 40, 45, 47, 48, 52, 59, 61, 64, 71, 75, 86, 89, 112, 115, 123, 148, 190, 192, 195, 197, 217, 226
 - autocatalytic 48
 - flammable 217
 - heating 64
 - hydrogen-oxygen 86
 - pulmonary 226
 - ventilation 195, 197

T

- Tetrahydrofuran 130
- Thermal 1, 6, 11, 18, 28, 29, 38, 39, 50, 73, 164
 - behavior 50
 - conductivity 38
 - decomposition 1, 18

- energy 11
- explosions 6, 28, 73
- power 29, 39, 164
- Thermodynamic(s) 26, 50, 156, 167, 201
 - analyses 50
 - approach 156
- Threshold limit values (TLV) 170, 182, 183, 184, 197, 205
- TNT 137, 150, 152, 156, 157, 158
 - equivalency method 137, 150, 152, 156, 157, 158
 - for selected hydrocarbons 156
- Traditional remediation techniques 243
- Transformation processes 226
- Transport 225, 226, 227, 232
 - mechanisms 225, 227
 - processes 226
 - properties 232
- Transporting 113, 184, 188
 - chemicals 184

V

- Vacuum 93, 138, 189, 190, 192, 193
 - pump 93
 - purging 189, 190, 192, 193
 - withstand 190
- Vapor cloud 158, 162, 166
 - burning 166
 - explosion (VCE) 158, 162, 166
- Vapor pressure 112, 186

W

- Waste 59, 224, 225, 230, 242, 248
 - disposals 224, 225
 - industrial 225
 - non-hazardous 248
- Water, contaminated 242