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Using historic accident data to estimate the potential fatalities due to chemical hazards

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Abstract

Inherent safety is that which is intrinsic to a chemical plant. Chemical plants should be designed to be acceptably safe and it is better if this can be achieved through inherent safety, which cannot be compromised, rather than added - on engineered safety. The earlier that inherent safety is considered, the greater are the benefits.

The aim of this project is to develop a method which can be used to assess the inherent safety of a chemical plant, by estimating the potential number of fatalities in the event of a catastrophic accident. This method is intended for use in the early phases of design when the major decisions on the chemical process are made. In the early stages, only limited information about equipment and plant layout exist as well as the reaction chemistry and the physical, chemical and toxicity properties of the chemicals involved.

Historical accident data for fire, explosion and toxic release accidents has been collected from all over the world. A number of statistical tests were conducted on this data in order to investigate the possibility of developing relationships predicting the number of fatalities caused by a chemical accident.

A number of relationships have been obtained from applying the mortality index (MI) approach. These relationships could predicte the potential number of fatalities in case of chemical accident. However, other factors have to be taken into consideration in order to improve the prediction accuracy.

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Chapter 1: Introduction

1.1. Inherent safety

Inherent safety is that which is intrinsic to something. A good example, used by Kletz, is the bungalow, which is inherently safer than a house. This is because the majority of accidents in the home are caused by stairs. Stairs are inherently unsafe but can be made safe by adding on safety features, for example hand rails, child-gates or non-slip carpets. The inherently safer choice is to remove the stairs that is to live in a bungalow. The inherent safety philosophy is to avoid or remove hazards rather than try to control them.

In the context of a chemical process, according to Hendershot (1996), a chemical manufacturing process could be described as inherently safer if it reduces or eliminates one or more hazards associated with the materials and operations used in the process, when compared to some alternative process, and this reduction or elimination is accomplished by characteristics which are permanent and inseparable parts of the process.

The traditional plant design philosophy and practice identifies hazards and then adds protective measures to control them. This method of secondary prevention reduces the probability of accidents. However, there is an alternative philosophy of Inherent Safety or primary prevention, where the possibility of accidents is removed, by the use of safer chemicals and operations. In the practical approach to Inherent Safety, called Inherently Safer Design (ISD), hazards are identified early and then avoided or at least minimised, rather than controlled so that accidents either cannot happen or their effects are minimal.

ISD as a general concept was first introduced by Kletz (1976) after the Flixborough, UK accident in 1974. It has attracted global interest since the early nineties after several major disasters occurred during the eighties, for example, Bophal, Mexico city, and Piper Alpha.

Kletz (1991) sets out major strategies in which the approaches to the design of inherently safer processes and plants can be achieved:

- **Intensification** – using less of hazardous material,
- **Attenuation** – using a hazardous material in a less hazardous form,
- **Substitution** – using a safer material instead,
- **Limitation** – minimising the effect of an incident,
- **Simplification** – reducing the opportunities for error and malfunction.

It is widely recognized that the timely and effective use of the above principles can make a process and plant cheaper to build and operate as well as improve safety. This is because conventional plant design often relies on extensive "add-on" engineered safety systems which are expensive to provide and maintain, and do little to improve the performance or operation of the plant. Therefore, if the basic process or plant design can be developed such that any hazards are avoided, eliminated or minimised at source, the need for these "add-on" systems or facilities may be removed or reduced and a plant can improve its inherent safety performance and lower capital and operating costs.

In spite of the attractive and the cost-effective approach of inherent safety, it has not been used as widely as other techniques such as HAZOP and risk assessment. Gupta and Edwards (2002) cited some reasons that are responsible for the limited adoption of inherent safety. The key reason is the non–availability of a systematic methodology and tools for measuring inherent safety.

Academic and industrial research personnel have worked on how to measure the inherent safety of the processes. A number of methods have been proposed but are too complicated for easy adoption by the industry which needs simple methods to measure ISD, Gupta and Edwards (2002) and (2003).

1.2. Aims and Objectives

The aim of this project is to develop a method which can be used to assess the inherent safety of a chemical plant. This model is intended to use in the early phases of design when the major decisions on the chemical process are made. In the early stages, only limited information on equipment and plant layout exist as well as the main reaction chemistry and the physical, chemical and toxicity properties of the chemicals involved.

The method is based on statistical analysis of historical accidents which have happened in the process industries. Analysing historical data can lead to a number of observations which help in hazard assessment, identifying the main sources of hazards, establishing which accidents are more prone to happen, showing the activities or operations in which effort is required to improve safety and estimating the probable number of fatalities from such accidents.

The method can be used in association with other hazard assessments to help process designers to apply good judgment in selecting the safest process. On the other hand, it is not vital that the assessment is quantitatively accurate, because the aim is an aid for decision-making in design. The method takes into consideration the three main classes of hazards with which process engineering is concerned, fire, explosion, and toxic release. Brief summaries of the topics of the remaining chapters of this thesis are as follows:

Chapter 2: introduces the concept of inherent safety and inherently safer design. It describes how the design can be made more inherently safe by applying the principles of inherently safer design. It describes some available tools for measuring inherent safety. It also covers the reasons for the limited adoption of inherently safer design.

Chapter 3: is a case study that has been applied to the inherent safety index which was developed by Edwards and Lawrence (1993). The case study is for testing two routes for manufacturing Adiponitrile in order to determine the safer route.

Chapter 4: presents the dust explosion which poses a major hazard in handling solid materials. The chapter describes the dust explosion phenomena, the factors that influence dust explosibility and reviews some tests used worldwide for measuring explosion properties. It also suggests a method to assess the hazards posed by dusts.

Chapter 5: is the major chapter in this thesis. This chapter starts with a survey of the fire and explosion accidents published in the literature and their analysis where available. It then illustrates the statistical tests which have been conducted on the fire and explosion accidents in order to develop a method which will be used to measure the inherent hazard of a chemical plant or the impact of a chemical or a process operation on people.

Chapter 6: summarises the main findings of the research and makes some recommendations for future work.

Chapter 2: Literature Review

2.1 Inherent Safety and Inherently Safer Design

The term inherent means "belonging by nature" or the "essential character" of some thing. An inherently safer plant is safe by its nature and by the way it is constituted, Scheffler (1996). In the typical approach to design and operation, safety measures are engineered near the end of the design process, leaving added-on control measures to be the only option available. Control measures added late in design require continual staffing and maintenance throughout the life of the plant, greatly adding to the lifetime costs as well as repetitive training and documentation upkeep, Khan and Amyotte (2003). Inherently safer design represents a fundamentally different approach. Firstly avoiding the hazard and if this is not possible, reducing the size of the hazard as much as possible.

The best known measure for safety is risk, which is defined as a measure of human injury, environmental damage, or economic loss in terms of both the incident likelihood and the magnitude of the injury, damage or loss, Hendershot (1997). Thus, any effort to reduce the risk arising from the operation of a chemical processing facility should be directed towards reducing the likelihood of incidents (incident frequency), reducing the magnitude of the injury, damage, or loss should an incident occur (incident consequences) or some combination of both. Traditional plant designs try to reduce the risk by adding protective equipment and following safe working methods, Kletz (1998).

A hazard is a condition with a potential for causing an injury or damage, Heikkila (1999). A chemical process normally has a number of potential hazards, for example raw material and intermediate toxicity and reactivity, energy release from chemical reactions, high temperatures, high pressures, quantity of material used. Each of these hazards impacts the overall process risk.

The concept of inherent safety can be incorporated at any stage of design and operation. However, its application at the earliest stages of process design when a process is being chosen or developed yields the best results, Khan and Amyotte (2003). At that time, the designer still has considerable freedom in technology selection. For a chemical process, the greatest opportunities lie in the selection of the chemical synthesis route to be used, including the raw materials, solvents, chemical intermediates, reaction steps, and other physical and chemical operations to be used. However, it is never too late to consider inherent safety.

The term "Inherently Safer Design" (ISD) was coined by Trevor Kletz three decades ago. Since the early nineties, this term has been recognized as the most worthwhile approach by the chemical process industry, regulators and researchers as is evident from the large number of papers published and presented at conferences, Gupta (2000).

Hazards can be reduced or eliminated by changing the materials, chemistry, and the process variables such that the reduced hazard is characteristic of the new conditions. The process with reduced hazards is described as inherently safer, that is a process is safer because of its very nature and not because equipment has been added to make it safer, Kletz (1998a). This terminology recognises that there can be no chemical process that is without risk, but that all chemical processes can be made safer by applying inherently safer concepts. The term "inherent safety" does not mean absolute safety.

2.2 The advantages of Inherently Safer Design (ISD)

Adopting an "inherent safety" approach offers several advantages. Minimizing the inherent hazards in the plant offers savings by reducing the need for expensive safety systems and instrumentation, which increase the plant complexity and provides opportunities for human error.

Reducing complexity reduces the need for instrumentation and operator supervision and decreases maintenance cost. Decrease the amount of material in the plant (inventory) means smaller plant and storage facilities, possibly lowering equipment costs together with costs related to the site size. Substitution for less harmful chemicals or processes could reduce the environmental impact of any wastes produced and the cost of dealing with the wastes.

It has been shown that, considering the lifetime costs of a process and its operation, an inherently safer approach is a cost optimal option, Khan *et al* (2004). Lifetime costs include the fixed cost of the facility, as well as the costs due to operations, maintenance, and safety measures. Conventional systems may be cheaper in terms of fixed and operational costs; however, considering maintenance and safety measure costs, these systems may turn out to be costlier than those based on the principles of inherent safety (which may well have higher fixed costs).

2.3 Strategy for reducing risks in the Chemical Industry

The strategy for reducing risk, whether directed toward reducing frequency or consequence of potential incidents, can be classified into four categories. These categories, in decreasing order of reliability and robustness, are, Bollinger *et al* (1996):

- ***Inherent:*** Eliminating the hazard by using materials and process conditions, which are non-hazardous.
- ***Passive:*** Minimizing the hazard by process and equipment design features, which reduce either the frequency or consequence of the hazard without the active functioning of any device.
- ***Active:*** Using controls, safety interlocks, and emergency shutdown systems to detect and correct process deviations. These systems are commonly referred to as engineering controls.
- ***Procedural:*** Using operating procedures, administrative checks, emergency response, and other management approaches to prevent incidents, or minimize the effects of an incident.

Risk control strategies in the first two categories, inherent and passive, are more reliable because they depend on the physical and chemical properties of the system rather than the successful operation of instruments, devices, procedures, and people. Table 2.1 gives examples of the four risk management strategies.

2.4 Inherent Safety Principles

Kletz (1998a) has defined the term "friendly plants" as plants designed such that any departures from ideal performance by operators, maintenance people, or equipment can be tolerated without serious effects on safety, output, or efficiency. He recommended some principles by which friendliness in plant design can be achieved. These are now described.

Table 2.1: Examples of Process Risk Management Strategies

Risk Management Strategy Category	**Example**	**Comments**
1. Inherent	An atmospheric pressure reaction using non-volatile solvents, which is incapable of generating any pressure in the event of a runaway reaction.	There is no potential for overpressure of the reactor because of the chemistry and physical properties of the materials.
2. Passive	A reaction capable of generating 150 psig pressure in case of a runaway, done in a 250 psig reactor	The reactor can contain the runaway reaction. However, if 150-psig pressure is generated, the reactor could fail due to a defect, corrosion, physical damage or other cause.
3. Active	A reaction capable of generating 150 psig pressure in case of a runaway, done in a 15 psig reactor with a 5 psig high pressure interlock to stop reactant feeds and a properly sized 15 psig rupture disk discharging to an effluent treatment system.	The interlock could fail to stop the reaction in time, and the rupture disk could be plugged or improperly installed, resulting in reactor failure in case of a runaway reaction. The effluent treatment system could fail to prevent a hazardous release.
4. Procedural	The same reactor described in Ex. 3 above, but without the 5 psig high pressure interlock. Instead, the operator is instructed to monitor the reactor pressure and stop the reactant feeds if the pressure exceeds 5 psig.	There is a potential for human error, the operator failing to monitor the reactor pressure, or failing to stop the reactant feeds in time to prevent a runaway reaction.

2.4.1 Intensification

Use smaller quantities of hazardous substances. This could be achieved through efficient continuous reactors (loop reactors, or tubular reactors) in place of batch reactors, reduced inventory of raw materials and in-process intermediates, and efficient process equipment. Friendly plants contain low inventories of hazardous materials so that they do not cause harm in case of a leak.

Application examples

A good example of an intensified process, mentioned by Kletz (1998a), is that of Nitroglycerine production. The product was originally made in ton batches in a mass transfer limited reactor. However, studies of the reaction rate revealed that the two-to-three hour batches needed only two minutes to go to satisfactory completion. This chemical discovery drove processing changes towards a small continuous reaction process where if the reactor exploded, very little damage resulted and a spare gram-size reactor would be ready to insert into the unit operation. Whereas, loss of the ton-capacity reactor was always disastrous for both production and life.

Khan and Amyotte (2003) cited a continuous process for phosgene manufacture on demand, that eliminating the need for storage of liquid phosgene. Various important issues such as quality control, understanding of transient reactor operation, and process control were successfully resolved by a fundamental understanding of the chemical reaction. This enabled the design of a system which met all of the user's requirements in an inherently safer way.

It is understood that mixing and gas-liquid phase mass transfer controls the rate and efficiency of chlorination reactions. Replacing a stirred tank reactor with a loop reactor, specifically designed to optimize mixing and gas-liquid phase transfer, has been shown to significantly reduce reactor size, processing time, and chlorine usage.

2.4.2 *Substitution*

This practice aims to replace the hazardous material with a less hazardous one. This could be achieved through water based paints and coatings, alternative chemistry using less hazardous materials, and less flammable or toxic solvents.

Application examples

The following two examples were described by Khan and Amyotte (2003) for the applications of substitution. Manufacture of acrylic esters by oxidation of propylene to produce acrylic acid, followed by esterification to manufacture the various esters is inherently safer than the older Reppe process, which used acetylene, carbon monoxide, and nickel carbonyl.

Disodium iminodiacetate (DSIDA), an intermediate used for agricultural chemicals, was traditionally manufactured using a process requiring ammonia, formaldehyde, hydrogen cyanide, and hydrogen chloride. Monsanto developed a new process for DSIDA which eliminates the use of hydrogen cyanide and formaldehyde, has a higher yield, is simpler, and produces a product of sufficiently high purity that purification is not required. Many cleaning and de-greasing operations have eliminated the use of organic solvents by substituting water based systems, Hendershot *et al.* (1999).

A polymerization process was conducted using a gradual addition batch process, with a large quantity of organic solvent being required to keep the system viscosity low enough for effective mixing and heat transfer. In the event of an uncontrolled (runaway) polymerization, a large quantity of flammable and toxic material would be ejected through the reactor rupture disk. Instead of relying on an expensive and elaborate emergency relief discharge system to control the potential hazard, the basic process chemistry was re-considered. It was found that it was possible to make the product using a suspension polymerization process in water. Because of the significantly lower amount of solvent required in the new process, in the case of a runaway reaction most of the material released would be water (with a small amount of solvent and unreacted monomer). Reaction runaway was also less likely because of the higher heat capacity of water, allowing it to absorb more of the heat of reaction during a process upset, Khan and Amyotte (2003).

2.4.3 Attenuation or moderation

Use less hazardous conditions, a less hazardous form of a material, or facilities which minimize the impact of a release of hazardous material or energy. This could be implemented through dilution, refrigeration of volatile hazardous materials, and granular product formulations in place of powders.

Application example

In the 1930s, ammonia plants typically operated at pressures up to 600 bar. Over the years, improved understanding of the chemistry has resulted in a downward trend in the operating pressure of ammonia plants; in the 1980s, plants operating in the range of 100-150 bar were common. The newer, low-pressure plants are inherently safer, cheaper, and more efficient than their high-pressure counterparts.

Some other examples of attenuation described by Khan and Amyotte (2003) are storing liquefied chlorine and ammonia as refrigerated liquids at atmospheric pressure instead of storing them under pressure at ambient temperature and handling powdered dyestuffs that might cause dust explosions as slurries.

2.4.4 Simplification

Design features that eliminate unnecessary complexity make operating errors less likely. Design teams engineer very complex processing systems to accommodate a variety of products that make the plant complex. Complex processing facilities provide many opportunities for error and create more expense since there is a great deal of cleanup and retool time consumed. Therefore, focusing just on the product at hand should be considered.

Application examples

An understanding of basic process chemistry allows process chemists and engineers to design simpler reaction systems and facilities. *One pot* and *in-situ* processes permit the generation of a hazardous intermediate in the vessel where it will be used, eliminating the need to store it, or to move it around the plant in piping systems. The inventory of hazardous material is thus limited to a maximum of one batch. This example illustrates the beneficial overlap that can occur with inherent safety principles (in this case, *simplification* and *minimization*).

On the other hand, simplification sometimes involves a trade off between the complexity of an overall plant and complexity within one particular piece of equipment. For example, a reactive distillation process for producing methyl acetate requires only three columns and the associated support equipment. The older process required a reactor, an extractor, and eight other columns, along with the associated support equipment. The new process is simpler, safer, and more economical, but the successful operation of the reactive distillation component is itself more complex and knowledge intensive, Bollinger *et al.* (1996).

2.4.5 Limitation of effects

The idea is to minimize the effect of an incident as much as possible. These are not planned exercises in design failure, but are careful use of technology to limit potential system losses. A good example is the use of gasket systems that only leak small amounts when they fail instead of gaskets that can totally blow-out. Another example mentioned by Kletz (1998) is the reactor type. A tubular reactor is better than a pot reactor because the leak rate is limited by the cross-section of one tube and can be stopped by closing a valve in the pipe.

2.4.6 Avoiding Knock-On Effects

This is to prevent any knock-on or un planned effect which might happen when incidents occur. For example, provide firebreaks between plants sections to restrict the spread of fire, or, if flammable materials are handled, the plants are built out-of-doors so that leaks can be dispersed by natural ventilation.

2.4.7 Making Incorrect Assembly Impossible (or at least difficult)

Friendly plants are designed so that incorrect assembly is difficult or impossible. For example, compressor valves should be designed so that inlet and exit valves cannot be interchanged. To prevent relief valves from being installed the wrong way round, their inlet and exit lines should have flanges of different sizes.

2.4.8 Make Status Clear

With friendly equipment it is easy to notice any wrong assembly and to find out whether it is in the open or shut position. Check valves should be marked so that installation the wrong way round is obvious. It should not be necessary to look for a faint arrow hardly visible beneath the dirt.

2.4.9 Tolerance

This is the ability of equipments to tolerate poor installation or operation without failure. Material of construction (MOC) evaluations early in the development of a chemical route is essential to provide greatest degree of inherent safety.

Good engineering design is also considered in tolerance. Piping stress analysis can lead to provision of expansion loops to compensate for thermal expansion of piping rather than using special fittings of convenience like bellows or hoses. Quality of the original equipment specification, likewise, has a potential effect on tolerance. If the equipment or control system is critical, its design should be made more fault-tolerant.

2.4.10 Ease of Control

Is the use of the known physical principles, when possible, to achieve the operating conditions rather than adding control equipment. For example, one flow can be made proportional to another by using flow ratio controllers, which may fail or be neglected, or, a better way, by letting one fluid flow through an orifice and suck in the other through a sidearm.

2.4.11 Administrative Controls/Procedure

Human error is the most frequent cause of loss of containment. Training and certification of personnel on critical procedures are permanent considerations. Also some other inherent safety principles, like ease of control, making status clear, tolerance and making incorrect assembly impossible, play a vital role.

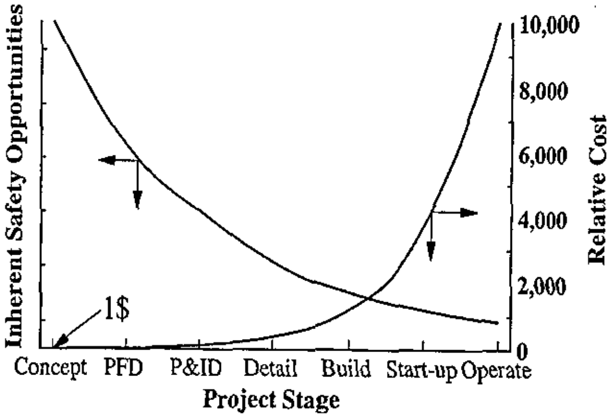


Figure 2. 1: Opportunity to Implement and Cost of Ignoring Inherent Safety.

2.5 Inherent safety in preliminary process design

As a process goes through the stages of the project, such as conceptual design, process flow sheet, construction and finally operation, opportunity of implementing inherent safety principles and cost of design changes have a varying trends. While the major decisions on process principle are done on the conceptual design phase, this phase gives the best opportunity of implementing inherent safety. In terms of cost, in the early stages of plant design the changes for safety will be most profitable, since nothing has been built or ordered yet and thus no expensive modifications are needed.

Figure 2.1 shows that the cost of any design/process changes are easier and cheaper early in the process life cycle (conceptual design) and any re-design done after the detailed design stage is extremely expensive. Table 2.2 shows the stages at which each feature of friendly design should be considered.

Table 2.2: Project stages at which each feature of friendly design should be discussed, (Kletz, 1998a)

Feature	Conceptual stage	Flowsheet stage	Line diagram stage
1. Intensification	X	X	
2. Substitution			
of chemistry	X		
of auxiliary materials		X	
3. Attenuation	X	X	
4. Limitation of effects			
by equipment design		X	X
by changing reaction conditions	X	X	
5. Simplification	X	X	
6. Avoiding knock-on effects			
by layout	X	X	
in other ways		X	X
7. Making incorrect assemble impossible			X
8. Making status clear			X
9. Tolerance			X
10. Ease of control	X	X	
11. Computer control		X	X
12. Passive features		X	X

2.6 The Constraints on Inherently Safer Design

Despite the clear benefits of adopting the concept of the inherently safer plant from both sides, process safety and cost, a number of reasons have been found that hinder the wider spread of the inherent safety principles. In order to know these reasons and the low profile of inherent safety, the European joint Industry-government Inside Project (for INherent Safety InDEsign) assessed the true extent of use of inherent safety in the process industries, Mansfield (1996).

The Inside team has surveyed more than 20 large, medium and small companies across Europe, representing a wide-range of the chemical process industries (CPI). A number of major design and engineering contractors and a process licensors were interviewed. These interviews provide insight into the way Safety, Health and Environment (SHE) issues are addressed in process development and design. The findings were as follows:

- Companies consider a lack of awareness and a conservatism in the design to be the main hurdles to adopting inherent SHE, Figure 2.2. Lack of awareness is attributed to the education that chemists and engineers receive. SHE management principles simply do not get sufficient attention in their studies and even when SHE topics are taught, they are treated as a separate subject rather than as an integral part of development and design.
- Governmental regulation can be either a hurdle or a stimulus to inherent safety. On the one hand, prescriptive regulatory requirement can hinder its attainment. On the other hand, an appropriate educational approach by the regulators can help raise awareness of SHE and how to attain it. Some companies have realised the benefits which can be gained by adopting the principles of inherent safety. In the U.K. under the COMAH (Control of Major Accident Hazards) legislation, there is a requirement to demonstrate that a hierarchical approach to process design, including SHE, has been taken.
- The relationship between client and contractor can have a key influence on SHE. A more-open relationships may be needed to encourage dialogue between the contract engineers and clients, and to ensure that the contractor takes steps to evaluate and optimise SHE-related design options. Pressure to reduce the cost and time of a project can likewise be a problem.

- The emphasis on modifying and expanding existing plants rather than building new ones places constraints on the design, which can inhibit the adoption of inherent SHE. However, such modifications and revamps often provide the opportunity to take into account the latest advances in production and SHE performance. Some speciality chemical manufacturer uses the same plant to make a wide variety of products. Such an activity requires special attention to SHE.

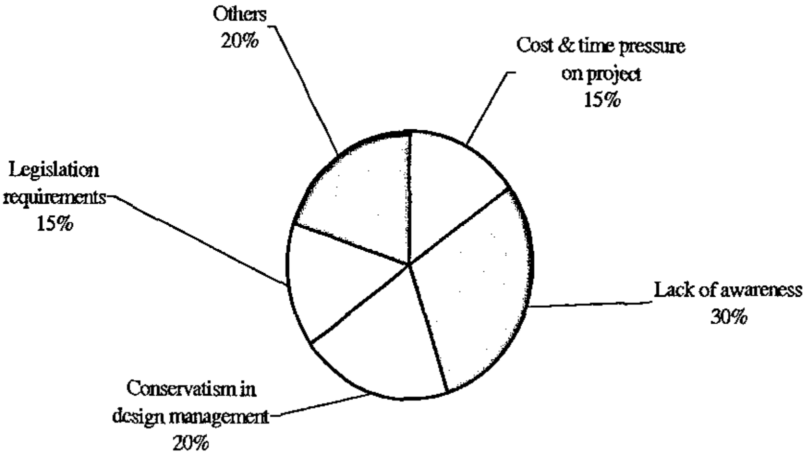


Figure 2. 2: The hurdles preventing the adoption of inherent safety

Kletz (1998) added some reasons to the Inside Project's findings such as the tendency of people to follow the procedures in plant design and to use tested designs rather than use new processes because the new designs might produce unforeseen problems which will delay the start-up or the achievement of flowsheet output.

Khan and Amyotte (2002) have proposed some suggestions by which inherently safer approaches to design can be promoted:

- Regulatory agencies must take the initiative in raising awareness and promoting discussion of inherently safer approaches to design.
- Researchers should be encouraged to work on the demonstration of inherent safety applications and these findings should be made available to all interested industries.

- Regulatory agencies must encourage the use of inherent safety by providing various incentives for collaborative research opportunities.
- A structured discussion paper needs to be developed on the use of inherent safety and its advantages. This could be achieved through collaboration among industries, regulatory agencies, and researchers.
- Efforts must be made to develop easier to use methodologies and tools for inherent safety application. The reality at present is that there are few systematic methodologies or tools available to evaluate inherent safety.
- Regulatory agencies and industry should encourage the inclusion of inherent safety principles and their application in training programs for safety specialists and designers. Such training would also be appropriate for senior managers and project managers so they are made aware of the principles and benefits of inherent safety.
- Research and development programs should be funded to address or encourage inherently safer technology, design and operation. Perhaps greater priority could be given to joint programs to develop and test new technologies that could provide inherently safer alternatives.
- Consideration should be given to practical ways of encouraging innovation and the search for inherently safer design solutions in projects. This might include providing more time or resources at the early stages of projects for these activities and by having more open and flexible contractual and working relationships.
- Universities should be encouraged to include more emphasis on safety in general, and inherently safer design of processes and plant in particular, as part of the curriculum for their engineering graduates.

In order to know whether there is a progress in the status of use of ISD in industry in the recent years and to discover the reasons for slow adoption, Gupta and Edwards (2002) carried out a survey amongst industrialists, academics and regulators. Questionnaires were sent to different sets of responders: industries and consultants; academics and R&D organizations; and regulators. 63 completed responses were received from 11 countries represent a whole spectrum, from those who have only recently heard of ISD to those who have practised it successfully for over two decades. The responding companies covered a very wide range of industrial activities. Amongst the reasons cited for limited adoption were: lack of case studies dealing with economic benefits; lack of a tried and tested yet simple methodology of application; lack of desire to change; lack of knowledge about ISD amongst research chemists, engineers, managers and regulators; no enforcing regulation; lack of specific research funds for academics in this area.

However, the results of this survey showed that awareness of inherent safety is progressing since almost all the responders were familiar with ISD. This is a significant and favourable development compared to the results of the Inside team survey (1997) in which lack of awareness was cited as the major hurdles to the ISD.

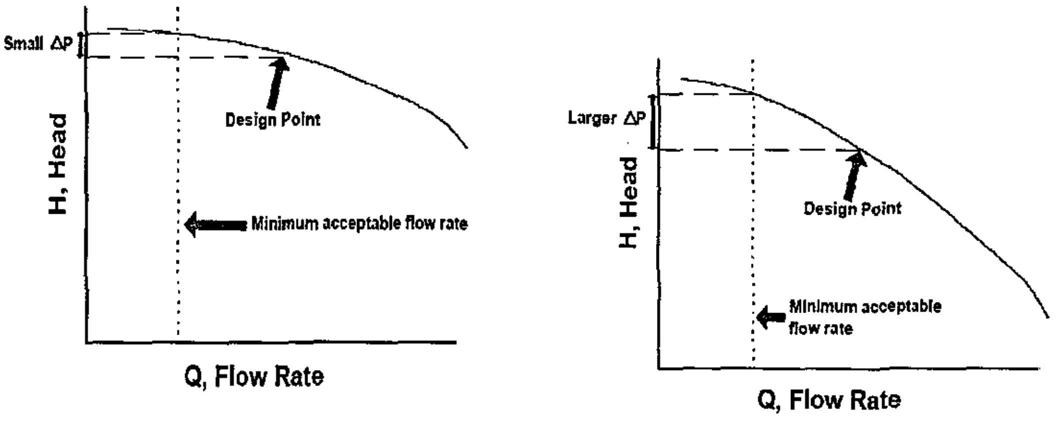
Though, many of the responders were not familiar with the current inherent safety indices. Those familiar have used them sparingly. Companies stated that the current indices are too elaborate, required a lot of process data and could not be used in early development stage. They recommended the need for quick, simple, well tested methods with enough examples to instill confidence in them.

2.7 Inherent Safety and reliability in process design

As mentioned before inherent safety principles can be applied at all stages in a process life cycle. In fact, there are many opportunities for enhancing the inherent safety and reliability of a plant at the detailed design stage. Hendershot and Post (2000) gave some specific examples for more reliable chemical plant design in the following sub - sections.

2.7.1 Pumps

When specifying a pump, the design should be robust enough to allow the pump to deliver the required flow rate over a wide range of operating conditions. In particular, the pump should be insensitive to variation in the downstream pressure, perhaps caused by fouling or plugging of pipes, valves stuck in a partially open position, failure of control valves, or operator error in setting manual valves. Figure 2.3 (A) shows a pump, which is very sensitive to an increase in downstream pressure. A better pump selection is shown in Figure 2.3 (B) – this pump will deliver the required flow rate with a much larger increase in downstream pressure. If the flow drops below the critical value, the plant will probably have to be shut down because of product quality or safety problems.



(A) (B)

Figure 2. 3: Pressure drop profile against flow rate for (A) Sensitive Pump Design, (B) More Robust Pump Design, Hendershot and Post (2000).

2.7.2 Compressors

Similar attention to performance curves can improve the reliability of a compressor design also. The vendors do provide this information for a good reason, and it is up to the plant designer to use the available data to specify a robust design which will provide acceptable performance over a wide range of operating conditions which may be encountered in plant operation. Figure 2.4 shows a sensitive compressor design, which can easily go into a surge condition with a slight variation in operating conditions. Figure 2.5 shows a much more robust design, which is much more tolerant of variation in operating conditions. Again, perhaps this compressor is a critical piece of equipment for plant operability or safety – for example, it might be the refrigeration compressor for the brine supply to a reactor with a highly exothermic reaction.

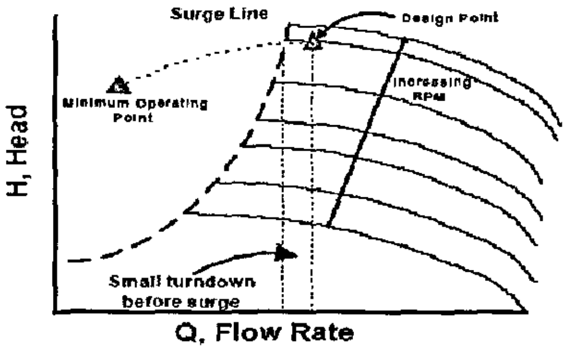


Figure 2. 4: A Sensitive Compressor Design, Hendershot and Post (2000).

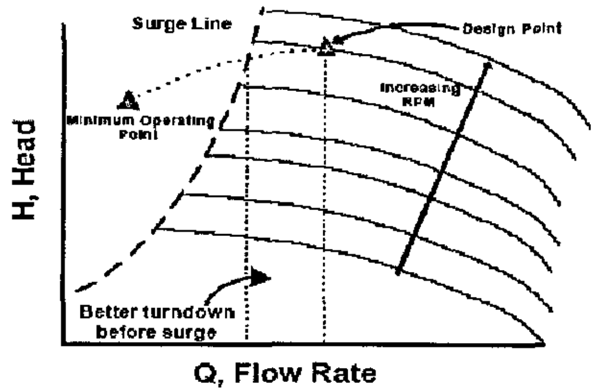
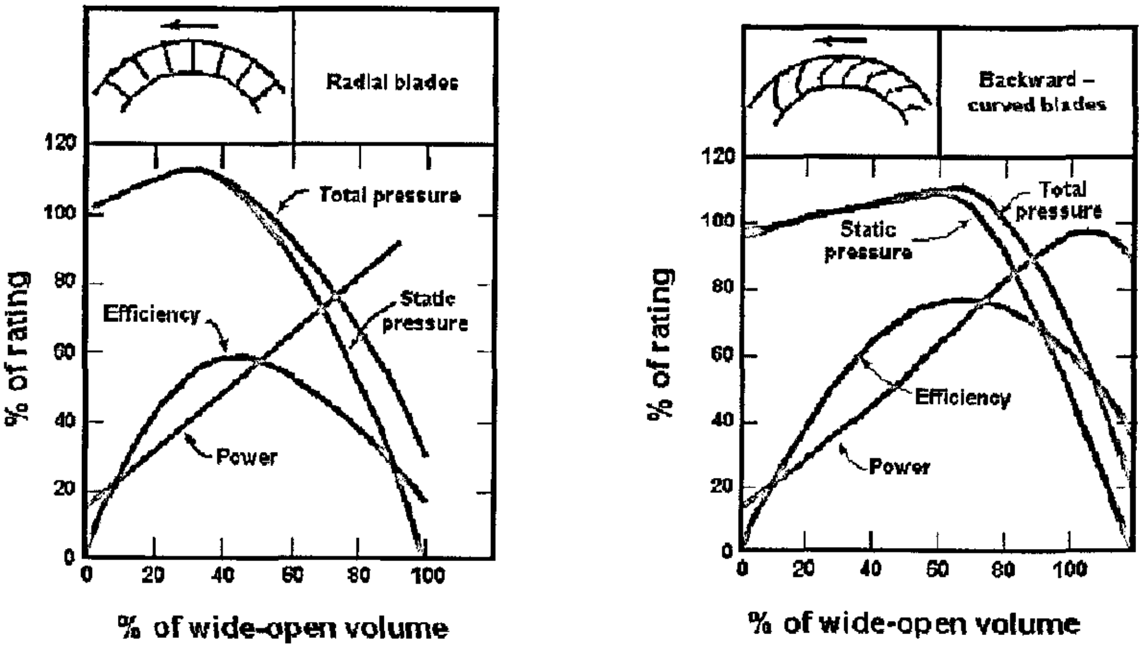


Figure 2. 5: A More Robust Compressor Design, Hendershot and Post (2000).

2.7.3 Fans

The selection of fan type can impact the robustness of a design, and the potential for the fan to trip out due to high power draw for the fan motor. The power draw for a radial blade fan increases as downstream dampers are opened, and it could reach a point where the motor would trip due to high power (Figure 2.6(A)). A fan with backward curved blades has a maximum possible power draw, and it is possible to design the system so the fan cannot trip due to high power (Figure 2.6 (B)).



(A) (B)

Figure 2. 6: Power Characteristics for (A) radial blade fan, (B) Backward Curved Blade Fans, Hendershot and Post (2000).

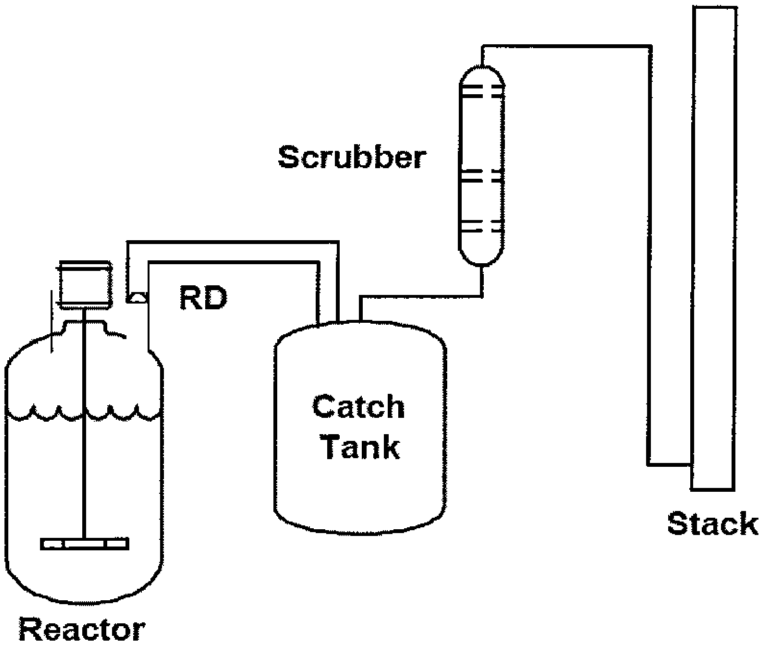


Figure 2. 7: A Complex Emergency Relief System for a Batch Reactor with a Potential Exothermic Runaway Reaction, Hendershot and Post (2000).

2.7.4 Vessel Design

Many years ago, emergency relief systems from reactors and other vessels discharged directly to the atmosphere, usually through a stack or to a building roof where potential exposure to people could be minimized. This is no longer acceptable for many vessels today because of environmental concerns, and a better understanding of the potential health and safety issues arising from an emergency relief system release. Therefore, it is often necessary to provide a complex system to treat the effluent from an emergency relief device. This might include equipment such as catch tanks, quench tanks, scrubbers, absorbers, or flare systems. Figure 2.7 shows an example system.

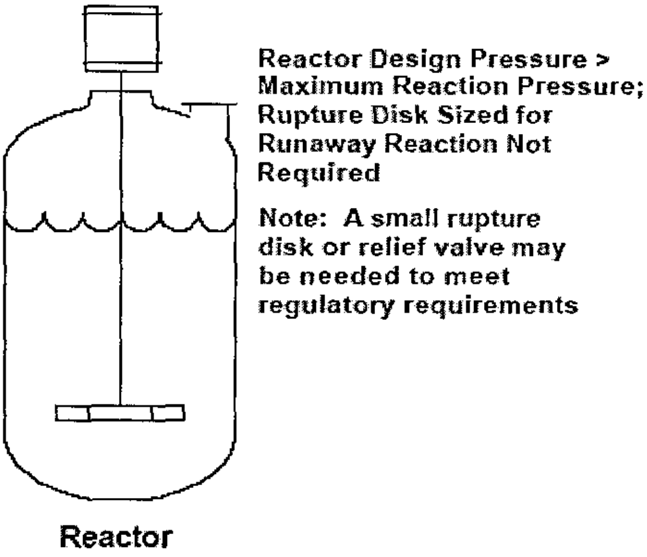


Figure 2. 8: A Reactor with a Higher Design Pressure May Eliminate the Need for the Complex Emergency Relief System, Hendershot and Post (2000).

Such systems are expensive to build and operate, and they can never be 100% reliable. Because they are emergency systems, which do not normally operate when the plant is functioning properly, failures may be hidden, detectable only by testing and other preventive maintenance programs. In many cases it may be possible to eliminate the need for complex emergency relief and effluent treatment systems by building a stronger reaction vessel, as shown in Figure 2.8. If the vessel can be designed to be strong enough to contain the maximum pressure from the worst credible runaway reaction event, the emergency relief system might be eliminated or greatly simplified while still complying with code and regulatory requirements. Of course, if this strategy is adopted, it is absolutely essential that the design engineers fully understand all chemical reactions, which can occur at the extreme conditions of temperature and pressure, which will result from a runaway reaction. Experimental data for all credible runaway scenarios must be available to confirm the maximum runaway pressure and temperature. It is essential that the chemistry, kinetics, thermodynamics, maximum temperature, and maximum pressure for the runaway reaction are thoroughly understood to properly design the reactor.

2.7.5 A Piping Design Example

To avoid over pressurization due to gas and heat generation from solid packing material, the column in Figure 2.9 must always be lined up either to the process flow (which will carry the gas and heat away) or vented to a collection and treatment system if the column is taken off line. Use of a three way valve which is designed to always be open to at least one of the flow paths (either to the process flow or to the vent system) will ensure that the column cannot be blocked in by closing the process feed valve without opening the vent valve.

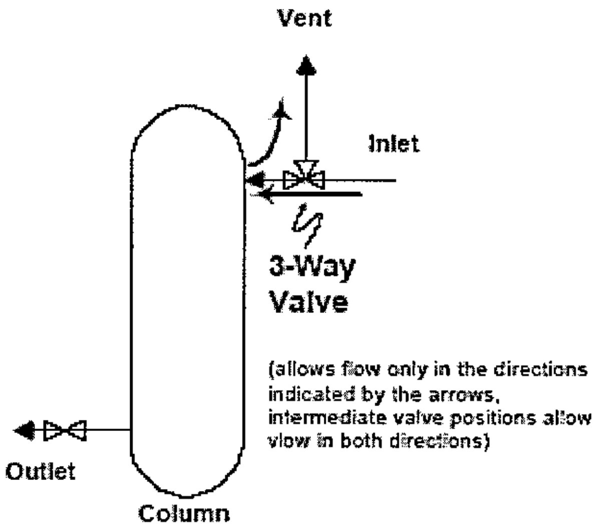


Figure 2. 9: A Three Way Valve Ensures that the Column Is Always either On Line or Vented, Hendershot and Post (2000).

2.8 Offshore Inherent Safety Potential

Khan *et al* (2004) and Khan and Amyotte (2002) discussed the applications of inherent safety in offshore oil and gas operations. They claimed that the main hazards on offshore installations are the process fluids and processing operations, the sea environment, and the process links between the reservoir and other installations. The following is some examples of inherent safety applications in offshore oil and gas fields.

2.8.1 Process facility layout

One of the most inherently safe means of managing risk to personnel associated with process facilities is to maximize the distance between the highest risk components of the processing facilities and the personnel. This methodology can be as fundamental as ensuring proper layout of the process facilities. Due to the high pressures involved, and relative ease of igniting the gas if released inadvertently, gas compression facilities are a significant risk contributor. It is therefore essential to maximize the distance between these facilities. Separation facilities also pose risks to personnel, and it is appropriate for these facilities to be located at the maximum reasonable distance from the accommodation module. The fuel gas system (relatively low pressure) can be located near the compression and separation facilities, while still maintaining a reasonable distance between the system and the facilities (including accommodation). Less hazardous systems such as power generation, utilities, etc. can be located closer to personnel quarters.

Incidents associated with gas compression and separation facilities are the most likely ones to impair escape routes back to the accommodation module. It is therefore critical that escape routes are designed to minimize these impairment risks.

There are two fundamental philosophies applied to the provision of escape routes: (i) fully enclosed tunnels and (ii) protected open walkways. Past studies have indicated that both philosophies can be applied successfully; however, protected open walkways are considered to be the more inherently safe option because there is no reliance on mechanical systems. The provision of two protected open walkways can be considered to achieve inherent safety through simplification of the design. A fully enclosed tunnel requires a pressurization system to achieve a similar performance level as that mentioned above for protected walkways. This reliance on an active system cannot be considered as inherently safe as a system reliant on only passive components. However, in certain scenarios a fully enclosed pressurized tunnel may be a more appropriate alternative. Therefore, as with all proposed risk reduction methodologies, there is a need for a case by case evaluation.

2.8.2 Offshore Process Operation

The sources of major hazards in offshore processing are the inventories of flammable materials in the associated pipelines of the reservoir, slug catchers, separators, contactors, heat exchangers, and high speed rotating equipment such as turbines, compressors, export pumps, and re injection pumps. Therefore, these items should be the main targets for inherently safer approaches.

Some inherent safety approaches can make a compromise in which safety enhancements are achieved as well as cost savings or improvements in process/structural performance.

For example, the elimination or reduction in size of equipment can lead to the use of simpler, smaller, more compact equipment which offers the promise of reduced hazard and risks, reduced weight and space requirements, and less maintenance. In this way inherent safety approaches can provide the most cost effective route to safety.

2.8.3 Separation processes

The use of static hydrocyclones is now an accepted technology for the treatment of oily water. These devices can reduce inventories and space and weight requirements by an order of magnitude compared to conventional technologies. They are very simple devices, more like a length of pipe than a separator; they need little maintenance and are also far less prone to leaks than older style flotation units. British Petroleum has carried out successful trials using hydrocyclones for well fluid dewatering. This study included the use of rotary as well as static hydrocyclones. The technology has cut residence times from minutes to seconds. Centrifuges potentially offer the best separation performance per unit volume, but maintenance requirements of the seal and the use of high speed rotating equipment are matters of concern. Alfa-Laval is reported to have developed a disk-stacked centrifuge that can be used to separate oil from water; this device is intended to replace existing coalescers for oily water treatment and recovery.

Power fluidics has also been used to develop a vortex choke valve for flow control, designed to reduce erosion and corrosion problems at chokes, and reduce maintenance requirements. The design, which requires no seal or gland for the main well stream flow, is said to last five times longer than a conventional choke valve.

Power fluidics is currently used mainly for oily water treatment. It is possible, however, that the technology could find wider application offshore for main stream separation, sand and solids separation, and glycol contacting, thus offering size and inventory reductions to about one-fifth that of conventional equipment.

2.8.4 Heat exchangers

It may also be possible to achieve further intensification by combining unit operations. Many fluidic devices can generate intense mixing, providing the basis for good heat transfer. In the future, heat exchangers could possibly be located within or around separators or contactors. In fact, the combining of unit operations/functions is a classic route to intensification, and should be given serious consideration in process development design. In recent years compact heat exchangers, especially plate-fin exchangers, have been specified for offshore duty. These are an order of magnitude smaller and lighter than conventional shell and tube designs, and hence have lower process inventories. They are, however, prone to fouling and are not as robust as other designs. 'Printed Circuit' heat exchangers (PCHEs) are an alternative compact design that has been used for compressor after-cooling, and has been claimed to offer a five-fold reduction in size and weight. The space and weight savings of the PCHE led to a cost saving of $1.50M compared to a conventional upgrade in a particular application.

Other developments have tried to improve the design of conventional shell and tube units; a Norwegian company claims to have developed a spiral baffle system which can enhance shell side performance leading to 25% weight and size savings.

2.8.5 Compressors

A study of compressor systems for offshore gas re-injection compared several alternatives using a simulation program. This work showed that a simpler system gave the best safety and process performance. The optimum design combined the inter-stage cooler and recycle coolers for stages 1 and 2 in the same unit, and also led to a reduction in the number of valves needed for recycle and surge control. This provides an example of how careful consideration of design alternatives can lead to inherently simpler and safer plant. The design eliminated the need for several valves and reduced the number of coolers from three to one, and probably reduced capital and operating costs accordingly.

2.9 Available Tools for Inherent Safety Evaluation

2.9.1 Hazard Indices

Several hazard indices have been developed as tools for chemical process loss prevention and risk management. These indices measure one or more aspects of inherent safety, usually implicitly (e.g. fire, explosion and/or toxic hazards), and it is generally necessary to use several indices to obtain a full understanding of the overall process characteristics. These indices can be calculated fairly quickly for a number of process options and design variations. Each gives a dimensionless index value that is defined relatively and may be combined with a decision analysis tool for setting priorities. Available indices include:

- Dow Fire and Explosion Index (F&EI), Dow (1994): Fire and explosion hazards. An interesting article by Gupta (1997) provides guidance on use of the Dow F&EI for process plants in developing countries. This may be regarded as an inherently safer application of an inherent safety tool, in that the premise of Gupta (1997) is that one should avoid a false sense of security by applying a tool based on U.S. experiences which may not transcribe exactly to other countries.
- Dow Chemical Exposure Index (CEI) Dow (1993): Acute chemical exposure hazards.
- Safety Weighted Hazard Index (SWeHI), Khan *et al.* (2001): Fire, explosion, and toxic release hazards. Provision is also made in the calculation procedure for evaluation of safety control measures.
- Environmental Risk Management Screening Tool (ERMST®) ERMST (1996): Environmental hazards, including air, ground water, surface water (human), surface water (ecological), and waste water.
- Transportation Risk Screening Model (ADLTRS®) ADLTRS (1994): Risk to people and the environment from chemical transportation operations.
- Hazardous Waste Index (HWI), Gupta and Babu (1999): Flammability, reactivity, toxicity and corrosivity hazards of waste materials.
- Mond Index, Tyler (1985): Fire, explosion and toxicity hazards.
- Toxicity Hazard Index, Tyler *et al.* (1996).

Most of these methods focus on existing plants and therefore required detailed information about equipment and plant layout. Other detailed methods developed for hazard evaluation (e.g., HAZOP, fault Tree Analysis (FTA), failure Mode Effect Analysis (FMEA)) can not be applied during early process design due to the huge amount of data required. Only a number of simplified methods exists (e.g., Inherent Safety Index (ISI), Inherent Safety Evaluation Toolkit (INSET), Environment, Health & Safety Index (EHS)) which are in principle applicable in early process design phases. Safety aspects are most effectively being considered early in chemical process development. However at early stages, only limited information on equipment and plant layout are exists. Thus, most existing methods cannot be applied directly in early process design.

2.9.2 The Mortality Index

Another way of quantifying hazards is to use potential loss of life as the primary measure of the size of hazard, Marshall (1987). This approach has been studied by Marshall (1977) who derived a relation between the number of deaths caused by a hazard, and the mass of material (explosive, toxic or flammable) causing the hazard. This relation is called the mortality index and is defined as the number of fatalities per tonne of hazardous material. Marshall examined historical records and from it he developed empirical relationships for fires and explosives.

The concept of the mortality index was first applied during the Second World War, to assess the success of bombing Germany. Marshall (1977) was the first to apply it to assessing chemical hazards. The idea is to derive a relation between the number of deaths caused by a hazard, and the mass of material (explosive, toxic or flammable) causing the hazard. The mortality index is defined as the number of fatalities per tonne of hazardous material.

Marshall examined historical records from the first and second world wars, covering bombings and the use of early chemical weapons. He developed the following empirical relationships from this data.

For explosives:

$$M_I = P_D \times Q^{-1/3} \qquad 2.1$$

Where,

M_I = mortality index, fatalities per tonne of explosive

P_D = population density in thousands per sq. km.

Q = mass of explosive, tonnes

For vapour cloud explosions and fireballs:

$$M_I = 3P_D \times Q^{-1/3} \qquad 2.2$$

Where,

Q = mass of flammable material, tonnes

For toxics, Marshall's research concluded that the mortality index was invariant with mass released. Therefore he gives the mortality index directly for four chemicals (in fatalities per tonne):

Chlorine $M_I = 0.5$

Mustard gas (bis-2-chloroethyl sulphide) $M_I = 0.8$

Ammonia $M_I = 0.02\text{-}0.052$

Methyl isocyanate $M_I = 12.5$

Vilchez *et al.* (2001) have applied the relationships proposed by Marshall to 352 explosions recorded in the Major Hazard Incident Data Service (MHIDAS). They obtained relationships that as they claimed have little predictive value. They attributed the weakness to some reasons such as the variation in population density and the difficulty of getting the real amount of material involved in the accidents as the amount listed in the databases does not necessarily coincide with the amount which was really involved in the explosion. However, they proposed new relations that enabled the estimation of the maximum number of fatalities which could be expected in an accidental explosion at a fixed installation by knowing the quantity of material involved as well as the probability of certain range of fatalities.

2.9.3 The INSIDE project Toolkit

The INSIDE (*IN*herent *S*HE *In DE*sign) project was a European government/industry project sponsored by the Commission of the European Community to encourage and promote inherently safer chemical processes and plants. The project has developed a set of tools, the INSET Toolkit, to identify inherently safer design options throughout the life of a process and to evaluate the options. These tools are described in more detail by the INSIDE (1997) Project.

The tools of particular interest with respect to measuring the inherent safety of chemical processes are the ISHE Performance. The inherent safety performance indices intentionally involve relatively simple computations. This enables a large number of process options to be rapidly evaluated. The various inherent safety, health, and environmental aspects of a process are evaluated using separate indices; no attempt is made to combine the indices into a single overall measure.

The INSET Toolkit instead recommends a multi-attribute decision analysis technique to evaluate the overall inherent safety aspects of the various process options. The INSET Toolkit is particularly interesting as an inherent safety measurement tool for two reasons, Mansfield (1996) and INSIDE (1997). First, it represents the consensus and combined expertise of a number of companies and organizations. Additionally, it is intended to consider safety, health, and environmental factors in one set of tools, an approach consistent with the recommendations of CCPS/CWRT (2001).

2.9.4 Inherent Safety Index

Heikkila (1996), of the Helsinki University of Technology, have proposed a new index for inherent safety evaluation. The index is relatively simple and is designed to consider a range of factors affecting the inherent safety of a process. These factors are grouped into two main categories: chemical and process inherent safety. The chemical inherent safety index describes the effect of the choice of raw materials and other chemicals on the inherent safety of the process through consideration of heats of reaction, flammability, explosiveness, toxicity, corrosiveness, and incompatibility of chemicals. The process inherent safety index describes the effect of the type of process equipment and process conditions on inherent safety. The parameters considered here are: inventory of chemicals, process temperature and pressure, the type of processing equipment, and the structure of the process. The separate chemical and process indices are summed to yield a total inherent safety index.

It appears that this work attempts to build on the prototype index of inherent safety of Edwards and Lawrence (1993) by extending beyond the choice of raw materials and the sequence of reaction steps. In a series of subsequent publications the group at the Helsinki University of Technology have described their use of:

- Case-based reasoning (using a design case database) to determine a process structure subindex Heikkila *et al.* (1998),
- A genetic algorithm for optimization of a process synthesis model, Heikkila and Hurme (1998), and
- Accident statistics and layout data to determine an equipment safety subindex Heikkila and Hurme (1998). Heikkila (2000) provides a summary of the progress to that date.

Palaniappan *et al.* (2001) have presented a new inherent safety index for ranking process routes and a graphical method for analysing reaction networks. The index consists of two parts, the first part is a systematic methodology for inherent safety analysis during process route selection stage and the second part is a methodology for inherent safety analysis during flowsheet development stage. They implemented the methodology by using an expert system called iSafe. They used the index to compare three routes for phenol manufacture.

2.9.5 Fuzzy Based Inherent Safety Index

Gentile *et al.* (2003), of the Mary Kay O'Connor Process Safety Centre at Texas A&M University, have attempted to improve on some of the subjective factors in the inherent safety index of Heikkila *et al.* (1996) by using fuzzy set theory. The modifications were essentially aimed at improving the sensitivity (either excessive or insufficient) in the ranges selected for each of the various index parameters.

The fuzzy logic system was used to calculate a proposed inherent safety index based on *if-then* rules that describe knowledge related to inherent safety. In this approach each factor is described by a linguistic variable whose range of interest is divided into fuzzy sets. For each set, a membership function is defined which has a specific shape describing the physical behaviour of the set, Gentile *et al.* (2003).

As noted by Gentile *et al.* (2003), the fuzzy based approach eliminates the problems presented by a traditional interval approach for parameter ranges, and is seen as a first step toward a more reliable and simple methodology for inherent safety evaluation. Further work identified by the authors, Gentile *et al.* (2003) includes: parameterization of inherent safety, unified membership functions, development of if-then rules, and reliable and robust methods of quantification.

2.9.6 Expert System for Inherently Safer Processes

Palaniappan and co-workers (2002a, b) have developed a systematic methodology and automated tools for inherently safer route selection and flowsheet development. Palaniappan *et al.* (2002a) describe the knowledge required for inherent safety analysis during route selection and how it can be formalized in the form of expert rules. The authors illustrate a new inherent safety index for ranking process routes and a graphical method for analyzing reaction networks. In the second part of their work Palaniappan *et al.* (2002b), they have proposed a methodology for implementing inherent safety during flowsheeting. The methodology is based on ranking flow sheets using indices that are based on ranking patterns proposed by Heikkila (2000).

2.9.7 Integrated Inherent Safety Index (I2SI)

Khan and Amyotte (2004) have developed a new indexing procedure: Integrated Inherent Safety Index (I2SI). The conceptual framework of the I2SI is shown in Figure 2.10. As illustrated, the I2SI is comprised of two main sub-indices: a Hazard Index (HI) and an Inherent Safety Potential (ISPI) Index. The hazard index is intended to be a measure of the damage potential of the process after taking into account the process and hazard control measures.

The inherent safety potential index, on the other hand, accounts for the applicability of the inherent safety principles (or guidewords) to the process. The HI is calculated for the base process (any one process option or process setting will be considered as the base operation or setting), and remains the same for all other possible options. The HI and ISPI for each option are combined to yield a value of the integrated index as shown in Equation 2.3.

$$I2SI = \frac{ISPI}{HI} \qquad 2.3$$

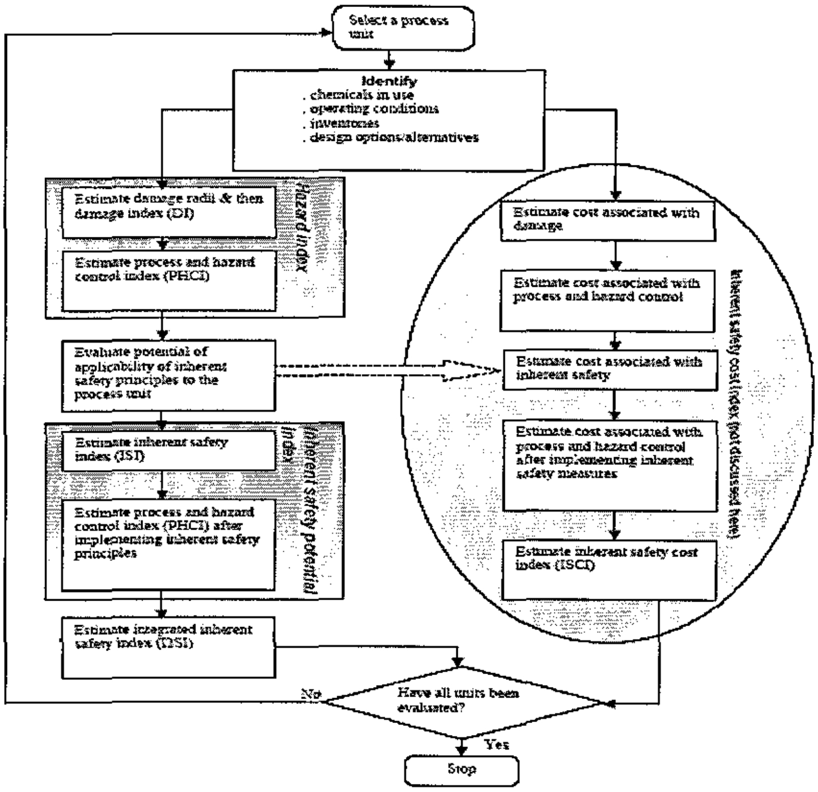


Figure 2. 10: Conceptual framework of the I2SI.

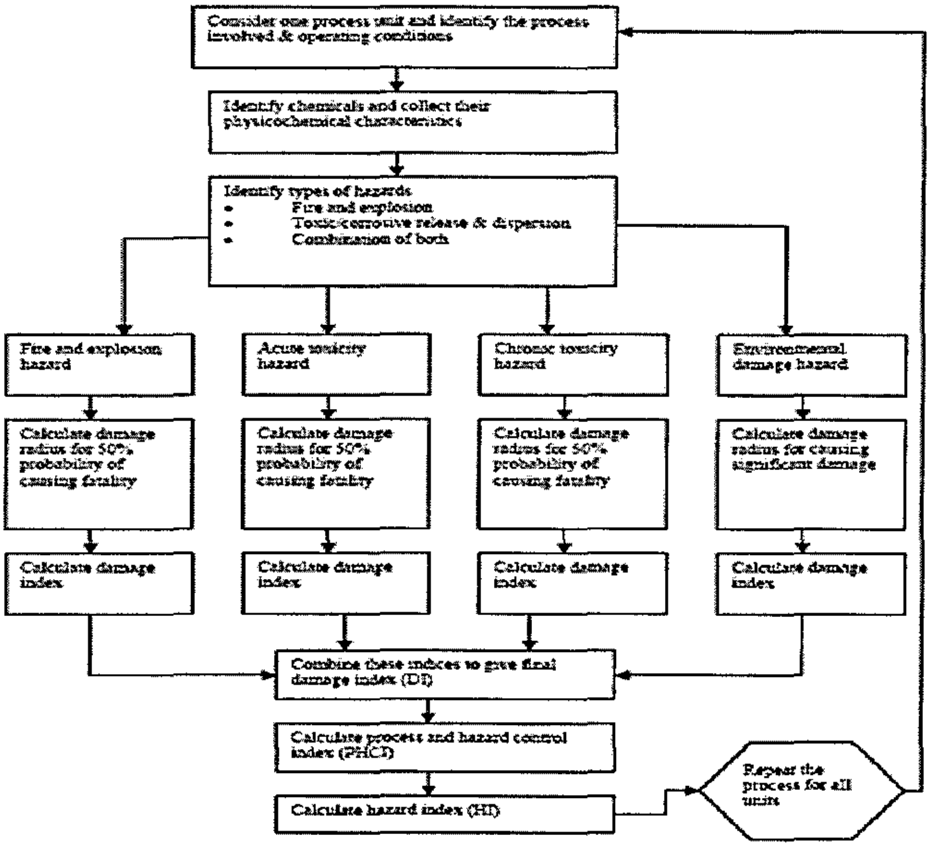


Figure 2. 11: Framework for hazard index (HI) computation.

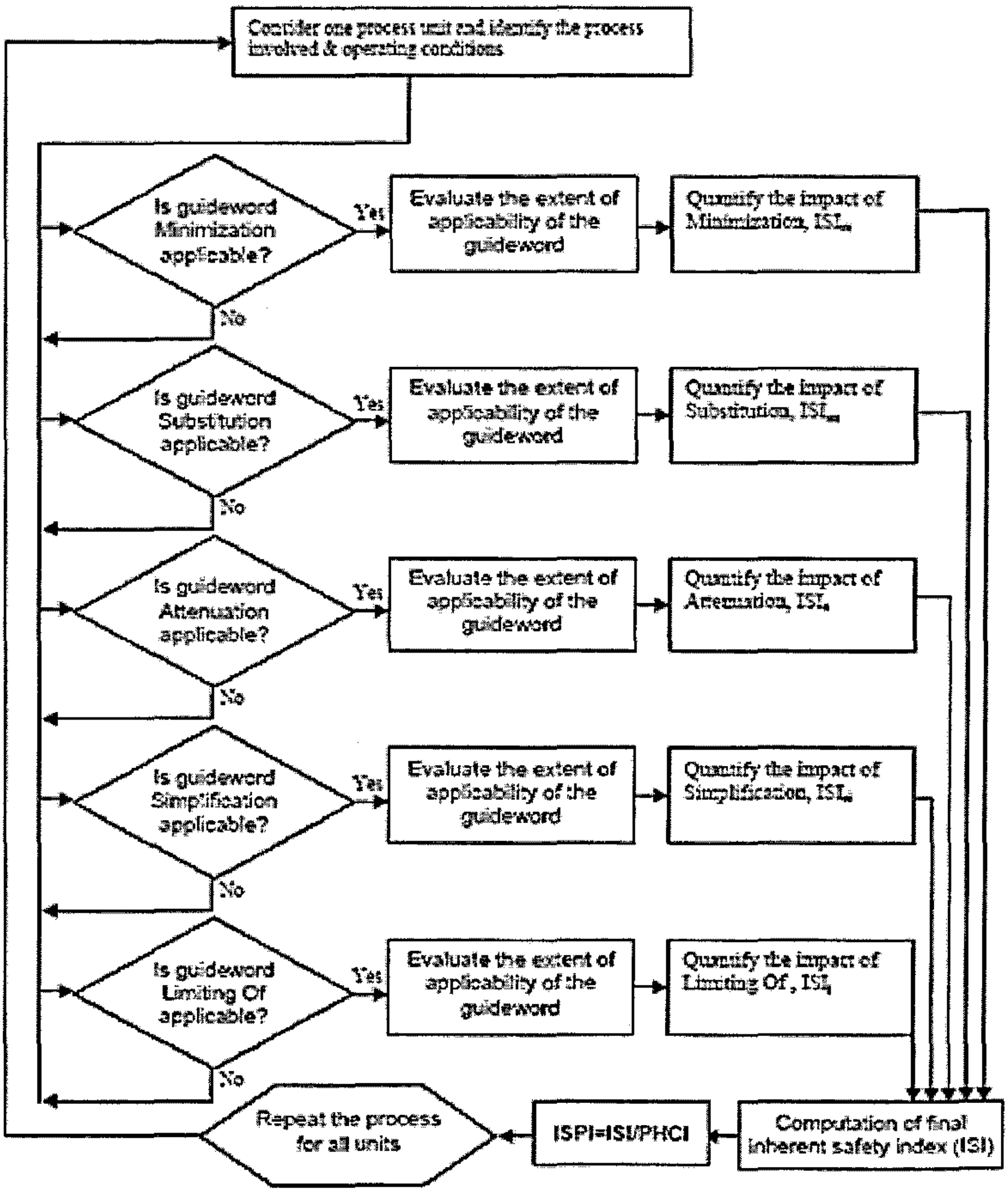


Figure 2. 12: Framework for inherent safety potential index (ISPI) computation.

Both the ISPI and HI range from 1 to 200; the range has been fixed considering the maximum and minimum likely values of the impacting parameters. This range gives enough flexibility to quantify the index. As evident, an I2SI value greater than unity denotes a positive response of the inherent safety guideword application (inherently safer option). The higher the value of the I2SI, the more pronounced the inherent safety impact.

The conceptual framework and sequence of steps involved in the computations of the HI and ISPI are shown in Figures 2.11 and 2.12 respectively. The details are available in Khan and Amyotte (2004).

2.9.8 Regulations and Legislation

Legal regulations are designed to ensure the safety and health of people. The first European Council directive concerned with controlling major accident hazards involving dangerous substances was adopted in 1982. Known as the 'Seveso' directive, (82/501/EEC), it was incorporated into UK law by means of the Control of Industrial Major Accidents Hazards Regulations 1984 (CIMAH). The regulations were primarily aimed at protecting people, and enforcing them was the responsibility of the Health and Safety Executive. In 1996, 'Seveso' was superseded by the 'Seveso II' directive (96/82/EC). The principal changes were a broadening of scope to include a wider range of dangerous substances and enhanced requirements to protect the environment. Most of the requirements of 'Seveso II' have been implemented by the UK Control of Major Accident hazards COMAH regulations 1999.

The general duty of the COMAH regulations is that 'Every operator shall take all measures necessary to prevent major accidents and limit their consequences to persons and the environment'. The regulations are implemented by a Competent Authority (CA), comprising the Health and Safety Executive working jointly with the Environment Agency and the Scottish Environment Protection Agency. This arrangement reflects the requirements to ensure the protection of both persons and the environment. The COMAH regulations apply to establishments that have the potential to cause major accidents because they use, or store, significant quantities of dangerous substances, such as oil products, natural gas, chemicals or explosives.

The requirement of the regulation operates at two levels defined in terms of a threshold quantity. At the first level, any activities that involve a quantity of a hazardous substance that is between 10% of the threshold quantity and the threshold quantity, are classified as a Lower-tier installation. Operators are required to produce documentation to demonstrate that the activity is being operated safely and also prepare an on-site Emergency Response Plan.

At the second level, any activities that involve quantities of hazardous substances that are above the threshold limit are classified as a major hazard installation, which require the operator to prepare a safety report called "COMAH Report" by a competent person and also prepare an Emergency Response Plan covering both on-site and off-site emergency services. The schedule of hazardous substances and threshold quantities can be found on the Health and Safety Executive (HSE) website.

2.9.9 Historical analysis of accidents

Historical analysis of accidents is one of the most frequently utilized auxiliary techniques in risk analysis. Its usefulness has essentially centred on its application to the identification of hazards in specific installations or operations and also because it offers promising possibilities for application in the estimation of human fatalities and property damage likely in specific accident.

Another interesting approach is that analyzing historical accidents such as fire and explosion or toxic releases lead to the identification of a number of features (origin of the accident, type of installation in which it has occurred most frequently, consequences, etc.) and to the reaching of conclusions which can be very helpful in risk assessment. The results of such an analysis can be used to identify the main sources of risk, to establish which accidents are more prone to happen, to show the activities or installations in which an effort is required to improve safety, to specify the order of magnitude of the probable consequences and to define safer operating procedures, Planas-cuchi *et al.* (1997).

2.10 Design and operate plants for inherent safety

Englund (1991) added some techniques to those suggested by Kletz, although some of the examples are already mentioned by Kletz, that can be used to design and operate plants so that they are inherently safer and to reduce the possibility of catastrophic incidents.

2.10.1 Clear responsibility

Competent and experienced people are responsible for decisions made from the start of plant design. Also it is the responsibility of the operations management to make certain that responsibility for safe design is clearly understood.

2.10.2 Critically review alternatives early in design

Identification of the hazards and alternatives available to remove or reduce them should be made early in the design. The alternatives may include adding protective equipment at the end of the design or after the plant is operating, both of which can be expensive and not entirely satisfactory.

Hazard and operability studies and other safety studies and reviews normally take place late in the design. At this stage it is usually too late to increase the design pressure of vessels, relocate electrical equipment and revise the layout or the process extensively. Critical reviews and evaluation of alternatives are needed in the early stages of design. This would involve an early hazard and operability (HAZOP) study using flow sheet before the final design begins.

2.10.3 Incorporate emergency planning into the original design

Emergency planning is often done after the plant is nearly complete and ready for start-up. At this point, it is necessary to live with the plant as built because it is not easy to make some of the desired changes for accommodating emergency planning. Emergency planning should cover items such as possible vapour releases from the proposed plant, nearby plants, proximity to public areas, accessibility of fire protection equipment to the plant, safe exit routes, etc.

2.10.4 Provide adequate spacing for process plants, tanks, and roads

Also it is not a good idea to have tank-car and tank-truck loading and unloading facilities close to the process area when hazardous materials are involved. Process and storage areas must be sited away from residential areas.

2.10.5 Storage

Another aspect which needs to be taken into consideration is the storage tanks. Process designers must question the need for all intermediate hazardous material storage and minimize quantities where storage is really needed, with grater attention to "just in time" supply.

Inventory in transfer lines can be a major factor in overall facility risk. Their length should be minimized by careful attention to pipe routing. Pipe size should be sufficient to handle the required amount of material and no more. It is desirable to design dikes that will not allow flammable or combustible materials to accumulate around the bottom of tanks or equipment in case of a spill. If liquid is spilled and ignites inside a dike where there are storage tanks or process equipment, the fire may be continuously supplied with fuel and the results can be severe. It is usually much better to direct possible spills and leaks to an area away from the tank or equipment and provide a fire wall to protect the equipment from most of the flames if a fire occurs. Figure 2.13 (A) shows schematically a traditional way to design diking and Figure 2.13 (B) shows a better design that has met with success.

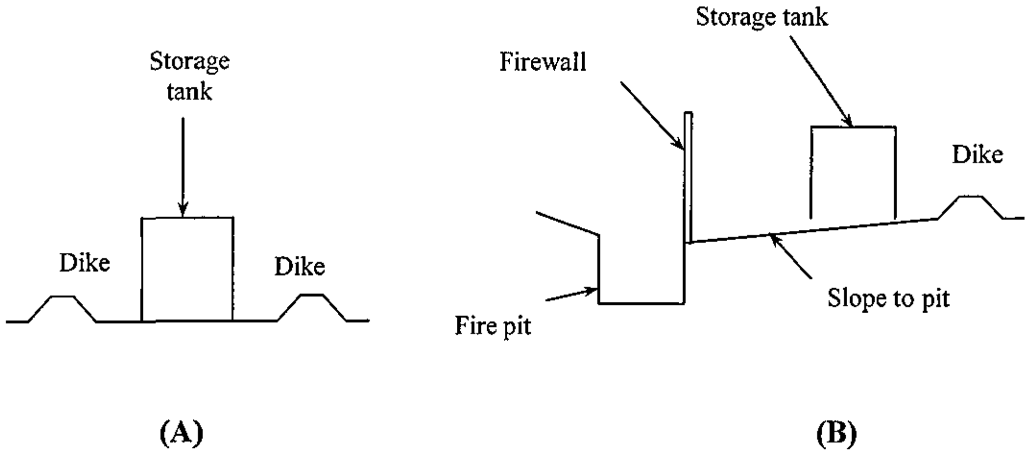


Figure 2. 13:(A) Traditional diking design method, (B) More desirable diking method.

2.11 Summary and conclusion

It can be seen from the above sections that the concept of inherent safety is very important. The inherently safer process avoids or reduces hazards instead of controlling them. It relies on naturally occurring phenomena and robust design and eliminates or greatly reduces the need for instrumentation or administrative controls, thereby reducing the costs related to safety and environment. This is normally accomplished by application of inherent safety principles throughout the design process, from conception until completion.

Major decisions on process principles are done in the process development and conceptual design phases. Therefore, the preliminary design phases give the best opportunities of implementing the inherent safety principles. In fact the possibility of implementing inherent safety decreases as the design proceeds. Thus, the inherent safety characteristics should be evaluated systematically as early as possible.

Despite the obvious importance of inherently safer design, there is limited adoption of its principles in the industry. Constraints such as lack of knowledge and inadequate inherent safety analysis tools are often cited as obstacles to application of inherent safety principles during process design.

A number of tools/indices were developed to evaluate inherent safety in the early design phases. These tools/indices are used in ranking process at the route selection stage. Other methods such as Dow and Mond indices and Marshall's mortality index have been suggested as measurements of inherent safety though not originally developed for that purpose, Rahman *et al.* (2005). In addition, analysing historical accident provide a great benefit since it can help in learning from past mistakes, make design improvements, and quantify the hazards associated with chemical and process industries.

As a conclusion, inherent safety is an exciting field that has caught the attention of researchers, plant designers, management and regulators worldwide. An inherent safety measurement method is needed to compare different processes for an end product. This method should work at the research stage itself and not require too much process data that can not be available in early design stages.

Chapter 3: Inherent Safety Index

3.1 Introduction

Edwards and Lawrence (1993) have proposed an index for ranking the inherent safety of chemical process routes. One of the recommendations suggested by Edwards and Lawerence (1993) is to try the index on more test data in order to examine the performance of it as well as to give more evidence of the benefits of inherent safety. This chapter presents a case study applied to the index in order to examine the performance of it as well as to give more evidence of the benefits of inherent safety. The case study is for the production of Adiponitrile.

3.2 Inherent safety index details

The inherent safety index serves three functions:

- It scores chemical routes allowing them to be compared against each other by inherent safeness.
- It is an additional method to compare chemical routes to a common product, rather than just looking at economic evaluations.
- It allows for the impact of changes to the route to be assessed.

The index is based on seven factors: inventory, flammability, width of explosive range, toxicity (threshold limit value), reaction temperature, reaction pressure, and reaction yield. Edwards and Lawrence used the index to compare six methods for the manufacture of methyl methacrylate (MMA) and have compared the results with assessments made by eight experts. The agreement was good. They have also compared the index values with the costs of making MMA by the six routes to see if the costs (capital and operating) of the inherently safer processes are less. They pointed out that inherently safer plants are cheaper because they require less added protective equipment, but this is not accounted for in the cost estimates. When alternative processes are compared, the total capital cost is usually estimated by factorial cost accounting, that is, by multiplying the cost of main plant items by a factor, and no allowance is made for different levels of protective equipment.

Each parameter was assigned a scoring table. Some tables are based upon tables and charts from the Dow and Mond indices. The steps are scored by summing the scores from the table for each parameter and finally the scores for all the steps are added together to score the route.

The score for a reaction step is divided into two parts. The first part is the process score. This is the score for the reaction parameters, that is temperature, pressure and yield. The scores for the three parameters are summed to give the process score.

The second part is the chemical score. This is the score for the hazard due to properties of the chemicals, that is inventory, toxicity, explosiveness and flammability. The scores for the four parameters are summed to give a score for each chemical in the step. The chemical score for the step is taken as the highest score out of the chemicals in the step, that is the scores for the most hazardous chemical, in a similar manner to the Dow and Mond indices.

The process score and the chemical score are summed to give the step score. The Inherent Safety Index for the route is the sum of the step scores. A high score means an inherently unsafe process.

3.3 Case Study

Adiponitrile is a nitrile, with formula $NC(CH_2)_4CN$, is manufactured principally for use as an intermediate to make hexamethylenediamine, which is a principle precursor of the polymer Nylon-6,6.

A literature survey has been made on the manufacture of Adiponitrile. The results showed that Adiponitrile is made by at least three different processes, and each is based on a different hydrocarbon. Data for only two routes could be found. The chemical and process details of the routes were taken from a report by Chem Systems International Ltd. (1983) for adipic acid and acrylonitrile routes. A process description of each route, including the main chemicals and reaction steps is given below.

3.3.1 Adiponitrile from adipic acid

A flow sheet is presented in Figure 3.1 for the vapour phase reaction of adipic acid with ammonia to form adiponitrile. Purification units for the adiponitrile include both distillation and chemical treatment. In this method solid adipic acid, with greater than 99.7 % purity is fed by a star feeder to a tank in which the acid melts and is kept in the liquid form at 200° C under an ammonia atmosphere. The heat of fusion is supplied by a heating coil. Fertiliser grade anhydrous ammonia is vaporised at 21°C and 8.9 bar in an evaporator, superheated to 275°C and passed to the bottom of the reactor. The reactor is a multi-tubular vessel made of stainless steel and packed with catalyst.

The liquid adipic acid from the melt tank is heated to 275°C and fed to the bottom of the reactor. The liquid enters the reactor mixing section through a series of nozzles specially designed to ensure atomisation of the liquid and minimum contact between the molten acid and the walls of the vessel. The vaporised acid, mixed with ammonia in a molar ratio of 1:10 is fed to the reactor tubes packed with a sintered mixture of boric and phosphoric acid particles. The reaction is strongly endothermic and the heat necessary to keep the reaction temperature around 275°C is supplied by condensing Dowtherm. The reaction is one of ammoniation followed by dehydration to the acid amide, and then to the nitrile.

The vapours leaving the top of the reactor are cooled down to 230°C and separated into a vapour and a liquid phase. The liquid phase contains adiponitrile and by-products while the vapour phase is composed primarily of ammonia, water, and small amounts of adiponitrile and partially converted adipic acid compounds.

The gas phase is sent to a column where water and ammonia are taken overhead, crude adiponitrile is removed as a side stream and a mixture of adiponitrile and partially converted acid is taken off as bottoms. The ammonia and water overhead is partially condensed, some of the aqueous layer is discarded while the rest is used as a reflux for the column. The non-condensed ammonia is purged in order to remove possible traces of carbone oxide and hydrogen cyanide that might be generated in the reactor.

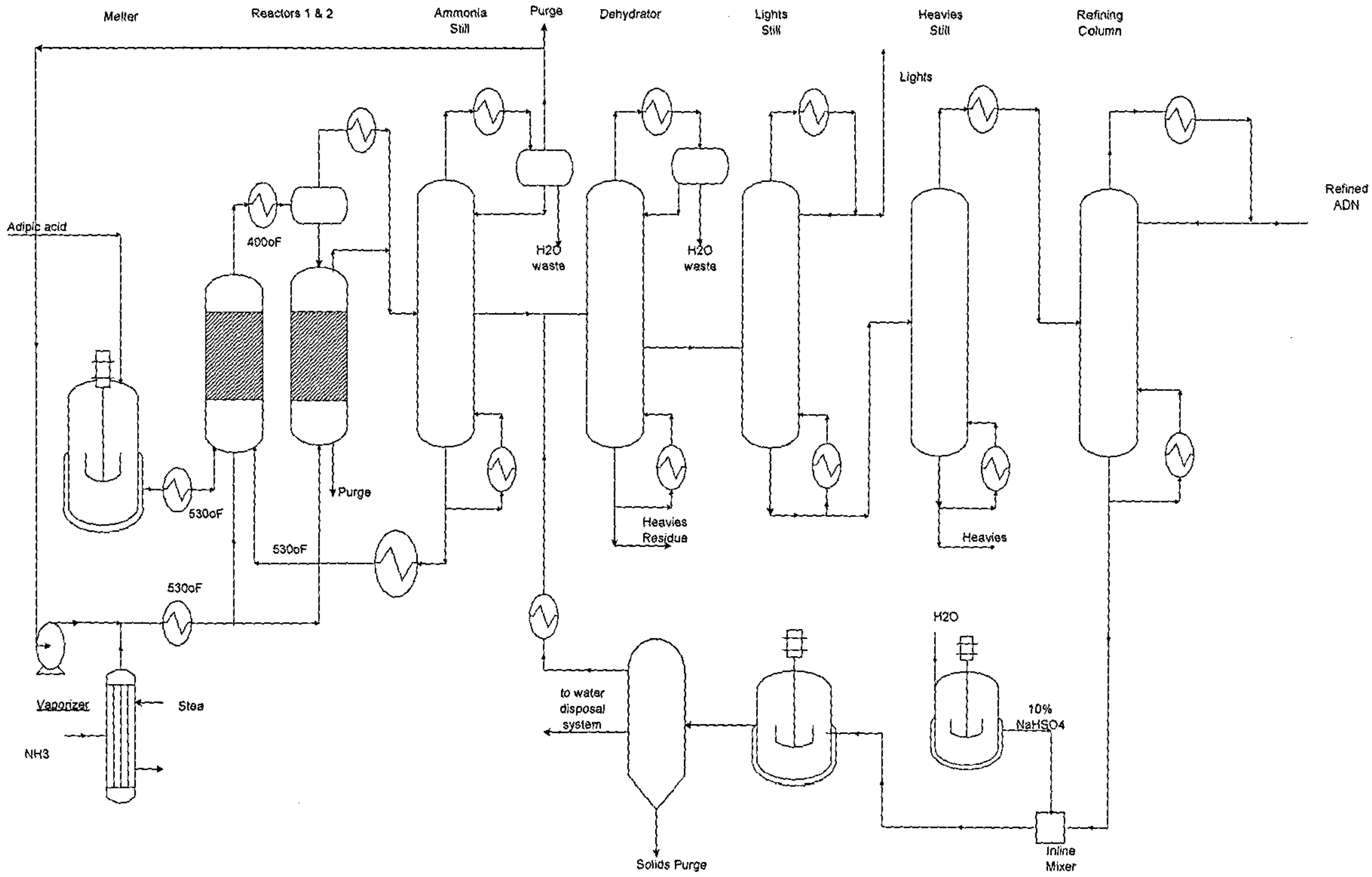


Figure 3. 1: Process Flow Diagram for the Adipic Acid Route.

The bottoms from the column, containing partially converted acid, are recycled back to the reactor. The liquid phase from the gas-liquid separator in the reactor section contains adipic acid, partially converted acid, adiponitrile and by-products of the reaction. This material is fed to a second reactor to complete the reaction of the partially converted acid. Ammonia at 275°C enters the bottom of the second reactor and contacts the liquid entering at the top. Dowtherm vapours condensing at 345°C provide the energy necessary to produce adiponitrile and water vapour by the reaction of the partially converted acid and the ammonia. The vapours leaving at the top of the film evaporator type reactor, containing ammonia, water and adiponitrile, are fed to the distillation column which is also fed by the vapours from the gas-liquid separator of the reactor unit. The reactor is purged in order to remove heavy impurities that collect at the bottom.

The adiponitrile side stream of the ammonia recovery column contains a wide assortment of organic contaminants and some water which must be removed prior to using the adiponitrile as a raw material for hexamethylenediamine production. The crude adiponitrile is sent to a dehydration column in which water is removed at the top and heavy by-products and solid residues are taken out at the bottom. A solid-free and dry adiponitrile side stream is taken off at a point substantially lower than the feed point. This is a provision necessary to obtain a water-free adiponitrile. The next step in the purification of adiponitrile is the removal of the light components in a vacuum distillation still. The adiponitrile withdrawn at the bottom is sent to the heavies vacuum still where the adiponitrile is removed at the top and the heavies are taken off as bottoms. In a subsequent distillation, refined hexamethylenediamine-grade adiponitrile is removed as the distillate stream. In this distillation unit, a substantial amount of adiponitrile is removed with the heavies components at the bottom of the column. A better separation is not attempted, in order to ensure that the purity of the adiponitrile withdrawn at the top of the column satisfies the requirements for hexamethylenediamine production. The bottoms of the adiponitrile refining still are subjected to chemical treatment with sodium bisulphate.

Treating crude adiponitrile streams with either acids or bases is used widely throughout the chemical industry as a convenient way to remove the by-product impurities. The specific treatment proposed in this processing scheme consists of mixing the adiponitrile-organic by-products bottoms from the refining column with a 10% weight sodium bisulphate aqueous mixture. An in-line mixer should be used to achieve rapid and complete mixing of the two streams. The in-line mixer is connected to a stirred tank with a residence time of approximately thirty minutes. The effluent from the agitated vessel is sent to a settling tank where solids overflow is recycled back to the purification section where it is mixed with the feed to the dehydration column. The aqueous phase is sent to the water disposal system.

3.3.2 Adiponitrile Production – Electrolytic Process From Acrylonitrile

The second process to produce Adiponitrile is the electrohydrodimerization of acrylonitrile. The electrolytic cells are the heart of the processing facility for the production of adiponitrile via electrohydrodimerisation of acrylonitrile. Figure 3.2 is a schematic diagram of the process. The reactions taking place at the electrodes are given below:

$$Anode: \quad H_2O \Rightarrow \quad 2H_2 + \frac{1}{2}O_2$$

$$Cathode: \quad 2CH_2 = CHCN + 2H_2O \Rightarrow \quad NC(CH_2)_4CN + 2OH$$

The reaction is carried out to about 50 percent molar conversion of the acrylonitrile with a selectivity close to 92 percent. The most important by-products are propionitrile and high boilers (oligomers of acrylonitrile). All impurities present with the adiponitrile are removed by distillation. Propionitrile is taken off at atmospheric pressure while the others are distilled under vacuum.

The catholyte mixture is prepared in an agitated blending tank where fresh acrylonitrile and water are mixed with recycle streams of these two components. An organic salt solution and make up salt are also fed into this tank. The catholyte solution is sent to a storage tank from which it goes to the tank of cells. The anolyte make-up, sulphuric acid and demineralised water, are mixed with recycled anolyte in a surge tank which also serves as the blending facility.

Both the anolyte and the catholyte solutions flow in parallel through numerous compartments in a tank of cells. Electric current passes through the same cell compartments in series and provides the electrons necessary for the formation of adiponitrile.

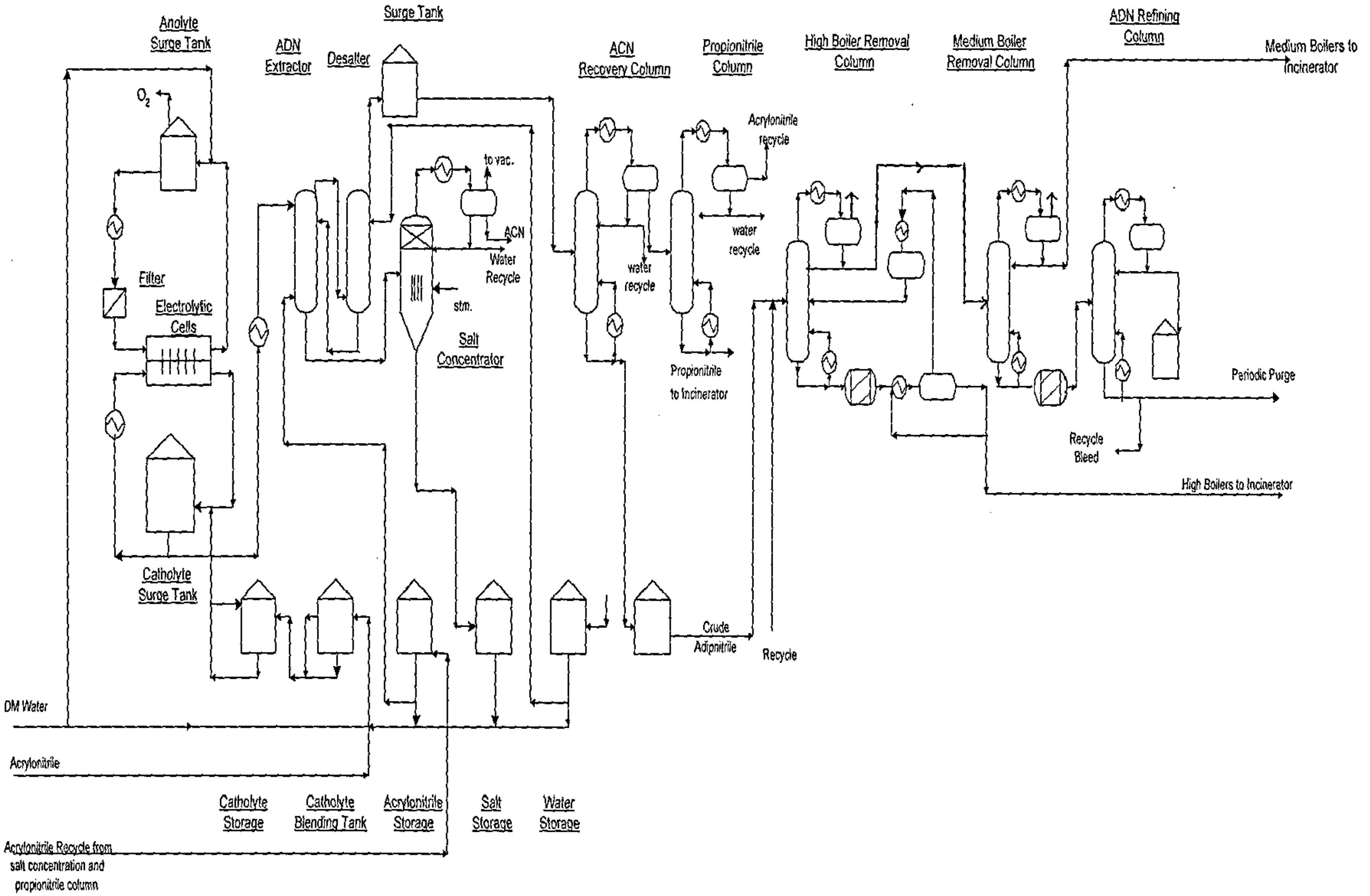


Figure 3. 2: Process Flow Diagram for Acrylonitrile Route.

The effluent catholyte from the cells is recycled through a cooler and back to the cells. A high rate of circulation through the cell keeps the temperature rise down to 3°C (5°F) and serves to keep the adiponitrile concentration low at the cathode surfaces. The anolyte effluent flows to the surge tank where the oxygen formed at the anodes is vented into the atmosphere. Prior to being recycled back to the cells, the anolyte is cooled down to 50°C (122°F).

A small quantity of the liquid circulating through the catholyte side of the cells is continously removed and sent to the purification-recovery section of the plant. The product stream is cooled down to 37°C (100°F) and sent to the top of the adiponitrile extractor. The adiponitrile is extracted with concentrated acrylonitrile. The aqueous phase leaving at the bottom of the extractor unit contains the salt used as solubiliser for the acrylonitrile.

The overhead effluent from the adiponitrile extractor contain the solvent, acrylonitrile, the extracted compound, adiponitrile, and relatively small amounts of salt and organic by-products. This mixture is sent to a second extractor where it is contacted with a 7.4 % by weight acrylonitrile solution in water. The remaining salt is extracted with this aqueous stream.

The aqueous bottoms from the second extractor containing the extracted salt are fed to the top of the first extractor unit. The overhead stream from the second extraction column, consisting of a mixture of acrylonitrile, adiponitrile, and organic by-products, is sent to the acrylonitrile recovery column.

The bottoms from the first extraction unit are sent to the salt concentrator where water and acrylonitrile are distilled off while a concentrated salt solution is drawn off at the bottom and sent to the salt storage tank. The organic phase containing almost exclusively acrylonitrile is sent to the acrylonitrile storage tank. The aqueous phase is sent to the water storage units with the exception of a small portion which is used as recycle for the concentrator.

The organic mixture of reactants and feed to the acrylonitrile recovery column is separated into crude adiponitrile bottoms and a two phase overhead distillate containing water, acrylonitrile and small amounts of propionitrile. A portion of the aqueous layer is used as a reflux to the column and the rest is sent to the water storage tanks. The organic phase is sent to the propionitrile removal column. In this unit propionitrile is removed as a bottoms while a two phase mixture is distilled overhead. The organic phase containing acrylonitrile and approximately 5 % by weight propionitrile is returned to the acrylonitrile storage units and recycled back to the cells. The aqueous phase amounts to only a negligible quantity and is also returned to the water storage area. The propionitrile bottoms are burned in an incinerator.

The crude adiponitrile leaving the acrylonitrile recovery still is sent to the adiponitrile purification section. The product purification train consists of three vacuum distillation columns and a small evaporator. In the first column, high boilers and some adiponitrile are withdrawn at the bottom of the still. The adiponitrile is separated from the high boiler removal column. The overhead from the first still is sent to the medium boilers column where these compounds are distilled off while adiponitrile and heavies are withdrawn at the bottom. The last purification unit, referred to as the refining column, separates adiponitrile from higher boiling compounds which are periodically purged.

3.4 Applying the Inherent Safety Index to the adiponitrile routes

In this section the index was tested on two routes to produce adiponitrile. Full details of the chemicals present including physical and chemical properties, are given in Table 3.1.

Adiponitrile is used as an intermediate for manufacture of Hexamethylenediamine (HMDA). A production of 75,000 ton/year of Hexamethylenediamine has been taken as a basis for the two routes and a backward calculation has been done in order to calculate the amount of chemicals involved in the reactions.

Table 3. 1: Adiponitrile (ADN) route details

Route	Reactants	Products	Temp. (°C)	Pressure (atm)	Yield (%)
Adipic acid	Adipic acid Ammonia	Adiponitrile water	275	1*	95*
Acrylonitrile	Acrylonitrile water	Adiponitrile propionitrile	55	1	90

* *kirk othmer – Encyclopedia of Chemical Technology*

3.4.1 Adipic acid route

Basis:

Capacity: 75,000 tonnes per year of (HMDA).

The process consists of two reaction steps, the first is to produce adiponitrile starting from adipic acid and the second is to produce HMDA. The reactions are as follows:

$$C_6H_{10}O_4 + 2NH_3 \rightarrow C_6H_8N_2 + 4H_2O \qquad 3.1$$

Adipic acid + ammonia → adiponitrile + water

$$C_6H_8N_2 + 4H_2 \rightarrow (CH_2)_6(NH_2)_2 \qquad 3.2$$

Adiponitrile + hydrogen → HMDA

Chemical	**Molecular weight (Mwt.)**
Adipic acid	146.16
Ammonia	17.04
Adiponitrile	108.16
Water	18
HMDA	116

Number of moles of HMDA = 75,000/116 = 646.5 tonne moles

__From reaction No. (2):__

Moles of adiponitrile required to produce 75,000 ton of HMDA =

$$= 646.5 \times {}^{1}\!/_{1} = 646.5 \quad \textit{tonne of moles}$$

$$= 646.5 \times 108.16 = 69{,}925 \quad \textit{tonne}$$

__From reaction No. (1):__

Moles of adipic acid required to produce 75,000 ton of HMDA

$$= 646.5 \times {}^{1}\!/_{1} = 646.5 \quad \textit{tonne of moles}$$

$$= 646.5 \times 146.16 = 94{,}492 \quad \textit{tonne}$$

Inventory of chemical (X), tonne = flow rate of the chemical, tonne/hr x hold-up time, hours. If the hold-up in the reactor is not known, a hold-up of 1 hour has been assumed here, working hours are assumed to be 8000 hr/yr.

$$\text{Adiponitrile inventory} = \left(\frac{69{,}925}{8000}\right)\times 1 = 8.74 \quad \textit{tonne}$$

$$\text{Adipic acid inventory} = 94{,}492\times\left(\frac{1}{8000}\right) = 11.81 \quad \textit{tonne}$$

The molar ratio of the adipic acid to the ammonia is 1:10

So, the amount of ammonia fed to the reactor per year =

$$= 646.5\times\left(\frac{10}{1}\right) = 6{,}465 \quad \textit{tonne moles}$$

$$= 6465\times 17.04 = 110{,}163.6 \quad \textit{tonne}$$

$$\text{Ammonia inventory} = \left(\frac{110{,}163.6}{8000}\right)\times 1 = 13.77 \quad \textit{tonne}$$

<u>From reaction No. 1:</u>

Actual moles of ammonia reacted $= 646.5\times\left(\frac{2}{1}\right) = 1{,}293 \quad \textit{tonne moles}$

$= 1{,}293\times 17.04 = 22{,}032.72 \quad \textit{tonne}$

The amount of unreacted ammonia $= 6{,}465 - 1293 = 5{,}172 \quad \textit{tonne moles}$

Moles of water produced $= 646.5\times 4 = 2{,}586 \quad \textit{tonne moles}$

$= 2{,}586\times 18 = 46{,}548 \quad \textit{tonne}$

Water inventory $= \left(\frac{46{,}548}{8000}\right)\times 1 = 5.82 \quad \textit{tonne}$

<u>Taking reaction No. 1:</u>

Adipic acid + ammonia ➔ adiponitrile + water

The scores for adipic acid are:

Inventory: 11.81 tonne scores 1 on the inventory table.

Toxicity: TLV = 0.005 ppm scores 7 on the toxicity table.

Explosiveness:U.E.L. = 5.04 – 1.37 = 3.67 scores 1 on the explosiveness table

Flammability: FP = 385 °F > 140 °F scores 1 on the flammability table.

So, the step score for adipic acid = 1 + 7 + 1 + 1 = 10

Using the same method, the scores for the other chemicals in reaction 1 are:

Ammonia	= 6
Adiponitrile	= 7
Water	= 1

Adipic acid chemical score is larger than the other chemicals, so it is used as the chemical score. Table 3.3 shows the process scores for the reaction. Again for each step, the parameters for the process are scored, for reaction No. 1

Temperature:	275°C scores 3 on the scoring table.
Pressure:	1 atm. Scores 1 on the scoring table.
Yield:	95% scores 1 on the yield table.

Process score = Temperature + Pressure + Yield

Process score for the step = 3 + 1 + 1 = 5

So, the step score = chemical score + process score

= 10 + 5 = 15

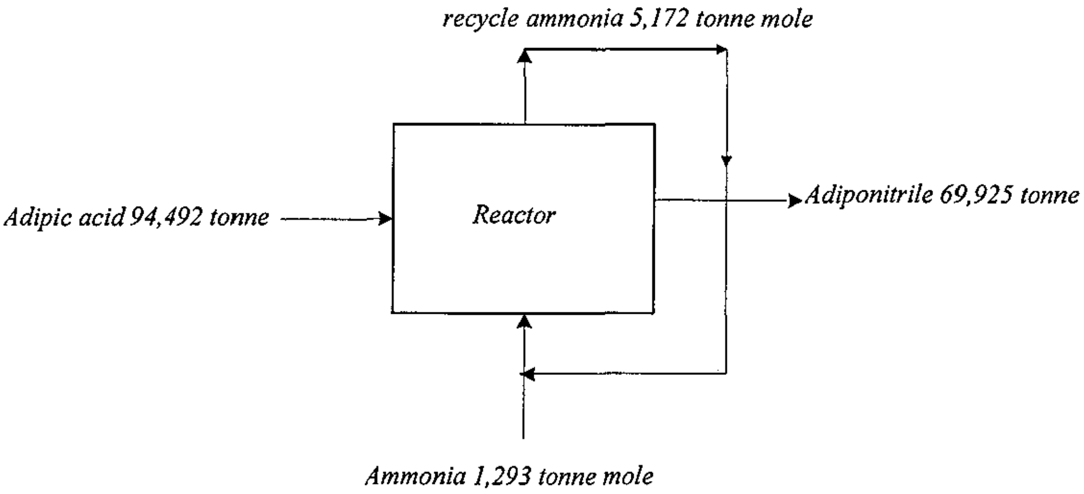


Figure 3. 3: Adiapic acid material balance

3.4.2 Acrylonitrile route

Basis:

Capacity: 75,000 tonnes per year of (HMDA).

The process consists of two steps reaction, the first is to produce adiponitrile starting from acrylonitrile and the second is to produce HMDA. The reactions are as follows:

$$2CH_2{=}CHCN + H_2O \rightarrow NC(CH_2)_4CN + \tfrac{1}{2} O_2 \qquad 3.3$$

acrylonitrile + water ➔ adiponitrile+ oxygen

$$C_6H_8N_4 + 4H_2 \rightarrow (CH_2)_6(NH_2)_2 \qquad 3.4$$

Adiponitrile + hydrogen ➔ HMDA

Chemical	Molecular weight (Mwt.)
Acrylonitrile	53.07
Water	18
Adiponitrile	108.16
Oxygen	32
HMDA	116

Number of moles of HMDA = 75,000/116 = 646.5 tonne moles

From reaction No. (4):

Mole of adiponitrile required to produce 75,000 ton of HMDA

$$= 646.5 \times \tfrac{1}{1} = 646.5 \quad \textit{tonne of moles}$$

$$= 646.5 \times 108.16 = 69{,}925 \quad \textit{tonne / yr}$$

Inventory of chemical (X), tonne = flow rate of the chemical, tonne/hr x hold-up time, hours. Assume 1 hour hold-up time and 8000 hr/yr operation.

$$\text{Adiponitrile inventory} = \left(\frac{69{,}925}{8000}\right) \times 1 = 8.74 \quad \textit{tonne}$$

From reaction No.(3):

Moles of acrylonitrile required to produce 75,000 tonne of HMDA

$$= 646.5 \times 2 = 1{,}293 \quad \textit{tonne moles}$$

$$= 1293 \times 53.07 = 68{,}619.5 \quad \textit{tonne/ yr}$$

$$\text{Acrylonitrile inventory} \quad = \left(\frac{68619.5}{8000}\right) \times 1 = 8.58 \quad \textit{tonne}$$

$$\text{Moles of water required} \quad = 646.5 \times \tfrac{1}{1} = 646.5 \quad \textit{tonne moles}$$

$$= 646.5 \times 18 = 11{,}637 \quad \textit{tonne}$$

Water inventory $= \left(\dfrac{11{,}637}{8000}\right) \times 1 = 1.45 \quad \textit{tonne}$

Moles of oxygen produced $= 646.55 \times \tfrac{1}{2} = 323.3 \quad \textit{tonne moles}$

$$= 323.3 \times 32 = 10{,}346 \quad \textit{tonne}$$

Oxygen inventory $= \left(\dfrac{10346}{8000}\right) \times 1 = 1.29 \quad \textit{tonne}$

Taking reaction No. 3

acrylonitrile + water ➔ adiponitrile + oxygen

The scores for acrylonitrile are:

Inventory: 8.58 tonne scores 1 on the inventory table.

Toxicity: TLV = 1 ppm scores 5 on the toxicity table.

Explosiveness:U.E.L. = 17 – 3.1 = 13.9 scores 2 on the explosiveness table

Flammability: FP = -117.4 °F < 100 °F

PB = *170.96 > 100* °F scores 3 on the flammability table.

So, the step score for acrylonitrile = 1 + 5 + 2 + 3 = 11

Using the same method, the scores for the other chemicals in reaction 3 are:

adiponitrile = 7

oxygen = 1

Water = 1

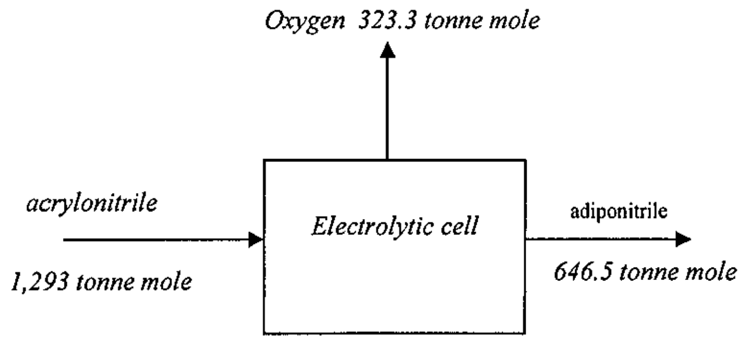


Figure 3. 4: Acrylonitrile material balance

Acrylonitrile has the highest chemical scores

Process score:

The step temperature: 55°C scores 1 on the temperature scoring table.

The step pressure: 1 atm. Scores 1 on the pressure scoring table.

The step yield: 90% scores 1 on the yield scoring table.

Process score = Temperature + Pressure + Yield

Process score for the step = 1 + 1 + 1 = 3

So, the step score = chemical score + process score = 11 + 3 = 14

Table 3. 2: Summary of components chemical scores.

Chemical	Inventory	Toxicity	Flammability	Explosiveness	Chemical Score
Adipic acid route					
Adipic acid	1	7	1	1	10
Ammonia	1	3	1	1	6
Adiponitrile	1	4	1	1	7
water	1	-	-	-	1
Acrylonitrile route					
Acrylonitrile	1	5	3	2	11
Adiponitrile	1	4	1	1	7
Oxygen	1	-	-	-	1
water	1	-	-	-	1

Table 3. 3: Summary of routes process scores.

Chemical Route	Temperature	Pressure	Yield	Process Score
Adipic acid				
Step no. 1	3	1	1	5
Acrylonitrile				
Step no. 1	1	1	1	3

The results obtained show that the adipic acid route and the acrylonitrite route have almost the same score values, 15 and 14 respectively.

3.5 Results and Discussion

The graph below shows the chemical and process scores from Tables 3.2 and 3.3 and the Inherent Safety Index for Adiponitrile production. The Adipic acid route has a higher process score than the Acrylonitrile route and conversely, Acrylonitrile route has a higher chemical score than the Adipic acid route.

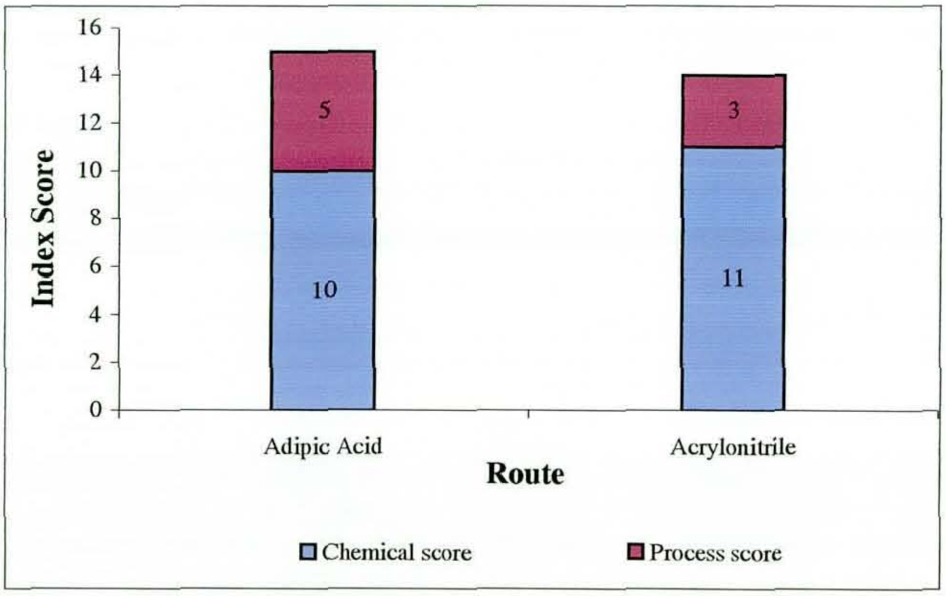


Figure 3. 5: Inherent Safety Index for Adiponitrile Production

By making an analogy between the two routes, it is noticed that both routes work at the same pressure and thus they have the same pressure scores. On the other hand, there is a significant difference between the routes temperature. The Adipic acid and Acrylonitrile routes temperature are 275°C and 55°C respectively. However their temperature scores are only 3 and 1 respectively. This might gives some doubts to the reliability of the temperature scores as they are not giving a fair equivalent to the large gap between the temperature values.

Looking at the chemical scores, the three chemicals involved in the Adipic acid route have the same explosiveness scores of 1. Following Gupta and Edwards (2003) explanation, and from explosiveness point of view, Ammonia is safer than Adipic acid and Adiponitrile, it requires a richer mixture of 16% in air before it will ignite, while both Adipic acid and Adiponitrile will need only 1.37% & 1.7% respectively of them in air to ignite. On the other hand, in the Acrylonitrile route the explosiveness score for Acrylonitrile is higher than the Adiponitrile one although the risk of ignition is anticipated to be first in the case of Adponitrile. This point might emphasize the need to reconsider the method of measuring explosiveness of a step route. Using the lower explosive limit as the criterion for explosiveness, since it is the more important parameter instead of using the difference between upper and lower explosiveness limits as Gupta and Edwards (2003) suggested might be a good trial.

A first attempt to computerize the index is presented using Visual Basic Editor (VBE), and Microsoft excel spreadsheet is used for running VBE. A copy of the program print out is shown in Appendix B.

3.6 Conclusion

It can be seen from the results of the case study that the adipic acid and the acrylonitrile routes have almost the same inherent safety index of 15 and 14 respectively which make it difficult to distinguish between them. Theses results were obtained even though the temperature difference between the two routes was significant. The index does not account for the large gap between the temperature values which might give some doubts about the realibility of the temperature scoring table. In addition, using the difference between the upper and lower explosive limits might not be a good representative of the explosiveness of a step route. Reconsideration of the method of measuring explosiveness as well as the temperature scoring table is needed in order to get more reliable results.

The above case study also showed that some chemicals can be present as solids causing different hazards known as dust explosion. A dust explosion results when divided combustible substance is dispersed into an atmosphere containing oxygen to permit combustion and a source of ignition of appropriate energy. The inherent safety index has not taken this type of hazard into consideration. The next chapter illustrates the dust explosion hazard in more details.

Chapter 4: Dust Explosion

4.1 Introduction

During the application of the inherent safety index to the manufacture of Adiponitrile in the last chapter, it was found that adipic acid presents as a solid. Handling solid materials pose a dust explosion hazard. The Edwards and Lawrence (1993) index does not cover the explosion of dusts. Therefore, it was imperative to extend the index to cover this new finding. This chapter introduces dust explosion hazards.

4.2 Historical view of dust explosions

Dust explosions have been recognized as a threat to humans and property since the time that man developed the windmill for grinding grain. Actually, the first known report of dust explosion dates back to the eighteenth century, the violent explosion of flour dust at Turin mill, Italy in 1785, Field (1982). It was thought at that time, that the dispersed dust had produced an inflammable gas, which had subsequently ignited.

Explosion in coal mines were also common during that period, but again it was assumed that flammable gas was the cause. No thought has been given to the possible effects of airborne coal dust, till the latter part of the nineteenth century when it was realised that coal dust could ignite and explode in the absence of gas, or that flour dust alone was responsible for the explosions in mills.

During the twentieth century, the frequency of dust explosions increased and a wider variety of materials became involved as industry developed. Galloway (1898) estimated that no fewer than 645 explosions occurred between 1835 and 1898 in the UK alone. Field (1982) described the starch factory explosion which took place in Iowa, USA at 1919, and in which 43 people were killed, as the most devastating dust explosion, in terms of loss of life, outside of the coal industry.

4.3 Dust explosions in USA 1900-1956

The National Fire Protection Association published a report of important dust explosions in the USA from 1900 to 1956 (NFPA 1957). The report gives details of a selection of 75 of the most serious and recent of the 1123 explosions recorded. The selection covers a wide range of dusts from all the categories wood, food and feed, metals, plastics, coal, paper and chemicals. In addition, each of the 1123 explosions is mentioned briefly by specifying the date, location, dust involved, probable ignition source, number of fatalities and injuries, and material losses.

Table 4.1 gives an overall summary of the consequences of explosions involving various dust categories. The table illustrates some interesting differences. For example, half of the dust explosions in the shows period involved food and feed dusts. They also give the highest percentage of fatalities and injuries. On the other hand, the metal dust explosions, representing 7.1% of the total number of explosions, were responsible for 16% of all the fatalities and 11.2% of all the injuries than food & feed dusts. However, metal dust gives the highest number of fatalities and injuries per explosion. The pulverized coal dust explosions (not mining), on the contrary, gave lower percentages of fatalities, injuries and material losses than their share of the total number of explosions. It has been also reported that between 1958 and 1977 the American grain industry experienced 220 explosions, which resulted in 48 deaths and 500 injuries.

Table 4. 1: Dust explosions in USA 1900-1956: fatalities, injuries and material losses in a sample of 1123 accidental explosions

Types of dust	Explosions		Fatalities			Injuries			Material losses	
	Number	%	number	%	Per explosion	Number	%	Per explosion	Million US$	Per explosion
wood & bark	162	14.5	38	5.6	0.23	160	9.0	0.99	11.4	0.070
Food & feed	577	51.4	409	60.5	0.71	1061	60.0	1.84	75.8	0.131
Metals	80	7.1	108	16.0	1.35	198	11.2	2.48	3.2	0.040
Plastics	61	5.4	44	6.5	0.72	121	6.8	1.98	3.7	0.061
Coal (not mines)	63	5.6	30	4.4	0.48	37	2.1	0.59	1.6	0.025
Paper	9	0.8	0	0.0	0.0	0	0.0	0.0	0.5	0.056
others	171	15.2	47	7.0	0.27	193	10.9	1.13	4.3	0.025
all	1123	100	676	100	0.60	1770	100	1.58	100.5	0.089

From Eckhoff (1977)

4.4 Dust explosions in F. R. Germany 1965-1985

The Institute of Safety at Work of the Trade Unions in F. R. Germany has conducted a programme of recording dust explosion accidents in F. R. Germany since the beginning of the 1960s. The first comprehensive report, covering 1965-1980 was published by Beck and Jeske in 1982. A condensed version of the findings was given by Beck in 1982. The comprehensive report contains a brief description of each explosion accident specifying the type of plant, the specific plant item, the type of dust, the likely ignition source, numbers of fatalities and injuries, and material losses. A further comprehensive report covering the explosions recorded from 1981 to 1985 was published by Jeske and Beck in 1987, and the corresponding short version by Beck and Jeske in 1988. Finally Jeske and Beck published in 1989 an informative overview covering the whole span 1965-1985, Eckhoff (1997).

The total numbers of explosions recorded were 357 for 1965-1980 and 69 for 1981-1985. It has been estimated by Beck and Jeske that the recorded explosions from 1965 to 1980 is about 15% of the total number of explosions that had actually occurred. The estimated number of actual dust explosions in F. R. Germany from 1965 to 1980 was therefore about 2400, i.e. about 160 per year. The number of explosions recorded per year for 1981-1985 was somewhat lower than for 1965-1980. Eckhoff (1997) claimed that, because of the low percentage of recorded explosions it might not be justified to conclude that the annual number of accidental explosions dropped significantly after 1980.

Table 4.2 gives some data from F. R. Germany which covers the period from 1965-1980. Eckhoff (1997) has compared the Germany data with the older data from USA in Table 4.1. He found some differences in the distribution of the number of explosion accidents on the various dust categories from the first to the second part of the century, and differences between the structure of the industry in USA and in the F. R. Germany. The food and feed dust for example represent 25% of all the explosions in F. R. Germany, whereas in USA the percentage was more than 50. However, the percentages of both fatalities and injuries for this dust group both in F. R. Germany and USA was higher than the percentage of explosions. On the other hand, the percentage of the explosions involving metal dusts was about twice as high in F. R. Germany as in USA. The higher percentage of both fatalities and injuries for metal dust explosions than the percentage of the number of explosions corresponded in both countries. He attributed that to the violence and temperatures of flames of metals like magnesium, aluminium and silicon.

Table 4. 2: Dust explosions in F. R. Germany 1965-1980: fatalities, injuries in a sample of 357 explosions.

Types of dust	Explosions		Fatalities			Injuries		
	Number	%	number	%	Per explosion	Number	%	Per explosion
Wood	113	31.6	12	11.7	0.11	124	25	1.10
Food & feed	88	24.7	38	36.8	0.43	127	26	1.44
Metals	47	13.2	18	17.5	0.38	91	18.5	1.94
Plastics	46	12.9	18	17.5	0.39	98	20	2.13
Coal / peat	33	9.2	7	6.8	0.21	39	8	1.18
Paper	7	2.0	0	0.0	0.0	0	0	0.0
others	23	6.4	10	9.7	0.43	13	2.5	0.56
all	357	100.0	103	100.0	0.29	492	100.0	1.38

From Eckhoff (1977)

4.5 Recent statistics on grain dust explosions in USA

Eckhoff (1997) presented some data for grain dust explosions in the USA as shown in Table 4.3. The data for the period 1900-1956 are from the same source as in Table 4.1. As Eckhoff stated, the trend is disturbing, as the annual number of explosions seems to increase rather than decrease. The annual number of fatalities is also higher for the last period 1979-1988 than for the previous one 1957-1975. The annual number of injuries for the last period is higher than for both previous periods. However, the deaths per explosion have gone down.

The above statistics indicate that dust explosions remain a persistent threat to human life and to property. However, if a dust explosion hazard can be recognised at the early stage when industrial plant is being designed, precautionary measures can be installed without difficulty and at much less cost and inconvenience than in an established plant.

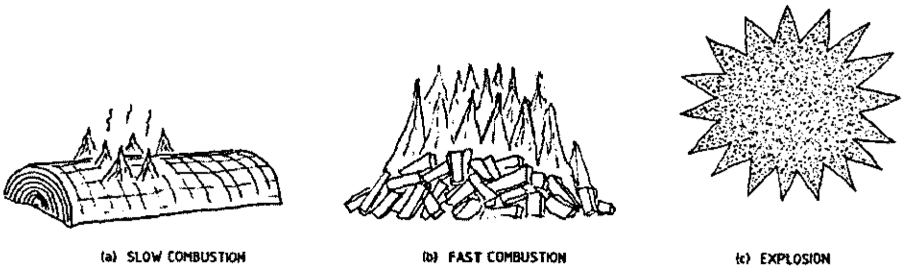
Table 4. 3: Grain dust explosions in USA

Loss category	1900 - 1956		1957 – 1975		1979 - 1988	
	Total	Per year	Total	Per year	Total	Per year
Number of explosions	490	8.6	192	10.1	202	20.2
Fatalities	381	6.8	68	3.6	54	5.4
Fatalities per explosion	0.78		0.35		0.27	
Injuries	991	17.4	346	18.2	267	26.7
Estimated damage to facility, Million US$, not inflated	70	1.3	55	2.9	169	16.9

From Eckhoff (1977)

4.6 Dust explosion phenomenon

A dust explosion results when divided combustible substance is dispersed into an atmosphere containing oxygen to permit combustion and a source of ignition of appropriate energy. The violence and the speed of explosion increase with increasing degree of sub-division of the material. Figure 4.1 from Eckhoff (1997) illustrates how a piece of wood, once ignited, burns slowly, releasing its heat over a long period of time. When cut in small pieces, as illustrated in Figure 4.1 (b), the combustion rate increases because the total contact surface area between wood and air has been increased. Also, the ignition of the wood has become easier. If the sub-division is continued right down to the level of small particles of sizes of the order of 0.1 mm or less, and the particles are suspended in a sufficiently large volume of air to give each particle enough space for its unrestricted burning, the combustion rate will be very fast, and the energy required for ignition very small. Such a burning dust cloud is a dust explosion.



(a) SLOW COMBUSTION (b) FAST COMBUSTION (c) EXPLOSION

Figure 4. 1: Illustration of how the combustion rate of a given mass of combustible solid increases with increasing sub-division.

4.7 Combustion of dusts

Many solid materials are combustible, that is they can be made to burn if a source of ignition is applied. The ease with which ignition occurs, or the size of the source required to initiate burning, depends on the nature and dimensions of the solids. Generally solids are ignited and burn more readily as their size decreases, and when reduced to powders or dusts the conditions are most favourable. Not only are dusts and powders relatively readily ignited, but they also burn more rapidly. Two of the reasons are that air, or oxygen, gains easier access to the whole mass if it is in powder form, and heat cannot be drained from the burning surfaces into the interior of the solid material when this is in the form of small particles.

A favourable arrangement for the rapid burning of dust is when the particles are separated from each other by relatively large distances, so that the air has ready access to each particle, as when the dust particles are dispersed as a cloud in the air. The optimum condition is when the particles are separated far enough to have sufficient air for complete combustion, but they are close enough for the heat release to support the burning of adjacent particles.

A number of conditions must be satisfied simultaneously for a dust explosion to occur:

- The dust must be combustible.
- The dust must be in suspension in an atmosphere which must contain sufficient oxygen to support combustion.
- The dust must have a particle size distribution that will propagate a flame.
- The dust concentration in the suspension must be within the explosible range.
- The dust suspension must be in contact with an ignition source of sufficient energy.

If these conditions are satisfied the hazard from a dust explosion depends upon the explosibility of the dust, the volume and characteristics of the vessel or chamber containing the dust suspension the dispersion and concentration of the dust suspension and the degree of turbulence in the vessel.

The explosibility of a combustible dust is greater if the particle size is reduced. The minimum ignition energy is reduced and the maximum explosion pressure and rate of pressure rise are increased with a decrease in particle size. In addition fine particles more readily stay in suspension than coarse particles so the probability of producing an explosible concentration is enhanced. Particles greater than about 500 μm diameter are unlikely to cause dust explosions, although the possibility of coarser materials producing fine dust by attrition during handling must be anticipated.

Minimum explosible concentrations in air are typically in the range 10-500g/m^3. Explosible concentrations are much higher than those associated with toxic hazards or nuisance problems (which might range from about 1-10 mg/m^3) and such explosible concentrations would most likely occur very close to a dust source or within an enclosed space where the dust cloud cannot spread.

4.8 Factors influencing dust explosibility

The explosibility of a dust may be regarded as increasing as the minimum explosible concentration, the minimum ignition temperature and the minimum ignition energy decrease and the burning velocity and the minimum rate of pressure rise increase.

The characterization of particles is a complex matter, but in general, characteristics which affect the behaviour of particles include those of the individual particle itself such as particle composition, density, size, shape, surface properties and moisture content and those of the bulk powder such as bulk density and flow properties. Some factors, which influence dust explosibility, are:

- Chemical composition.
- Particle size.
- Moisture content.
- Oxygen concentration
- Inert gas
- Admixed inert dust concentration.

Nagy and Verakis (1983) give a large number of plots showing the effect of these factors on the dust explosibility parameters, mainly for particular dusts.

There are certain chemical groups such as COOH, OH, NH_2, NO_2, $C \equiv N$, $C = N$ and $N=N$, which tend to be associated with higher dust explosibility and certain others such as Cl, Br and F with lower explosibility. Dusts of pure metals generally react with air to form metallic oxides. In this case the explosive increase pressure is due to expansion of the nitrogen of the air caused by the heat release. In some cases metals actually react violently with the nitrogen itself to form a metallic nitride.

Volatile matter in the dust tends to enhance the explosibility, although there is generally little increase for volatile contents below 10%. Coal dust in particular can contain a high proportion of volatile matter. Interestingly, according to Nagy and Verakis (1983), pure carbon dust does not explode. They speculate that the reaction rate of pure carbon with oxygen is too low. But carbon dust containing 8% volatile matter is explosive. If the dust contains inert material this reduces its explosibility.

Dust explosibility is strongly affected by particle size. Particle size is usually defined in terms of an equivalent particle diameter. Generally, a dust with a particle diameter greater than 500 μm is unlikely to initiate an explosion, though it may undergo combustion in one already occurring. At the other end of the range, reduction in particle size below about 50-74 μm does not normally result in any significant increase in explosibility. The particle diameter of dusts used in dust explosibility testing normally does not exceed 75 μm.

A dust usually contains a range of particle sizes. A relatively small proportion of fine particles enhance the explosibility of a dust. Moreover, it should be borne in mind that attrition caused by handling the dust tends to generate fine particles.

Moisture content has a strong effect on dust explosibility, although the effect is generally weak for moisture contents below 10%. At the other end of the range, dust with moisture content greater than 30% is unlikely to be responsible for initiation of an explosion.

The oxygen concentration in the surrounding atmosphere has strong effect on dust explosibility, which increases as the oxygen concentration increases and visa versa especially in the inert gas environment. Dust explosibility is affected by the concentration of any admixed inert dust, although the effect is generally weak for inert dust concentrations below 10-20%.

4.9 Explosibility tests in the UK

The tests described in the following sections are those currently being used, the methods being agreed with the Health and Safety Executive's Factory Inspectorate, who have the responsibility of ensuring industry's compliance with the relevant safety standards, Field (1982). The available tests are as following

4.9.1 Explosibility classification

This test determines whether a dust cloud will explode when exposed to an ignition source. It results in a material being classified as either combustible or non-combustible. In the UK the dust explosibility classification used over a number of years is:

- Group A - Dusts which ignite and propagate a flame in the test apparatus.
- Group B - Dust which do not propagate flame in the test apparatus.

Tests are made using the Modified Hartmann Tube apparatus, Figure 4.2. The apparatus consists of a 1.2-liter vertical tube mounted onto a dust dispersion system. Powder or dust samples of various sizes are dispersed in the tube and attempts are made to ignite the resultant dust cloud using a 10 J constant arc ignition source. If the material fails to ignite in the Modified Hartmann Tube apparatus, A/B testing is continued in the 20-litre sphere apparatus. Powder or dust samples of various sizes are dispersed inside the sphere and are exposed to a 10,000 J ignition source (chemical igniters).

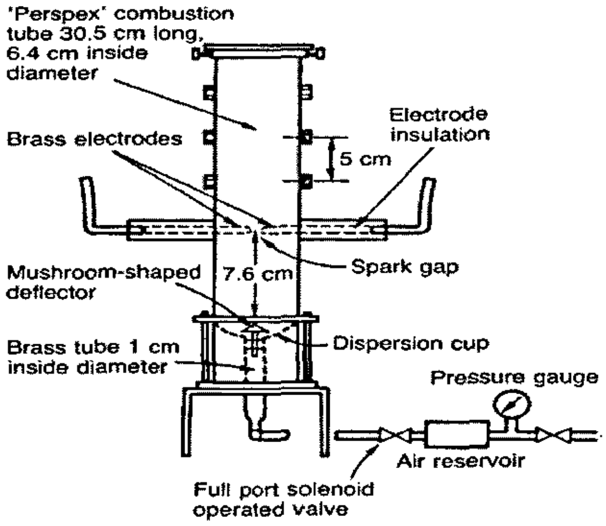


Figure 4. 2: Hartmann Tube apparatus, from Lees (1996).

Field (1982) claimed that, the classification test does not afford a means of quantitatively assessing the severity of an explosion hazard. Consequently, it is not possible to specify explosion protection methods from the results of a classification test alone.

4.9.2 Minimum ignition temperature

The minimum ignition temperature (MIT) test determines the lowest temperature at which dust dispersed in the form of a cloud can ignite. The MIT is an important factor in evaluating the ignition sensitivity of dusts to ignition sources, such as heated environments, hot surfaces, electrical apparatus and friction sparks.

MIT testing is performed using the Godbert-Greenwald Furnace shown in Figure 4.3. Powder or dust samples of various sizes are dispersed into the furnace and the minimum wall temperature capable of igniting the dust cloud is determined.

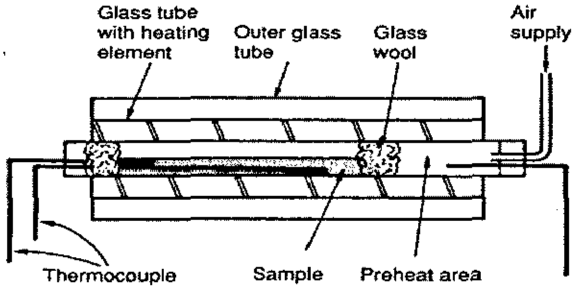


Figure 4. 3: Godbert-Greenwald Furnace, from Lees (1996).

4.9.3 Minimum explosible concentration

The minimum explosible concentration (MEC) test determines the smallest concentration, in g/m^3 of material in air that can give rise to flame propagation upon ignition when in the form of a dust cloud. It gives an indication of the hazardous concentration in the plant. The test involves dispersing powder or dust samples in a vertical tube apparatus and attempting to ignite the resulting dust cloud with an electric spark as a source of ignition. Trials are repeated for decreasing sample sizes until no explosion occurs. The mass of the smallest quantity of dust giving an explosion is divided by the volume in which the explosion occurred to give the MEC in air.

4.9.4 Minimum ignition energy

The minimum ignition energy (MIE) test determines the lowest spark energy capable of igniting a sample when dispersed in the form of a dust cloud. The test is used primarily to assess the potential vulnerability of powders and dusts to electrostatic discharges, but is also relevant to frictional sparks. Powder or dust samples of various sizes are dispersed in the vertical tube apparatus. Attempts are made to ignite the resultant dust cloud with discrete capacitive sparks of known energy.

4.9.5 Maximum permissible oxygen concentration to prevent ignition

This is the maximum amount of oxygen that can be tolerated before a dust suspension explodes. The test carried out in the open Hartmann vertical tube using spark ignition. A weighed quantity of the dust is placed in the dispersion cup. The dust is dispersed and the criterion for indicating an explosion is propagation of flame away from the igniting source. When an explosion occurs the amount of dust is reduced and the testing continued until no explosion is observed in at least ten tests at the same dust concentration. The mass of the minimum quantity of dust with which an explosion occurs, divided by the total volume of the tube, is taken as the minimum explosible concentration in air.

4.9.6 Maximum explosion pressure and maximum rate of pressure rise

The maximum explosion pressure and the maximum rate of pressure rise are obtained by measuring the pressure-time profile in a stronger form of the vertical tube apparatus. A typical pressure-time curve is shown in Figure 4.3. The maximum explosion pressure P_{max} is normally calculated as

$$P_{\max} = P_2 - P_1 \qquad 4.1$$

Where, P_{max} is the maximum explosion pressure, P_1 is the initial pressure caused by the entry of dispersing air into the vessel, and P_2 is the pressure defined in Figure 4.4. The maximum rate of pressure rise $(dP/dt)_{max}$ is determined from the maximum slope pressure rise curve a/b and the average rate of pressure rise $\left(\frac{dP}{dT}\right)_{av}$ *is calculated as* $\frac{(P_2 - P_1)}{(t_2 - t_1)}$.

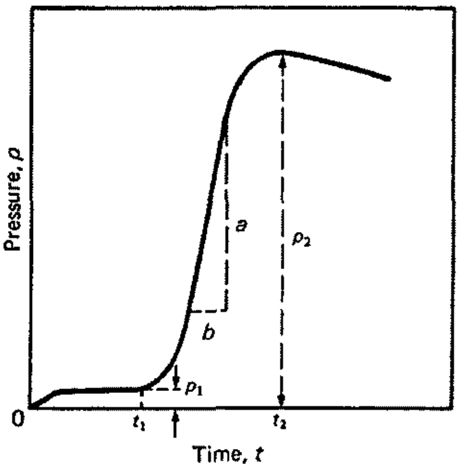


Figure 4. 4: Determination of P_{max} and $(dP/Dt)_{max}$ from pressure – time curve in test apparatus

4.10 Relative explosion hazard rating

An empirical index of explosibility was developed by the US Bureau of Mines to facilitate the evaluation of the dust explosion. It is not based on theoretical considerations but on research findings which suggested that the explosion hazard of a dust is related to its ease of ignition and the severity of the explosion. It is considered that the ease of ignition is dependent upon the minimum ignition temperature, the minimum explosible concentration, and the minimum ignition energy, while the severity of an explosion can be thought in terms of the maximum explosion pressure and the maximum rate of pressure rise.

A numerical rating and a relative hazard are obtained by comparing the experimental data to those of a standard material. The US Bureau of Mines selected a specific grade of Pittsburgh coal dust as the standard due to the availability of its information from both the laboratory scale and the experimental coal mines. Based on the above concept two terms the ignition sensitivity and the explosion severity were developed as follows:

$$Inginition\ Sensitivity = \frac{(Min.\ Ign.Temp.\times Min.\ Ign.\ Eng.\times Min.\ Expl.\ Conc.)_{Pittsburgh\ Coal\ Dust}}{(Min.\ Ign.Temp.\times Min.\ Ign.\ Eng.\times Min.\ Expl.\ Conc.)_{Sample\ Dust}} \qquad 4.2$$

$$Explosion\ Severity = \frac{(Max.\ Expl.\ \Pr essure\times Max.\ Rate\ \Pr essure\ rise)_{Sample\ Dust}}{(Max.\ Expl.\ \Pr essure\times Max.\ Rate\ \Pr essure\ rise)_{SPittsburgh\ Coal\ Dust}} \qquad 4.3$$

an over all index of explosibility is then determined such that

$$Index\ of\ Explosibility = Ignition\ Sensitivity\times Explosion\ Severity \qquad 4.4$$

The ignition sensitivity, explosion severity, and the explosibility index are dimensionless and numerical values greater than unity indicate a relative hazard greater than that of coal dust. The standard data used in these explosion hazard ratings and derived from Pittsburgh coal are given in Table 4.4.

Table 4. 4: Pittsburgh coal dust explosion properties

Cloud ignition temperature	610°C
Minimum ignition energy	0.06 J
Minimum explosive concentration	0.055 g/l
Maximum explosive pressure	83 psig
Maximum rate of pressure	2300 psi/sec

Table 4. 5: Relation between explosion hazard rating and index of explosibility

Relative explosion hazard rating	Ignition Sensitivity	Explosion Severity	Explosibility Index
Weak	< 0.2	< 0.5	< 0.1
Moderate	0.2 – 1.0	0.5 – 1.0	0.1 – 1.0
Strong	1.0 – 5.0	1.0 – 2.0	1.0 – 10
Severe	> 5.0	> 2.0	> 10

A relative explosion hazard rating is obtained by the empirical correlations shown in Table 4.5 and permits the type of explosion to be described as weak, moderate, strong, or severe.

The index of explosibility is a relative one and is to this extent less independent on the apparatus used. The use of an explosibility index coupled with a relative explosion hazard rating system provides a useful means for obtaining a general guide to the explosion hazard of a dust, particularly of novel materials. A dust having an explosibility index much greater than coal (unity) would be expected to present a major dust explosion hazard, while a dust having an explosibility index less than 0.1 probably presents no real explosion hazard, although a fire risk probably exists, Field (1982).

4.11 Prevention and Mitigation Frameworks for Dust Explosion

There are some existing prevention and mitigation frameworks described in the literature for explosions in general and dust explosions in particular. They provide a level of guidance for reducing the potential explosion hazard. These include the following methodologies:

- Fire triangle,
- Fire triangle for dusts,
- Explosion pentagon,
- Guides and standards, and
- Strategies suggested in established reference work; e.g. texts by Field (1982) & Eckhoff (1997).

The most well-known scheme in this area is the fire triangle, Figure 4.5. It illustrates the three necessary elements which must occur simultaneously to cause a fire: fuel, oxidant and ignition source. These elements form the three legs of the fire triangle and by removing any one of these elements, a fire becomes impossible. This simple concept provides industrial practitioners several approaches to explosion prevention. For example removal of fuel by good housekeeping and removal of electrostatic ignition sources by grounding will prevent fire from occurring.

On the other hand, the explosion pentagon, Figure 4.5 shows the five necessary elements which must occur concurrently to cause an explosion. They are: fuel, oxidant, ignition source, suspension and confinement. Like the fire triangle, removing any one of these requirements would prevent an explosion from propagating. Remembering the three sides of the fire triangle and the five sides of the explosion pentagon is important in preventing fires and explosions at any facility. By eliminating the possibility of either suspension or confinement, an explosion can not occur, but a fire may occur. By eliminating the fuel, the source of ignition, or the oxygen requirements, neither a fire nor an explosion can occur. The explosion pentagon, as described by Amyotte and Khan (2002) and illustrated in Figure 4.5, expands the basic fire triangle to include thorough mixing of the fuel and oxidant and confinement of the combustible mixture. This visualization of explosion requirements leads to identification of engineered safety measures for explosion mitigation such as venting.

Figure 4.6 presented by Amyotte and Khan (2002) is the Institution of Chemical Engineers (IChemE) guidelines for dust explosion mitigation. It illustrates that in order for a dust to be considered a fuel, it must be explosible, airborne, have a particle size distribution capable of propagating flame, and have concentration within the explosible range.

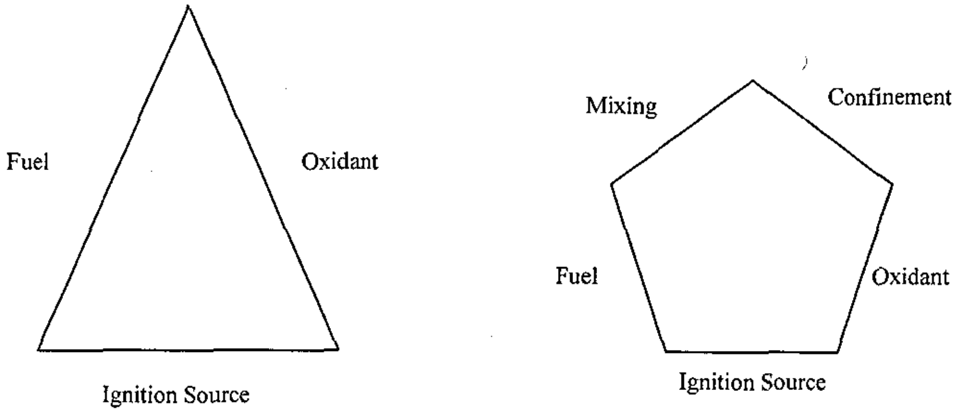


Figure 4. 5: Fire triangle and Explosion Pentagon

In addition to the basic prevention measures indicated by the fire triangle, the modified triangle shown in Figure 4.6 begins to partially address the issue of inherent safety. For example, by incorporating particle size into the graphical representation, the suggestion is made that an increase in particle size can provide a non-explosible material. This is an application of one of the inherent safety principles, which is attenuation or moderation (using hazardous materials in their least hazardous forms). The same practice can be made for concentration. If the quantity of dust in suspension is less than the attainable range, explosion would still not be possible.

Further advice on explosion prevention and protection can be found in a number of guides and standards available worldwide. In the USA, information documented by the National Fire Protection Association (NFPA) is widely followed. For example, NFPA 654 provides guidance on where explosion protection is required, and NFPA 68 and 69 are helpful as, respectively, a guide on venting and a standard on engineered measures such as suppression and isolation.

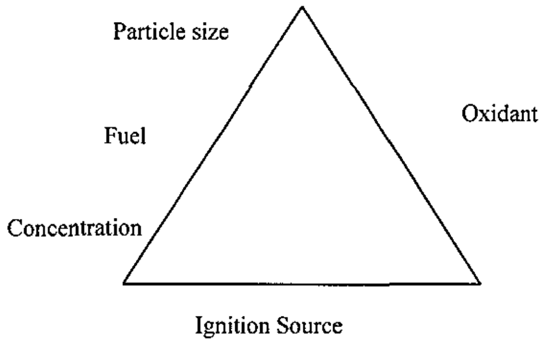


Figure 4. 6: Fire triangle for dusts.

The strategy for dust explosion prevention and protection presented by Field (1982) is given in Figure 4.7. This graphical/text representation starts with the hazard identification step and proceeds through explosion prevention measures based on the fire triangle and protection measures that are primarily engineered and procedural in nature. There are also inherent safety features evident in Figure 4.7. The recommendation to control process and surface temperatures is an example of attenuation in the case of normal operation of a process below the minimum ignition temperature (dust cloud or layer as the situation warrants). Strengthening of plant, leading to pressure resistance with or without deformation, can be viewed as an application of error tolerance in that equipment is made more robust and able to withstand process upsets.

In Figure 4.8 Eckhoff, (1997) has expanded on the scheme suggested by Field (1982) by making several significant modifications. Explosion prevention and mitigation measures and directly related to the measures such as the need for good housekeeping, that is by keeping the concentrations of dust down and possibly keeping the dust damp. and the use of hot work permits are explicitly identified. In addition to that mentioned before, Eckhoff provides a clear statement of the need for personnel training and the ultimate responsibility of management for process safety matters

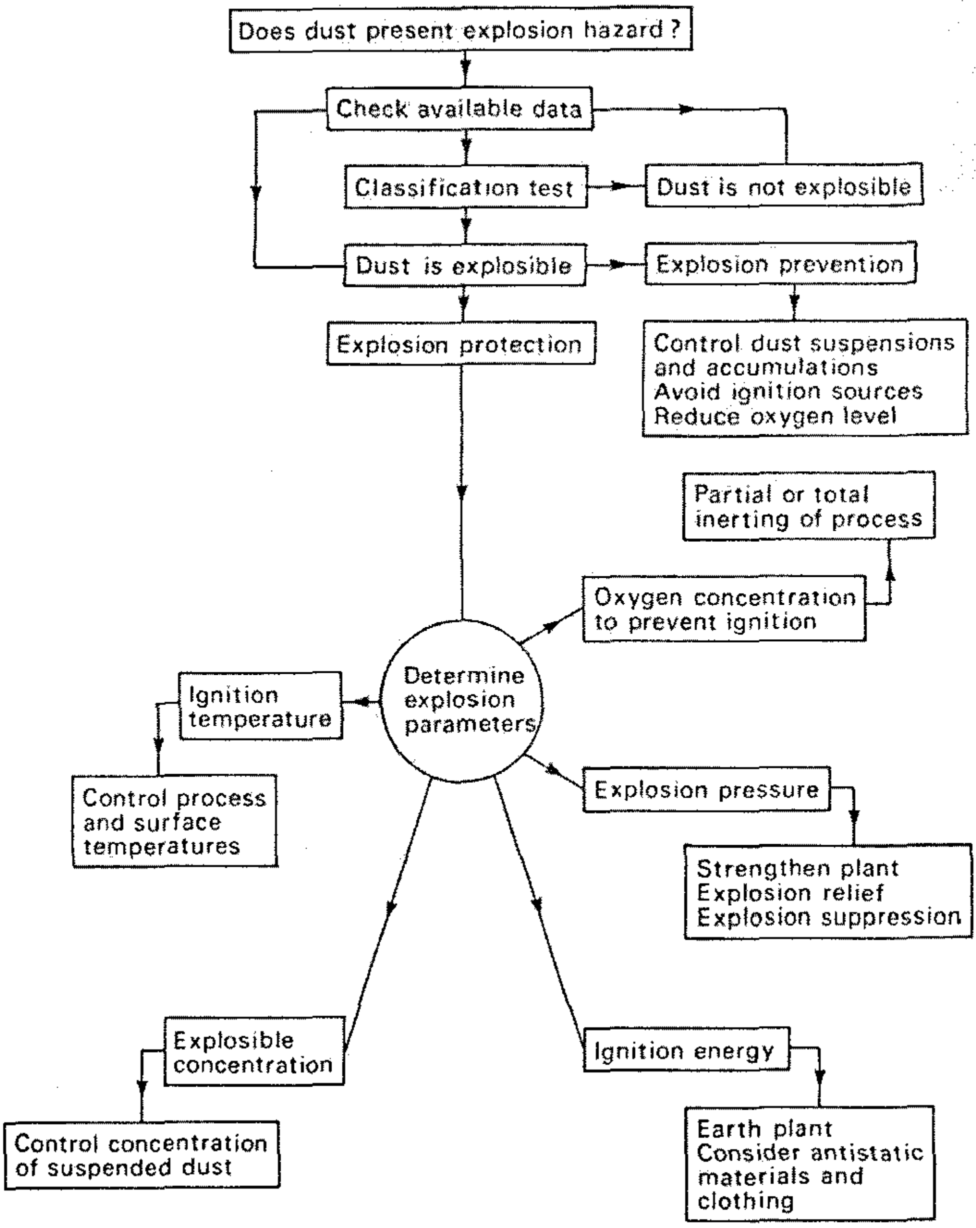


Figure 4. 7:Field's framework.

Amyotte and Khan, (2002) have proposed a framework for dust explosion prevention and mitigation, Figure 4.9. They built up their proposal on various heuristics available in the literature.

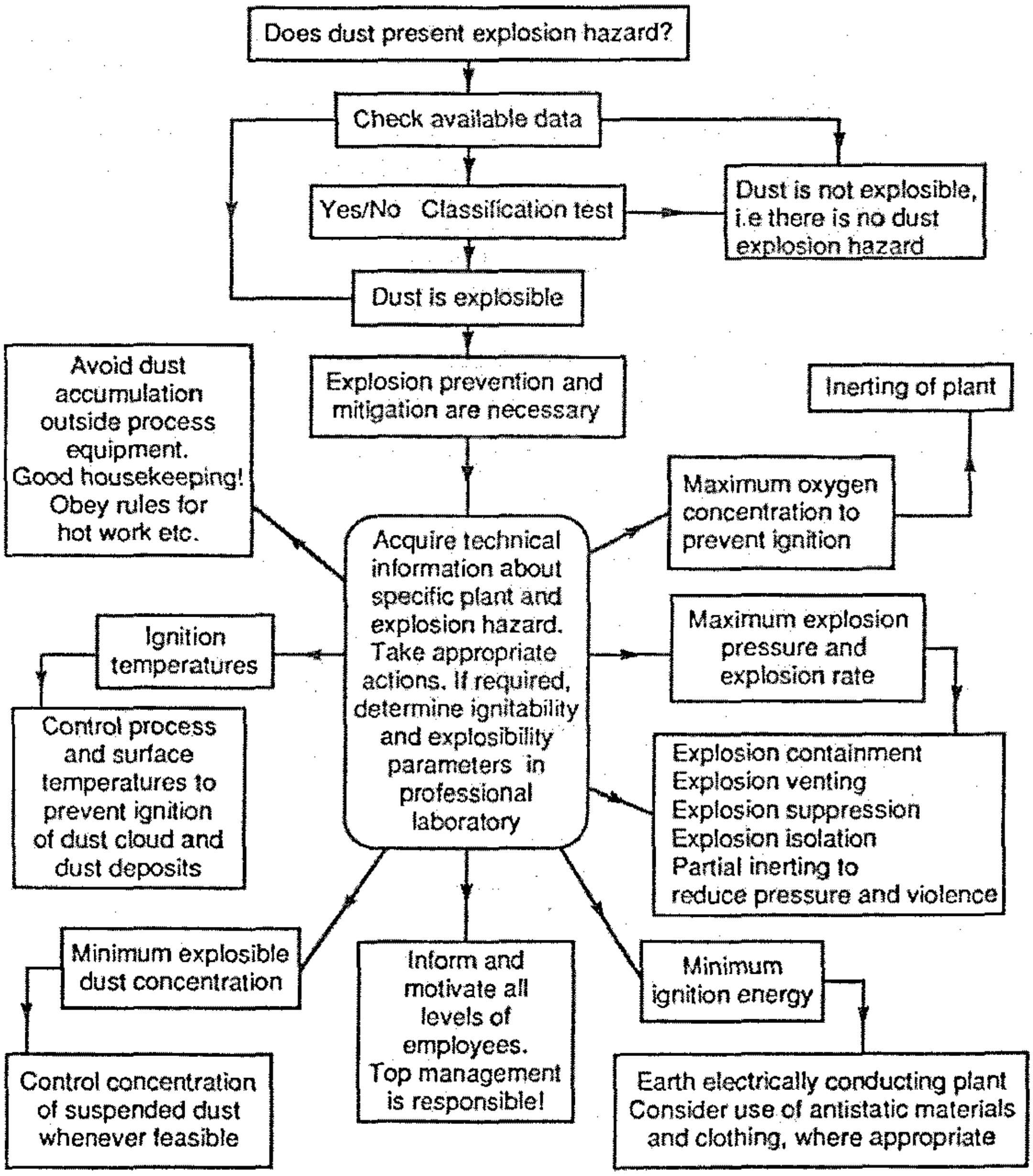


Figure 4. 8: Eckhoff's framework

The proposal provides a hierarchy in which inherent safety principles are considered first, followed by engineered and procedural safeguards. They identified some requirements such as:

- A clear identification of responsibilities at all organizational levels, especially management.
- Mapping of existing engineered and procedural measures into the framework.

- Applications of specific inherent safety principles to provide example-based guidance to framework users. In addition to the examples mentioned previously, intensification by waste/by-product removal. Substitution can also be applied to reduce the degree of hazard of some dusts. Amyotte *et al.* (2003) have investigated experimentally the dust explosion hazard in fossil fuel-fired power plants. They studied the substitution of petroleum coke for coal. They found that petroleum coke is an inherently safer fuel than either Columbian coal or Powder River Basin coal from the perspectives of explosion pressure and rate of pressure rise.

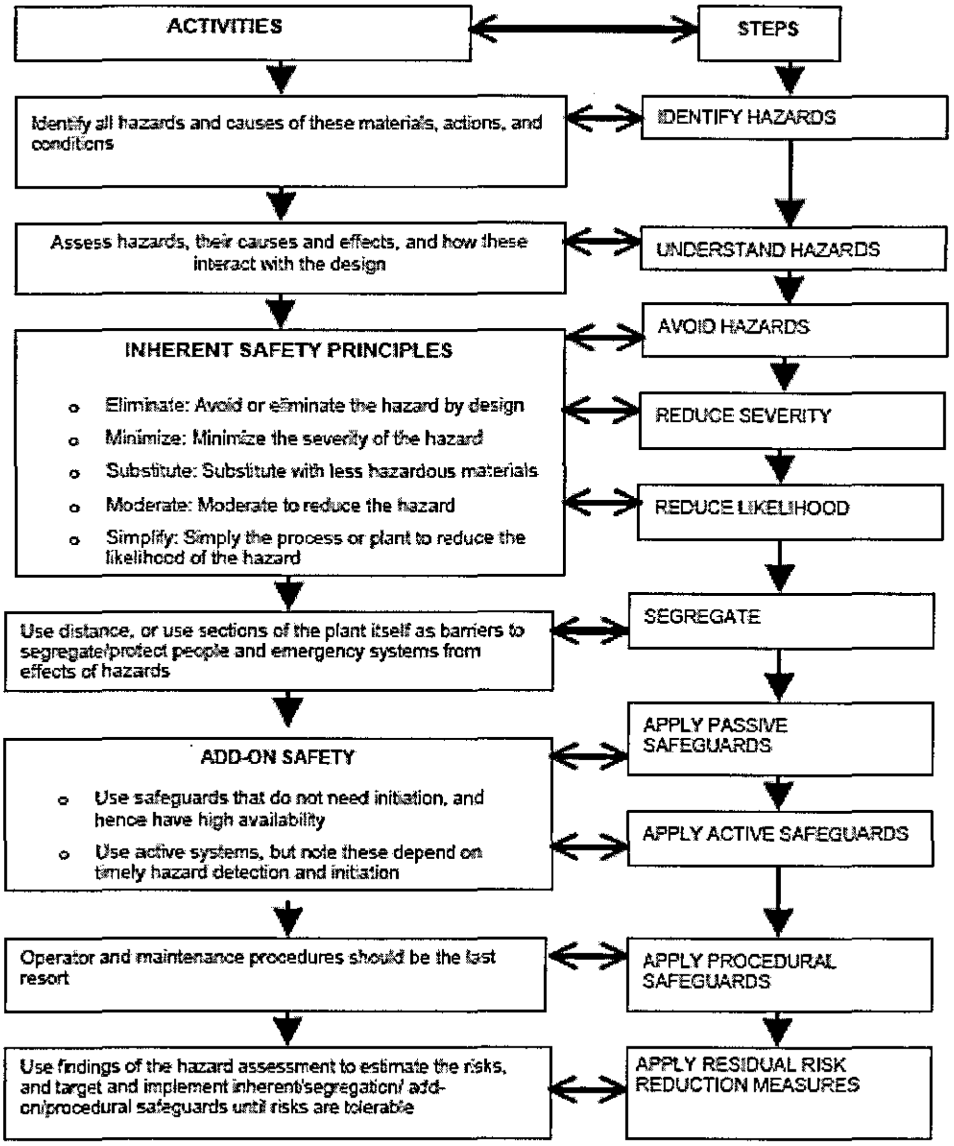


Figure 4. 9: A systematic approach to loss prevention.

4.12 Assessing dust explosion hazard

The potential for a dust explosion exists in all industrial processes in which combustible material is either manufactured or handled. The material may be a final product or unwanted by-product. If a dust explosion hazard can be anticipated in the early stages of design, precautionary measures can be installed.

In this section a method is proposed to assess the inherent hazard of dusts. It is developed by the US Bureau of Mines and it ranks dusts relative to Pittsburgh coal. The method has been described in details in section 4.10. It based on a comprehensive data in which it has been experimentally approved their influence on dust explosion. The approach is an index of explosibility which is basically consists of two parameters, the dust Ignition Sensitivity (IS) or the dust ease of ignition which is dependent on the minimum ignition temperature, minimum explosible concentration, minimum ignition energy, and Explosion Severity (ES) of dusts which can be thought of in terms of the maximum explosion pressure and maximum rate of pressure rise. The index of explosibility can be obtained as follows:

1. Calculate the Ignition Sensitivity (IS):

$$Inginition\ Sensitivity = \frac{(Min.\ Ign.\ Temp. \times Min.\ Ign.\ Eng. \times Min.\ Expl.\ Conc.)_{Pittsburgh\ Coal\ Dust}}{(Min.\ Ign.\ Temp. \times Min.\ Ign.\ Eng. \times Min.\ Expl.\ Conc.)_{Sample\ Dust}} \qquad 4.5$$

2. Calculate the Explosion Severity (ES):

$$Explosion\ Severity = \frac{(Max.\ Expl.\ \Pr essure \times Max.\ Rate\ \Pr essure\ \ rise)_{Sample\ Dust}}{(Max.\ Expl.\Pr essure \times Max.\ Rate\ \Pr essure\ rise)_{Pittsburgh\ Coal\ Dust}} \qquad 4.6$$

3. Calculate the Explosion Index (EI):

$$EI = IS \times ES \qquad 4.7$$

4. Obtain the explosion hazard rating as follows:

• If EI > 1	dust in question would be expected to present a major dust explosion hazard.
• If EI = 0.1 – 1.0	dusts with EI in this range can still present explosion hazard.
• If EI < 0.1	dusts do not present explosion hazard.

4.13 Conclusion

The above approach can give a general guide to the potential hazard of a particular material. It gives the scale of the severity of dust explosion. However, in order for this approach to be contributed to Edwards and Lawrence index and assess the dust hazard quantitatively, the explosion index values need to assign scores instead of ratings so it can be easily added to the scores resulted from assessing the hazard for gasses and liquids. This point needs more investigation and can be presented as a recommendation for future work.

Chapter 5: Data analysis for fire and explosion accidents

5.1 Introduction

The aim of this work is to develop a method for assessing the inherent safety of a chemical plant. This method is intended to be used in the early stages of plant design when the materials in process are known and their amount can be roughly estimated. This method is intended to predict the number of people that might be killed in case of a chemical accident involving a certain mass of specified chemical. It is not vital that such a method is to be very accurate as it aims to help process designers to apply good judgment in selecting the safest process in a phase when limited design data are available.

In order to do this, historical analysis of accidents, a technique utilizes in risk analysis is applied as a trial to derive a separate method for measuring the inherent safety of chemical plants. A number of statistical tests were conducted on historical accident data in order to investigate the possibility of developing relations predicting the number of fatalities caused by a chemical accident. These relations would be used to build a model which can predict the number of people that might be killed in case of a chemical accident per unit mass of a specified chemical.

The chapter starts by reviewing published accident data and its analysis where this is available. It then illustrates the statistical tests that were conducted on the fire and explosion accident data in order to develop a method which will be used to measure the inherent safety of a chemical plant.

The major hazards with which the chemical industry is concerned are fire, explosion and toxic release. Of these three, fire is the most common but explosions are more significant in terms of damage potential, often leading to fatalities and damage to property. Toxic release has possibly the greatest potential to kill a large number of people.

5.2 Definition of accidents

According to Lees (1996), an event can be classified as an accident if it is unexpected, unavoidable and unintended. He proposed the following three characteristics with which to classify an event as an accident: (1) degree of expectedness, (2) degree of avoidability and (3) degree of intention.

Secondary characteristics are: (1) degree of warning, (2) duration of occurrence, (3) degree of negligence and (4) degree of misjudgement. An event is an accident if it gives little warning, happens quickly, or if there is a large element of negligence and misjudgement leading to it.

5.3 Review of accident statistics

The purpose of publishing accident statistics is to emphasise the hazards of flammable materials and highlight common accident scenarios in the hope that relevant people may recognize particular situations and react before an accident occurs. In order to understand the mechanisms of accidents and to develop accident prevention and control strategies, it is essential to know about and learn from past accidents. Several researchers have published papers dealing with accident data. The following reviews published accident data and its analysis where this is available.

A study of worldwide industrial accidents has been conducted by Khan and Abbasi (1999b) covering the period 1926 to 1997. They listed reports of 3222 accidents relating to handling/transportation/processing/storage of chemicals. They stated that the actual number may be higher as reports of all accidents are not available in the literature. Of the 3222 accidents, 1744 (54%) occurred during different stages of operations in fixed installations, 1320 (41%) were transportation accidents and the remaining 160 (5%) happened during loading or unloading of chemicals, Figure 5.1.

Of the 1744 fixed installation accidents, 441 (25%) involved fires and explosions, and 1247 (71%) involved toxic release. The remaining accidents (4%) featured a combination of fire, explosion and toxic release.

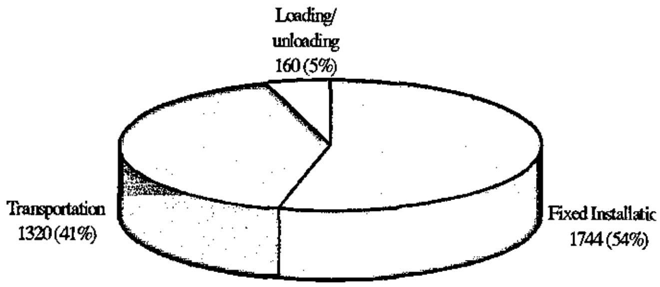


Figure 5. 1: Accident classification

The 1320 transportation accidents were classified according to the different mode of transportation. Such classification indicates that 37% occurred during rail transport, 29% during road transport, 6% during marine transport, 18% during pipeline transport, 4% during inland waterway transport, and the remainder during loading and unloading of chemicals.

Khan and Abbasi (1999b) have cited a study carried out by Norstorm (1982) in which he analysed fire and explosion accidents separately as shown in Tables 5.1 and 5.2. He found that about 18% of fires are due to release and overflow of flammable gases and/or liquids. Fires contributed about 20% of the total number of accidents; in comparison, explosions contributed about 75% to the total loss. His analysis concluded that failure to control chemical reactions is the most frequent cause leading to accidents; it contributed 35% to the total number of accidents. He also found that the processing area is the most susceptible location for accidents; it composed 47% to the total number of accidents.

Table 5. 1: Main causes of large fires in the chemical and allied industries (Khan & Abbasi)

Causes	Proportion (%)
Flammable liquid or gas (release, overflow)	17.9
Overheating, hot surfaces, etc.	15.7
Pipe or fitting failure	11.1
Electrical breakdown	11.1
Cutting and welding	11.1
Arson	4.4
Others	28.7
Total	100

Table 5. 2: Information related to explosions in the chemical and allied industries (Khan & Abbasi)

	Proportion (%)
Main cause	
Chemical reaction uncontrolled	20.0
Chemical reaction accidental	15.0
Combustion explosion in equipment	13.3
Unconfined vapour cloud	10.0
Overpressure	8.3
Decomposition	5.0
Combustion sparks	5.0
Pressure vessel failure	3.3
Improper operation	3.3
Others	16.8
Total	100
Location of occurrence	
Enclosed process or manufacturing buildings	46.7
Outdoor structures	31.7
Yard	6.7
Tank farm	3.3
Boiler house	3.3
Others	8.3
Total	100
Occupancy	
Chemical reaction process, batch	27.3
Storage tank	10.2
Boiler	8.4
Chemical reaction process, continuous	7.3
Compressor	5.4
Evaporation	4.0
Recovery	4.0
Transfer	4.0
Liquefaction	4.0
Others	25.4
Total	100

Table 5. 3: UK fires, explosions and related incidents in 1998/1999

Type of event	No. of incidents	No. of injuries			
		Fatal	major	minor	total
Incident involving:					
Fire alone	322	4	67	109	180
Explosion alone	104	3	28	58	89
Fire and explosion	67	1	30	28	59
Near miss	472	0	0	12	12
other	22	0	4	8	12
not classified	13	0	1	1	2
total	1010	8	130	216	354

Table 5. 4: UK fires, explosions and related incidents in 1999/2000

Type of event	No. of incidents	No. of injuries			
		Fatal	major	minor	total
Incident involving:					
Fire alone	371	6	73	137	216
Explosion alone	87	0	17	36	53
Fire and explosion	90	3	21	36	60
Near miss	529	0	3	9	12
other	39	2	20	8	30
not classified	94	0	2	2	4
total	1210	11	136	228	375

A review of incidents in the UK reported to the Health and Safety Executive during 1998/1999 and 1999/2000 involving fires, explosions, runaway chemical reactions and releases of flammable materials was conducted by Bradley and Baxter (2002). Tables 5.3 and 5.4 give the number of incidents and injuries as a function of the type of event.

During the 2-year periods, 354 injuries (including 8 fatalities), which resulted from fire and explosion related incidents were reported in 1998/1999 and 375 injuries (including 11 fatalities) in 1999/2000. Bradley and Baxter (2002) mentioned that the accidents which were classified as (not coded) are known to have occurred but could not be analysed due to the lack of information. The overall numbers for the 2-year reported accidents are compared to the preceding 8 years, from 1990 to 1997, in Table 5.5.

Table 5.5: Fires and explosions incidents statistics

Category		90/91	91/92	92/93	93/94	94/95	95/96	96/97	97/98	98/99	99/00
Flammable solids	Incidents	223	106	200	213	169	169	153	151	121	156
	Injuries	158	101	113	132	96	107	121	91	57	86
	Fatalities	1	5	5	7	5	5	3	4	1	3
Flammable liquids	Incidents	447	411	359	318	299	225	245	211	252	211
	Injuries	232	217	172	151	156	132	139	108	109	91
	Fatalities	12	8	7	10	3	3	6	3	5	5
LPG	Incidents	90	75	61	62	66	45	46	32	34	36
	Injuries	92	66	46	45	48	40	26	24	27	25
	Fatalities	1	3	0	0	4	1	2	0	0	0
Flammable gases and oxygen	Incidents	277	299	251	241	246	189	372	367	536	637
	Injuries	194	209	139	171	135	124	163	91	129	120
	Fatalities	4	1	1	0	1	0	0	2	1	1
Exothermic chemical reaction	Incidents	60	50	37	61	69	49	53	33	29	38
	Injuries	24	25	23	38	28	24	50	20	13	17
	Fatalities	0	1	5	1	0	0	0	0	0	2
Miscellaneous	Incidents	230	251	153	97	143	107	29	22	25	38
	Injuries	183	179	156	74	140	106	23	16	17	32
	Fatalities	0	5	2	1	1	1	1	0	1	0
Not coded	Incidents	0	0	0	0	0	0	0	0	13	94
	Injuries	0	0	0	0	0	0	0	0	2	4
	Fatalities	0	0	0	0	0	0	0	0	0	0
Totals	Incidents	1327	1192	1061	992	992	784	898	816	1010	1210
	Injuries	883	797	649	620	603	533	522	350	354	375
	Fatalities	18	23	20	19	14	10	12	9	8	11

Table 5. 6: Characteristics of accidental release from pipework and in-line equipment.

	No. of incidents	%
A Location type		
Chemical plant	278	30.3
Unknown	232	25.3
Factory	187	20.1
Refinery	96	10.5
Storage depot	47	5.1
Other	38	4.14
Tank yard	28	3.1
Fuel station	15	1.63
Total	921	100
B Site status		
Normal operations	343	38.8
Maintenance	146	16.52
Unknown	128	14.5
Storage	103	11.65
Start-up	42	4.75
Other	40	4.53
Loading/unloading	33	3.73
Contractor work	18	2.03
Shut-down	18	2.04
Modification	8	0.90
Testing	5	0.57
Total	884	100
C Materials released		
Ammonia	54	10.7
Hydrocarbons (unspecified)	54	10.7
Chlorine	50	9.86
Hydrogen	37	7.3
Benzene	33	6.5
Crude oil	28	5.52
Steam	25	4.93
Natural gas	24	4.73
Propane	20	3.94
Butane	18	3.55
Fuel oil	18	3.55
Hydrochloric acid	16	3.16
Sulphuric acid	16	3.16
Ethylene	16	3.16
Hydrogen sulphide	14	2.76
Water	13	2.56
Nitrogen	13	2.56
Oxygen	13	2.56
Vinyl chloride	12	2.37
LPG	12	2.37
Styrene	11	2.17
Naphtha petroleum	10	1.97
Total	507	100

Table continued next page…

Continue Table 5.6…

	No. of incidents	%
D Material phase		
Liquid	393	49.25
Gas	260	32.58
Liquid + gas/vapour	120	15.04
Vapour	13	1.63
Solid	9	1.13
Solid + gas/vapour	3	0.38
Total	798	100
E Unignited material dispersion		
Liquid	212	19.5
Spill	186	17.11
Vapour cloud	180	16.56
Flammable	127	11.68
Toxic	123	11.78
Corrosive	97	8.92
Unignited gas	96	8.83
Flammable/toxic	47	4.32
Spray	10	0.92
Jet/spurt	8	0.74
Irritant	1	0.09
Total	1087	100
F Fire or explosion event		
Fire	145	46.2
Explosion followed by fire	77	24.5
Explosion	63	20.1
Flash fire	11	3.50
Fireball	7	2.23
Pool fire	4	1.27
BLEVE	4	1.27
Explosion followed by flash fire	2	0.64
Jet fire	1	0.32
Total	314	100

Note: BLEVE stands for boiling liquid expanding vapour explosion.

Marshall (1977); Bellamy *et al* (1989) have reported data for various release accidents, Table 5.6, in which the accidents are ranked in terms of the amount of vapour released. Their report suggested that large releases often result in explosions rather than fires.

Vilchez *et al.* (1995) have compiled data for 5325 accidents from the MHIDAS database starting from 1900 until 1992. The survey includes accidents from 95 countries, particularly the USA, the UK, Canada, France and India.

Kirchsteiger (1999) has analysed data on major industrial accidents involving dangerous substances from the Member States of the European Union.

5.4 Data sources and description

Information on the accidents surveyed was gathered from a number of published sources in the literature. The majority of the data was from the comprehensive accident data lists in Marshall (1987), King (1990), Marsh & McLenan (1985), Lenoir and Davenport (1993) and Lees (1996). They have compiled data related to chemical and petrochemical plants and oil refineries.

Accident data are also quoted in a number of papers such as by Khan and Abbasi (1999a, b), Bradley and Baxter (2002). However, these papers are quoting data from the above mentioned sources.

Furthermore, there are a number of databases specifically dealing with accident histories. They include the following:

- Major Hazards Incident Data System (MHIDAS) and the corresponding explosives data system EIDAS. These are operated by SRD (Safety and Reliability Directorate), UK Atomic Energy Authority.
- The FACTS incident database.
- The Major Accident Reporting System (MARS).
- The Process Safety Incident Database.
- The FIRE incident database for chemical warehouse fires.
- The offshore Hydrocarbon Release (HCR) database.
- The ICHEME Database.

Tables 1 and 2 in appendix A are a comprehensive chemical accidents list covering the period from 1911 to 2000. The following is an explanation of the information contained in the various columns of Table 1:

- Date and location of the accident. Knowing these two factors was useful not only for identifying individual events but also for identifying other aspects. For example, accidents which occurred a very long time ago with a high number of fatalities could be due to a lesser regard for safety which was prevalent at that time. Also, accidents with high number of casualties in poorer or underdeveloped countries may be due to a similar lack of priority for safety and inferior technology.

- The type of accidents in terms of fire, explosion or toxic release has to be known. This can help in classifying the accidents according to the type of accident.

- The chemical involved in the accident and its quantity is major pieces of data. In fact getting the quantity of the chemical involved in the accident was the most difficult task. This information was available for only a few of the numerous accidents published in the literature. In some cases where the release was from a vessel or a container, the entire vessel capacity is considered as the amount released. Other accidents quoted an estimate or range; in this case an average figure was assumed. It was the lack of this particular figure that caused a lot of data to be unusable.

- Another important piece of data is the number of fatalities. The number used is the fatalities which were immediately attributable to the fire, explosion or toxic release. Fatality figures which occurred some time after the accident were ignored. The number of injuries was not used in the analysis although it is another indicator of the severity of the accident.

- The equipment indicates the unit operation in which the accident took place. This can help in classifying the accidents according to the unit operation in order to determine the most hazardous unit.

Accident data have been collected from the various sources mentioned above covering the period from 1911 to 2000. The accidents relate to handling, transportation, processing and storage of chemicals. Accidents were not included where no ignition occurred. On the other hand, no accident was excluded because some information on it was lacking. In the data, accidents are classified into two types: toxic releases and fire and explosion. During that period a total of 631 of these classes of accidents happened. The number of fire and explosion accidents was 512, whilst there were 119 toxic accidents. The fire and explosion accidents involved numerous chemicals from a large number of industries. Tables 1 and 2 in Appendix A list all the fire and explosion, and the toxic release accidents respectively.

Some accidents involving highly explosive chemicals such as, TNT, munitions and explosives are reported in historical accident data base. Those chemicals have been discarded from the data since they have a potential for serious accidents which is significantly greater than the rest.

5.5 Fire and explosion accidents

5.5.1 Classification of accidents over time

The distribution of fire and explosion accidents over time measured in decades is presented in Figure 5.2. As can be seen, there is a significant difference between the number of accidents that took place before and after the 1950s. During the early period, most of the accidents were due to dust explosions, in particular explosions in the windmills which were commonly used for grinding grain into flour. After the 1950s, the considerable increase in the number of accidents was due to the appearance of hydrocarbon accidents. The fire and explosion accidents have increased dramatically to the end of the eighties. This might be attributed to the start of developments, which resulted in great changes in the chemical, oil and petrochemical industries in that period. These changes involved a severe increase in the process operating conditions such as pressure and temperature, an increase in the size of plants, which resulted in large equipment items, such as compressors and distillation columns. Consequently, this gave rise to an increase in the potential for major accidents, usually arising from loss of containment and taking the form of serious fire, explosion or toxic release, Lees (1996). The late nineties exhibited a decline in the number of accidents.

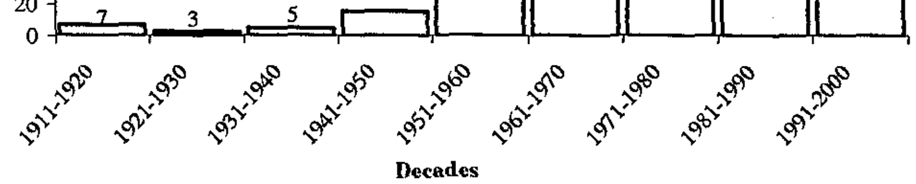


Figure 5. 2: Distribution of fire and explosion accidents as a function of time.

Figure 5.3 shows the distribution of the total number of fatalities resulting from the fire and explosion accidents. The figure shows a fluctuation in the number of fatalities during the early decades until the late fifties. The number of fatalities increased exponentially during the 60s, 70s and 80s. Actually, the number of fatalities which were reported in the period 1971 to 1980 was about four times the number in the previous decade, from 345 to 1270. A considerable number of accidents resulting in 10s and even 100s of fatalities happened in that decade. For example two accidents occurred in Spain. One was a propylene road tanker fire in 1978 causing the death of 216 persons and the other was a propane storage vessel explosion in 1980 causing 51 fatalities.

The number of fatalities continued to rise and peaked in the period 1981 to 1990. The reason for this peak is the two catastrophic accidents which were in 1984. The first one was the fire and explosion that took place in a petrol pipeline in Brazil. The pipeline was passing through a shanty town and a fire devastated the houses killing 508 people. The second was the LPG terminal fire in Mexico City which happened in a residential area and caused the death of 650 persons.

Figures 5.2 and 5.3 illustrate that there is a rough correspondence in the trend of the number of accidents and the number of fatalities during the period. Both decline during the last decade of the twentieth century.

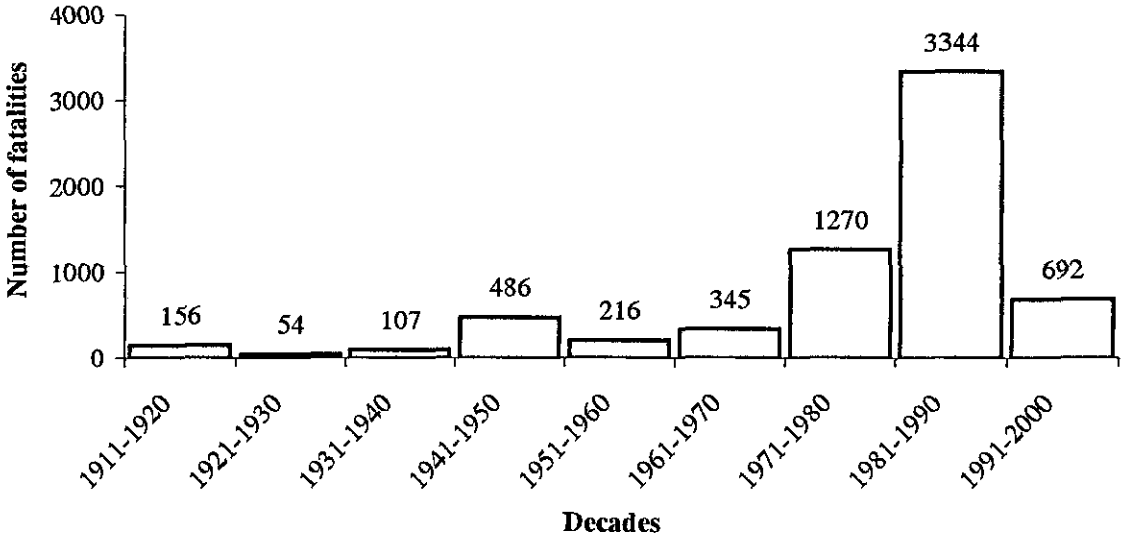


Figure 5. 3: Fire and explosion fatalities as a function of time

5.5.2 Classification of accidents by origin

The accident data are classified according to the unit operation in which the accidents took place. The accidents are categorised as follows:

- Process accidents are accidents which happened during processing or transformation of chemicals from one form to another. In some accidents the origin was named as plant without mentioning in which specific operation the accident took place, for example ethylene plant or propylene plant. These accidents were considered to have a process origin.
- Storage accidents are accidents which happened in storage tanks holding the final product or raw/intermediate materials waiting to be used, or accidents that happened in warehouses involving stored raw materials or products.
- Utility accidents are accidents that took place in equipment that supports the operating plant, such as pumps, compressors, heat exchangers and boilers.
- Transportation accidents are accidents that happened during the transport of chemicals, including transport by car, rail, ship and pipelines.

Of the 512 fire and explosion accidents reported, only 60 about (12%) are of unknown origin. For the rest 452 (88%), the distribution according to origin is presented in Figure 5.4. It can be seen that the principle origin of fire and explosion accidents is process, with (44%) of cases. Then, come in descending order, transport, storage and utilities accidents.

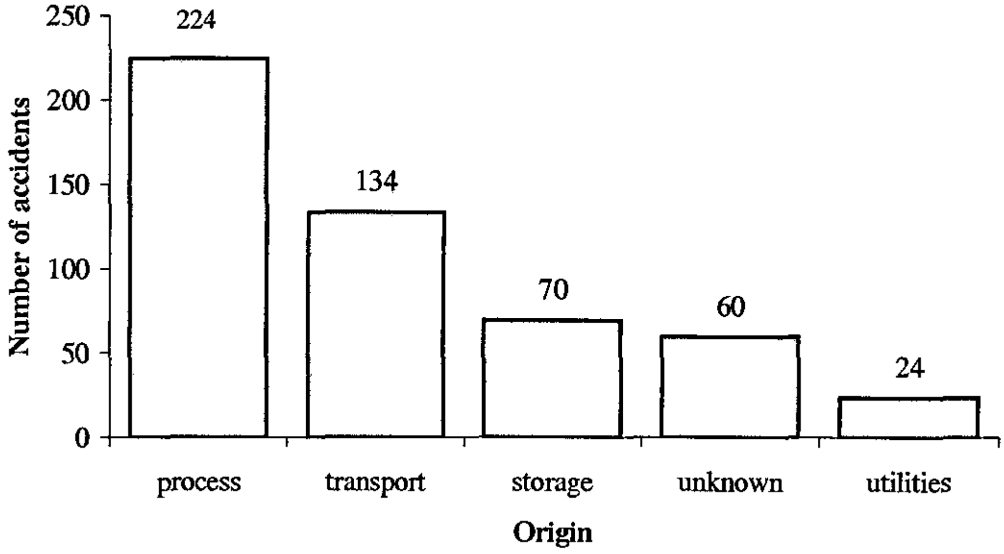


Figure 5. 4: Origin of accidents

In contrast, Figure 5.5 shows the rank of accidents in terms of the total number of people killed. As can be seen, accidents that happened during transporting materials have the highest number of deaths of 3088 people.

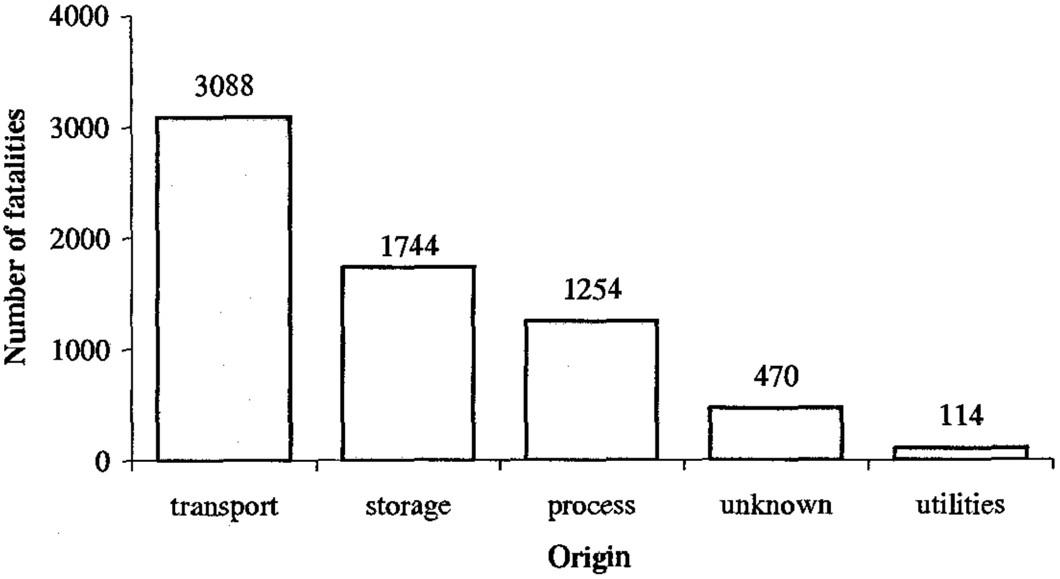


Figure 5. 5: Classification of accidents according to the number of fatalities

The initial step in the exploration of a data set is to examine the distribution of every variable in the data set. The starting point of this process is most typically the examination of the frequency distributions. This section aims to examine the distribution of the variables in question in order to detect asymmetry of distribution and thus to know the ability of each variable to approximate to a normal distribution.

Table 5.7 gives a summary of the two variables in question, the mass of chemicals involved in the accidents and the resulting number of fatalities. The table shows the 101 accidents (N) out of the 501 in which the mass of the chemicals involved is available. The table also shows the minimum and the maximum values for every variable, the mean, the median and the standard deviation. It can be seen that for both variables there is a wide range between the minimum and the maximum values. The standard deviation values are large which also indicates that data has a large spread. Table 5.7 also shows that the data are not normal because the mean and the median values are far apart and they are away from the centre of the distribution. This raises a concern about the validity of the tests that are only applicable in the case of a normal distribution. Table 3 in appendix A lists the 101 accident.

Table 5.7: Descriptive Statistics

Variables	N	Minimum	Maximum	Mean	Median	Standard Deviation
Number of fatalities	101	0	650	18.57	2	73
Mass of chemicals (tonne)	101	0.002	95,000	2043	18	10,704

N is the number of accidents

Figures 5.6 and 5.7 show the frequency distribution for the mass of chemicals involved in the accidents and the number of fatalities that resulted respectively. Figure 5.6 shows only the 88 accidents from the total of 101, the accidents which involved more than 500 tonnes were left out of the graph in order to show the distribution of the accidents with small mass of chemicals. It can be noticed that a large number of the accidents, 63, involve a small mass of chemical, in the range (0.002-33.33 tonnes) where as accidents involving large quantities of chemicals occurred less frequently.

Figure 5.7 shows the 88 accidents which yielded fewer than 100 fatalities. It can be seen that accidents with no fatalities or with a low number of fatalities happened much more often than accidents that yielded high number of fatalities. In fact 25 accidents out of 88 did not result in any fatalities.

It can be seen that in both cases the high number of accidents with small masses and the accidents that did not cause fatalities yielded patterns that are very different from a normal distribution. This distribution can be said to be positively skewed. That is, the tails of the curves or the extreme values are on the right side.

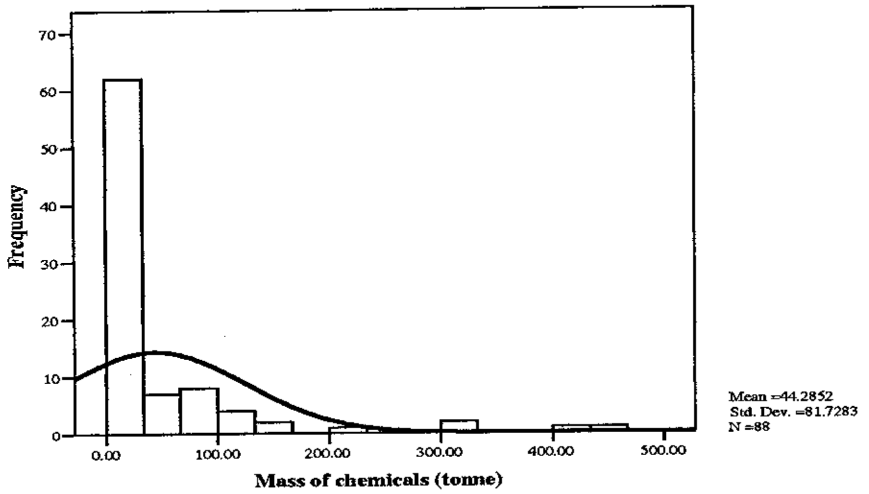


Figure 5.6: Frequency distribution for mass of chemicals

For the purposes of statistical testing, the original data can be transformed to make the distribution more symmetrical. There are great varieties of possible data transformations, from adding constants to multiplying, squaring or raising to a power, converting to logarithmic scales, and taking the square root of the values.

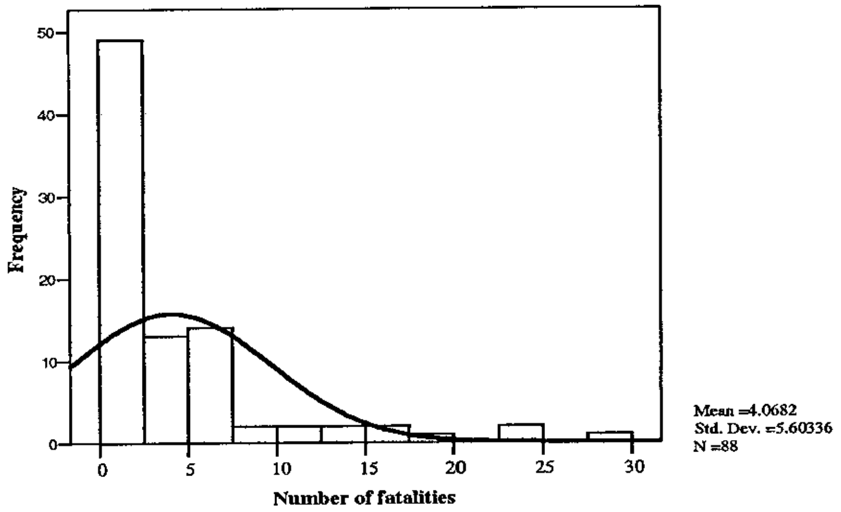


Figure 5.7: Frequency distribution for number of fatalities

The most commonly used transformation that is appropriate for data which are skewed to the right is the log transformation. However, if a data set contains values of zero, a constant must be added to move the minimum value of the distribution in order to take the log.

This solution cannot be applied in this case as it will change the consequence of an accident from an accident with no fatalities to an accident with one fatality. Therefore, the accidents which caused no fatalities are excluded from the distribution graph in order to take the logs. Figures 5.8 and 5.9 show the histograms of the logs of the original data.

The transformation has clearly reduced the skewness of the mass of chemicals distribution but the number of fatalities distribution is still skewed. This suggests that parametric tests or tests which can be used when the data is normally distributed are not applicable and so non parametric tests that do not make assumptions about population distributions will be used. The following section describes the nonparametric statistics.

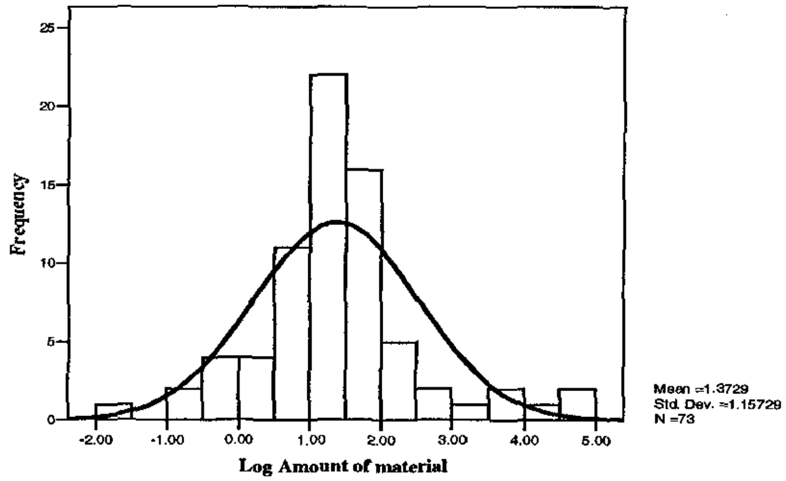


Figure 5.8: Frequency distribution for mass of chemicals

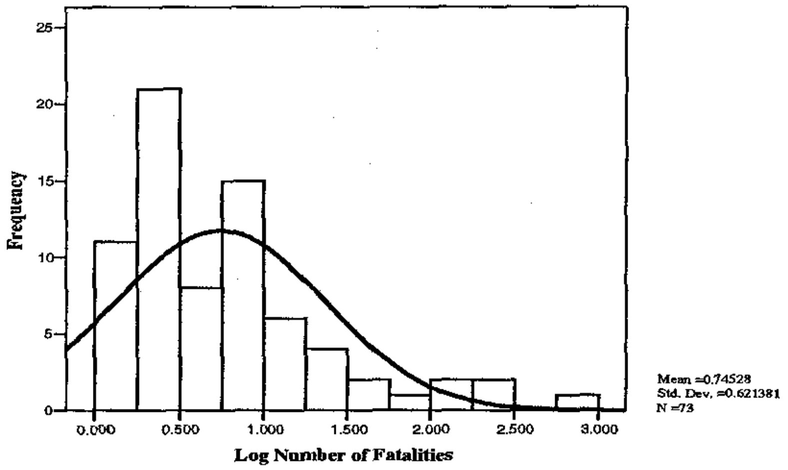


Figure 5.9: Frequency distribution for number of fatalities

5.6 Nonparametric statistics

As mentioned above, sometimes data is not normally distributed. That is, the distribution would not look like a symmetrical bell-shaped or normal curve, with most subjects having values in the mid range and with similar small numbers of participants with both high and low scores. A distribution that is asymmetrical with more high than low scores (or vice versa) is skewed. Nonparametric tests are tests which can be used in cases where the normal distribution in data is not fulfilled.

5.6.1 Correlations between the number of fatalities and the amount of chemicals

In this section the Spearman's rank correlation is calculated to examine if there is any relationship between the number of fatalities and measurable characteristics of the chemicals involved in the accidents. This has been calculated for all the accidents and separately for the three different types of accidents: process, storage and transport.

5.6.1.1 Spearman's rank correlation

Spearman's rank correlation measures the strength of association between quantitative variables. The Spearman correlation performs the analysis on the ranks of the values instead of an actual data values. It is applied to the values after they have been ranked from the smallest to the largest on the two variables separately. It is used when the values are markedly asymmetrical (skewed) on a variable. It ranges in size from a maximum of +1.00 through 0.00 to -1.00. The Spearman correlation can still be used even when the relationship between two variables is non-linear.

Spearman's correlation has been calculated in order to investigate if any correlation exists between the number of fatalities and the mass (in tonnes) of chemicals involved in the accidents. Table 5.8 shows the correlation coefficient for all accidents.

Table 5.8: Spearman's rank Correlation for all accidents

Correlation Coefficient	0.3
Significance, p value	0.012
N (number of accidents)	101

It can be seen from Table 5.8 that the correlation coefficient is 0.3. The significance (p-value) is used to assess the significance of the correlation. If the p-value is less than 0.05, the results can be considered as statistically significant. In this case p is less than 0.05 which indicates that there is statistical evidence for a correlation between the number of fatalities and the amount of chemicals involved in the accidents. The correlation is positive which suggests that on the whole the two variables increase together. However, the value is quite low, suggesting that there are other factors that may be important.

Figure 5.10 shows the scatter plot of the number of fatalities and the amount of chemicals. When the data was plotted on a linear-linear scale, it showed clustering close to the origin which obscured examination of any relationship. Therefore the data was all log-transformed. As can be seen, there is rough increase in the trend of the number of fatalities as the mass increases. The amount of variability between the data points is very high which suggests that any relationship obtained from this graph would not predict accurately the number of fatalities from knowing the mass of chemicals.

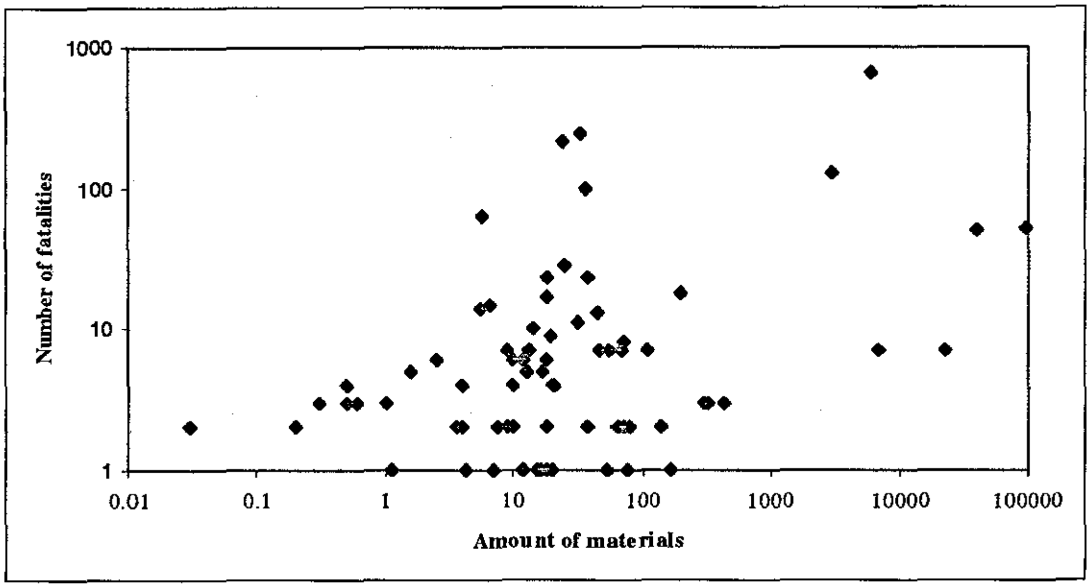


Figure 5.10: All fire and explosion accidents

The same analysis has been conducted between the number of fatalities and the mass of chemicals for each type of accident. Tables 5.9, 5.10 and 5.11 show the outputs of these analyses.

Table 5.9: Spearman's rank correlations for process accidents

Correlation coefficient	0.312
Significance, p value	0.042
N (number of accidents)	43

Table 5.10: Spearman's rank correlations for storage accidents

Correlation coefficient	0.343
Significance, p value	0.164
N (number of accidents)	18

Table 5.11: Spearman's rank correlations for transport accidents

Correlation coefficient	0.037
Significance, p value	0.835
N (number of accidents)	34

Table 5.9 shows that the Spearman's correlation ($r_s = 0.312$) and $p < 0.05$, which indicates that there is a significant correlation between the number of fatalities and the mass of chemicals in case of process accidents. However, the low value of the correlation coefficient suggests that on the whole the two variables are going up together but as for all accidents, the relationship is not strong.

The results from tables 5.10 and 5.11 show that there is no significant correlations between the number of fatalities and the amount of chemicals in the cases of storage and transport. This might be attributed to the lack of storage accidents with a known amount of chemicals (18 accidents) since the smaller the size of the sample the less significant the correlation. The non significant transport correlation might be due to the different types of transportation included in the data. It includes rail tank cars, road tankers and oil tankers. Also the circumstances of the accidents vary widely for example happening in the middle of a built-up area or where there are no people.

The correlation coefficients for process and storage accidents are very similar in contrast to transport where there was no correlation. This suggested eliminating the transport accidents as they might weaken any potential correlation that might exist between the mass of the chemicals and the number of fatalities. In addition, the transport accidents are of minor concern in this study since the main aim is to estimate the hazard of process plants. However, eliminating the transport accidents did not make a big difference in the value of the correlation coefficients. Table 5.12 shows Spearman's correlation excluding the transport accidents.

Table 5.12: Spearman's rank correlation for accidents without transport

Correlation coefficient	0.237
Significance, p value	0.055
N (number of accidents)	66

5.6.2 Box Plots

The type of accidents data was graphically represented using box and whisker plots as shown in Figure 5.11. Boxplots are particularly useful for identifying outliers and extreme cases in data sets.

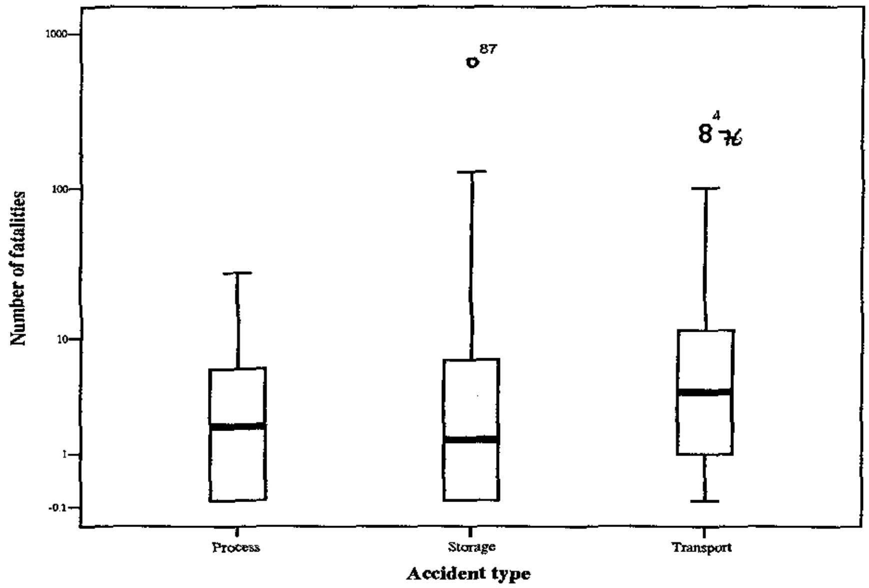


Figure 5.11: Boxplots for accidents type

Figure 5.11 shows the three types of accidents. The box itself represents that portion of the distribution falling between the 25th and 75th percentiles, i.e. the lower and upper quartiles. The thick horizontal line across the interior of the box represents the median. The vertical lines outside the box, which are known as whiskers, connect the largest and smallest values that are not outliers or extreme cases. An outlier (o) is defined as the value more than 1.5 box-lengths away from the box, and extreme case (*) as more than 3 box-lengths away from the box.

The o^{87} above the storage boxplot indicates the existence of an outlier and that it is the value for accident number 87. This accident is the LPG vapour cloud fire which took place in Mexico City in 1984 and in which 650 people were killed. This value is well above the average fatalities and it therefore responsible for skewing the distribution of the data.

The other two outliers are the points above the transport type. They are for the Dimethyl ether rail tank car vapour cloud explosion which happened in Germany in 1948 and in which 245 people lost their lives and for the propylene road tanker vapour cloud fire that took place in Spain in 1978 and in which 216 people were killed. In general Figure 5.11 shows that there is not much difference in the median number of fatalities between the three accidents types. It should point out that Figure 5.11 shows only the accidents in which the mass of chemicals involved was available.

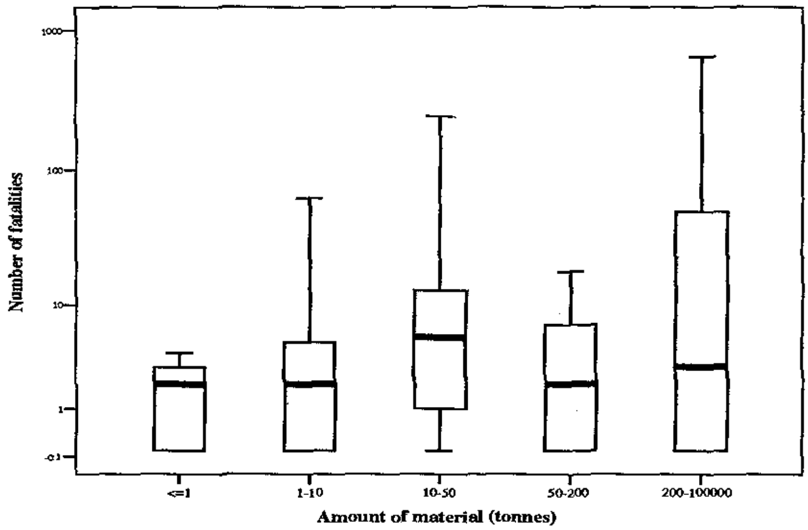


Figure 5.12: Box plot for amount of chemicals

Figure 5.12 shows the median number of fatalities when the accidents are grouped by mass of materials. It can be seen that there are neither outliers nor extremes in the data, though, the long whiskers indicate that there are some points which are away from the median. The eccentric positions of the median lines in all the amount of material categories, however, indicate that the number of fatalities in those groups have skewed distributions.

Figure 5.13 shows the boxplots for the chemicals when they are categorized by risk phrases (R). Risk phrases are approved phrases for describing the risks involved in the use of hazardous chemicals and have validity in the United Kingdom and throughout the countries of the European Community. These phrases should be used to describe the hazards of chemicals on data sheets for use and supply; for labelling of containers, storage drums, tanks, etc, Royal Society of Chemistry (1989). Due to the small groups of chemicals which have similar risk phrases (R), the chemicals were divided into two groups. The first group consists of extremely flammable liquefied gas R13, and the second group contains R10, R11 and R12 which represent flammable, highly flammable and extremely flammable chemicals respectively.

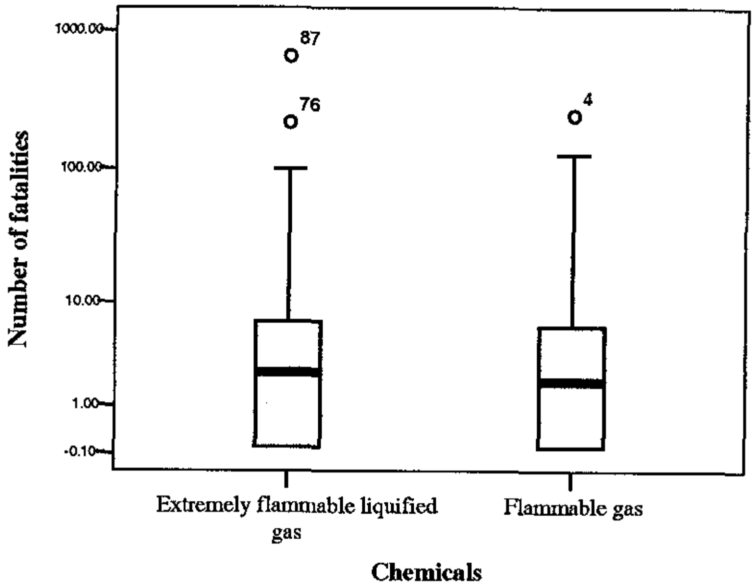


Figure 5.13: Box plot for chemical type

There are two outliers in the extremely flammable liquefied gas group. One of them is the LPG vapour cloud fire which took place in Mexico City causing 650 fatalities and the other one is the Propylene road tanker vapour cloud fire that took place in Spain in 1978 and caused the death of 216 people. There is only one outlier in the flammable gas group, it is again the Dimethyl ether rail tank car vapour cloud explosion which happened in Germany in 1948 and in which 245 people lost their lives. Figure 5.13 shows that the median number of fatalities for the two chemical groups is almost the same.

5.6.3 Kruskal-Wallis and Mann-Whitney tests

This section aims to establish a ranking system for the accidents and to investigate whether there are any differences between the median number of fatalities for each type. The Kruskal-Wallis test is used to compare three or more groups while the Mann-Whitney test is used for comparing two groups.

5.6.3.1 Type of accidents

The Kruskal-Wallis test was applied to the accidents grouped by type of operations in order to investigate any differences in the median number of fatalities. This can help to know if one type poses more hazards to people than the others. The test results are shown in Table 5.13.

Table 5.13: Kruskal-Wallis test

Operation type	N	Median No. of fatalities	Significance, p value
Process	43	4.0	0.131
Storage	18	6.0	
Transport	34	7.0	
Total	95		

N is the number of accidents

The test shows that there are differences in the median number of fatalities for the three operation types. The lowest one is the process and the highest is the transport. However, since the p-value is greater than 0.05 it indicates that there is no statistical evidence for significant differences between the three types of operations.

5.6.3.2 Amount of chemicals involved in the accidents

The Kruskal-Wallis test has been carried out for the amount of chemicals involved in the accidents in tonnes, subdivided into ranges. Table 5.14 shows the output from the test.

Table 5.14 shows that there is fluctuation in the median number of fatalities between the five mass groups. The median was equal in three groups while it was relatively higher in the range of 200 to 100,000 and it gets very high in the range of 10 to 50 tonne. The high median in the range of 200 to 100,000 is due to the two storage accidents which resulted in 128 and 650 fatalities while for masses between 10 and 50 tonnes it is due to the three transport accidents which resulted in 245, 216 and 100 fatalities. Since the p-value is less than 0.05 it suggests that there are significant differences in the median number of fatalities between the quantity ranges. This corresponds with the result of Figure 5.12 which shows the differences between the median numbers of fatalities for each amount of material groups. However, conducting the same test without the transport accidents resulted in p-value of 0.414 which indicates non significant differences in the median number of fatalities.

Table 5.14: Kruskal-Wallis test

Amount of material (tonne)	N	Median number of fatalities	Significance, p value
<=1	15	2	0.024
1-10	25	2	
10-50	30	6	
50-200	18	2	
200-100000	13	3	
Total	101		

N is the number of accidents

5.6.3.3 Type of chemicals

The Mann-Whitney U test has been carried out to assess whether there are differences in the median number of fatalities by type of chemicals. In this test the chemicals were classified according to their risk phrases (R).

Table 5.15 is the output of the Mann-Whitney test. It shows that the median for the two chemical groups are almost the same. The p-value ($p > 0.05$) confirms that there is no statistical evidence for any differences between the median number of fatalities in the two chemical groups. This confirms the results of Figure 4.13 which shows that there are no differences between the median number of fatalities for the two chemical groups. There was no difference in the result of the test when the transport accidents were excluded.

Table 5.15: Mann-Whitney test

Chemical type	Number of accidents	Median Number of fatalities	Significance, p value
Extremely flammable liquified gas	66	3	0.131
Flammable gas	35	2	
Total	101		

5.6.4 Accidents without zero fatalities

In this section the previous analyses were repeated for the accidents after excluding the accidents which did not cause any fatalities. This has been done in order to investigate whether these accidents have a significant impact on the results. The following tables show the results of the tests excluding the zero accidents.

Table 5.16: Descriptive Statistics

Variables	N	Minimum	Maximum	Mean	Median	Standard Deviation
Number of fatalities	73	1	650	26	4	85
Amount of material (tonne)	73	0.03	95000	2424	18	12258

N is the number of accidents

Table 5.17: Spearman's rank Correlations

	All accidents	Process	Storage	Transport
Correlation Coefficient	0.3	0.31	0.713	-0.151
Significance, p value	0.011	0.096	0.021	0.443
N (number of accidents)	73	30	10	28

Comparing Table 5.17 to Tables 5.8, 5.9, 5.10 and 5.11 show that in the case of applying all the fire and explosion accidents, the Spearman's correlations were the same in case of including and excluding the accidents that did not cause any fatalities, (r_s = 0.3). Comparing the type of accidents shows that the correlations obtained from process accidents were also similar in both cases, (r_s = 0.31). Storage correlation was much stronger for the case of excluding the accidents with no fatalities (r_s = 0.713). It also changed from a non significant correlation (p = 0.164) to a significant correlation (p = 0.021). There was no transport correlation in both cases.

The Kruskall–Wallis and the Mann-Whitney tests were conducted on the accidents without zero fatalities grouped by amount of chemicals, the type of accidents and the type of chemicals that were involved in the accidents. Tables 4.18, 4.19 and 4.20 show the results from these tests.

Table 5.18: Kruskal-Wallis test for amount of material

Mass of chemicals (tonne)	N	Median number of fatalities	Significance, p value
<=1	8	3	0.05
1-10	17	4	
10-50	26	7	
50-200	13	2	
200-100000	9	7	
Total	73		

Table 5.19: Kruskal-Wallis test for type of accidents

Accidents type	N	Median number of fatalities	Significance, p value
Process	30	4	0.35
Storage	10	6	
Transport	28	7	
Total	68		

Table 5.20: Mann-Whitney test for chemical type

Chemical type	N	Median number of fatalities	Significance, p value
Extremely flammable liquified gas	49	5	0.79
Flammable gas	24	4	
Total	73		

Comparing the results obtained from both data sets, with and without the zero fatalities accidents showed that both of them resulted in positive correlation between the number of fatalities and the amount of chemicals involved in the accidents. These correlations were significant in both cases. Correlating the same variables by the accident type showed that the process operations resulted in the same correlation coefficients. The storage correlation became stronger when the zero fatalities accidents have been excluded, it jumped from non significant correlation (r = 0.343, p = 0.164) to a significant correlation (r = 0.713, p = 0.021). There was no transport correlation in both data sets.

The Kruskal-Wallis test showed that in both data sets there were no significant differences in the median number of fatalities between the process, storage and transport accidents. Applying the same test to the amount of chemicals as groups showed that there is an increase in the median number of fatalities as the amount of chemicals increase to the range of 10 to 50 tonnes then it fluctuates, which is the same results obtained from including the accidents with zero fatalities in the data. The Mann-Whitney test showed that there is no significant difference between the two chemical groups in the case of including or excluding the accidents that did not cause any fatalities. Conducting the two tests excluding the transport accidents did not change the results.

It can be seen from the results obtained from the two sets of data that there is statistical evidence that the amount of chemical has an impact on the number of fatalities. However, plotting the two variables together has not resulted in a clear relationship that can be used to predict the number of fatalities from knowing the amount of chemical. This can be due to the non consistency of the data as it represents accidents with different chemicals which took place in different countries with different regulations and different design standards. In addition, the accidents happened in very wide range of time since it includes very old accidents when safety was of less concern compared to nowadays. This may explain why the number of fatalities in many cases did not bear any relation to the amount of chemical involved. For example 1 tonne killed 6 people while 60 tonnes did not kill anybody.
This raised a concern about the validity of using the raw data to compare accidents happening in different situations and different circumstances, for example different locations, different population densities and historic time period. This suggested that there are more factors that can play role in the consequences of accidents.

5.6.5 Accident by location and time

This section aims to investigate if the relationship between the number of fatalities and the mass of chemicals varies according to place and date. In order to do this, accidents were divided into three groups by location and three groups by time. The next sections show the analysis according to location and time.

5.6.5.1 Accident by location

The three groups by location are as follows: the first group is for the accidents which took place in the United States of America and Canada and they are labelled as (US), the second group is for the accidents happened in the European countries and are labelled as (EU). These accidents happened in the United Kingdom, France, Germany, Netherlands, Spain, Sweden, and Norway. The last group is labelled as others and it consists of accidents that happened in less developed countries such as Mexico, Turkey, Saudi Arabia, Qatar, Czechoslovakia and Lithuania. The two accidents which happened in Japan are not included in the analysis as it was not known if Japan uses the American or the European regulations or if it has its own regulations.

Tables 5.21, 5.22 and 5.23 show the output from calculating the Spearman's rank correlation between the number of fatalities and the amount of chemicals involved in the accidents for the US and the EU and the accidents that are labelled as others.

Table 5.21: Spearman's rank correlation for US

Correlation Coefficient	0.063
Significance, p value	0.7
N (number of accidents)	40

Table 5.22: Spearman's rank correlation for EU

Correlation Coefficient	0.3
Significance, p value	0.2
N (number of accidents)	21

Table 5.23: Spearman's rank correlation for others

Correlation Coefficient	0.34
Significance, p value	0.34
N (number of accidents)	10

As can be seen there was no correlation between the number of fatalities and the amount of chemicals in the case of the US accidents while there were positive correlations for both EU and for the less developed countries accidents. It can also be noticed that the correlations that obtained from EU and others are similar to the one obtained from all the accidents except that both of them are not significant. However, the reason for that might be the small sample sizes. Figures 5.14, 5.15 and 5.16 show the shape of the relationships between the two correlated variables for the three groups.

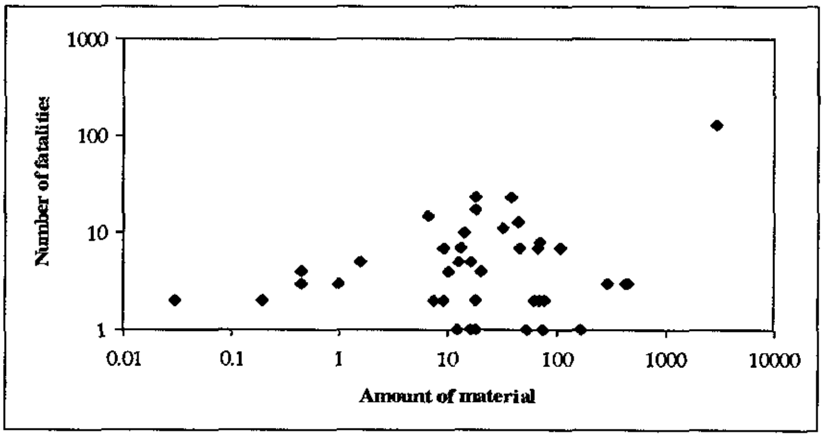


Figure 5.14: The United States (US) accidents

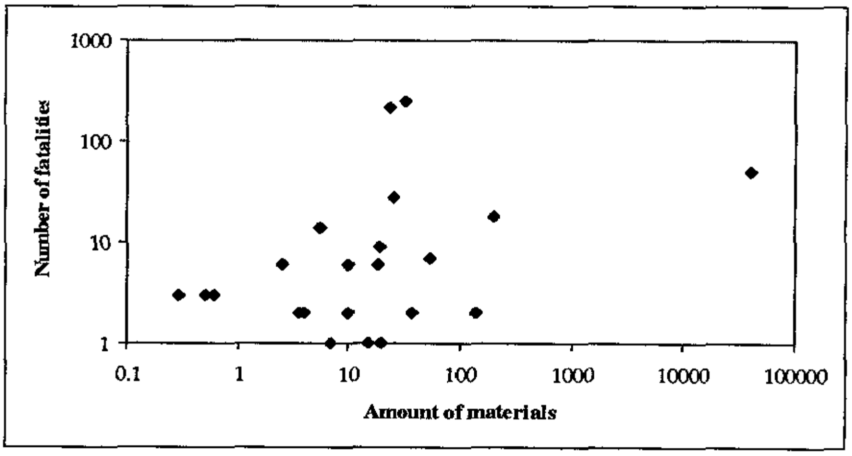


Figure 5.15: The European Union (EU) accidents

It can be seen from Figures 5.14, 5.15 and 5.16 that the scatter plots in the three cases show no clear relationship that can not be used to predict the number of fatalities.

The Kruskal-Wallis test was applied to the three accidents groups in order to determine whether there were any differences in the median number of fatalities between the three groups of accidents. Table 5.24 shows the results of this test.

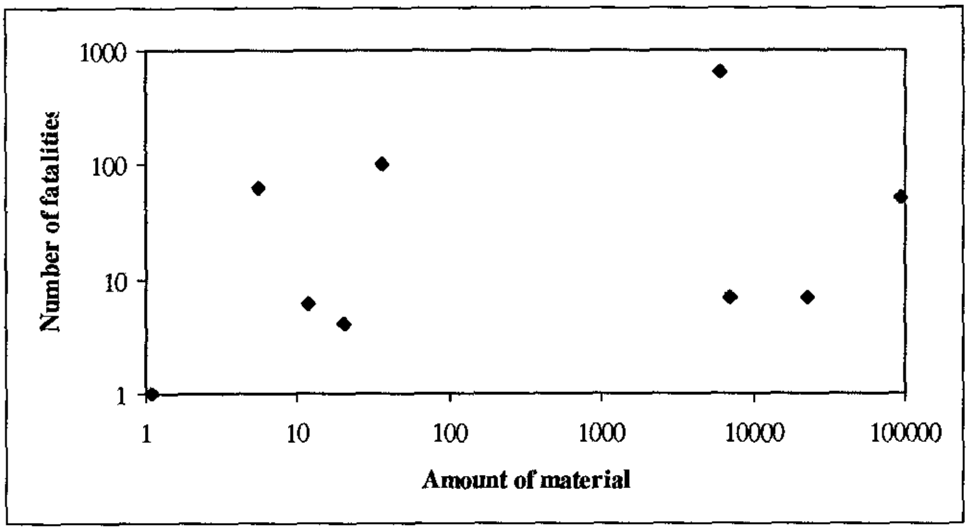


Figure 5.16: The less developed countries (others) accidents

Table 5.24: Kruskal-Wallis test

Locations	N	Median number of fatalities	Significance, p value
US	40	4	0.05
EU	21	5	
Others	10	7	
Total	73		

The Kruskal-Wallis test shows that the US have the lowest median number of fatalities followed by the EU. The others group which represents the less developed countries have quite high median number of fatalities. This seems to be logical as safety regulations could be less strict in these countries compared to the developed ones. The p value suggests that the differences in the median between the three groups are significant which indicates that the location of accident is an important factor that affects the accident consequences.

5.6.5.2 Accidents by time

The same procedures as in the accidents by locations were applied to the accidents after they classified according to time. Accidents were divided into three periods as follows:

from 1921 to 1950, which represents very old accidents when safety was less concern compared to nowadays; from 1951 to 1980, representing the appearance of hydrocarbons which resulted in great changes in the chemical, oil and petrochemical industries; and from 1981 to 2000 which represent recent accidents and showed decline in the number of fire and explosion accidents. Figure 5.2 in section 5.7.1 show the basis of the division. Tables 5.25, 5.26 and 5.27 show the Spearman's rank correlations.

Table 5.25: Spearman's rank correlation (1921 – 1950)

Correlation Coefficient	0.72
Significance, p value	0.17
N (number of accidents)	5

Table 5.26: Spearman's rank correlation (1951 – 1980)

Correlation Coefficient	0.22
Significance, p value	0.11
N (number of accidents)	54

Table 5.27: Spearman's rank correlation (1981 – 2000)

Correlation Coefficient	0.24
Significance, p value	0.42
N (number of accidents)	14

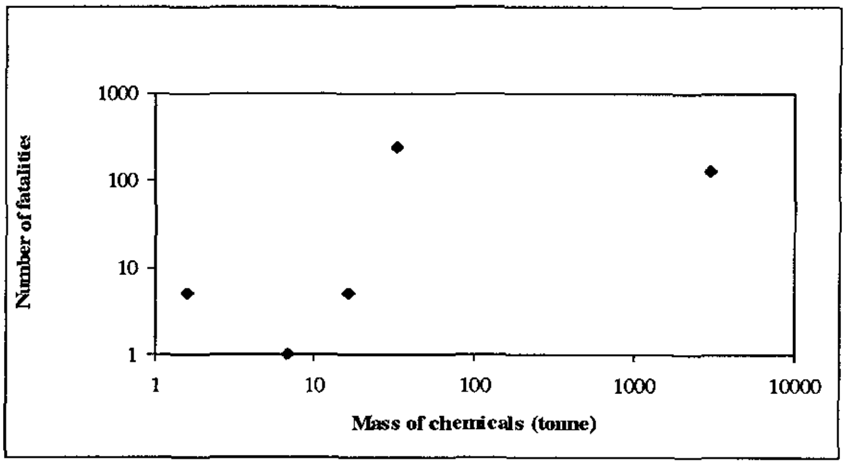


Figure 5.17: Accidents from 1921 to 1950

It can be seen from the above tables that none of the groups yielded significant correlation. Figures 5.17, 5.18 and 5.19 are the scatter plot for the three periods.

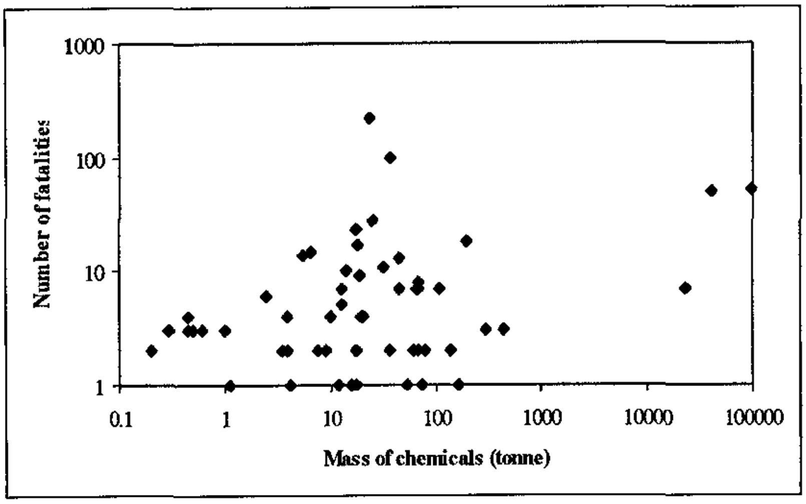


Figure 5.18: Accidents from 1951 to 1980

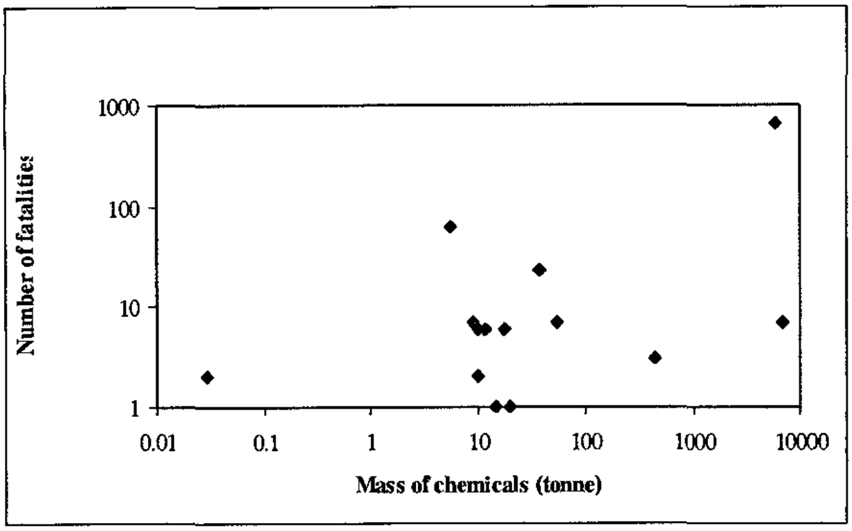


Figure 5.19: Accidents from 1981 to 2000

It can be seen from the above tables that correlating the mass of chemicals and the number of fatalities for the three showed periods of time did not result in significant correlations. Despite the high correlation coefficient in the period of 1921 to 1950 of 0.72, the value of p = 0.17 suggests that no reliable relationship can be obtained from the two correlated variables. The scatter plots for the three periods of time showed that no clear relationships exist between the mass and the number of people killed.

5.6.6 Conclusion

In conclusion these results indicate that the amount of materials does have an impact on the number of fatalities. The reason for the weak relationship between the number of fatalities and the amount of materials might be the non consistency of the data. In other words, taking into consideration only the amount of material involved in the accidents might not be sufficient. Other factors such as the location of the accident (for example, in densely populated city or in the middle of a desert), or the country of operation are also important. In fact conducting the Kruskal-Wallis test on the accidents classified by countries showed that there are differences in the median number of fatalities between developed and less developed countries. More rigorous classification, by grouping countries that use the same regulations and same design standards, could produce more accurate results.

The time of the accident is also a factor because the consequences of an accident might be different if it happened during day or night, or if it happened during a weekday or at a weekend. If these information were available it would be possible to compare accidents which took place in similar circumstances (the same quantity, the same time, the same location, the same population density, etc..). These factors might generate basis for further analysis in which stronger relationships could be obtained.

5.7 Estimating the number of people killed by type of chemicals

In the previous part, chemicals were classified by hazard type or risk phrases into extremely flammable liquefied gases and flammable gases. In the following sections hazards will be assessed by type of chemical. Accidents will be classified by chemical type in order to investigate whether specific chemicals pose more hazards to people than others and subsequently to estimate the number of fatalities per mass of those chemicals.

As stated before, the accident data collected shows that the mass of the chemicals involved in the accidents is often missing. This hindered the estimation of the number of fatalities for every chemical that was involved in fire and/or explosion accidents. However, quantities of chemicals involved were available for some groups of hydrocarbons. They may be classified according to the number of carbon atoms in the molecule as follows:

- One carbon atom (methane): this is often handled as a refrigerated liquefied gas.
- Two carbon atoms (ethane, ethene): these are usually handled as refrigerated liquefied gases.
- Three and four carbon atoms (propane, butane and corresponding unsaturated compounds): these are handled as liquefied vapours.
- Five or more carbons (pentane, hexane): these are liquids at ambient temperatures.

Chemicals were classified according to the above classification. The one carbon atom class contains methane (natural gas) and Liquefied Natural Gas (LNG). It was not possible to assess the hazard of these hydrocarbons due to the unavailability of the mass involved for most of these accidents. There were 45 accidents in total and the mass was available in only 3 accidents.

The second hydrocarbon group is the two carbon atoms which are represented by ethylene. The following section describes the estimation of the number of fatalities from ethylene accidents.

5.7.1 Estimating the number of fatalities per mass of ethylene (C2)

Ethylene was found to be involved in 23 fire and explosion accidents resulting in 165 fatalities. The mass of ethylene was available for 12 of these accidents. Figure 5.20 shows the relation between the number of fatalities and the mass of ethylene involved for the accidents that caused one or more fatalities. The figure does not show the accidents that did not cause fatalities.

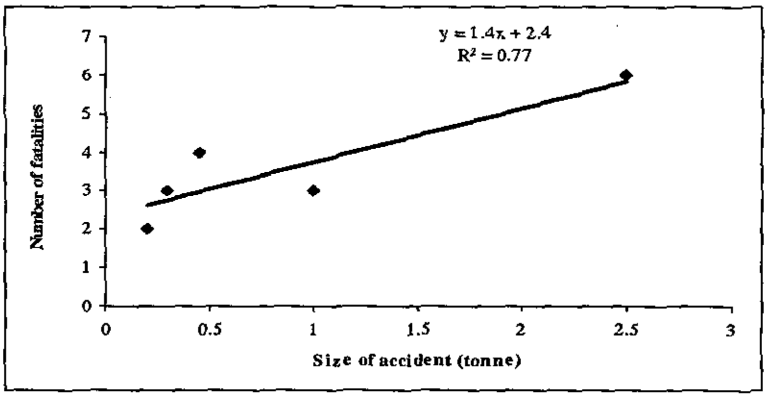


Figure 5. 20: Ethylene accidents

From Figure 5.20 it can be seen that there is a roughly proportional relationship between the mass of ethylene and the number of fatalities. The more ethylene involved, the greater the number of people killed. In seven accidents fortunately no one was killed.

The accident which took place in 1982 at Alberta, Canada, involving 2.9 tonnes of ethylene killed no-one because the explosion happened in an unmanned compressor building. There is no detailed information available about the other six accidents that resulted in no fatalities.

Fitting a line to the ethylene accidents with fatalities, as shown in Figure 5.20 leads to the following relation between the number killed and the mass of ethylene involved:

$$[No\ Killed, if\ any] = 1.4(m_E) + 2.4 \qquad 5.1$$

Where $m_{E,}$ is the mass of ethylene involved in the accident in tonnes. Although of the significance of Equation 5.1 ($R^2 = 0.77$), it can not be considered as a model to predict the number of fatalities from ethylene accidents. It will be inappropriate to base a model on five accidents. Additionally, with the non-availability of detailed information about the accidents which caused no fatalities, it would be difficult to know if these accidents were in situations where no-one was around. If more information is made available, specifically the mass of ethylene for more accidents, it might be possible to establish a more reliable relationship between the fatalities and the mass of ethylene.

The third group of the classification is those hydrocarbons with three or four carbon atoms which contain LPG, propane/propylene, butane. The next section assesses the hazards of these hydrocarbons.

5.7.2 Estimating the number of fatalities per mass of LPG, propane/propylene, butane

Among the various chemicals handled in a refinery Liquefied Petroleum Gas (LPG) is the most common and most hazardous, it is extremely flammable and is handled in huge quantities. Numerous accidents involving LPG have been reported in the accidents statistics involving more than 1000 injuries of varying seriousness, and several hundred deaths, Khan and Abbasi (1990).

The term Liquefied Petroleum Gas (LPG) covers several mixtures of C_3 and C_4 hydrocarbons. It is widely used as a fuel in industrial and domestic heating systems and as a feed for petrochemical processes as well, Speight and Ozum (2002). It is a vapour at atmospheric temperature and pressure and is held in the liquid state by pressure to facilitate storage, transport, and handling.

Marshall and Ruhemann (2001) have argued that the term "liquefied petroleum gases" is scientifically inappropriate, as they are vapours. The vapour phase is a sub phase of the gas phase and it is that phase where the temperature lies below the critical temperature. Only below that temperature can the gas be liquefied by pressure alone. The term "liquefied gases" should be reserved for liquids with a critical temperature below ambient which are kept at, or around, their normal boiling points by means of refrigeration.

Petroleum vapours may flow along surfaces for substantial distances, reach a source of ignition and flash back. They are often heavier than air, and may accumulate in pits and other low-lying areas where they may displace air.

LPG was found to be involved in 47 accidents. The mass of LPG was available for 13 accidents; this made it impossible to analyse all the LPG accidents. Figure 5.21 shows the relation between the number of fatalities and the amount of LPG. It can be seen that the number of people killed in a lot of accidents do not bear any relation to the amount of LPG. Thus, it can be concluded that there is no relationship between the number of people killed and the amount of LPG that was involved in the accidents.

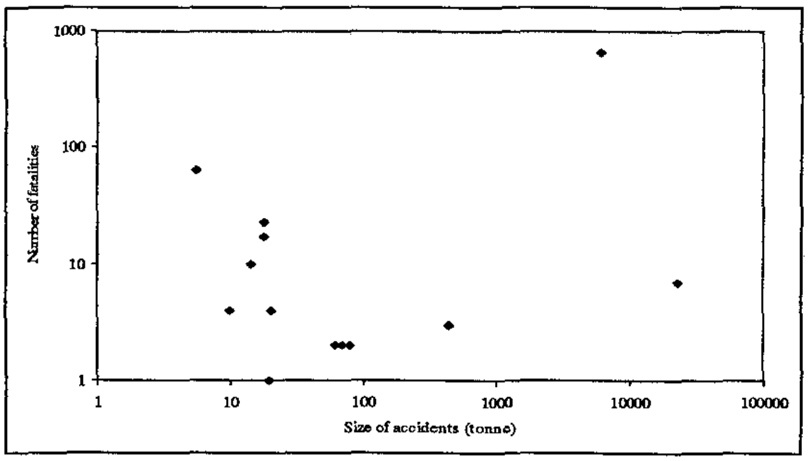


Figure 5.21: LPG accidents

Propane/Propylene were involved in 51 accidents resulting in 246 fatalities. Figure 5.22 shows the 13 accidents in which the amounts of the propane/propylene involved were available. There is no clear relationship between the amount of the propane/propylene involved and the number of fatalities that resulted. For example a vapour cloud explosion in which 53.5 tonnes of propylene exploded killed one person while 23.5 tonnes caused 216 fatalities. This is more evidence that the amount of material is not the only factor which affects the impact of accidents. Factors such as the accident time (day or night), the location of the accident and other chance events can play a major role in the consequences of an accident. Figure 5.23 shows the nine butane/isobutane accidents in which the quantity of materials involved were available.

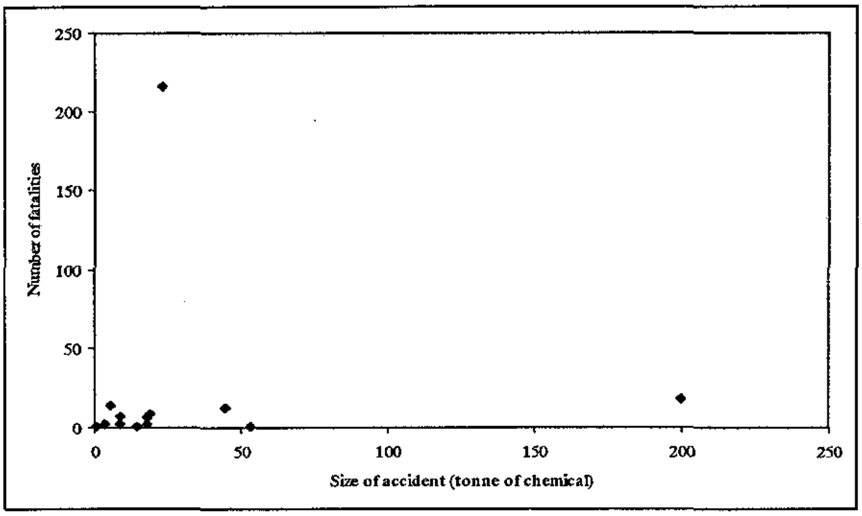


Figure 5. 22: Propane / Propylene accidents.

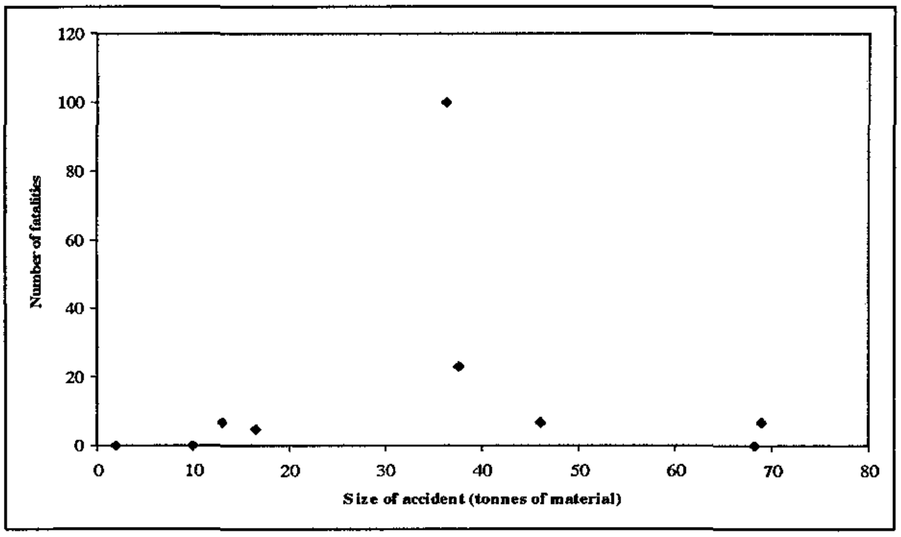


Figure 5.23: Butane accidents

Figure 5.24 shows all the LPG accidents where the mass of LPG was available. It also shows pure propane and pure butane accidents and the only two accidents that are available for propane-butane. The figure shows that there was no clear relationship between the mass and the number killed by the LPG. It can be seen that it was not possible to predict the number of fatalities from the LPG accidents in case of using the C3, C4 hydrocarbons individually or considering all the LPG components as one component.

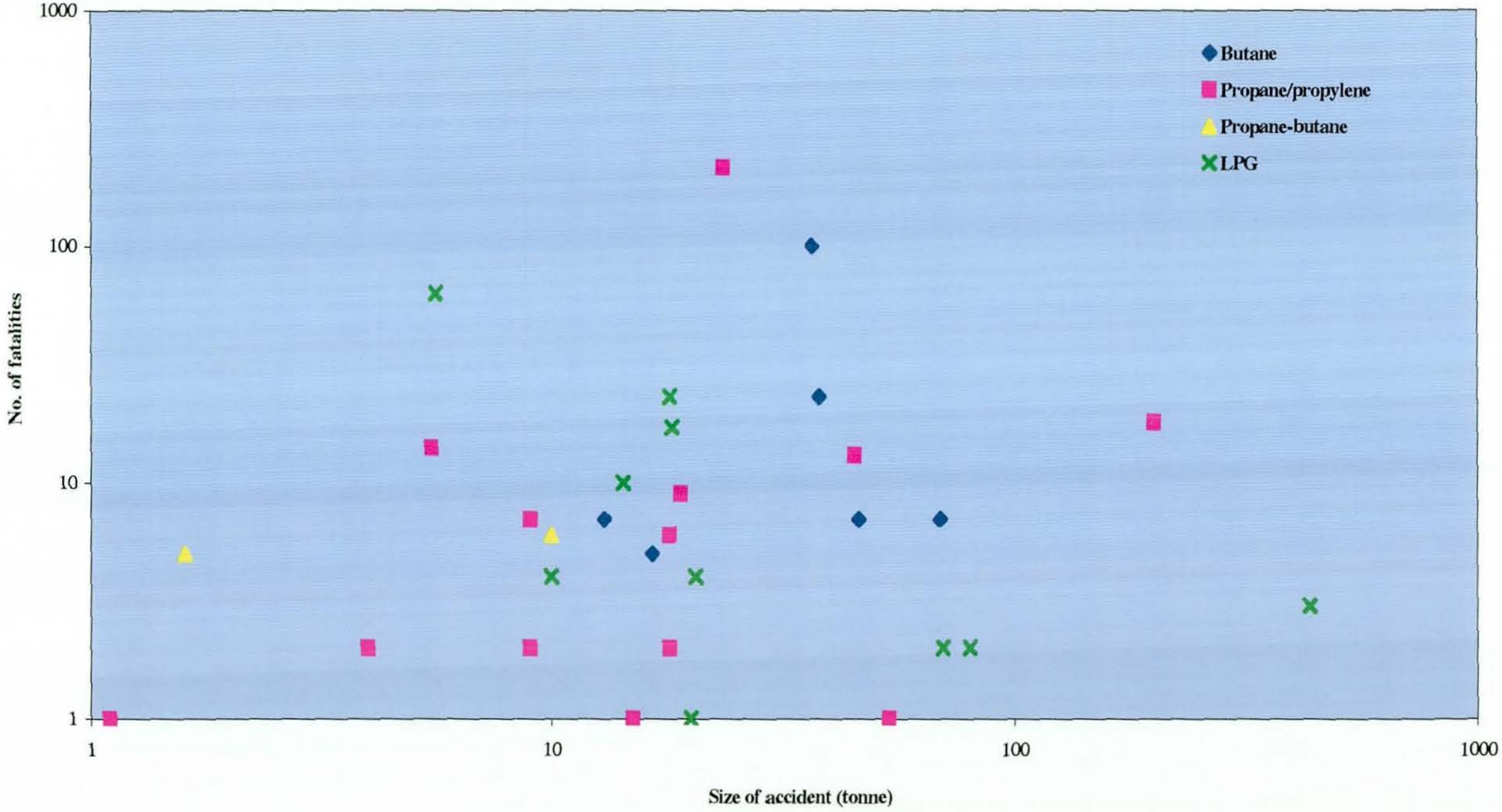


Figure 5. 24: LPG, propane and butane accidents

5.7.3 Estimating the number of fatalities per mass of liquids with more than five carbon atoms

A number of chemicals with five or more carbon atoms were found in the fire and explosion accident data. They are: pentane, naphtha, benzene, cyclohexane and petrol. Data for amount of chemicals involved in the accidents was available only for cyclohexane.

The only serious accident in which Cyclohexane was involved happened in Flixborough, UK in 1974 in which 28 people lost their lives. Figure 5.25 shows the number of fatalities per mass of cyclohexane exploded.

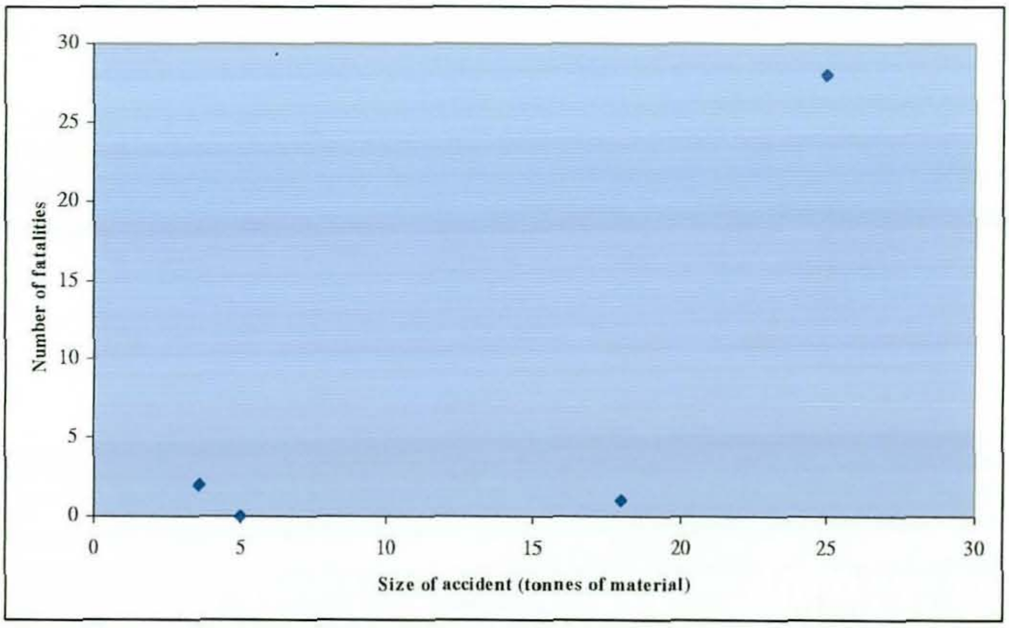


Figure 5.25: Cyclohexane accidents

5.7.4 Conclusion

The above section aimed to assess the hazards posed by the chemicals which were involved in the historic accidents. The idea was to correlate the mass of a certain chemical and the number of people killed by that chemical. Hydrocarbons were dominant in the accidents data so groups of hydrocarbons were classified by the number of their carbon atoms. It was thought to classify the hydrocarbons by phase and to obtain relationships between the numbers of people killed by certain phase. These relationships can then be used to estimate the potential number of fatalities for certain phases, for example: gas, vapour, liquefied gas, liquefied vapour, and to find out whether the accident happened in process or in storage operation. The analysis has been obstructed by the unavailability of the mass of chemicals for every accident, which prevented a large number of accidents from being used.

However, an equation to assess the hazard posed by ethylene has been obtained. This equation can be presented as a model if more information about the quantities of ethylene involved in the accidents is available.

5.8 Mean and median number of fatalities ranking index

As an alternative to estimating the number of fatalities per mass of chemical involved, the mean and the median number of fatalities were calculated for the chemicals involved in fire and explosion accidents in order to rank the chemicals by mean/median fatalities they yielded. From the 512 fire and explosion accidents listed in Table 1 in Appendix A, the chemicals that occurred most frequently in these accidents are summarized in Table 5.28. It can be seen that hydrocarbons were dominant in the fire and explosion accidents. Therefore, more account will be given to hydrocarbon accidents.

Table 5. 28: Table of most frequent occurring accidents caused by hydrocarbons

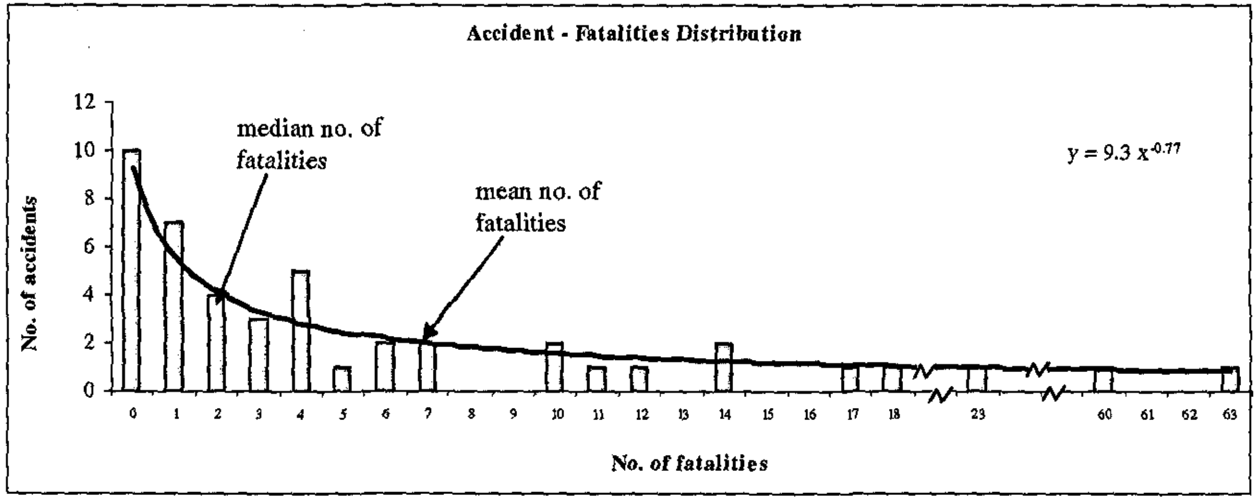
Chemical	Number of occurrence
LPG	47
Natural gas	30
Ethylene	23
Hydrocarbons (unspecified)	22
Butane	19
Propane/propylene	51
Crude oil	14
Total	206

5.8.1 Calculation of the mean & median numbers of fatalities by type of chemical

The accident fatalities distribution for LPG, propane/propylene and butane are plotted in Figures 5.26, 5.27 and 5.28. The number of fatalities is plotted against the number of accidents. The LPG, propane/propylene and butane charts appear to have a similar curve profiles. They show an exponential decay trend with a few very large fatality accidents; these are best fitted by power curves.

It has been found that LPG was involved in 47 accidents of various types for example, in storage, transportation (road, rail and pipelines) and accidents that happened in refineries. The mean number of fatalities was 7 persons per accident. The Mexico City vapour cloud fire which happened in a residential area and in which 650 people were killed and the pipeline accident which occurred in Russia in 1989 and caused 462 fatalities were excluded from this calculation. The median number of fatalities was 3. If the Mexico City and the Russian accidents are included, the mean number of accidents jumps to 30 people per accident while the median remains the same. This is a good example of why the median is a better statistic than the arithmetic mean as the few accidents with a large number of casualties skew the mean. Propane/propylene and butane were found to have the same mean and median number of fatalities (10 and 2 respectively), although the number of accidents and number of fatalities for propane are twice that of butane. Isobutylene, a chemical with a similar number of carbon atoms to butane, was involved in only one accident resulting in 7 fatalities from a pipeline explosion. Thus, it has been added to the butane accidents. Figure 5.29 shows the accidents – fatalities distribution for LPG, propane/propylene and butane accidents together. It can be seen that the trend of the accidents is the same in case of plotting the accidents individually or together.

No. of fatalities	No. of accidents
0	10
1	7
2	4
3	3
4	5
5	1
6	2
7	2
8	
9	
10	2
11	1
12	1
13	
14	2
15	
16	
17	1
18	1
23	1
60	1
61	
62	
63	1

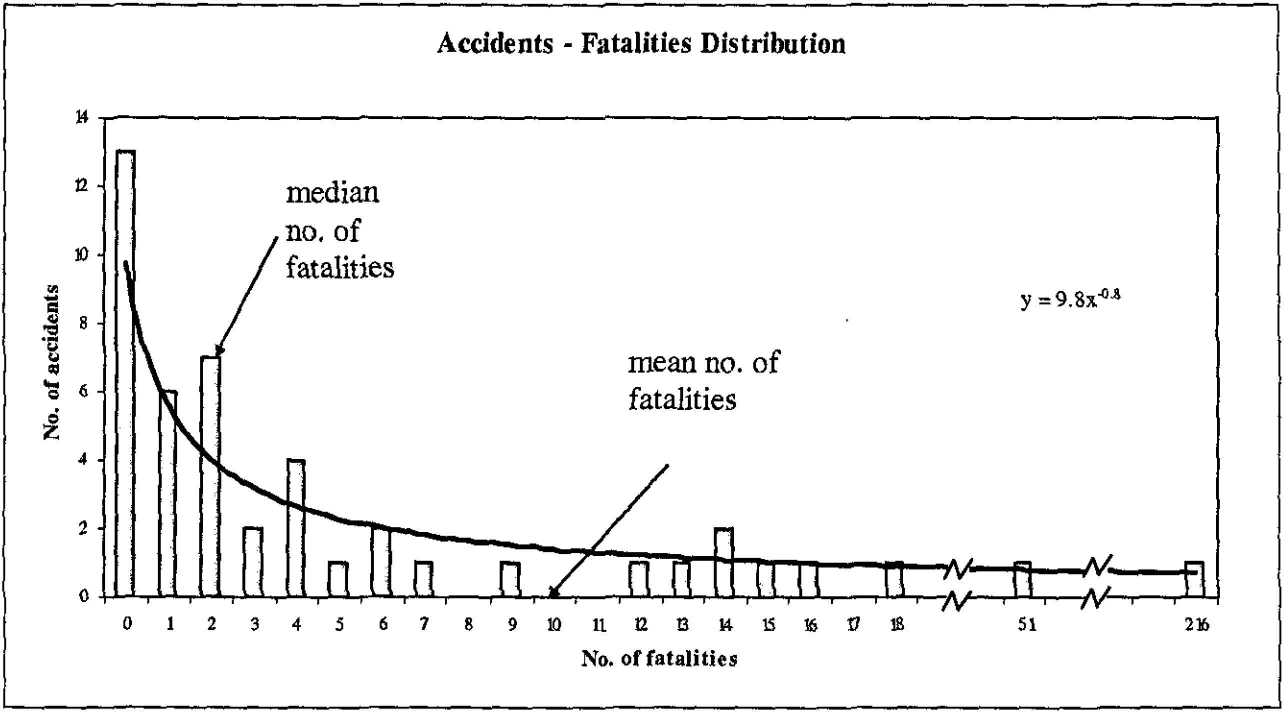


Total number of LPG fatalities = 327
Total number of accidents = 47

mean number of fatalities = 327/47 = 7
median number of fatalities = 3

Figure 5. 26: Distribution of the number of fatalities for Liquefied Petroleum Gas (LPG) accidents

No. of fatalities	No. of accidents
0	13
1	6
2	7
3	2
4	4
5	1
6	2
7	1
8	
9	1
10	
11	
12	1
13	1
14	2
15	1
16	1
17	
18	1
51	1
216	1

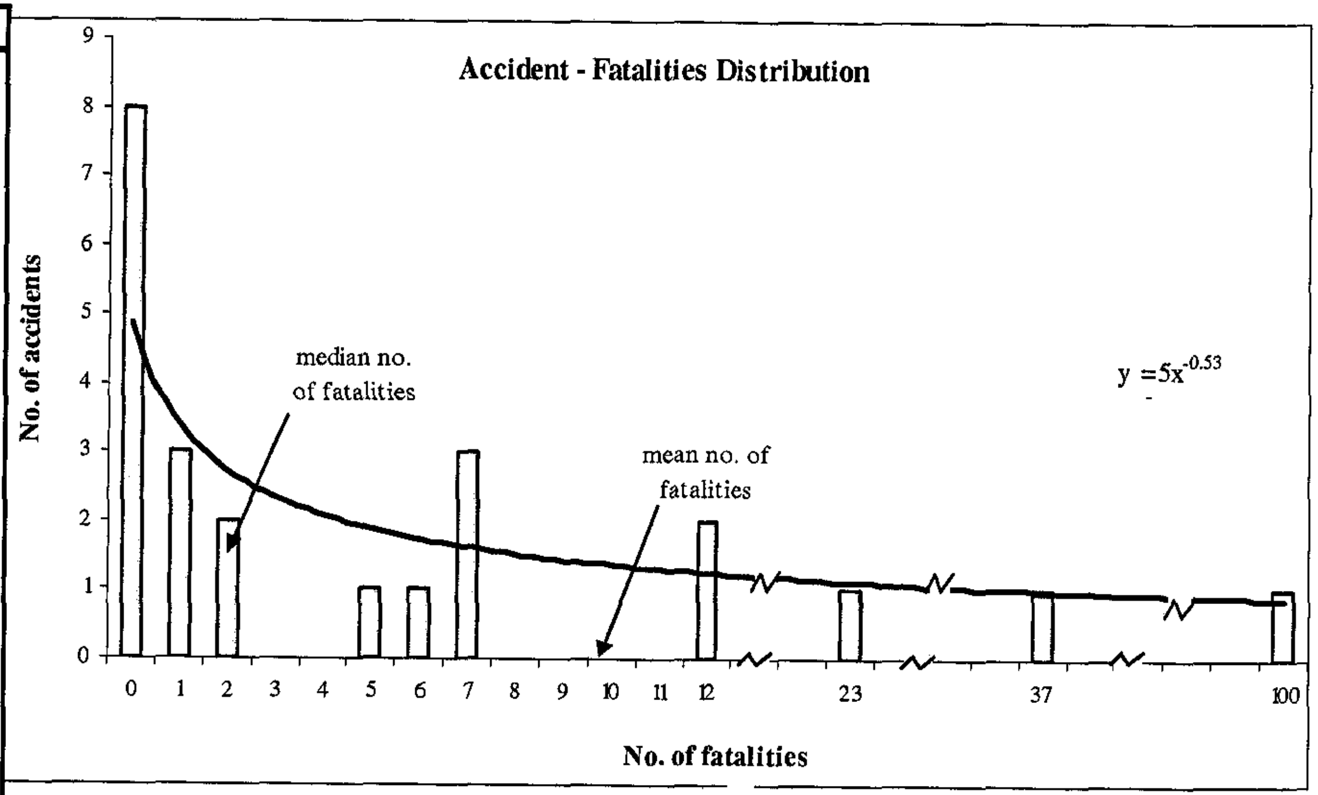


Total number of propane fatalities = 444
Total number of accidents = 46

mean number of fatalities = 444/46 = 10
median number of fatalities = 2

Figure 5. 27: Distribution of the number of fatalities for propane/propylene accidents.

No. of fatalities	No. of accidents
0	8
1	3
2	2
3	
4	
5	1
6	1
7	3
8	
9	
10	
11	
12	2
23	1
37	1
100	1

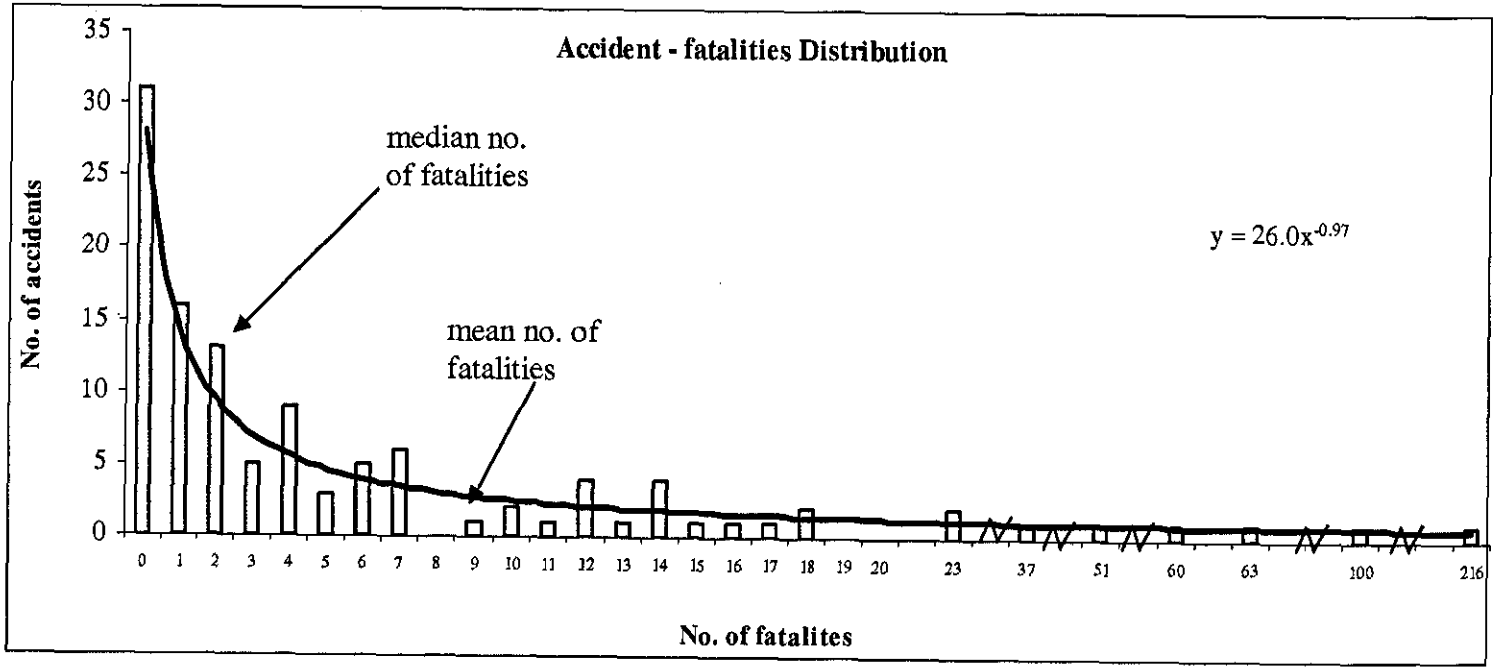


Total number of Butane fatalities = 233
Total number of accidents = 24

mean number of fatalities = 233/24 = 10
median number of fatalities = 2

Figure 5. 28: Distribution of the number of fatalities for butane accidents.

No. of fatalities	No. of accidents
0	31
1	16
2	13
3	5
4	9
5	3
6	5
7	6
8	
9	1
10	2
11	1
12	4
13	1
14	4
15	1
16	1
17	1
18	2
19	
20	
23	2
37	1
51	1
60	1
63	1
100	1
216	1



Total number of fatalities = 1004

Total number of accidents = 117

mean number of fatalities = 1004/117 = 9

median number of fatalities = 2

Figure 5. 29: Distribution of the number of fatalities for LPG, propane/propylene and butane accidents

Liquefied Natural Gas (LNG), is mainly methane that has been liquefied for ease of transport by cooling it to (-162°C), Speight and Ozum (2002). LNG was involved in 10 accidents with a total number of fatalities of 242 people. The mean number of fatalities for LNG was 24 persons per accident, while the median was 2. The data is shown in Figure 5.30. The high mean number can be attributed to the storage tank fire and explosion accident, which happened in 1944 at Cleveland, Ohio, in which 126 people were killed. The high number of fatalities was due to the massive quantity of material spilled, about 3000 tonnes of LNG in total. Furthermore, the plant was located in the middle of a densely population area containing a mixture of housing and business places, Marshall (1987). It can be seen that the LNG distribution of the number of fatalities is different from the LPG and propane. This is probably due to the lack of data compared to that for LPG and propane.

Natural gas is a gaseous mixture that is predominantly methane but also contains other combustible hydrocarbon compounds, Speight and Ozum (2002). It is lighter than air (density 0.584), so it can disperse readily and it rises even when it is cold. It has been found that it was responsible for the death of 173 people from 35 accidents with a mean number of fatalities of 5 persons per accident and a median of 3 as can be seen in Figure 5.31.

Crude oil was involved in 21 fire and explosion accidents, killing 193 people with a mean of 9 deaths per accident. The median number of fatalities for crude oil was 1, Figure 5.32

There were 12 accidents in which the material involved is known as a hydrocarbon causing 105 fatalities with a mean number of fatalities of 9 persons per accident and a median of 1.

Natural gas liquids (NGL) are the hydrocarbon liquids that condense during the processing of hydrocarbon gases that are produced from oil or gas reservoir, Speight and Ozum (2002). They were involved in 4 accidents. All of them took place during transporting by pipeline. One of these accidents was the explosion that happened in 1989 in Ufa, USSR and caused the death of 645 people. Excluding this accident, NGL had a mean number of fatalities of 4.

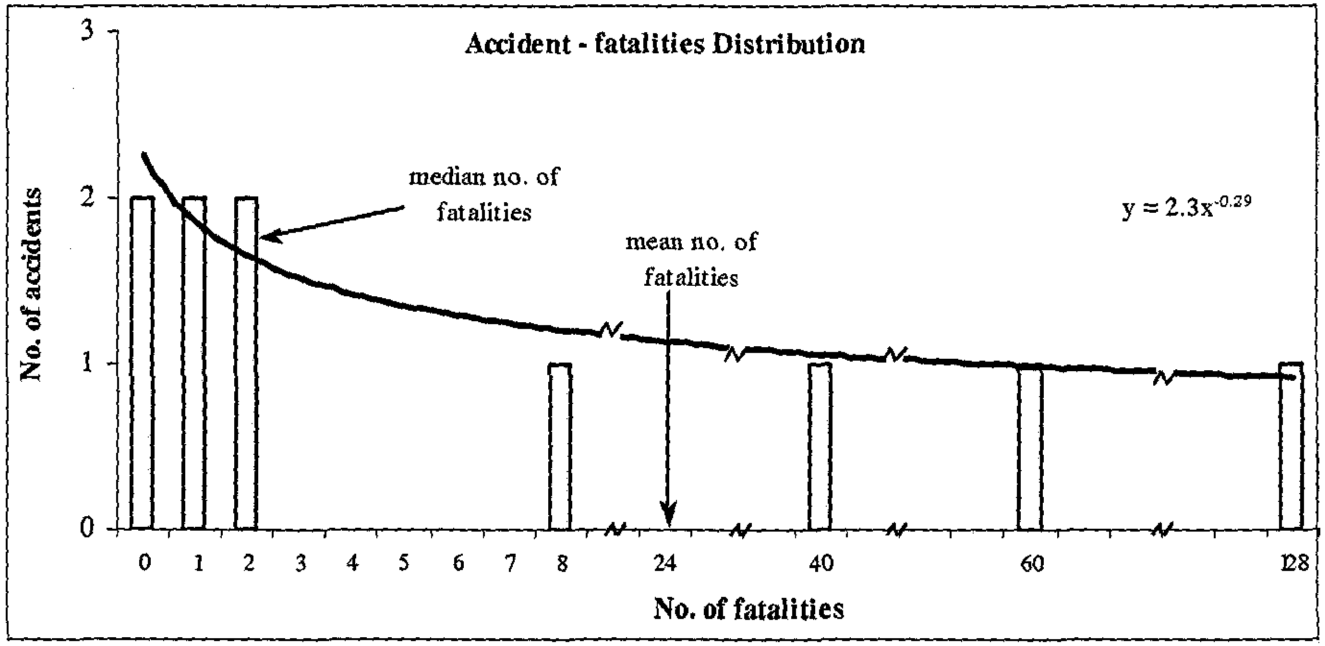
Table 5.29 gives the mean and the median number of fatalities per accident for some hydrocarbons. Table 5.30 compares the heat of combustion of the substance to the heat of detonation of TNT (4652 KJ/Kg), the energy ratio. This ratio shows that the energy of combustion of hydrocarbons is about ten times the energy of detonation of TNT. It can be noticed that the energy ratio for hydrocarbons is almost the same, ranging from 9 to 11 despite the difference in their phase.

Table 5. 29: The mean and the median number of fatalities for some hydrocarbons

Substance	Formula	No. of accidents	No. of fatalities	Mean fatalities	Median fatalities
Hydrogen	H_2	13	278	21	4
LNG	CH_4	10	242	24	2
Methane/natural gas	CH_4	35	173	5	3
Ethylene	C_2H_4	23	165	7	1
LPG	$C_3 - C_4$	47	327	7	3
Propane/propylene	C_3H_8 /C_3H_6	46	444	10	2
Butane/butylene	C_4H_{10}	24	233	10	2
Pentane	C_5H_{12}	2	3	2	1
Naphtha	$C_5 - C_9$	9	72	8	2
Light HCs	-	6	10	2	2
Benzene	C_6H_6	2	1	-	-
Cyclohexane	C_6H_{12}	5	35	7	2
Petrol	$C_7 - C_{11}$	20	611	31	3
Crude oil	-	21	193	9	1
Hydrocarbons (unspecified)	-	12	105	9	1

Table 5.31 ranks the hydrocarbons according to their median number of fatalities. For ease of ranking, it is convenient to group some hydrocarbons together and order them in terms of their number of carbons and their median number of fatalities.

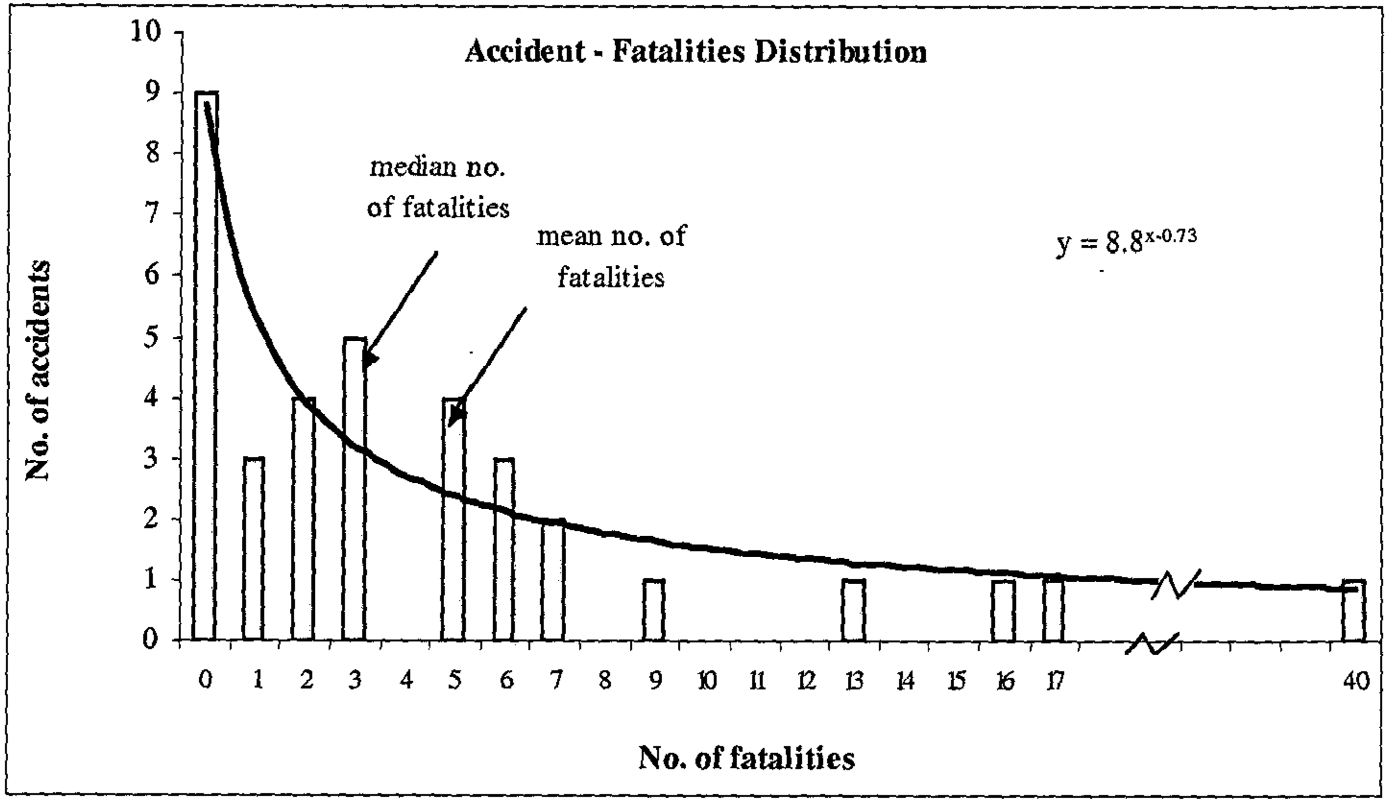
No. of fatalities	No. of accidents
0	2
1	2
2	2
3	
4	
5	
6	
7	
8	1
24	
40	1
60	1
128	1



Total number of LNG fatalities = 242
Total number of accidents = 10
mean number of fatalities = 242/10 = 24
median number of fatalities = 2

Figure 5.30: Distribution of the number of fatalities for Liquefied Natural Gas (LNG) accidents

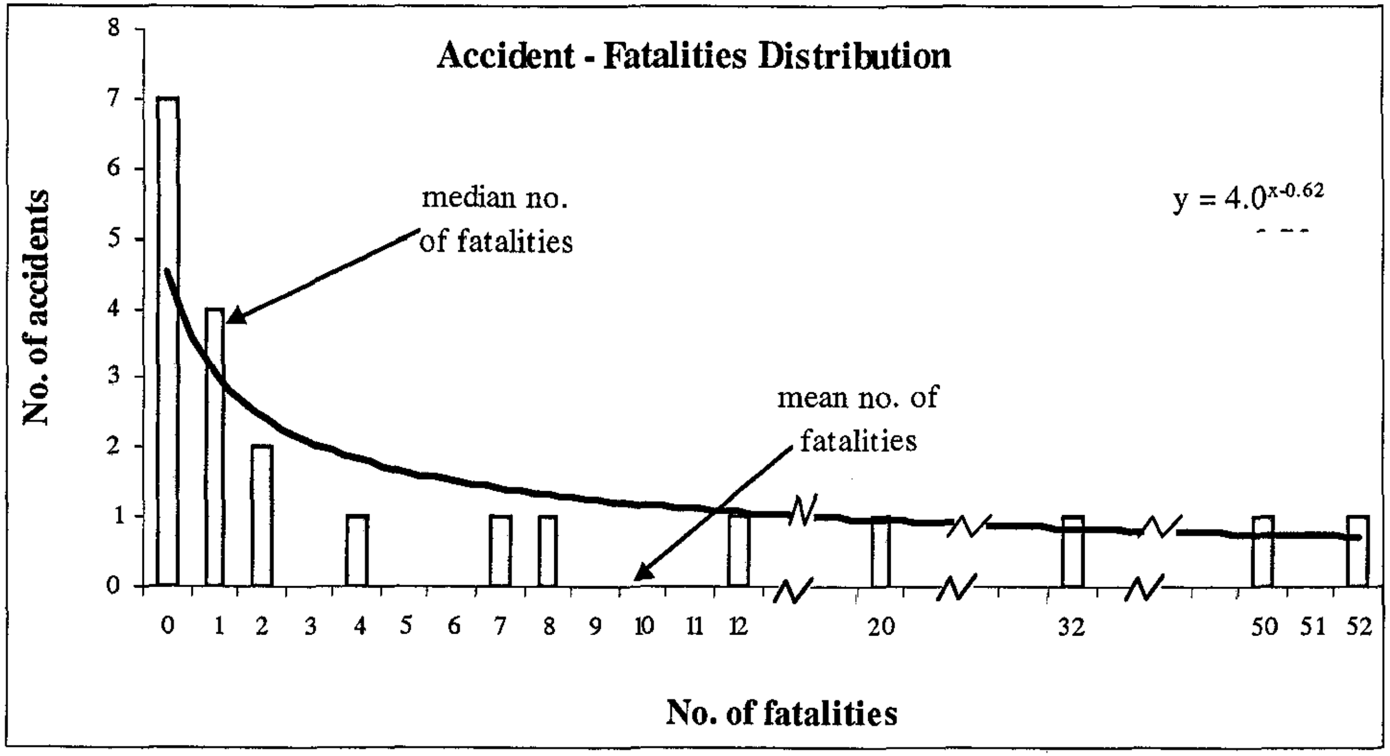
No. of fatalities	No. of accidents
0	9
1	3
2	4
3	5
4	
5	4
6	3
7	2
8	
9	1
10	
11	
12	
13	1
14	
15	
16	1
17	1
40	1



Total number of fatalities = 173
Total number of accidents = 35
mean number of fatalities = 173/35 = 5
median number of fatalities = 3

Figure 5. 31: Distribution of the number of fatalities for natural gas accidents

No. of fatalities	No. of accidents
0	7
1	4
2	2
3	
4	1
5	
6	
7	1
8	1
9	
10	
11	
12	1
20	1
32	1
50	1
51	
52	1



Total number of crude oil fatalities = 193
Total number of accidents = 21
mean number of fatalities = 193/21 = 9
median number of fatalities = 1

Figure 5.32: Distribution of the number of fatalities for crude oil accidents

Table 5.30: The energy ratio for some hydrocarbons

Substance	Formula	Heat of combustion (KJ/Kg)	Energy ratio
Hydrogen	H_2	- 120,034	26
Methane	CH_4	- 50, 470	11
Ethylene	C_2H_4	- 47,192	10
Propane	C_3H_8	- 46,386	10
Propylene	C_3H_6	- 45,813	10
Butane	C_4H_{10}	- 45,771	10
Pentane	C_5H_{12}	- 45,384	10
Benzene	C_6H_6	- 40,171	9
Cyclohexane	C_6H_{12}	- 43,470	9

Hydrogen came at the top of the list; it has the highest mean and median number of fatalities, (21 and 4 respectively). This can be attributed to the high energy of hydrogen as evidenced by its high energy ratio of 26. Hydrogen has also a wide range of flammability (4% to 74%) and, when diluted with inert gas, it can still burn with only 5% oxygen compared with about 11% for hydrocarbon gases. Hydrogen has a high burning velocity compared with hydrocarbon gases, and it can be ignited by low energy sparks as it requires only about 1/10 of the energy that is required by hydrocarbon gases, Marshall (1987). However, it is an extremely light gas and does not pool on the ground like petrol or LPG and is therefore less hazardous when not confined. Figure 5.33 shows the mean and the median number of fatalities for hydrogen accidents.

Table 5.31: Hydrocarbons ranking

Substance	Formula	No. of accidents	No. of fatalities	Mean no. of fatalities	Median no. of fatalities
Hydrogen	H_2	13	278	21	4
LNG+methane	CH_4	45	415	9	3
LPG	C_3 - C_4	47	327	7*	3
Petrol	$C_7 - C_{11}$	19	103	5^+	3
Light HCs	$C_2 - C_6$	108	914	8	2
Naphtha	$C_5 - C_9$	9	72	8	2
HC (unspecified)	-	12	105	9	1

* this value is excluding the Mexico city (650 fatalities) and the Russian (462 fatalities) accidents.

+ this value is excluding the pipeline accident took place in Brazil and caused 508 fatalities.

Some releases are not pure hydrogen, but also contain other materials. Lees (1980) cited that the addition of hydrocarbons narrows the flammable range and reduces the burning velocity. This might explain the reason behind the four accidents shown in Table 5.32 in which hydrogen contained hydrocarbons and in which nobody was killed.

Table 5.32: Hydrogen/hydrocarbons accidents

Date	Chemical	Type	Fatalities	Location	Equipment
1973	Hydrogen, HCs	Fire	0	St.Croix, Virgin Islands	Hydrodesulphurizer
1975	Hydrogen, Naphtha	VCE	0	Cologene, FRG	-
1987	Hydrogen, HCs	Fire	0	Mississauga, Ont.	Hydrotreater
1989	Hydrogen, HCs	Fire or Explosion	0	Martinez, CA	Hydrotreater

Liquefied natural gas (LNG)/methane, liquefied petroleum gas (LPG) and petrol came at the second position in the list with a median number of fatalities of 3.

Gasoline and petrol accidents are added together as they are one component with different names, Speight and Ozum (2002). Petrol was involved in 20 accidents and caused the death of 611 people with a mean of 31 and a median of 3, as shown in Table 5.29. If the pipeline accident, which took place in Brazil in 1984 and resulted in 508 fatalities is excluded from the calculation of the mean and the median number of fatalities, the mean goes down to 5 and the median remains the same.

Naphtha is a generic term applied to refined, partly refined, or unrefined petroleum products and liquid products of natural gas, the majority of which distill below 240°C (464°F), It is a complex mixture of more than 100 components of C_5 – C_9 paraffins, naphthene, and aromatic hydrocarbons, Speight and Ozum (2002). Naphtha was involved in 9 accidents resulting in 72 fatalities. Figure 5.35 gives the trend of the accidents. There was not a clear pattern; this could be because there are too few data points.

Light hydrocarbons are defined in Speight and Ozum (2002) as the hydrocarbons with molecular weights less than that of heptane (C_7H_{16}). Based on this definition, the $C_2 - C_5$ hydrocarbons accidents have been added together and named as light hydrocarbons. Table 4.33 below lists the components which are now considered as light hydrocarbons. LPG and LNG are treated separately.

Light hydrocarbons and naphtha found to have the same level of hazard as both of them give the same mean and median number of fatalities of 8 and 2 respectively.

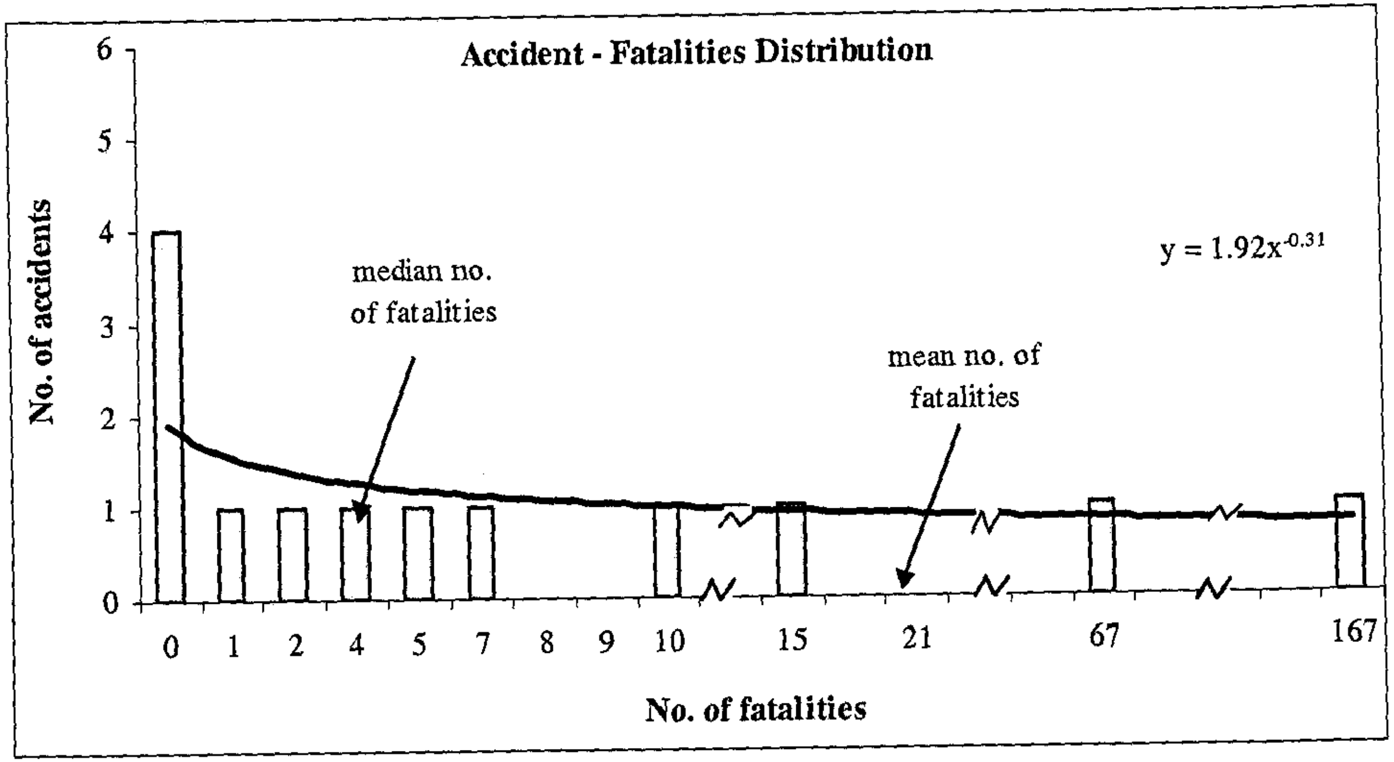
Unspecified hydrocarbons, which are accidents for hydrocarbons (unspecified), oil and petroleum, gave the lowest median number of fatalities of 1.

Table 5.33: Light hydrocarbons accidents and fatalities

Hydrocarbon	No. of accidents	No. of fatalities
Ethane & propane	3	34
Ethylene	23	165
Propane/propylene	48	458
Propane & butane	3	11
Butane/butylenes	24	233
Pentane	2	3
Light hydrocarbons	5	10
Total	108	914

It can be seen from Table 5.31 that there is not much difference between hydrocarbons in terms of the mean and the median number of fatalities. The median number of fatalities range from 1 to 3 with the highest number for liquefied gases and liquefied vapours. The mean number of fatalities range from 5 to 9.

No. of fatalities	No. of accidents
0	4
1	1
2	1
4	1
5	1
7	1
8	
9	
10	1
15	1
21	
67	1
167	1



Total number of hydrogen fatalities = 278
Total number of accidents = 13
mean number of fatalities = 278/13 = 21
median number of fatalities = 4

Figure 5.33: Distribution of the number of fatalities for hydrogen accident

No. of fatalities	No. of accidents
0	2
1	2
2	5
3	1
4	1
5	2
6	1
7	4
40	1

Total number of petrol fatalities = 103
Total number of accidents = 19
mean number of fatalities = 103/19 = 5
median number of fatalities = 3

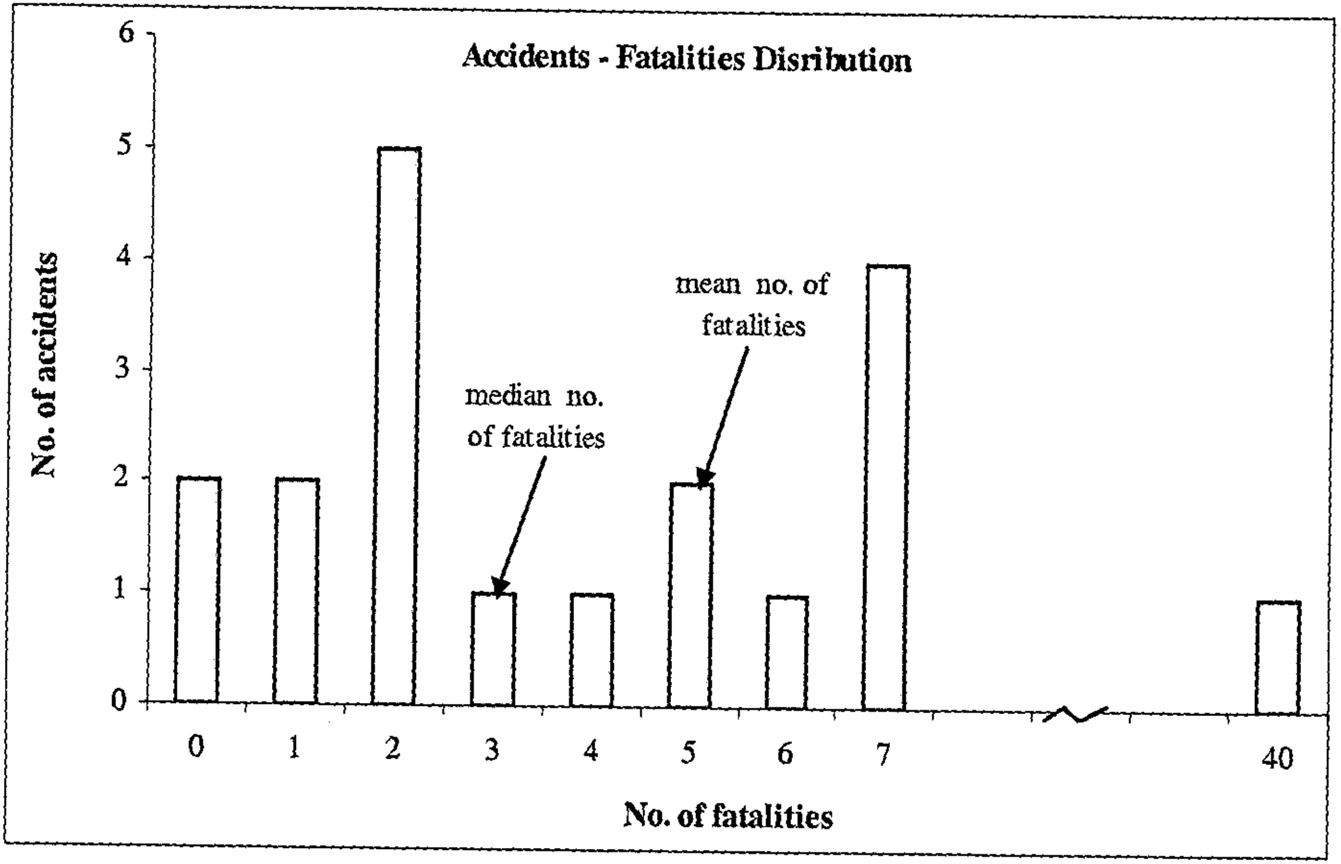
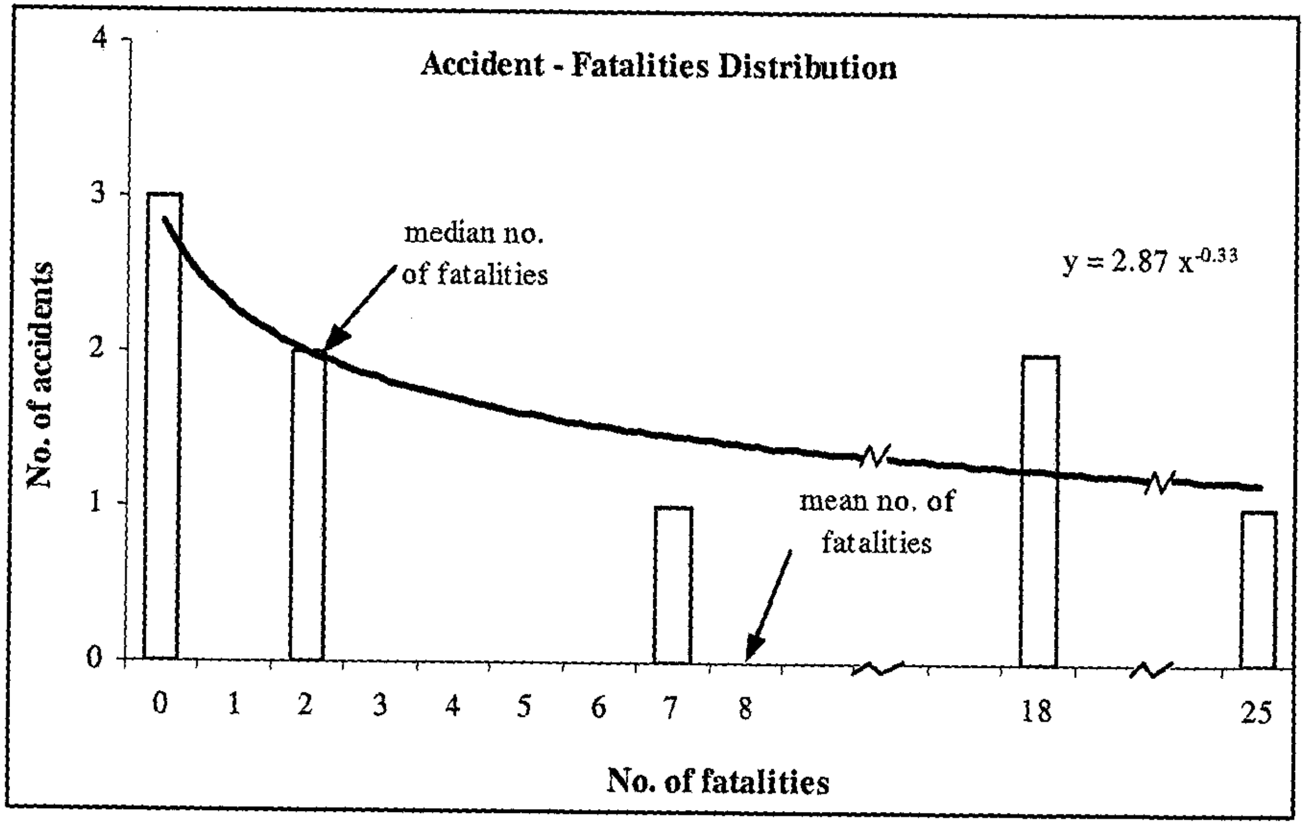


Figure 5. 34: Distribution of the number of fatalities for petrol accidents

No. of fatalities	No. of accidents
0	3
1	
2	2
3	
4	
5	
6	
7	1
8	
18	2
25	1



Total number of naphtha fatalities =72
Total number of accidents = 9
Average number of fatalities = 72/9 = 8
median number of fatalities = 2

Figure 5. 35: Distribution of the number of fatalities for naphtha accidents

5.8.2 Calculation of the mean and median numbers of fatalities by type of process operation

As mentioned in section 5.5.2, the accidents have been classified as process, storage, transport and utilities. In this section the mean and the median number of fatalities are calculated for each class.

5.8.2.1 Process accidents

The mean and median number of fatalities for process accidents is calculated for the 171 process accidents. The 53 accidents in which it was unknown whether there are fatalities or not have been discarded. The mean number of fatalities was 7 people per accident while the median was 2. In Figure 5.36 the trend shows a clear power curve.

5.8.2.1.1 Reactor accidents

The mean and the median number of fatalities for reactor accidents have been determined. It was found that reactors were involved in 30 accidents resulting in 83 fatalities with a mean of 3 people per accident. The median number of fatalities for the reactor accidents is 1. The distribution is shown in Figure 5.37.

5.8.2.2 Storage accidents

Figure 5.38 shows all the 70 accidents which happened during storing materials. The number of fatalities caused from storage accidents was 1744 people with a mean of 25 people per accident while the median number of fatalities was 2.

5.8.2.3 Transport accidents

Transport accidents are classified by type of transport, rail, road, ship, and pipeline and the mean and median number of fatalities were calculated for each class. Table 5.34 summarise the data and statistics for transport accidents by category.

From Table 5.34, it can be seen that during the period from 1911 - 2000, 134 transport accidents happened in which 3088 people were killed, with a mean of 23 persons per accident. Looking at the categories individually, it can be noticed that pipeline accidents tend to yield more fatalities than the other methods of transport. Among the 3088 people killed in transport accidents in general, 1939 people were killed by pipeline accidents, while the remaining 1149 fatalities were distributed between rail, road and ship accidents. Transport by pipeline has the highest mean number of fatalities because large quantities of petroleum products and crude oil are transported by this means. Road transport tends to kill more people than rail and ship; this may be because roads often pass through populated areas, especially in developing countries. Figure 5.39 shows the mean and the median number of fatalities for transport accidents.

Table 5.34: classification of transport accidents, 1911-2000

Transportation type	Rail	Road	Ship	Pipeline	Total
No. of accidents	35	25	12	62	134
No. of fatalities	491	495	163	1939	3088
Mean fatalities	14	20	14	31	23
Median fatalities	1	6	5	3	3

5.8.2.4 Utilities accidents

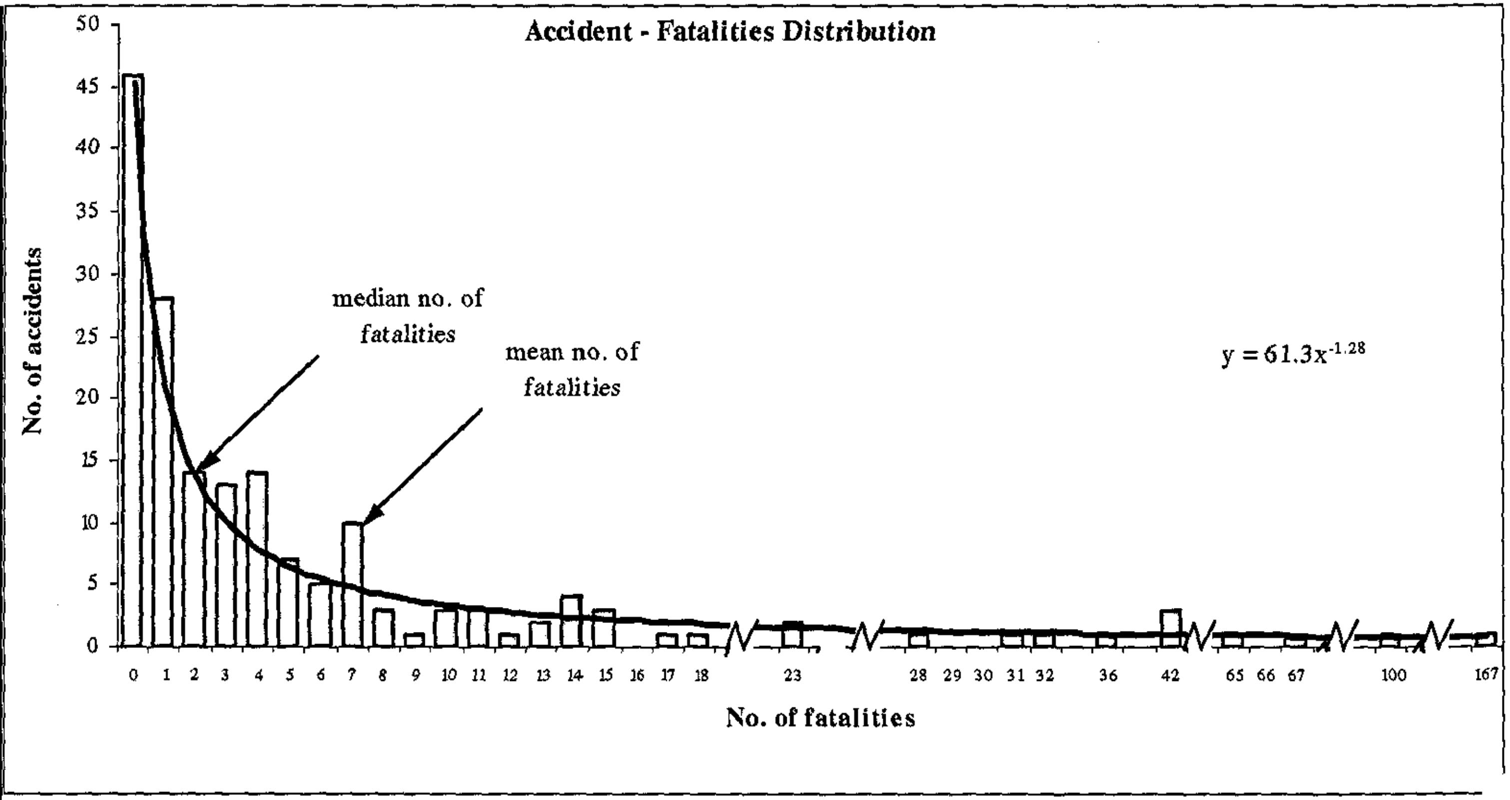
As mentioned in section 5.7.2, utility accidents are accidents that took place in equipment that supports the operating plant; such as pumps, compressors, heat exchangers and boilers. It has been found that those equipment were involved in 23 accidents causing the death of 114 people with a mean of 5 persons per accident and a median of 2. Figure 5.40 shows the distribution.

5.8.3 Conclusion

Table 5.35 ranks the types of accidents by their median number of fatalities. Transport appears to be the most hazardous class of accidents as it caused the highest median number of fatalities while the other three classes, - storage, process and utilities - have the same level of hazard. In terms of the mean number of fatalities, storage and transport accidents have almost the same mean number of fatalities although of the difference between the number of accidents and the number of fatalities they caused.

On the other hand, although the process and utility accidents have the same median number of fatalities, process accidents can be considered as more hazardous from the number of accidents involved and the number of people killed compared to the utilities accidents.

No. of fatalities	No. of accidents
0	46
1	28
2	14
3	13
4	14
5	7
6	5
7	10
8	3
9	1
10	3
11	3
12	1
13	2
14	4
15	3
16	
17	1
18	1
23	2
28	1
29	
30	
31	1
32	1
36	1
42	3
65	1
66	
67	1
100	1
167	1



Total number of process fatalities = 1254

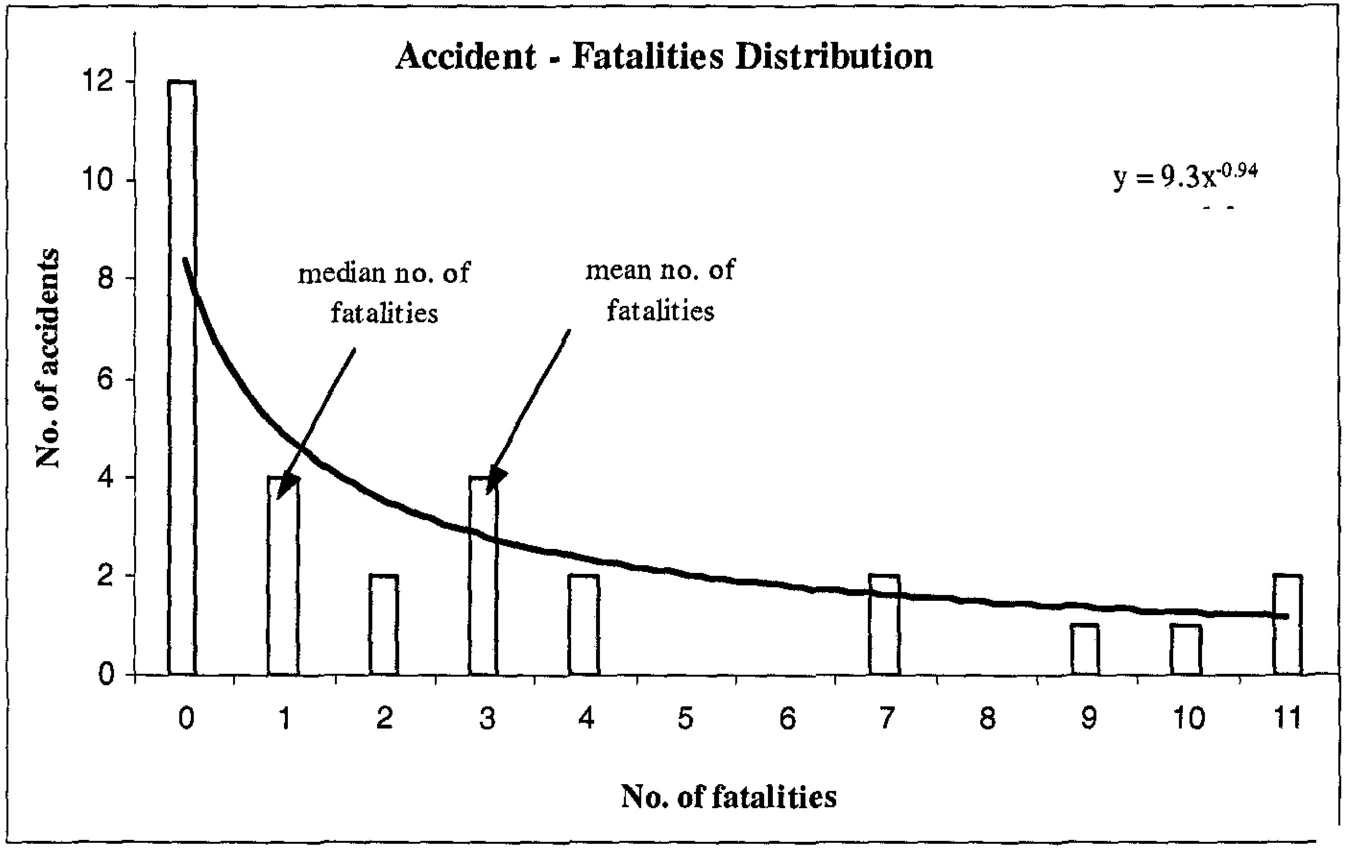
Total number of accidents = 172

mean number of fatalities = 1254/172 = 7

median number of fatalities = 2

Figure 5. 36: Distribution of the number of fatalities for process accidents

No. of fatalities	No. of accidents
0	12
1	4
2	2
3	4
4	2
5	
6	
7	2
8	
9	1
10	1
11	2



Total number of reactors fatalities =83

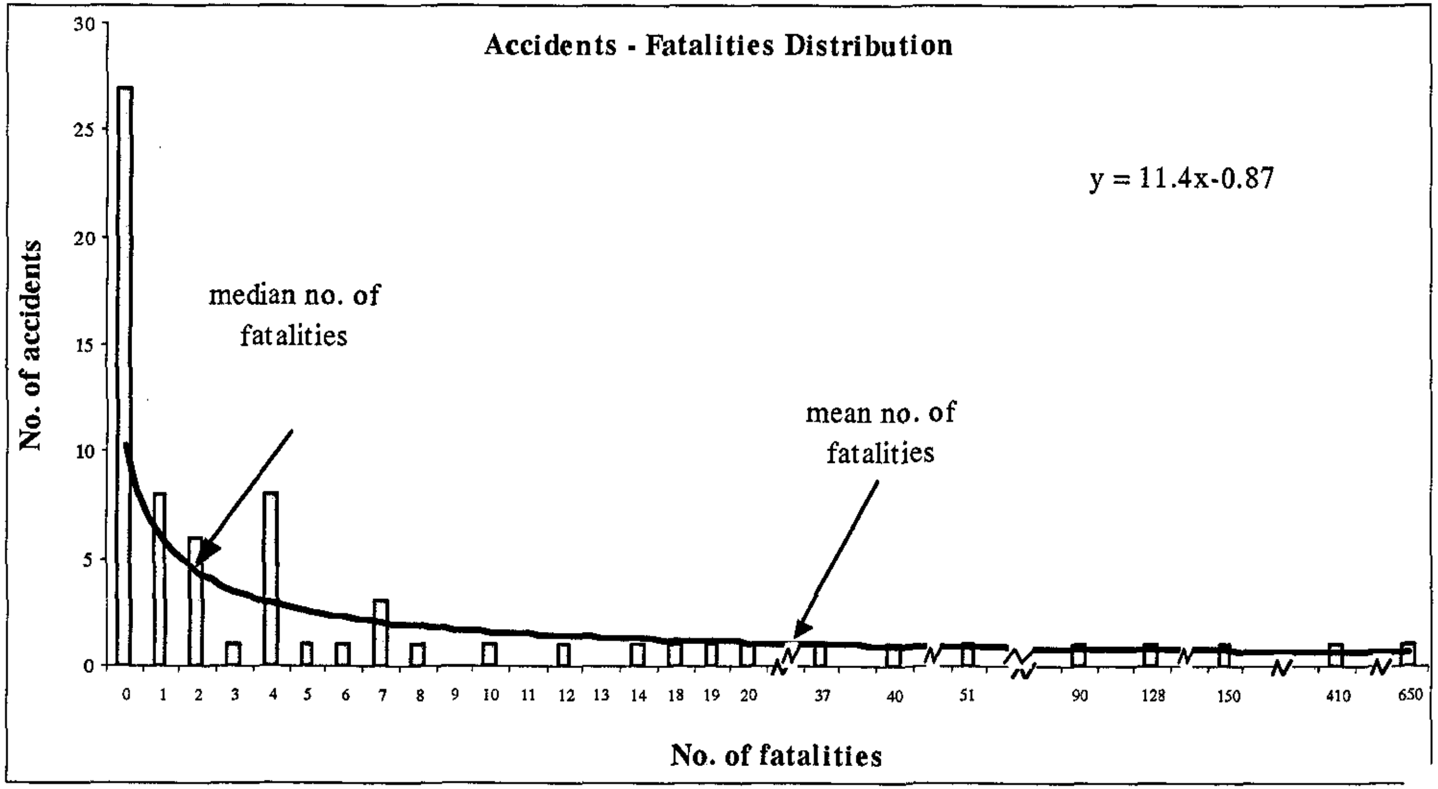
Total number of accidents = 30

mean number of fatalities = 83/30 = 3

median number of fatalities = 1

Figure 5.37: Distribution of the number of fatalities for reactors accidents

No. of fatalities	No. of accidents
0	27
1	8
2	6
3	1
4	8
5	1
6	1
7	3
8	1
9	
10	1
11	
12	1
13	
14	1
18	1
19	1
20	1
37	1
40	1
51	1
90	1
128	1
150	1
410	1
650	1



Total number of storage fatalities = 1744

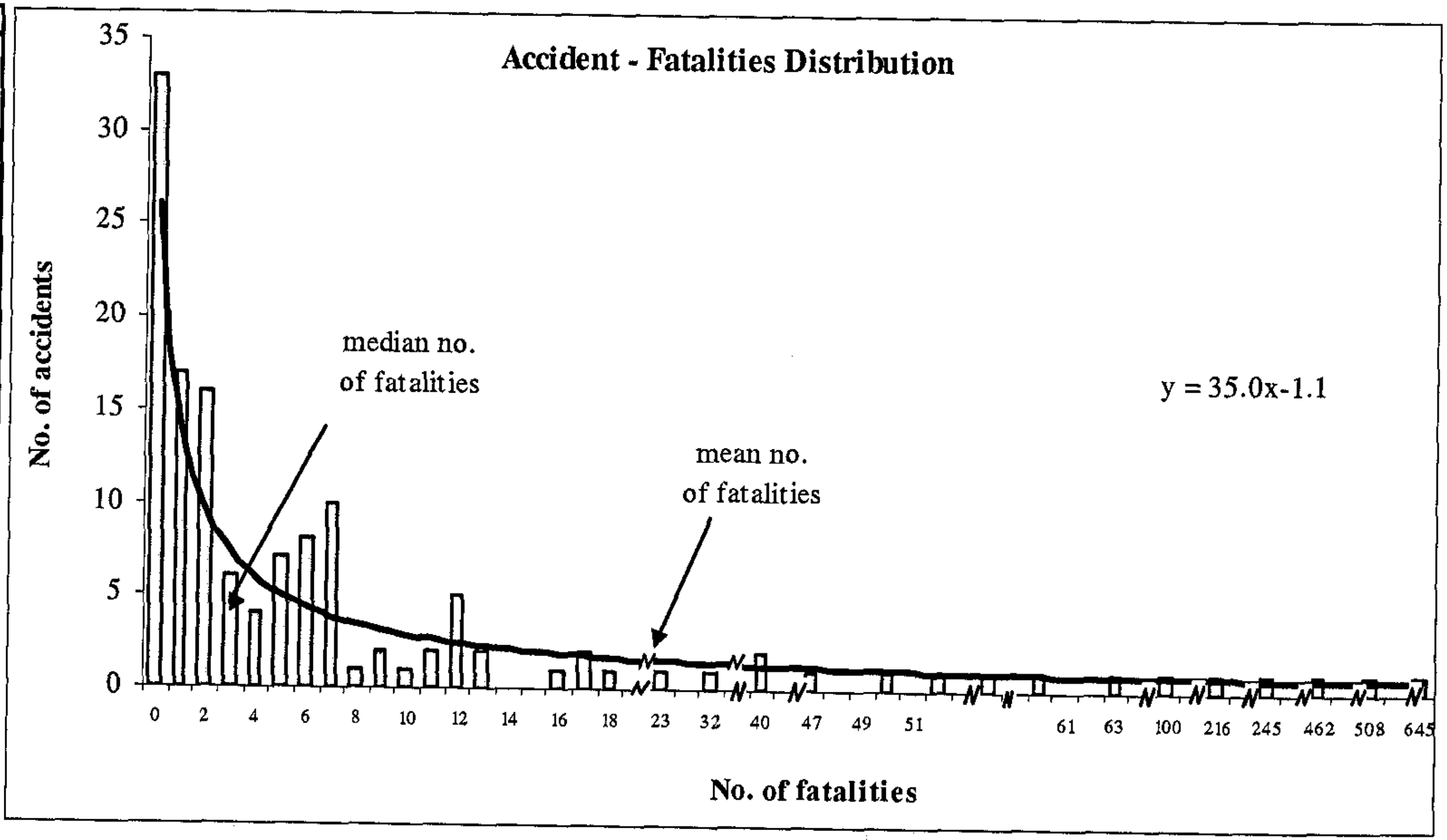
Total number of accidents =70

mean number of fatalities = 1744/70 = 25

median number of fatalities = 2

Figure 5. 38: Distribution of the number of fatalities for storage accidents

No. of fatalities	No. of accidents
0	33
1	17
2	16
3	6
4	4
5	7
6	8
7	10
8	1
9	2
10	1
11	2
12	5
13	2
14	
15	
16	1
17	2
18	1
23	1
32	1
40	2
47	1
48	
49	
50	1
51	
52	1
57	1
60	1
61	
62	
63	1
100	1
216	1
245	1
462	1
508	1
645	1

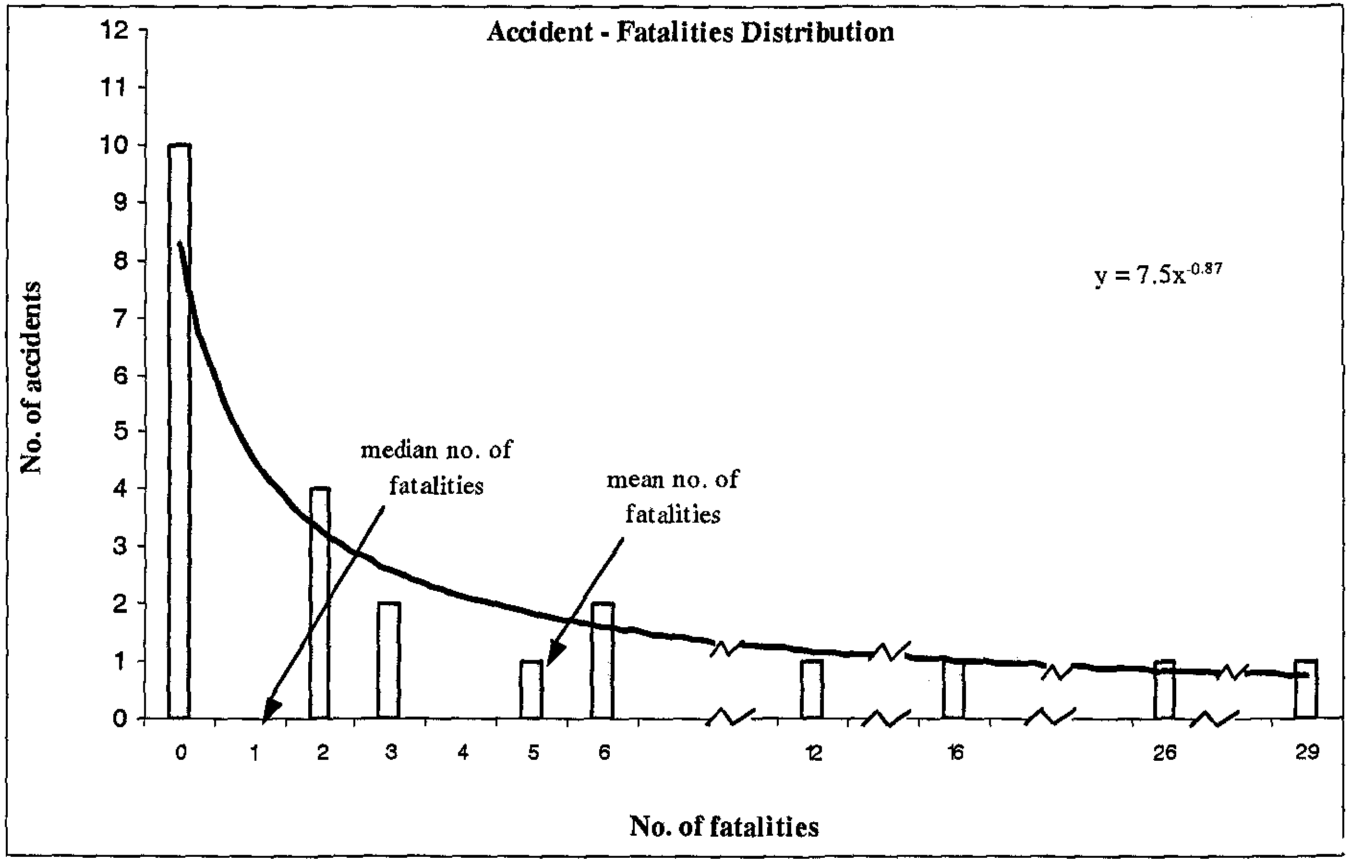


Total number of transportation fatalities = 3088
Total number of accidents = 134

mean number of fatalities = 3088/134 = 23
median number of fatalities = 3

Figure 5.39: Distribution of the number of fatalities for transport accidents

No. of fatalities	No. of accidents
0	10
1	
2	4
3	2
4	
5	1
6	2
12	1
16	1
26	1
29	1



Total number of process fatalities = 114
Total number of accidents = 23
mean number of fatalities = 114/23 = 5
median number of fatalities = 1

Figure 5.40: Distribution of the number of fatalities for utilities accidents

Table 5.35: Ranking types of accidents

Type of accident	No. of accidents	no. of fatalities	mean no. fatalities	median no. fatalities
Transport	134	3088	23	3
Storage	70	1744	25	2
Process	224	1247	6	2
Utilities	23	114	5	2

5.9 The Mortality Index

This section presents another methodology for estimating the possible number of fatalities due to fire and explosion accidents, as a function of the quantity of flammable substance involved. The method is called the mortality index and was developed by Marshall (1977). The mortality index value is expressed in terms of the mean number of fatalities per tonne of chemical involved.

The mortality index is intended to apply to the historical accident data in order to develop a method which will be used as a basic tool for measuring the inherent safety of a chemical plant in conceptual design stage. This method is supposed to be able to predict the number of fatalities from knowing the quantity of chemical that involved in a chemical accident. As mentioned before, it is not vital that such a method is to be very accurate as it will be used in association with other hazard assessment methods to help in selecting the safest process in a phase when limited design data are available.

The data set studied in this section consists of 101 fire and explosion accidents that happened during process, transport, and storage where the mass of material involved was available, see Table 5.36. These accidents were divided into 13 classes according to the mass of material involved. Each class is defined by lower and higher bounds on the mass of material. The higher bound is equal to the lower bound multiplied by $10^{0.5}$, i.e. by 3.17. When there are no accidents in a class, two classes are combined together. Marshall (1977) used this division into classes in deriving the mortality index. The first interval has been chosen arbitrarily according to the data as in an article by Vilchez *et al.* (2001) in which the same methodology was used.

Figure 5.41 shows a histogram for the frequency of accidents occurring in each class. As can be seen, the numbers of accidents is low in the first three classes which represent accidents with masses between 0 and 1.4 tonnes of chemicals. This could be attributed to the safety of dealing with small inventories, or as Marshall (1977) claimed, to the failure of recording small accidents, especially if not accompanied by fatalities. On the other hand, the mass range from 1.44 to 144 tonnes seems to be critical since it has the highest number of accidents, 58 accidents. Accidents involving masses of more than 500 tonnes tend not to happen often.

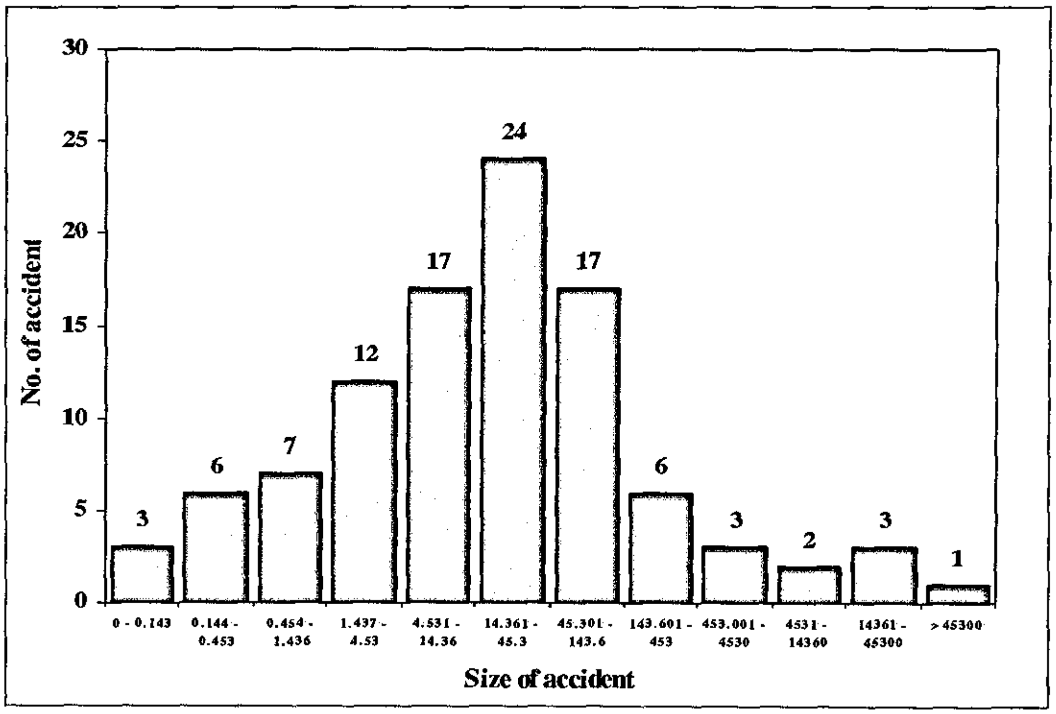


Figure 5.41: Fire and explosion accidents

5.9.1 Mortality index for all fire and explosion accidents

The first column of Table 5.36 shows the range, in tonnes of hazardous material, for the classes. The following three columns show: the total number of fatalities over all the accidents in the classes, the total mass of material involved in the accidents in the class and the number of accidents in each class.

The last three columns show, respectively, the mean number of fatalities per accident, the mass involved per accident (mean) and the mortality index (MI). The mortality index (MI) was calculated for each class and plotted on log/log scale against the mean mass for each class, as shown in Table 5.36 and Figure 5.42. After applying linear regression of log/log values and transforming back to the original scale, the following equation has been obtained:

$$MI = 2.22m^{-0.68} \qquad \textbf{5. 2}$$

where, MI, is the mortality index (fatality per tonne of material involved).
m, is the quantity of material in tonne.

Table 5.36: All fire and explosion accidents.

Size of accident (tonne)	Total fatalities in class (1)	Total mass in class (2)	Total no. of accidents in class (3)	Average fatalities (1)/(3)	Average tonnes (2)/(3)	MI (fatalities per tonne) (1)/(2)
0 - 0.143	2	0.142	3	0.67	0.05	14.0845
0.144 - 0.453	12	1.95	6	2.00	0.33	6.1538
0.454 - 1.436	10	6.11	7	1.43	0.87	1.6367
1.437 - 4.53	20	35.8	12	1.67	2.98	0.5587
4.531 - 14.36	145	159.2	17	8.53	9.36	0.9108
14.361 - 45.3	712	577.7	24	29.67	24.07	1.2325
45.301 - 143.6	53	1386.7	17	3.12	81.57	0.0382
143.601 - 453	28	1828	6	4.67	304.67	0.0153
453.001 - 4530	128	6390	3	42.67	2130.00	0.0200
4531 - 14360	657	13000	2	328.50	6500.00	0.0505
14361 - 45300	57	88000	3	19.00	29333.33	0.0006
> 45300	52	95000	1	52.00	95000.00	0.0005
Total	**1876**	**206,386**	**101**			

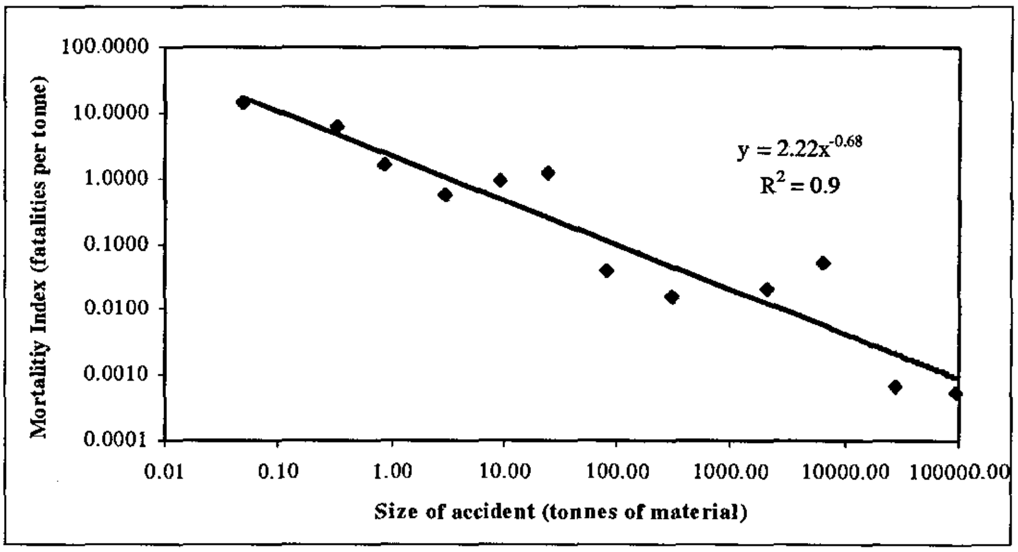


Figure 5.42: Fire & explosion accidents

In Figure 5.43 the same procedures as above were applied for only the accidents that caused one or more fatalities. The regression factor for this relation was ($R^2 = 0.9$) which indicates a good fit. The following equation can be used to estimate the MI:

$$MI = 3.7m^{-0.7} \qquad 5.3$$

It can be seen that both including and excluding the accidents that did not cause fatalities resulted in strong relationships. It should point out that the high regression factors for these relationships is expected since regression is done using mean values for both the size of accident and the mortality index.

Table 5.37:Fire and explosion accidents (caused one or more fatalities).

Size of accident (tonne)	total fatalities in class (1)	total mass in class (2)	total no. of accidents in class (3)	mean fatalities (1)/(3)	mean tonnes (2)/(3)	MI (fatalities per tonne) (1)/(2)
0 - 0.143	2	0.03	1	2	0.03	66.6667
0.144 - 0.453	12	1.4	4	3.00	0.35	8.5714
0.454 - 1.436	10	3.21	4	2.50	0.80	3.1153
1.437 - 4.53	20	19.9	6	3.33	3.32	1.0050
4.531 - 14.36	145	144.2	15	9.67	9.61	1.0055
14.361 - 45.3	712	487.4	20	35.60	24.37	1.4608
45.301 - 143.6	53	899.5	12	4.42	74.96	0.0589
143.601 - 453	25	1100	4	6.25	275.00	0.0227
453.001 - 4530	131	3455	2	65.50	1727.50	0.0379
4531 - 14360	657	13000	2	328.50	6500.00	0.0505
14361 - 45300	57	63000	2	28.50	31500.00	0.0009
> 45300	52	95000	1	52.00	95000.00	0.0005
Total	**1876**	**177,111**	**73**			

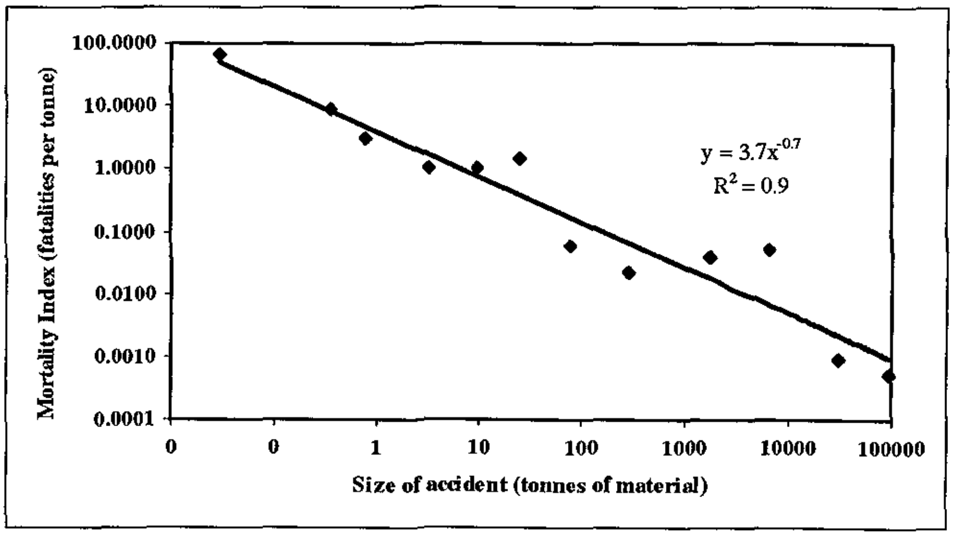


Figure 5.43: Fire & explosion accidents.

5.9.2 Mortality index by type of process operation

The fire and explosion accidents were classified by the type of accidents. Tables 5.38, 5.39 and 5.40 show respectively, the process, storage and transport accidents analysis and Figures 5.44, 5.45 and 5.46 show the relationships between the mortality index and the size of accidents by type of accident. It should be pointed out that the storage and transport relationships are not valid for accidents with small masses.

Table 5.38: Fire and explosion for process accidents.

Size of accident (tonne)	total fatalities in class (1)	total mass in class (2)	total no. of accidents in class (3)	mean fatalities (1)/(3)	mean tonnes (2)/(3)	MI (fatalities per tonne) (1)/(2)
0 - 0.143	2	0.032	2	1	0.016	62.50
0.144 - 0.453	12	1.65	5	2.4	0.33	7.27
0.454 - 1.436	6	4.4	5	1.20	0.88	1.36
1.437 - 4.53	18	26.2	9	2.00	2.91	0.69
4.531 - 14.36	63	98.4	10	6.30	9.84	0.64
14.361 - 45.3	66	208.6	8	8.25	26.08	0.32
45.301 - 143.6	14	237	3	4.67	79.00	0.06
143.601 - 453	3	328	1	3.00	328.00	0.01
Total	**184**	**904**	**43**			

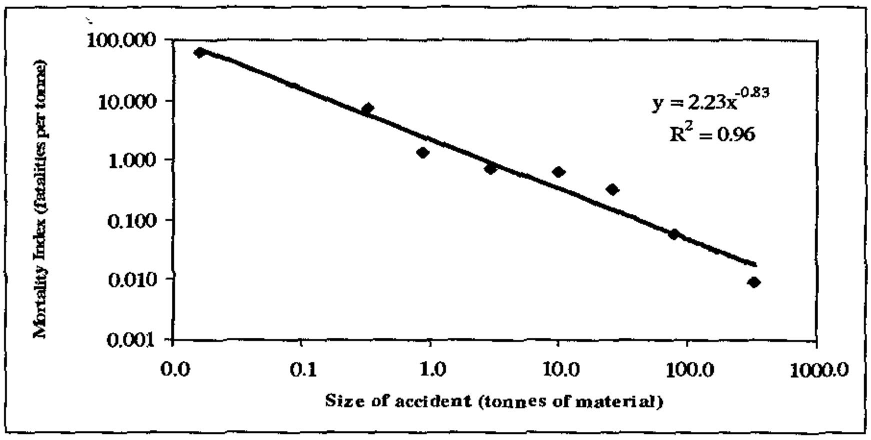


Figure 5.44: Fire and explosion process accidents.

Table 5.39: Fire and explosion for storage accidents.

Size of accident (tonne)	total fatalities in class (1)	total mass in class (2)	total no. of accidents in class (3)	mean fatalities (1)/(3)	mean tonnes (2)/(3)	MI (fatalities per tonne) (1)/(2)
0 - 0.143	0	0.11	1	0	0.11	0
0.144 - 0.453	0	0.3	1	0	0.3	0
0.454 - 1.436	4	1.71	2	2	0.86	2.34
1.437 - 14.36	4	15	2	2.00	7.50	0.27
14.361 - 45.3	4	20	1	4.00	20.00	0.20
45.301 - 143.6	2	208	2	1.00	104.00	0.01
143.601 - 453	18	600	2	9.00	300.00	0.03
453.001 - 4530	128	6390	3	42.67	2130.00	0.02
4531 - 14360	657	13000	2	328.50	6500.00	0.05
14361 - 45300	7	48000	2	3.50	24000.00	0.0001
Total	**824**	**68,235**	**18**			

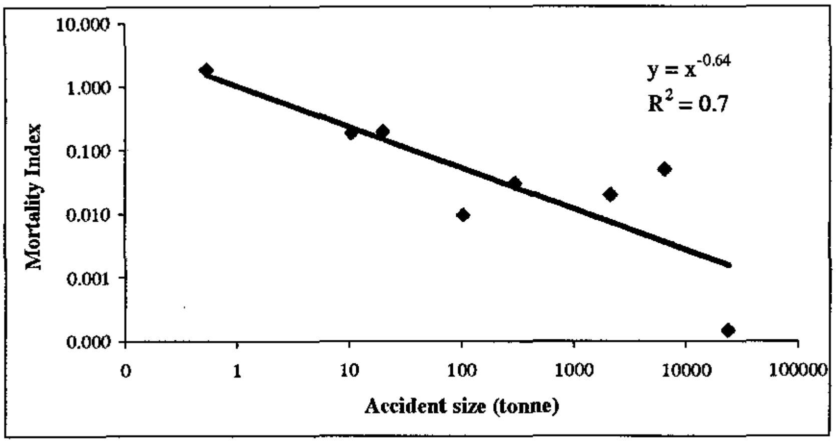


Figure 5.45: Fire and explosion storage accidents.

Table 5.40: Fire and explosion accidents for transport accidents.

Size of accident (tonne)	total fatalities in class (1)	total mass in class (2)	total no. of accidents in class (3)	mean fatalities (1)/(3)	mean tonnes (2)/(3)	MI (fatalities per tonne) (1)/(2)
0 - 0.143	-	-	-	-	-	-
0.144 - 0.453	-	-	-	-	-	-
0.454 - 1.436	-	-	-	-	-	-
1.437 - 14.36	75	34.5	5	15.00	6.90	2.17
14.361 - 45.3	635	314.6	13	48.85	24.20	2.02
45.301 - 143.6	37	814.7	11	3.36	74.06	0.05
143.601 - 453	7	900	3	2.33	300.00	0.01
453.001 - 45300	50	40000	1	50.00	40000.00	0.001
> 45300	52	95000	1	52.00	95000.00	0.001
Total	**856**	**137,064**	34			

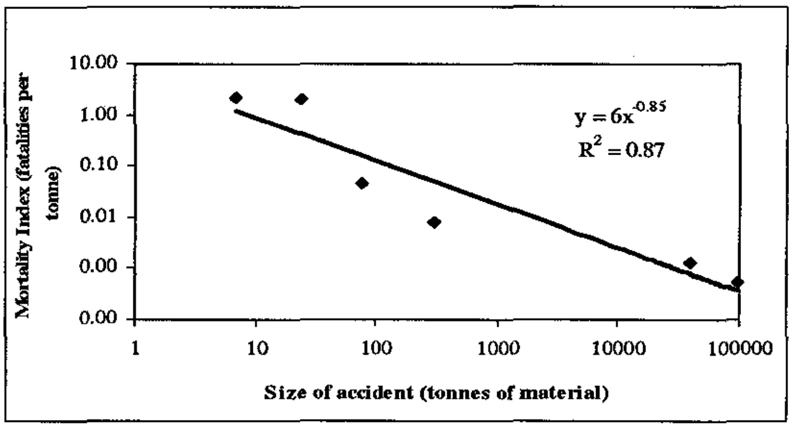


Figure 5.46: Fire and explosion transportation accidents.

5.9.3 Mortality index by type of chemical

The same analysis as that made for all fire and explosion accidents was applied to the 71 hydrocarbon accidents in which the mass of hydrocarbons were known. Table 5.41 shows the analysis and Figure 5.47 shows the relationship between the MI and the size of accident in tonnes of hydrocarbons. It can be seen that the relationship between the two variables is strong, giving a regression factor of ($R^2 = 0.85$). The following equation can calculate the mortality index for hydrocarbon accidents:

$$MI = 2.55m^{-0.67} \qquad 5.4$$

Analysing hydrocarbon accidents excluding the accidents which did not result in any fatalities yielded the same results as that given including the accidents with zero fatalities. The regression factor was ($R^2 = 0.87$) in the first case and ($R^2 = 0.85$) in the second case as shown in Figures 5.48 and 5.47.

Table 5.41: Hydrocarbon fire and explosion accidents.

Size of accident (tonne)	total fatalities in class (1)	total mass in class (2)	total no. of accidents in class (3)	mean fatalities (1)/(3)	mean tonnes (2)/(3)	MI (fatalities per tonne) (1)/(2)
0 - 0.143	0	0.11	1	0	0.11	0
0.144 - 0.453	9	0.95	3	3.00	0.32	9.47
0.454 - 1.436	7	4.5	5	1.40	0.90	1.56
1.437 - 4.53	19	31.6	11	1.73	2.87	0.60
4.531 - 14.36	122	121.7	13	9.38	9.36	1.00
14.361 - 45.3	451	415.4	17	26.53	24.44	1.09
45.301 - 143.6	31	900.7	11	2.82	81.88	0.03
143.601 - 453	24	935	3	8.00	311.67	0.03
453.001 - 4530	128	5190	2	64.00	2595.00	0.02
4531 - 14360	650	6000	1	650.00	6000.00	0.11
14361 - 45300	57	88000	3	19.00	29333.33	0.0006
>45300	52	95000	1	52.00	95000.00	0.0005
Total	**1550**	**196,600**	**71**			

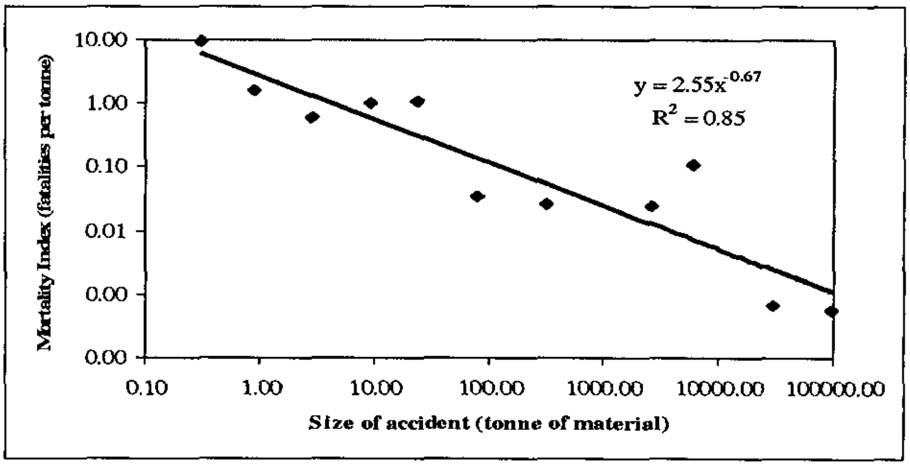


Figure 5.47: Hydrocarbons accidents.

Table 5.42: Hydrocarbon fire and explosion accidents

(caused one or more fatalities)

Size of accident (tonne)	total fatalities in class (1)	total mass in class (2)	total no. of accidents in class (3)	mean fatalities (1)/(3)	mean tonnes (2)/(3)	MI (fatalities per tonne) (1)/(2)
0 - 0.143	-	-	-	-	-	-
0.144 - 0.453	9	0.95	3	3.00	0.32	9.47
0.454 - 1.436	7	2.6	3	2.33	0.87	2.69
1.437 - 4.53	19	15.7	5	3.80	3.14	1.21
4.531 - 14.36	122	106.7	11	11.09	9.70	1.14
14.361 - 45.3	451	386.4	16	28.19	24.15	1.17
45.301 - 143.6	31	591.5	8	3.88	73.94	0.05
143.601 - 453	24	935	3	8.00	311.67	0.03
453.001 - 4530	128	3000	1	128.00	3000	0.04
4531 - 14360	650	6000	1	650.00	6000	0.11
14361 - 45300	57	63000	2	28.50	31500	0.001
> 45300	52	95000	1	52.00	95000	0.001
Total	**1550**	**169,039**	**54**			

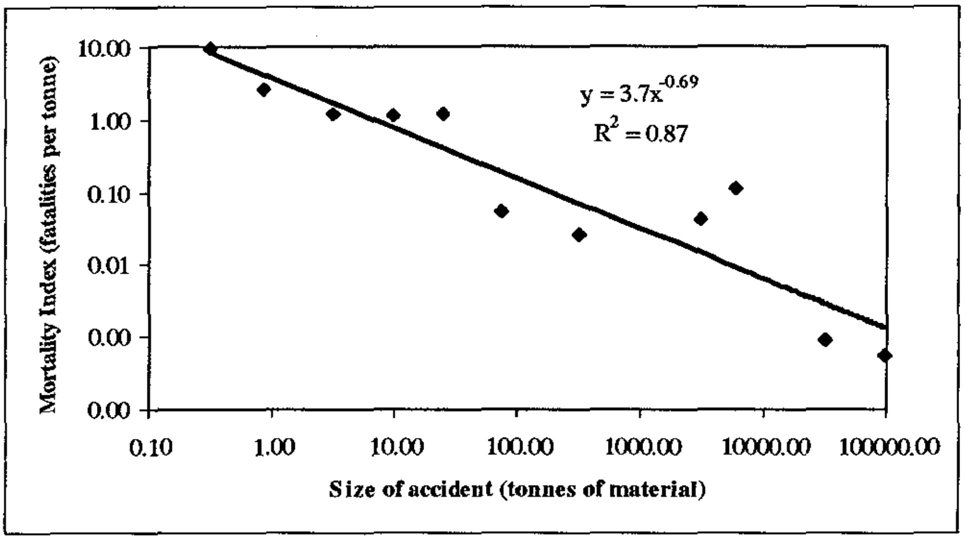


Figure 5.48: Hydrocarbon accidents that caused one or more fatalities

Table 5.43: The mortality index relationships for fire and explosion accidents.

Type of accident	Equations	R^2	0 fatalities accidents included	No. of accidents	No. of fatalities	Total mass involved
All F & E accidents	$MI = 2.22\ (m)^{-0.68}$	0.90	Yes	101	1876	206,386
All F & E accident	$MI = 3.7\ (m)^{-0.7}$	0.90	No	73	1876	177,111
Process F & E accidents	$MI = 2.23\ (m)^{-0.85}$	0.96	Yes	43	184	904
Storage F & E accidents	$MI = \ (m)^{-0.65}$	0.70	Yes	18	824	68,235
Transport F & E accidents	$MI = 6.0\ (m)^{-0.85}$	0.87	Yes	34	856	137,064
HC F & E accidents	$MI = 2.55\ (m)^{-0.67}$	0.85	Yes	71	1550	196,600
HC F & E accidents	$MI = 3.7\ (m)^{-0.69}$	0.87	No	54	1550	169,039

F & E: fire and explosion

HC: hydrocarbons

MI: Mortality Index (no. of fatalities/tonne of chemical)

m: amount of chemical (tonne)

Table 5.43 summarises all the relationships observed between the MI and the mass of chemicals involved.

It can be seen from Table 5.43 that for all fire and explosion accidents, the number of process accidents are much higher than the number of storage accidents. Among the 101 accidents with known amount of chemicals, 43 took place during processing while 34 and 18 happened during transport and storing operations respectively. In terms of the number of fatalities, process operations have yielded a lower number of fatalities than storage and transport. Process accidents caused the death of 184 people, while storage and transport caused 824 and 856 fatalities respectively. Calculating the amount of chemicals involved in the three operations shows that process operations involved a smaller amount of chemicals than storage and transport operations.

It can be noticed from Tables 5.36 to 5.42 that in most cases, the MI is higher for accidents that involve a smaller quantity of material. This can be due to the failure of reporting small incidents unless they involve fatalities which lead to high values for the mortality index for small incidents.

On the other hand, the number of accidents which happened in transporting chemicals was almost twice the number that took place in storage. Also the mass of chemicals involved in transport operations was twice that of storage. However, the fatalities toll from storing and transporting chemicals were almost the same.

Table 5.43 also summarises all the relationships observed between the MI and the mass of chemicals involved. Although the curves fit the data well, as indicated by the high values of R^2, it is not expected that these equations will have particularly good predictive values as they are obtained from plotting the mean mass and the mean mortality index within bands (as detailed in Table 5.36). This will reduce the variability between the data points and give a high correlation.

It should be pointed out that the number of fatalities resulting from a chemical accident will depend not only on the accident's physical effect but also on the distribution of the population in the area affected by the accident. Thus, it is necessary to look more closely at likely population densities and the mortality index may have to take account of variations in population density. Attention also has to be called to the fact that there are differences in population densities between office hours and outside office hours.

The above relationships do not take the population density into consideration. Population density in the area surrounding the source of the explosion is not uniform and in order to include such a factor, population data for both on site and off site is required as well as data for the actual population density at the time of accident. The information about process location, local population or number of employees is not known at the conceptual design phase. In addition, it was not possible to obtain data of the actual population density at the time of accident. Therefore, the exact number of people affected is unlikely to be accurately predicated from these equations.

5.9.4 Validation of results

In order to examine the validity of the mortality index relationships shown in Table 5.43, the mean mass for every class was used to predict the mortality index using equation 5.3. The predicted number of fatalities was plotted against the actual ones as shown in Figure 5.49. The figure shows that the method predicted fatalities up to about 1000 for accidents involving between 0.03 and 100,000 tonnes of chemicals.

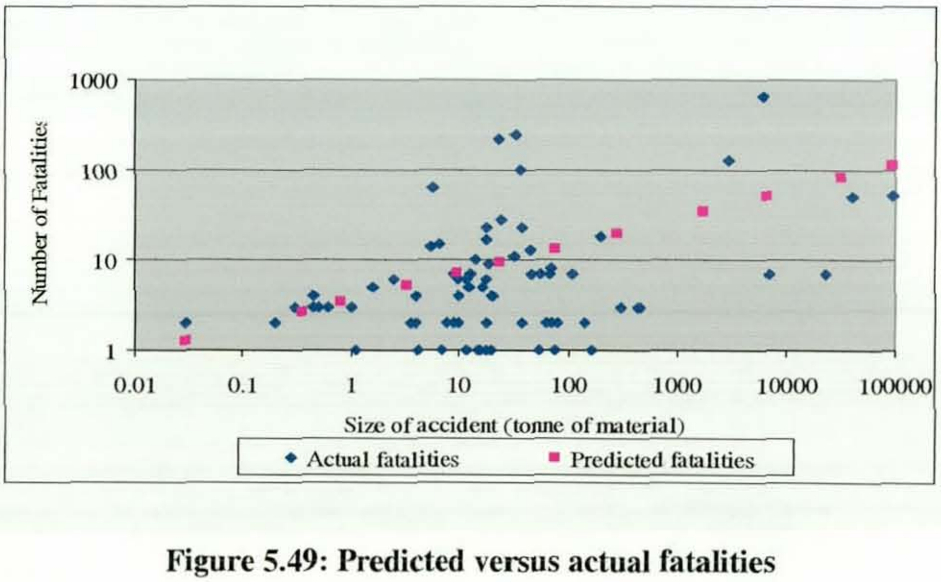


Figure 5.49: Predicted versus actual fatalities

Comparing the predicted number of fatalities to the actual ones showed that there are sometimes large differences between the actual and the predicted numbers. For accidents involving small quantities of chemicals, up to one tonne, the agreement between the actual and the predicted fatalities is reasonably close. However, variability exists that appears to increase somewhat with increasing quantity of material. As the quantities increased the actual fatalities range became too broad to suggest a specific pattern.

It can be seen that accidents with fatalities exceeding 100 are for the two storage accidents which happened in Cleveland, Ohio (1944) and the Mexico City fire (1984) in which the location of the plants in densely populated areas were responsible for the high death toll of 128 and 650 respectively. The other two accidents with more than 100 fatalities are the San Carlos, Spain (1978) and the Ludwigshafen, Germany (1948) transport accidents in which the former took place in a camp of about 500 people and the latter occurred in very large population density place. In addition these accidents happened a long time ago when safety issues and risk planning were of less concern compared with those that are used nowadays. It is believed that it would be inappropriate to take accidents that happened in such extraordinary circumstances which would not be tolerated today into consideration in a method that is intended to assess the hazards of plants that will be located outside built-up areas.

Therefore, due to the above reasons, it is believed that not taking those accidents into consideration reduces the variability of the actual data and thus makes the prediction slightly more accurate. Figure 5.50 shows that actual and the predicted fatalities after excluding the above accidents.

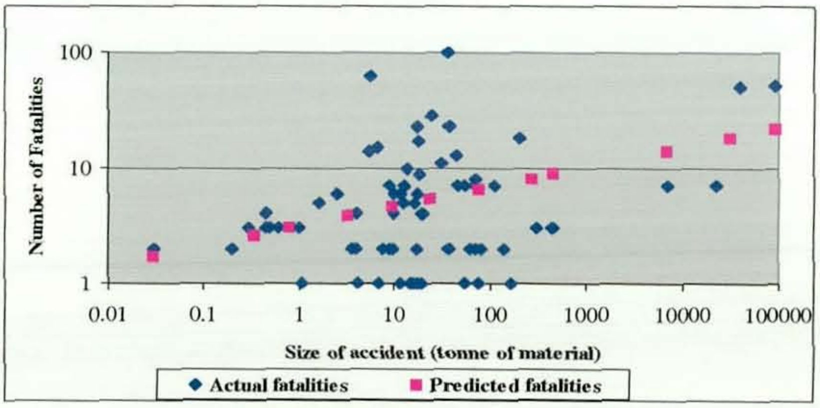


Figure 5.50: Predicted versus actual fatalities

(no high number of fatalities accidents)

The proposed method is valid for predicting fatalities for accidents involving chemicals between 0.03 and 100,000 tonnes. For quantities below and above that range, extrapolation is needed to obtain the number of fatalities. However, although it is possible to predict fatalities for quantities below 0.03 and above 100,000 tonnes, these results could not be validated due to the lack of actual data for these lower and higher quantities. If more data were available for accidents involving large quantities of chemicals it would provide means for validating results for accidents involving very low or very high quantities of chemicals.

A close look at the relations obtained for different operations show that the fit between the actual and the predicted fatalities for process and storage were reasonably acceptable. The process method predicted fatalities between about one and ten for quantities between about 0.01 and 1000 tonnes while in the case of storage the predicted number of fatalities was between 1 and 100. As mentioned before, the higher differences between the actual and the predicted fatalities for storage accidents are due to the presence of the two accidents which resulted in very high fatalities due to certain circumstances. The agreement between the actual the predicted fatalities in the transport accidents were very poor. Figures 5.51, 5.52 and 5.53 are the actual versus the predicted fatalities for process, storage, and transport accidents.

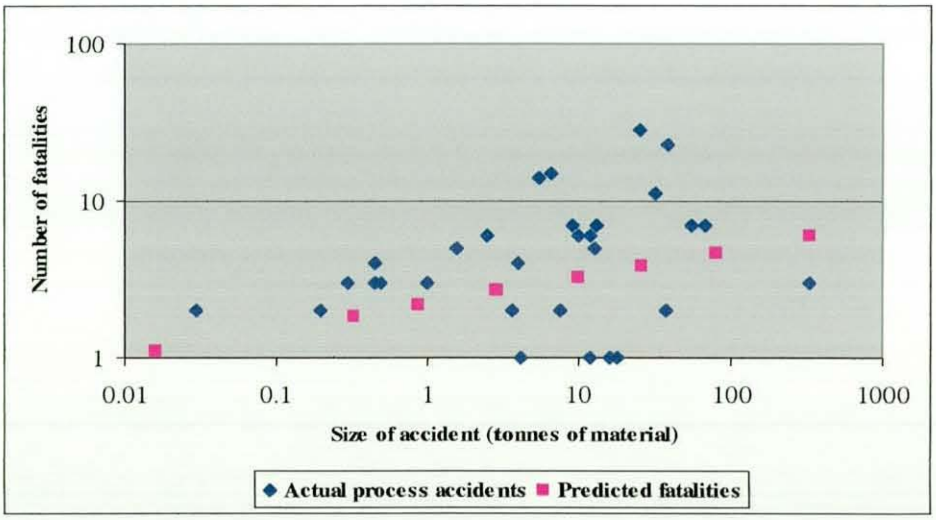


Figure 5.51: Predicted versus actual fatalities for process accidents

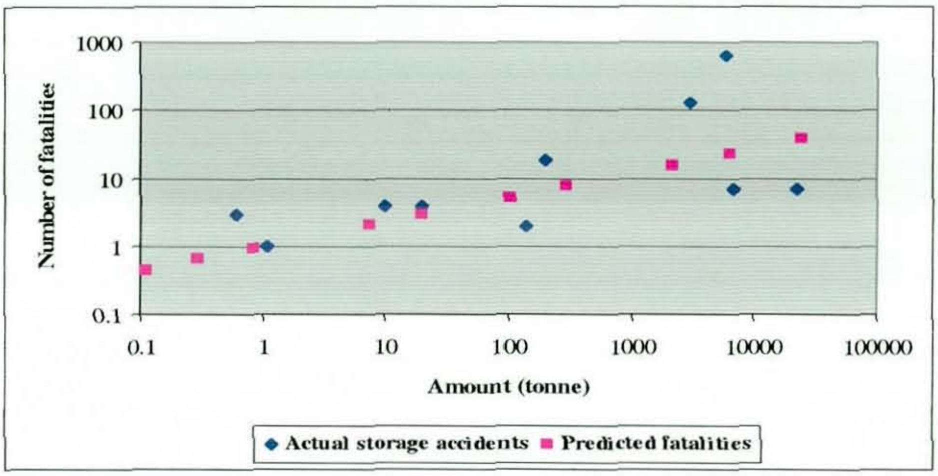


Figure 5.52: Predicted versus actual fatalities for storage accidents

It can be seen that the accuracy of prediction for the obtained equations is quite low, except for storage accidents involving less than 1000 tonnes. The difference between the actual and the predicted number of fatalities for equation 5.3 which was obtained from applying all the fire and explosion accidents that caused one or more fatalities was sometimes up to 70 fatalities for quantities more than 1 tonne. Unlike the accuracy of the equations obtained from the process and the storage accidents, the maximum difference between the predicted and the actual fatalities was about 20 for process and 7 for storage.

It is difficult to allocate criteria for an acceptable limit between the theoretical and the actual approach. On the other hand, it is not vital that an assessment method which will be used in association with other hazard assessments to help process designers to apply good judgment in selecting the safest process in a conceptual design phase to be very accurate. In addition, the method is still novel and as mentioned earlier it did not take the variation of population density into consideration. It is believed that if data about population density becomes available as well as the possibility to obtain the quantity of chemicals for the rest of accidents it could help to reduce the big difference between the theoretical and the actual fatalities and thus to increase the accuracy of the method. The accuracy of the transport equation was very poor. As mentioned earlier in section 5.6.1.1, this could be due to the different types of transportation included in the data. It includes rail tank cars, road tankers and oil tankers. Also the circumstances of the accidents vary widely for example happening in the middle of a built-up area or where there are no people.

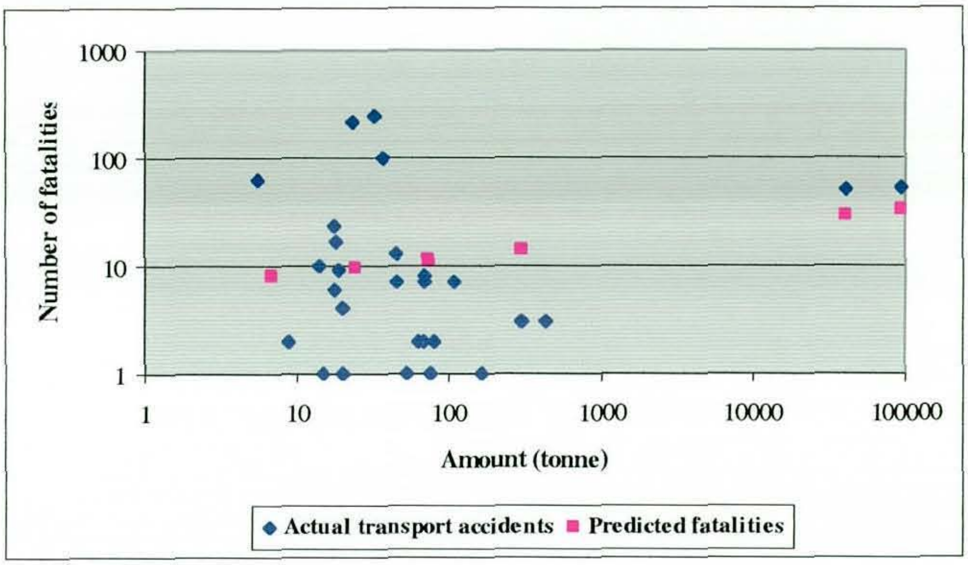


Figure 5.53: Predicted versus actual fatalities for transport accidents

5.9.5 Conclusion

Another method of assessing hazards from chemical accidents is the mean mortality index approach in which the ratio fatalities to size of release are determined. Mortality Indices were obtained for general chemicals and for hydrocarbons as well as for accidents by process operations. These indices allowed prediction of the potential number of fatalities from a chemical accident by knowing the quantity of the potential release. Comparing the actual to the predicted fatalities showed that there are sometimes large differences between the actual and the predicted number of fatalities. However, the fit between the actual and the predicted number were reasonably acceptable in the case of process and storage accidents, especially if the accidents which resulted in very high number of fatalities due to extraordinary circumstances were not taken into account.

5.10 Overall conclusion

The aim of this chapter was to develop a method for assessing the inherent safety of a chemical plant. This method is intended to predict the number of people that might be killed in case of a chemical accident involving a certain mass of specified chemical.

The major concern was to quantify the hazard posed by the chemicals that were involved in the accidents data. This has been done by estimating the number of people that could be killed in case of an accident per unit mass of a certain chemical released or exploded. It was also intended to investigate if the number killed is associated with other factors.

A trial has been made to seek and measure whether any correlation exists between the number of fatalities and the mass of chemicals involved in the accidents. The results indicated that there is a positive relationship between the number of fatalities and the amount of chemicals, the two variables increase together. However, the low value of the correlation suggests that there are other factors that maybe important in such relationship.

The results also showed that factors such as the location and time of accident, and the country of operation affect the consequences of a chemical accident.

A trial has been made to investigate whether certain chemicals or phases pose more hazards than others. Hydrocarbons, which were found to be dominant in the accident data, were classified by the number of their carbon atoms. The analysis was obstructed by the unavailability of the mass of chemicals for every accident. However, an equation to assess the hazard posed by ethylene has been obtained which still needs validation.

As an alternative to estimating the number of fatalities per mass of chemicals, the mean and the median number of fatalities were calculated for the chemicals involved in the accidents. This method did not involve the mass of chemicals which allowed the use of all the fire and explosion data. The results revealed that hydrocarbons were the most frequent chemicals involved in the accidents. The results allowed ranking of the hydrocarbons by median number of fatalities as well as by type of accident.

Another method of assessing hazards from chemical accidents is the mean mortality index approach in which the ratio fatalities to size of release are determined. Mortality Indices were obtained for general chemicals and for hydrocarbons as well as for accidents by process operations. These indices allowed prediction of the potential number of fatalities from a chemical accident by knowing the quantity of the potential release. Comparing the actual to the predicted fatalities showed that there are sometimes large differences between the actual and the predicted number of fatalities. However, the fit between the actual and the predicted number were reasonably acceptable in the case of process and storage accidents, especially if the accidents which resulted in a very high number of fatalities due to extraordinary circumstances not taken into account. There was no agreement between the actual and the predicted fatalities in the case of transport.

Despite this, it can be concluded that the mortality index could be an appropriate method to measure the inherent safety of a chemical plant. The weakness of the prediction accuracy is because the mortality index equations have not considered the variations in population density. This is due to the unavailability of this particular data in the conceptual design phase. If this data were available the mortality indices could then be corrected to take account of population density factor. This might improve the accuracy of the predicted equations. Use of the median number of fatalities instead of the mean did not change the accuracy of prediction.

Chapter 6: Data analysis for toxic release accidents

6.1 Introduction

The other major hazard after the fire and explosion is a release of a toxic chemical. A very large release of toxic chemical is usually regarded as having a disaster potential greater than that of fire or explosion. This is because toxic releases have possibly the greatest potential to kill a large number of people. However, according to Lees (1996), a large toxic release is a much less frequent occurrence than a large fire or explosion. In this chapter toxic accidents are analysed in order to assess the hazards posed by toxic chemicals. Table 2 in Appendix A is a list of the toxic accidents.

6.2 Classification of toxic accidents over time

As mentioned in chapter 5, section 5.5, there were 119 toxic release accidents with reported data between 1914 and 1999. Table 2 in Appendix A is a list of the toxic accidents . Figure 6.1 shows the distribution of toxic accidents over time.

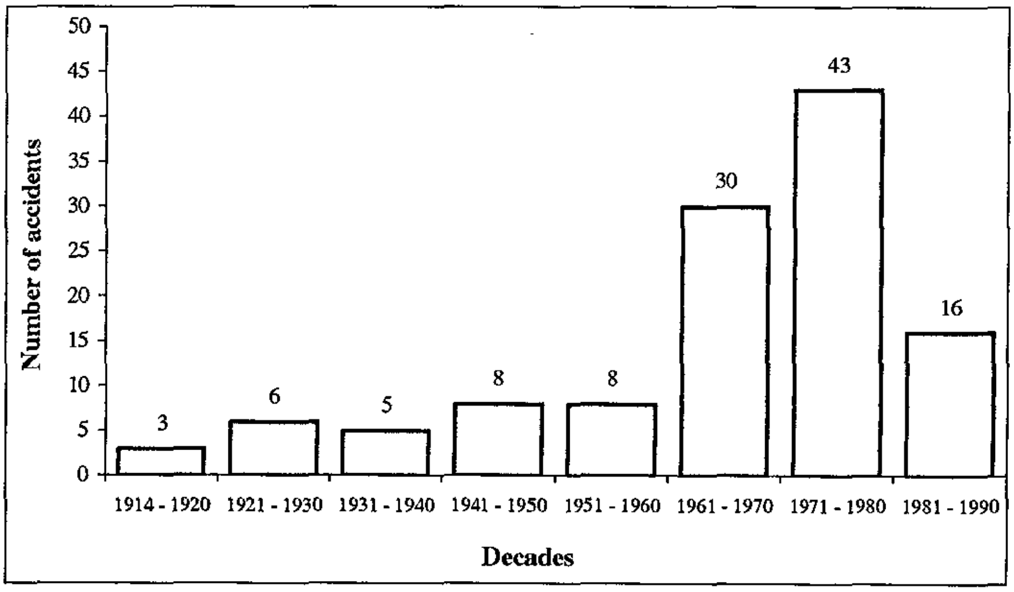
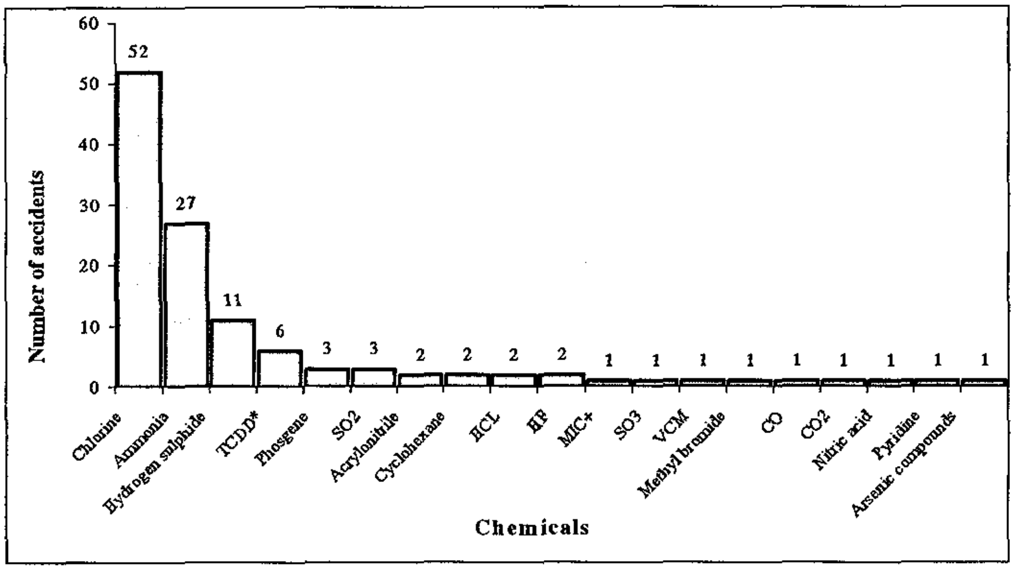


Figure 6.1: Distribution of toxic accidents as a function of time.

As can be seen from Figure 6.1, there were few releases during the first half of the twentieth century. The number varied from 3 to 8 accidents per decade, until the 1960s, when a significant rise in the number of toxic release accidents was observed. This rise was maintained during the seventies before it fell in the nineties.

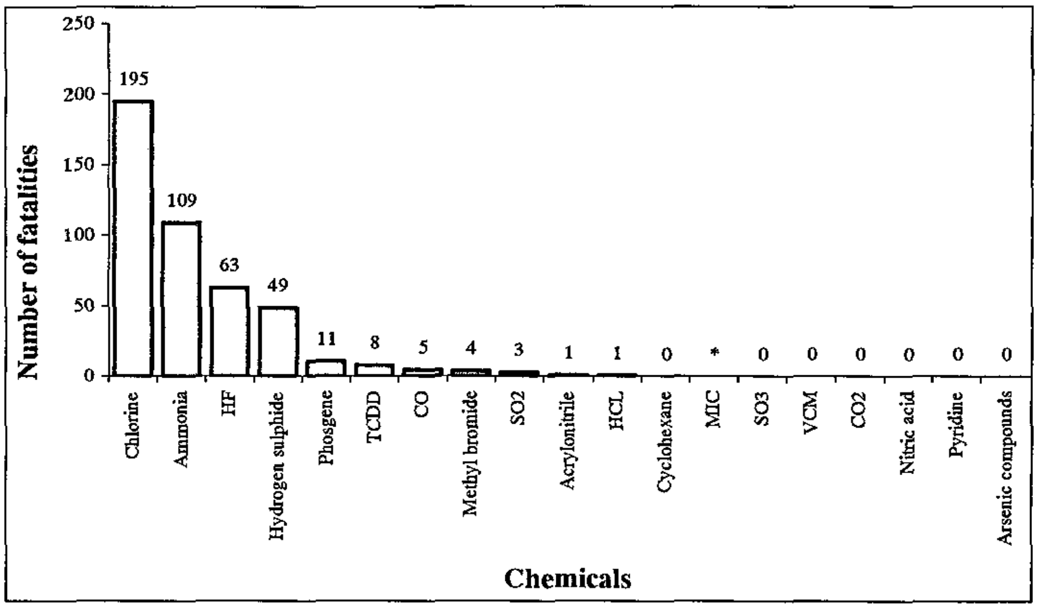
A number of chemicals were found to be responsible for these toxic releases in different frequencies. Figure 6.2 shows the number of accidents for each chemical.



*TCDD: Tetrachlorodibenzoparadioxin

+MIC: Methyl isosyanate

Figure 6.2: Number of toxic releases by chemical released



* MIC caused 8000 deaths from the only one accident.

Figure 6.3: Number of fatalities from toxic releases.

As can be seen from Figure 6.3 chlorine is the dominant chemical, accounting for 44% of the toxic accidents, followed by ammonia with 23%. The number of accidents involving chlorine is about double the number of ammonia accidents that took place in the same period. Hydrogen sulphide and Tetrachlorodibenzoparadioxin (TCDD) accounted for 9% and 5% respectively. The other 19% were for the chemicals shown in Figure 6.2.

Chlorine and ammonia were dominant in terms of the number of fatalities caused as well. Chlorine was found to be responsible for the death of 195 people from the 52 accidents it caused. In 8 accidents there was no information available as to whether or not there were fatalities. Ammonia was been found to cause 109 fatalities. Figure 6.3 shows the number of fatalities caused by the toxic accidents. Fatalities caused by Methyl Isocyanate (MIC) were left out of the figure for scale purpose.

6.3 Origin of toxic accidents

Reviewing the toxic accidents data revealed that toxic releases varied in their origin. The data showed that accidents happened in process plants, storage, transport and during loading terminals. Of the 119 toxic releases reported, 11% are of unknown origin. For the rest, the distribution according to origin is presented in Figure 6.4. It is obvious from the figure that most of the accidents took place during transportation of the chemicals (42%). The transport methods included rail tank cars (31 accidents), road tankers (3 accidents) and only one accident on a ship and it includes transporting by pipelines (15 accidents). Process accidents came second (24%) followed by storage accidents (16%). The last two categories are for accidents happening in chlorine cylinders (4%) and for accidents that happened in loading terminals (3%).

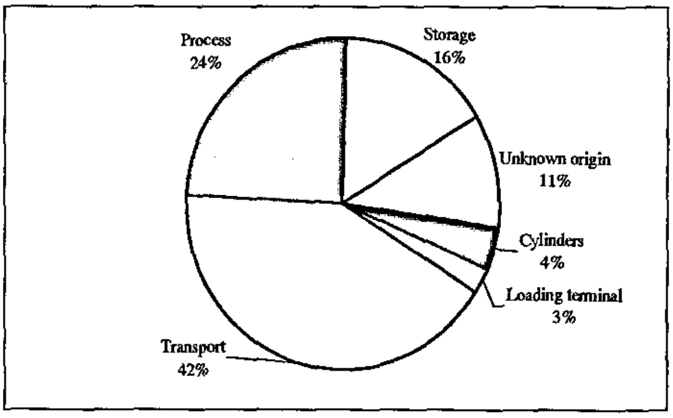


Figure 6.4: Origin of toxic release accidents.

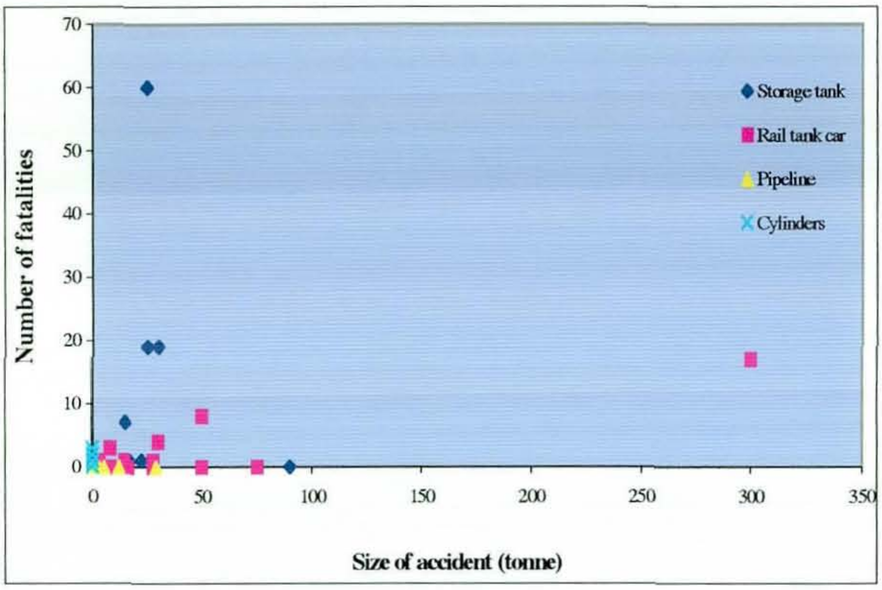


Figure 6.5: Chlorine accidents.

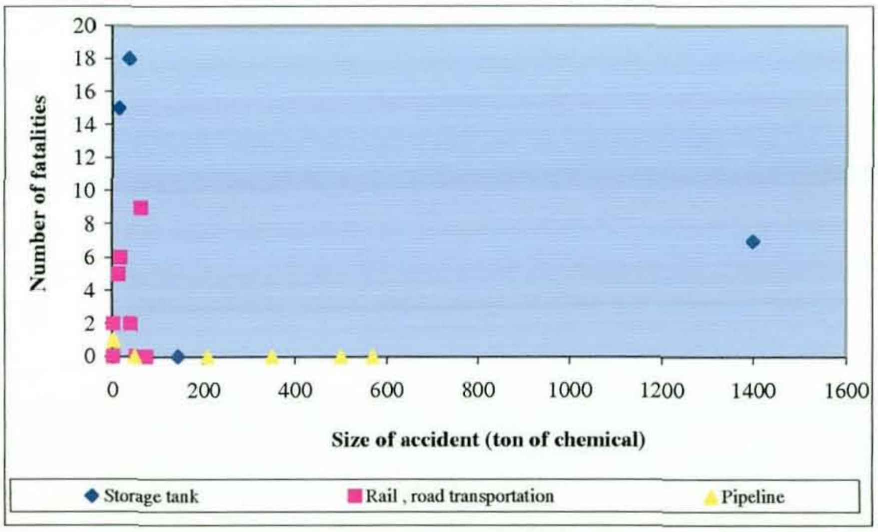


Figure 6.6: Ammonia Accidents.

Figures 6.5 and 6.6 make a comparison between chlorine and ammonia spills in terms of the size of the spill in tonnes and the number of people killed. It can be seen that in the case of chlorine, accidents involving fixed storage tanks tended to cause more fatalities per tonne released than did accidents involving rail tanks and pipelines. This might be attributed to the relatively small number of people exposed in transportation accidents, compared with production plant accidents. Ammonia accidents caused a greater number of fatalities due to rail tank cars but these still caused less fatality than storage tanks.

The sizes of chlorine containers are as follows. Storage is typically in large pressure vessels or refrigerated atmospheric tanks containing 1000 or 2000 tons each. Barges usually carry four pressure vessels each containing 275 tons, making 1100 tons total capacity. Rail tank cars are pressure vessels ranging in size from 16 to 90 tons, but only the latter size is now made. Road tankers are also pressure vessels and normally have a capacity of 16 tons. Cylinder sizes are usually 1 tons, 150 lb or smaller.

6.4 Toxicity

Toxicity is a measure of the ability of a material to harm the health of living organisms. Toxic materials can be classified into those that cause severe impact upon short term exposure, and others that generate noticeable effects or permanent damage only on long-term exposure.

Toxicity is typically measured in terms of the concentration of the material in mg/m^3 or ppm (parts per million), and exposure time, which can be seconds, minutes or even years. Common measures of toxicity are the TLV (threshold limit value), LD (lethal dose) and ED (effective dose). TLV refers to concentrations that cannot cause harm in the lifetime or workers who are exposed to such materials during normal working hours of 40h/week. Lethal dose refers to a dose of material that if inhaled, produces lethal effects or can cause death or permanent damage. The smaller the lethal dose, the higher the toxicity and the more inherently unsafe the material is. Effective dose is the dose of a material that if inhaled, creates minor and reversible effects such as eye irritation.

Lethal dose is usually expressed as LD_{50}, which is defined as that dose administrated orally or by skin absorption which will cause the death of 50% of the test group within a 14-day observation period, King (1990). It is generally expressed as mg or μg of substance per kg of body weight of the animal. Another unit, the lethal concentration LC_{50}, is used for airborne materials which are inhaled. It is defined as the concentration of airborne material, the four-hour inhalation of which results in the death of 50% of the test group within a 14-day observation period, King (1990).

6.5 Assessing the hazard of toxic material

An important part of choosing a process is establishing just how hazardous a particular material is. To do so it is important to know the effect of toxic material to people by one of *the known measurements of toxicity, for example LD_{50}.*

Marshall (1987) has suggested considering the number of lethal doses for quantifying toxic hazards. His idea is to categorise chemicals by how much is required to produce 10^7 or 10^8 lethal doses, based on the LD_{50} value of the chemical. Masses of hazardous chemicals can be converted to numbers of doses that would have a certain effect on a human by using the following formula:

The number of possible human lethal doses is:

$$PLD = \frac{Q}{M_H \cdot LD_{50}} \qquad 6.1$$

Where,

PLD = number of possible lethal doses
Q = mass of toxic chemical (mg)
LD_{50} = Lethal dose (mg of chemical /kg of body weight)
M_H = average mass of person = 70 kg

For example, the number of lethal doses from 1 tonne of formaldehyde, LD_{50} = 800 mg/kg

$$PLD = \frac{1000{,}000{,}000}{(70 \times 800)} = 17857.1 \qquad 6.2$$

Realistically, it would be extremely difficult to kill this many people from a release of formaldehyde. For example 300 tonnes of ammonia (LD_{50} = 350 mg/kg) only killed 12 people in Montana, Mexico, Marshall (1987), whereas the number of possible lethal doses is 12.2 x 10^6. The value is not representative of the hazard as the method overestimates greatly the number of potential deaths from a release. Therefore the method is rejected and another possible method is suggested.

Marshall (1987) introduced the concept of the mortality index (MI) as a means of determining the potential number of fatalities in the chemical process industry. This index was the mean number of fatalities per tonne resulting from the realisation of the potential of given hazards.

Marshall examined historical records from the first and Second World War, covering bombings and the use of early chemical weapons. From that data he developed empirical relationships for explosives and for vapour cloud explosions and fireballs. For toxics, his research concluded that the mortality index was invariant with mass released. Therefore, he gives the MI directly for some chemicals, namely chlorine, ammonia and methyl isocyanate (MIC) in fatalities per tonne, Table 6.1.

Table 6.1: MI and LD_{50} for some chemicals.

Chemical	LD_{50} (mg/kg)	Mortality Index (deaths/tonne)
Chlorine	3.5	0.5
Ammonia	21	0.052
Mustard gas (MG)*	10.5	0.1
Phosgene	0.3	1
HCL	10.25	0.61

*Mustard gas [bis (2-chloroethyl sulphide)]

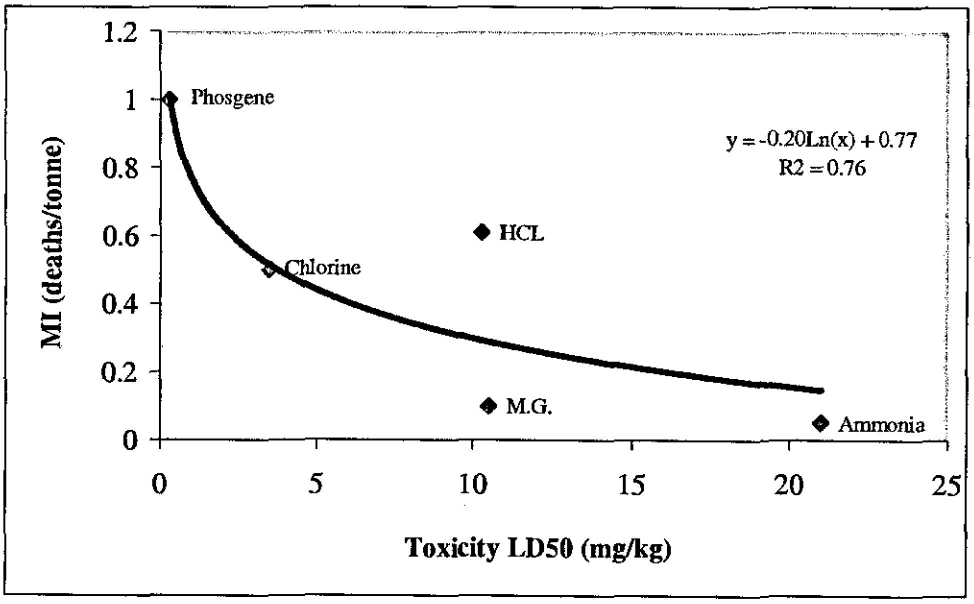


Figure 6.7: Toxicity verses mortality index.

An attempt has been made to assess the hazard posed by toxic releases by relating the mortality index (MI) of the chemicals that Marshall has calculated, with the LD_{50} values. The average mortality index for phosgene and hydrochloric acid has been calculated from the data obtained. Unfortunately no data were available for more chemicals to calculate the mortality index. Table 6.1 shows the MI and the LD_{50} for each chemical.

In Figure 6.7 Methyl isocyanate has been left out as the mortality index is calculated from only one incident, where there was a very high population density near to the plant. It is possible to derive the following relationship:

$$MI = -0.2\ln(LD_{50}) + 0.77 \qquad 6.3$$

Equation 6.3 can be used to estimate the MI for a chemical knowing its LD_{50} value. Where LD_{50} is expressed as mass of toxic agent per kg of body weight (for an average human adult, the body weight is about 70 kg).

When the lethal concentration (LC_{50}) is available, instead of the LD_{50}, the following formula can be used to obtain the LD_{50}, Marshall (1987).

$$Dose\left({}^{mg}\!/_{kg}\right) = \frac{Toxic\ \ concentrat\ \ ion\left({}^{mg}\!/_{m^3}\right) \times time\ (\min)}{10^4\left(kg.\min/_{m^3}\right)} \qquad 6.4$$

Where the lethal concentration is given in parts per million, this may be converted to (mg /m^3) by multiplying by (mol. wt. of toxic x 0.0423)

6.6 Conclusion

The aim of this chapter was to assess the hazards posed by toxic materials. A number of chemicals were found to be involved in the toxic accidents in different frequencies. However, ammonia and chlorine were found to be dominant in terms of both the frequency of occurrence and the number of fatalities caused. Data also showed that most of the toxic accidents took place during transporting chemicals followed by process accidents.

The mortality index approach was also used to assess the hazards posed by toxic chemicals. The mortality index values for few chemicals, the chemicals that Marshall has calculated, were used in conjunction with the toxicity expressed by LD_{50} to derive a relationship that can be used to predict the potential fatalities caused by a toxic chemical. LD_{50} was used as it is a property that can be obtained in early design stages.

Although of the significance of the obtained relationship approved by the regression factor of ($R^2 = 0.76$), it should be pointed out that it is based on few chemicals in which data for MI were available. It will be inappropriate to base a model on few accidents. In addition, this relationship is still primary and needs validation. If more MI data is available, it might be possible to establish a more reliable relationship in which the potential number of fatalities for toxic chemicals can be estimated by knowing their LD_{50}.

Chapter 7: Summary and Conclusion

7.1 Introduction

In order to avoid hazards the studies of process alternatives have to be carried out early in a design, for example at the conceptual stage when it is decided which product to make and by which operations. The aim of this research was to develop a method for assessing the inherent safety of a chemical plant which could be used in the early stages of plant design when the materials in process are known and their amount can be roughly estimated. This method is intended to predict the number of people that might be killed in case of a chemical accident involving a certain mass of specified chemical.

Historical accident data for 631 Fire, explosion and toxic release accidents has been collected from all over the world from 1911 to 2000. A number of statistical tests were conducted on this data in order to investigate the possibility of developing relationships predicting the number of fatalities caused by a chemical accident.

In order to determine the type of tests to be applied, the distribution of the mass of chemicals and the number of fatalities were examined. The results revealed that both variables in question are not normally distributed which suggests that parametric tests or tests that are used when the data is normally distributed are not applicable and so non parametric tests or tests that do not make assumptions about population distribution should be used. The following is a review of the different tests that were applied.

7.2 Statistical analysis

7.2.1 Spearman's rank correlation

The Spearman's rank correlation was calculated to examine whether any relationship exists between the number of fatalities and the mass of chemicals. Correlations were also sought between the number of fatalities and the mass of chemicals for the three different types of accidents: process, storage and transport.

The results showed that for all fire and explosion accidents, there is a positive significant correlation which suggests that the number of fatalities increases as the mass of chemicals increase but the low value of the correlation (r_S = 0.3) suggests that there are other important factors that may affect the consequence of a chemical accident.

Calculating the same correlation for the different type of accidents showed that the number of fatalities increases as the mass increase for the process accidents. However, as for all the fire and explosion accidents the low value of the correlation ($r_S = 0.3$) indicates that the relationship is not strong. It can be noticed that the correlation coefficient for all the accidents and for the process accidents are similar. Applying the same test to storage accidents resulted in positive but non significant correlation ($r_S = 0.343$). There was no correlation in the case of transport ($r_S = 0.037$).

The Spearman's rank correlation was applied to the fire and explosion accidents classified by location and time in order to investigate if the relationship between the number of fatalities and the mass of chemicals varies according to place and date. The accidents were classified as (US) which are accidents that happened in the United States of America and (EU) for the accidents that took place in Europe. The rest were the few accidents that happened in the Gulf countries, in some Far East countries and in some less developed countries. These were classified as (others). The results showed that there was no correlation for the US. The results also showed that in the case of both the EU and the less developed countries there were positive correlations and they were similar to the correlation that obtained from applying all the fire and explosion accidents ($r_s = 0.3$). However, even though the correlations are similar they were not significant in the cases of EU and less developed countries, this might be due to the small sample sizes.

The same tests as applied to the accidents by location were applied to the accidents classified by time. Accidents were divided into three periods as follows: from 1921 to 1950, which represents very old accidents when safety was less of a concern compared to nowadays; from 1951 to 1980, representing the appearance of hydrocarbons which resulted in great changes in the chemical, oil and petrochemical industries; and from 1981 to 2000 which represent recent accidents and showed decline in the number of fire and explosion accidents.

The results from the tests showed that correlating the mass of chemicals and the number of fatalities for the three mentioned periods of time did not result in significant correlations. Despite the high correlation coefficient in the period of 1911 to 1950 of (r_s = 0.72), the value of $p = 0.17$ suggests that no reliable relationship can be obtained from the two correlated variables. The scatter plots for the three periods of time showed that no clear relationships exist between the mass and the number of people killed.

7.2.2 Kruskal – Wallis and Mann – Whitney tests

In a trial to examine whether there are differences between the median number of fatalities in the three types of accidents: process, storage and transport, the Kruskal - Wallis test was made. The result from this test indicates that there is no statistical evidence for significant differences between the three types of accidents ($p = 0.131$). It should be pointed out that in this test only a portion of the data was involved, the accidents in which the mass of chemicals was available.

The same test was carried out to determine whether the median number of fatalities varies with the amounts of chemicals involved in the accidents. The results showed that there is statistical evidence that mass of chemicals does have an impact on the number of fatalities.

The Kruskal – Wallis test was applied to the accidents by location in order to determine whether place has an impact on the number of fatalities caused by a chemical accident. The result of this test showed that the location of accident is an important factor that affects the accident consequences.

The Mann – Whitney U test was conducted to assess whether there are differences in the median number of fatalities by type of chemicals. In this test chemicals were classified by risk phrases (R). Chemicals were divided into two groups. The first group consists of extremely flammable liquefied gas which is R13, and the second group contains combination of chemicals that are R10, R11 and R12 which represent flammable, highly flammable and extremely flammable chemicals respectively.

The results showed that there was no statistical evidence for any differences between the median number of fatalities in the two chemical groups. The box plots were also used to graphically represent the differences between the three types of accidents, the amount of chemicals and the chemical types.

7.3 Estimating the number of people killed by type of chemicals

In this section accidents were classified by chemical type in order to investigate whether specific chemicals pose more hazards to people than others and subsequently to estimate the number of fatalities per mass of those chemicals. The idea was to classify chemicals by phase. This analysis has been obstructed by the unavailability of the mass of chemicals for every accident, which prevented a large number of accidents from being used. However, quantities of chemicals involved were available for some groups of hydrocarbons namely: ethylene, LPG, propane/propylene, butane, and cyclohexane. It should be pointed out that in the previous analysis only part of the data was used, the accidents in which the mass of chemicals was known. A relationship between the number of fatalities and the ethylene mass was obtained which still needs more investigation to the circumstances of the accidents which resulted no fatalities to ensure its validity. No relationships were obtained from the other hydrocarbons.

7.4 Mean and median number of fatalities ranking index

As an alternative to estimating the number of fatalities per mass of chemicals, the mean and the median number of fatalities were calculated for the chemicals involved in the accidents. Unlike the previous analysis, this method did not involve the mass of chemicals which allowed the use of all the fire and explosion data. The results revealed that hydrocarbons were the most frequent chemicals involved in the accidents. The results allowed ranking the hydrocarbons by median number of fatalities as well as by type of accident. Hydrogen was the most hazardous chemical with a median number of fatalities of 4. Hydrogen was also found to have the highest energy ratio as shown in Table 5.30.

On the other hand, hydrocarbons were less hazardous than hydrogen as they gave a smaller median number of fatalities, ranging from 1 to 3. This also corresponded with the hydrocarbon energy ratio values that ranged from 9 to 11. In terms of type of accidents, transport accidents were found to be the most hazardous operations since they have the highest median number of fatalities. Even though, there was a big difference in the number of accidents between the process, storage and utilities operations, they all yielded the same level of hazard giving 2 as a median number of fatalities.

7.5 The mortality index (MI)

The Mortality Index represents another methodology for estimating the possible number of fatalities due to fire and explosion accidents. The MI is expressed in terms of mean fatalities per tonne for any given size of fire or explosion accident. In this method, 101 out of 512 fire and explosion accidents were analysed. A number of relationships between the MI and the mass of chemicals were obtained for all the fire and explosions and for the three types of accidents: process, storage and transport.

Comparing the predicted fatalities from applying the MI approach to the actual fatalities showed that there are sometimes large differences between the actual and the predicted fatalities. This could be due to not considering the variation of population density. However, the fit between the actual and the predicted fatalities for process and storage were reasonably acceptable while it was very poor in the case of transport.

7.5.1 Toxic accidents

119 toxic release accidents were reported among the historic data. A number of chemicals were found to be involved in the toxic accidents in different frequencies. However, ammonia and chlorine were found to be dominant in terms of both the frequency of occurrence and the number of fatalities caused. The mortality index was also used to assess the hazards posed by toxic chemicals. The mortality index values for few chemicals, the chemicals that Marshall has calculated, were used in conjunction with the

toxicity expressed by LD_{50} to derive a relationship that can be used to predict the potential fatalities caused by a toxic chemical. LD_{50} was used as it is a property that can be obtained in early design stages.

Although of the significance of the obtained relationship approved by the regression factor of ($R^2 = 0.76$), it should be pointed out that it is based on few chemicals in which data for MI were available. It will be inappropriate to base a model on few accidents. In addition, this relationship is still primary and needs validation. If more MI data is available, it might be possible to establish a more reliable relationship in which the potential number of fatalities for toxic chemicals can be estimated by knowing their LD_{50}.

7.6 Dust explosion index

The dust explosion phenomenon was studied in depth in chapter 4. The outcome of this research had suggested an "Index of Explosibility" (IE) which consists of two parameters, the dust Ignition Sensitivity (IS) or the dust ease of ignition and Explosion Severity (ES) of dusts. This index could be used to assess and possibly predict the dust explosion hazard as it based on properties of dusts which can be available in conceptual design stage. The index of explosibility needs more investigation and scores have to be assigned instead of rating in order to be added to Edwards and Lawrence (1993) index.

7.7 Conclusion

A number of statistical tests were made in different ways on historical accident data in order to derive a method that can be used to estimate the potential number of fatalities from a chemical accident. In conclusion the above analysis showed that the amount of materials does have an impact on the number of fatalities. The reason for the weak relationship between the number of fatalities and the amount of materials might be the non consistency of the data. For example, in many data cases the amount of material was not known. In addition, the number of people killed in lots of cases does not seem to bear any relation to the amount of material.

In other words, taking into consideration only the amount of material involved in the accidents might not be sufficient. Other factors such as the location of the accident (for example, in a densely populated city or in the middle of a desert) are important. Actually population density in the area surrounding the source of explosion is usually not uniform. So, two accidents with identical characteristics can cause different number of fatalities. The key point is the number of people present in the affected area just at the time of the accident. However, this is an unpredictable factor.

Another important factor is the country of operation. In fact, conducting the Kruskal-Wallis test on the accidents classified by countries showed that there are differences in the median number of fatalities between developed and less developed countries. More rigorous classification, by grouping countries that use the same regulations and same design standards, could produce more accurate results.

The time of the accident is also a factor because the consequences of an accident might be different if it happened during day or night, or if it happened during a weekday or at a weekend. If these information were available it would be possible to compare accidents which took place in similar circumstances (the same quantity, the same time, the same location, the same population density, etc..). These factors might generate basis for further analysis in which stronger relationships could be obtained.

Despite the differences between the theoretical and the historical data for the equations that have been obtained from applying the mortality index approach, it is believed that the mortality index could be an appropriate method to measure the inherent safety of a chemical plant. It assesses the hazards posed by the chemicals by quantifying their impact on people represented by the potential fatalities. It might be concluded that there are many reasons behind the weakness of the relationships. The first is that small incidents tend to be under-reported unless they involve fatalities which lead to high values for the mortality index for small incidents. The other reason is that the equations do not take account of the variation in population density.

It should be highlighted that the mortality index approach was used as an available method for quantifying hazards. The intention was to apply this method to the historic accident data to test its capability of measuring the inherent safety of chemical plants at the conceptual design stage. There was no intention to update or improve Marshall's work. However, if a new data set for chemical accidents were available the obtained relationships and Marshall's relationships could be compared.

It should also pointed out that there are some statistical analyses which can be used to predict the number of fatalities from historic data such as probit equations which are a familiar method in quantitative risk analysis. The use of probit equations was considered, but it was not possible because of the lack of getting information about the people who were exposed to risk at the time of the accidents. The other method that could be used for prediction is the logistic regression. The output from this method is dichotomous such as yes/no, pass/fail, and lived/died type, hence it cannot predict how many people will be killed in case of an accident. However, it allows prediction of whether there will be any fatalities or not.

7.8 Recommendations for future work

During data collection extensive efforts are required in order to integrate information from different data sources. A common problem of using various sources is duplication of accidents. This caused some accidents to appear to be different when in fact they were the same. The main reason for duplication is that the way of reporting accidents usually depends on the knowledge and the information available to the person reporting the event. For example, the name of the chemical involved in the accident can be reported by chemical name or trade name, or the chemical may have different names in different countries. In addition, spelling errors of addresses and chemical names and even the way of reporting the exact location and address can cause an accident to be repeated more than one time. An appropriate solution to this problem would be to establish a universal database for industrial accidents which unites the individual sources of information in one source and facilitates the researcher's task. It would also provide researchers with comprehensive accident data.

Another problem in estimating chemical hazards is the lack of an important piece of data, the quantity of the chemical involved in the accidents. It was the lack of this particular data that caused a lot of data to be unusable. Obtaining the quantity of chemicals would make it possible to estimate the potential number of fatalities per unit mass for all the chemicals which were involved in industrial accidents. It would be also possible to analyse accidents by phase and by process conditions. In this case it would be possible to obtain relationships between the number of people killed by certain phase. These relationships can then be used to estimate the potential number of fatalities for certain phases, for example gas, vapour, liquefied gas, liquefied vapour, and to find out whether the accident happened in process or in storage operations.

There are different types of data which represent the severity of an accident, such as number of fatalities and number of injuries. In this study the potential of chemical hazards was quantified as potential fatalities since it represents the extreme end of the spectrum of chemical hazards. However, the number of injuries can provide valuable information as an indicator of the potential hazards caused by a chemical accident. In fact, the number of injuries can represent a very important indicator of the severity of the accident. For example, the release accident which happened in Seveso, Italy, on 10th July 1976, was characterised by hundreds of cases of injury, but without fatalities. However, the Seveso accident led to the Seveso Directive, which has been the mainspring of much European legislation in the field of process safety.

It would be important to investigate other possible methods as a measure of potential chemical hazard in addition to the number of fatalities. Near-miss data are less likely to be a valuable measure for chemical hazards as they are not taken seriously due to no damage or hurt being incurred on the worker or in the process operations. However, near-misses provide valuable information on how to prevent incidents and the ability to predict possible consequences.

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Appendices

Table 1: All Fire and Explosion Accidents (1911 - 2000).

Date	Chemical	Type	Amount Released (Tonne)	Fatalities	Injuries	Location	Equipment
1911	-	Dust explosion		5	8	Glasgow, UK	-
1911	-	Dust explosion		37	100	Liverpool, UK	-
1911	-	Dust explosion		3	5	Manchester, UK	-
1912	Steam	Internal explosion		26	32	San Antonio, TX	Loco boiler
1913	-	Dust explosion		3	5	Manchester, UK	-
1915	Petrol	Fire		40		Ardmore, OK	Rail tank car
1919	Corn starch	Dust explosion		42		Cedar Rapids, IA	Starch plant
1921	Hydrogen	Explosion	6.9	1		Hull, UK	Airship
1924	Corn starch	Dust explosion		42		Peking, IL	Starch plant
1930	-	Dust explosion		11	32	Liverpool, UK	-
1932	LPG	-		0		Detroit, MI	Storage
1933	Town gas	Explosion		65	100+	Neunkirchen, Germany	Gas holder
1934	Town gas	Fire		42	46	Hongkong	Gas holder
1939	Butane	Vapour cloud explosion		0		Newark, NJ	-
1939	Crude oil	Internal explosion		0	1	Wichita Falls, TX	Pipeline
1941	-	Dust explosion		6	40	Liverpool, UK	-
1943	Butane	Vapour cloud fire	16.5	5	> 25	Los Angeles, Calif	-
1943	Butadiene	Vapour cloud explosion		57	37	Ludwigshafen, Germany	Rail tank car
1944	LNG	Fire & explosion	3000	128	300	Cleveland, OH	Storage tank
1944	LPG	Fire		10	45	Denison, Tex.	Tank
1944	Corn mill	Dust explosion		4	20	Kansas City, KS	Grain dust
1945	Butane	Vapour cloud explosion		0		Los Angeles, CA	Storage
1947	Acetic anhydride, etc.	Explosion		17	130	Los Angeles, CA	Electrolysis plant
1948	Dimethyl ether	Vapour cloud explosion	33	245	2500	Ludwigshafen, Germany	Rail tank car
1948	Butane	Fire		2		Sacramento, CA	Road tanker
1949	HCs	Fire		4	26	Perth, N. J	Storage tank
1949	Propane, butane	Vapour cloud explosion	1.6	5		Detroit, IL	Catalytic cracker (refinery)

1949	LPG	Fire		1		Winthrop, MO	Rail tank car
1950	Styrene, latex, butadiene	Explosion	1	0	0	Midland, MI	Reactor
1950	Propane	Vapour cloud fire		2		Wray, CO	Road tanker
1950	Propane, butane	Vapour cloud explosion		0	0	Georgia, USA	Storage tank
1951	Oil	Fire & explosion		2		Avonmouth, Bristol, UK	Storage tank
1951	C5 HCs	Vapour cloud explosion		2		Baton Rough, LA	Naphtha treating
1951	Propane	VCF, BLEVE		0	14	Pert Newark, NJ	Storage
1951	LPG	VEEB		14		St. Paul, MN	Storage tank
1951	Butadiene	Explosion		0	0	Ontario, Canada	butadiene separation equipment
1952	Resin dust	Dust explosion		5	21	Bound Brook, NJ	Phenolic resin plant
1952	LPG	Vapour cloud explosion		2		Kansas City, KS	Terminal LPG filling station
1953	Gasoline	Vapour cloud explosion		2		Campana, Argentina	Refinery recovery unit
1953	Organic peroxides	Explosion		11	27	Tonawanda, NY	Organic peroxides plant
1954	Kerosene	Fire		32	16	Bitburg, Germany	-
1954	LPG	Fire		4	0	California, USA	Storage tank
1954	Acrolein	Internal explosion	19	0		Institute, WV	Rail tank car, polymerization
1955	Ethylene	Vapour cloud explosion	1	0		Freeport, TX	Polyethylene plant
1955	-	BLEVE		?	2	Ludwigshafen, FRG	Rail tank car
1955	Grain dust	Dust explosion		3	13	Waynesboro, GA	Feed plant
1955	Naphtha	Explosion		2	30	Whiting. IN	Hydroformer
1955	Butane	Vapour cloud explosion		0		Wilmington, CA (sic)	Gasoline plant
1956	Oil	Fire ball		20	> 32	Amarillo, TX	Storage tank
1956	Butylene	Vapour cloud explosion	10	0		Baton Rouge, LA	Alkylation unit
1956	LPG	BLEVE		12	12	Cottage Grove, OR	Storage
1956	HCs	BLEVE		19	32	Dumas, TX	Storage vessel
1956	Ethylene	Vapour cloud explosion	2.5	0		North Tonawanda, NY	Polyethylene plant
1956	Steam	Internal explosion		2	9	Uskmouth, Wales	Turbogenerator
1957	Butane	BLEVE		1	0	Montreal, Quebec	Storage vessel
1957	LPG	Vapour cloud explosion		1		Sacramento, CA	Loading terminal
1958	Butane	Fire		1	4	Alma Michigan, USA	Storage tank
1958	Nitromethane	Explosion		?	200	Niagara Falls, N.Y.	Rail tank car

1958	Oil froth	Fire, BLEVE		2	34	Signal Hill, CA	Tank farm
1958	LPG	Vapour cloud explosion		1	16	Augusta, GA	Loading terminal
1958	LPG	Vapour cloud explosion		1		Ardmore, OK	Loading terminal
1958	-	Explosion		?		Celle, FRG	Rail tank car
1959	LPG	Vapour cloud explosion	18	23	78	Meldrin, GA	Rail tank car
1959	LPG	BLEVE		0	2	McKittrick, CA	Storage
1959	LPG	BLEVE		11	10	Deer Lake, PA	Rail tank car
1959	Gasoline	Fire		5		Kansas City, MO	-
1959	Lubricating and seal oil	Explosion		6	6	Phillipsburge, N.J.	compressor
1959	Ammonia	Explosion	-	11	40	Ube, Japan	Reactor
1960	Allyl dichloride, propylene chloride	Explosion		6	14	Freeport, Tex.	-
1960	benzene,mononitrobenzene,nitric acid, water	Detonation	6.6	15	60	Kingsport, TN	Nitrobenzene plant, *process*
1961	Cyclohexane	Vapour cloud explosion	18	1	5	Freeport, TX	Cyclohexane plant, valve failure
1961	Oxygen	Explosion		15		FRG	Air separation plant
1961	Butane	Vapour cloud explosion		2		Lake Charles, LA	Alkylation unit
1961	Vinyl chloride monomer	VEEB	-	4	10	Minimata, Japan	Reactor
1961	Acrylonitrile	Fire		6	5	Galveston, USA	marine tanker / collision
1962	Ethylene oxide	Internal explosion, VCE	16	1	19	Bradenburg, Kentucky	Reactor
1962	LPG	Vapour cloud explosion	14.3	10	75	Berlin, NY	Road tanker
1962	Propane	Fire	1.1	1	115	Ras Tanura, Saudi Arabia	Storage vessel
1962	Acrylic polymer reaction	Explosion		10	46	Toledo, OH	Reactor
1962	HCs	Vapour cloud explosion		0	0	Fawley, UK	Catalytic cracker
1962	P-Nitrodiphenlamine	Internal explosion		2	18	FRG	Reactor
1962	Gasoline	Vapour cloud explosion		2	2	Houston, TX	Tank farm
1962	Benzene	Explosion		1	3	Marietta, OH	benzene stripper column
1962	Grain dust	Dust explosion		2	34	St Louis, MO	Feed plant
1962	Organic peroxides	Explosion	20	4	4	Norwich, CT	Transport tank
1963	Ethylene	Vapour cloud explosion	0.9	0	7	Plaquemine, L.A	Ethylene plant
1963	Reaction mixture, including TCDD	Internal explosion		8	14	Amsterdam, Netherlands	Trichlorochenol plant
1963	Propylene	Internal explosion		?	0	Texas, U.S.A.	Ethylene plant
1963	Acetylene, diacetylene	Internal explosion		7	6	RRG	Acetylene plant

1963	Cumene hydroperoxide	Fire & explosion		4	9	-	Storage, decomposition
1964	Ethylene oxide	Internal explosion		4	20	Antwerp, Belgium	Reactor
1964	Vinyl chloride monomer	VEEB	68	7	40	Attleboro, MA	Reactor
1964	Oxygen	Internal explosion		?		FRG	Oxygen plant
1964	Acrylamide reaction mixture	Internal explosion		1	3	FRG	Reactor
1964	Propane	Vapour cloud explosion		0		Liberal, KS	Compressor station
1964	Ethylene	Vapour cloud explosion	0.2	2		Orange, TX	HP Polyethylene line
1964	-	Dust explosion		5	2	Paisley, UK	-
1964	PVC	Internal Explosion		7	27	Hebronville, MA	Polyvinyl chloride plant
1964	Ethylene	Explosion		2	34	Texas, U.S.A.	-
1965	Monovinyl acetylene	Internal explosion		12	60	Louisville, KY	Compressor
1965	Natural gas	Internal explosion		17	56	Natchitoches, LA	Pipeline
1965	Benzene	Vapour cloud explosion		?		Baltimore, MD	Detergents plant
1965	Ethyl chloride	Vapour cloud explosion	19.3	0	?	Baton Rouge, LA	Reactor
1965	Flour	Dust explosion		5	32	Bow, London, UK	Flour mill
1965	Hydrogen, carbon monoxide	Vapour cloud explosion	0.07	?		Escambia, USA	Chemical plant
1965	Ethyl chloride	Explosion		12		Houston, TX	Ethyl chloride plant
1965	Ethylene	Vapour cloud explosion		0		Lake Charles, LA	Ethylene plant
1965	Hydrogen, ammonia	Fire		2	3	Pasadena, TX	Ammonia plant
1965	Butane	Fire		?		Texas	Chemical plant
1965	Naphtha	Explosion		0	0	Whiting, IN	Reactor, separator
1965	Ammonia	Explosion	-	2	3	Pasadena, TX	Reactor
1966	Propane	BLEVE	200	18	6	Feyzin, France	Storage vessel
1966	NGL	Fire		7	20	Larose, LA	Pipeline
1966	Polystyrene	Explosion	32	11	10	LaSalle, Quebec	reactor
1966	Cumene, benzene & propane	Vapour cloud fire		?		Philadelphia, PA	Refinery
1966	Methane	Vapour cloud explosion	0.5	3	83	Raunheim, FRG	Ethylene unit
1966	Light HCs	Fire & Explosion		?	0	FRG	Storage vessel
1966	Butadiene	Vapour cloud explosion	0.45	3		Scotts Bluff, LA	Reactor
1966	Ethylene	Explosion	0.3	3	83	Germany	Compressor, pipework
1967	Vinyl chloride monomer	Fire	-	4	33	Antwerp, Belgium	-
1967	Propane	Fire		?	100	Buenos Aires, Argentina	-
1967	-	Explosion		2	16	Hawthorne, N. J.	-

1967	Isobutylene	Vapour cloud explosion	46	7	13	Lake Charles, LA	Pipeline
1967	Town gas	Internal explosion		?	300	Santos, Brazil	Gas holder
1967	Fuel oil	Fire		?		El Segundo, CA	Fuel oil reservoir
1967	Cyclohexane	Fire & explosion		4	0	-	Pipeline, storage tank
1968	Vinyl chloride monomer	Explosion	-	24		East Germany	-
1968	Acetic acid	Internal explosion		2	13	Hull, UK	-
1968	-	Internal explosion		?		Paris, France	Petrochemicals plant
1968	Light HCs (<C10)	Vapour cloud explosion	140	2	85	Pernis, Netherlands	Slop-oil tank, refinery
1968	Propane	Explosion		1	2	Tamytown, U.S.A.	Chemical plant
1968	LPG	Fire		5		Yutan, NE	Pipeline
1969	Dinitrochloraniline reaction mixture	Explosion		3	31	Basle, Switzerland	Reactor
1969	-	Explosion		6		Dudgeons Wharf, London UK	Tank dismantling
1969	Vinyl chloride monomer	Vapour cloud explosion	-	0	1	Glendora, MS	Rail tank car
1969	Propane	Vapour cloud explosion		4	3	Escombreras, Spain	Storage
1969	Hydrogen, naphtha	Vapour cloud explosion	23	0		Fawley, UK	Hydroformer
1969	Vinyl chloride monomer	Explosion	-	0	0	Flemington, NJ	Reactor
1969	Natural gas	Vapour cloud explosion		0	9	Houston, TX	Pipeline
1969	LPG	BLEVE	63	2	33	Laurel, Mississipi	Rail tank car
1969	Petroleum	Internal explosion		1	83	Long Beach, CA	Tank
1969	Naphtha	-		0		Rawley, England	-
1969	Light HCs	Fire		5	23	Puerto la Cruz, Venezuela	Crude unit
1969	LPG, propylene	Fire		0		Repesa, Spain	Refinery
1969	Carbone dioxide	Explosion		9	23	Repcelak, Hungary	-
1969	Butadiene	Internal explosion, VCE		3	13	Texas City, TX.	Butadiene recovery unit
1969	Cyclohexane	Vapour cloud explosion	3.6	2	23	Wilton, UK	Oxidation plant
1969	Ethylene	Internal explosion		4		Wilton, UK	Polyethylene plant
1970	Gas	Explosion		29	10	Agha Jari, Iran	Compressor station
1970	Oil	Fire		?		Beaumont, TX	-
1970	Olefins	Vapour cloud explosion		0		Big Springs, TX	Alkylation unit
1970	Oxygen	Fire		2	30	Brooklyn, NY	Road tanker
1970	Propane	BLEVE	75	?	66	Crescent City, IL	Rail tank car
1970	LPG	Fire		6		Hudson, OH	Road tanker

1970	Propane	Fire	4	2		Hull, UK	-
1970	Grain dust	Dust explosion		6	18	Kiel, FRG	Grain silo
1970	C10 HC	Vapour cloud explosion	114	0	40	Linden, N.J.	Refinery reactor
1970	LPG	Internal explosion		0		Mitcham, UK	-
1970	-	Explosion		7	42	Philadelphia, PA	Catalytic cracker
1970	Propane	Vapour cloud explosion	29	0	10	Port Hudson, MO USA	Pipeline
1970	Natural gas	Internal explosion		0	25	St. homas Island, Virgin Islands	-
1971	Butadiene	Explosion		8	21	Amsterdam, Netherlands	Refinery
1971	Ethylene	Vapour cloud explosion	3.6	0	21	Baton Rouge, LA	Rail tank car
1971	Formic acid, hydrogen peroxide	Fire & explosion		1	many	Emmerich, FRG	Oxidation plant
1971	Vinyl Chloride monomer	BLEVE	165	1	50	Houston, TX	Rail tank car
1971	Butadiene	Vapour cloud explosion	12	1	6	Houston, TX	Butadiene plant
1971	Trichlorethylene, perchlorethylene	Vapour cloud fire		4	3	Lake Charles, LA	Chemical plant
1971	Ethylene	Vapour cloud explosion	0.45	4	60	Longview, TX	Polyethylene plant
1971	Ethylene oxide, oxygen	Internal explosion		?	4	Morris, IL	Ethylene oxide plant
1971	Petroleum	Fire & explosion		7		Raunheim, FRG	Tankship
1971	Ethylene	Vapour cloud explosion	1	3	6	Texas, USA	reactor
1972	Butane	Vapour cloud fire		1	4	Billings, MT	Alkylation unit
1972	Propylene	Vapour cloud explosion	53.5	1	230	East St. Louis, IL	Rail tank car
1972	Crude oil	Fire		1	2	Hearne, TX	Pipeline
1972	Propane	Fire ball	9	2	5	Lynchburge, VA	Road tanker
1972	Hydrogen	Internal explosion		4	40	Netherlands	-
1972	Propane	Fire		2	28	NJ Turnpike, N.J.	Road tanker
1972	Butane	Explosion		37	53+	Rio de Janeiro, Brazil	Storage vessel
1972	-	Fire		2	21	Tewksbury, MA	Storage tank
1972	Crude oil	Fire		0		Trieste, Italy	Terminal
1972	Coke	Explosion		10	10	Weirton, WV	Coke plant
1973	LNG	Fire	70	8	21	Austin, Tx.	Pipeline
1973	Vinyl Chloride monomer	Explosion	-	4	2	Cologne, FRG.	Polyvinyl chloride plant
1973	Ethylene oxide	Vapour cloud fire		?	29	Freeport, TX	Tank
1973	Cumene	Fire (decomposition)		0	0	Gladbeck, FRG	Pipe to cumene reactor
1973	Hexane, propylene	Explosion	4	4		Goi, Japan	reactor

1973	Propane	BLEVE	45	13	95	Kingman, AZ	Rail tank car
1973	Methanol	Vapour cloud fire		7		Lodi, NJ	Reactor
1973	Vinyl Chloride monomer	Vapour cloud explosion	4.2	1	16	Noatsu, Japan	Vinyl chloride plant
1973	Town gas	Explosion		4	24	Sheffield, UK	Gas works
1973	Propane	Vapour cloud explosion	19	9	37	St-Amand-les-Eaux, France	Road tanker
1973	Hydrogen, HCs	Fire		0?		St Croix, Virgin Islands	Hydrodesulphurizer
1973	Vinyl Chloride monomer	Vapour cloud explosion	-	1	23	Shinetsu, Japan	Chemical plant
1973	LNG	Fire		40	3	Staten Island, NY	Storage tank
1973	Ethylene	Vapour cloud explosion		1	4	Tokuyama, Japan	Ethylene plant reactor
1973	Propylene	Fire & explosion	-	1	4	Chiba Area, Japa	Polypropylene plant
1973	Distillate	Explosion	0.61	3	29	Sheffield, UK	Tank
1973	Natural gas	Explosion		3	2	West Virginia, USA	Pipeline
1973	Natural gas	Fire		3	1	Maryland, USA	Pipeline
1973	Natural gas	Explosion		6	2	Texas, USA	pump station pipeline
1974	Cumene/cumene hydroperoxide	Fire		0	0	UK	reactor
1974	Butane	Fire ball	2	0		Aberdeen, U. K.	Road tanker
1974	Vinyl Chloride monomer	Vapour cloud fire	-	0		Barcelona, Spain	Chemical plant
1974	Gas	Fire		0	-	Bealeton, VA	Pipeline
1974	Isoprene(>C5 HC)	Vapour cloud explosion	7.6	2	10	Beaumont, TX	Isoprene plant
1974	Vinyl Chloride monomer	Vapour cloud explosion	110	7		Climax, TX	Rail tank car
1974	Vinyl Chloride monomer	Vapour cloud explosion	-	0	3	Cologne, FRG.	Vinyl chloride plant, separator
1974	Isobutane	Vapour cloud explosion	69	7	152	Decatur, IL	Rail tank car
1974	Ethylene	Vapour cloud explosion	1.8	0		Fawley, UK	Polyethylene plant
1974	Cyclohexane	Vapour cloud explosion	25	28	104	Flixborough, UK	Caprolactam plant (nylon)
1974	Propane	Fire		0		Griffith, IN	Cavern storage
1974	Propane	Vapour cloud explosion		0		Holly Hill, FL	Road tanker
1974	Butadiene	Vapour cloud explosion	75	1	235	Houston, TX	Rail tank car
1974	Organic peroxides	Explosion		0		Los Angeles, CA	Loading terminal
1974	Natural gas	Fire		5	0	Mississipi, USA	Pipeline

1974	Natural gas	Fire		3	0	Farmington, New Mexico	Pipeline, in the desert
1974	Natural gas	Fire & explosion		0		Munroe, LA	Pipeline
1974	LPG	BLEVE		0	0	USA	Rail tank car
1974	Butane	Vapour cloud explosion	2190	0	24	Petal, Mississippi USA	storage
1974	Propylene	Vapour cloud fire	-	?	0	Plaquemine, LA	Cracking plant
1974	HCs	Fire		?		Rotterdam, Netherlands	Petrochemicals plant
1974	Ethylene	Vapour cloud explosion		100		Pitesti, Roumania	Ethylene plant
1974	Pentanes	Vapour cloud explosion		2		Texas	Chemical plant
1974	Monomethylamine nitrate	Explosion		2	66	Wenatchee, WA	Rail tank car
1974	LPG	BLEVE	10	4	6	West St Paul, MN	Storage vessel
1974	Ethylene	Vapour cloud explosion		14	79	Zaluzi, Czechslovakia	Ethylene plant
1975	Ethylene	Vapour cloud explosion	2.5	6	13	Antwerp, Belgium	Polyethylene plant
1975	Oil	Fire		?		Avon, CA	Refinery
1975	Propylene	Vapour cloud explosion	5.5	14	107	Beek, Netherlands	Naphtha cracker column
1975	Hydrogen, naphtha	Vapour cloud explosion		0		Cologne, FRG.	Cyclic hydroformer
1975	Ethylene	Vapour cloud fire		1	4	Deer Park, TX	Polyethylene plant
1975	LPG	BLEVE		0	3	Des Moines, IA	Rail tank car
1975	LPG	Fire		4		Devers, TX	Pipeline
1975	LPG	Fire ball	18.2	17	34	Eagle Pass, TX	Road tanker
1975	Hydrogen, oxygen	Explosion		1	3	Ilford, UK	Electrolysis plant
1975	Crude oil	Fire		0		Lima, OH	Terminal
1975	Oil, phenol	Fire		?		Marcus Hook, PA	Oil tanker, tankship
1975	Crude oil	Explosion (VCF)		8	20	Philadelphia, PA	Tank farm
1975	Gasoline	Vapour cloud explosion	37.5	2		Rosendaal, Netherlands	Line leak
1975	-	Fire		?		Seattle, WA	Road tanker
1975	Methane	Fire	-	7	7	South Africa	-
1975	Hydrogen	Vapour cloud explosion	0.3	0		Watson, CA	Crack in tank
1975	NGL	Explosion		4	0	Texas, USA	Pipeline
1976	NGL	Vapour cloud explosion		1	4	Texas, USA	Pipeline
1976	LPG	BLEVE	80	2	22	Belt, Mt	Rail tank car
1976	Ethyl benzene	Explosion		13	2	Chalmette, LA	Refinery
1976	Petrol	Fire ball		4	28	Gadsden, AL	Tank farm

1976	Ethylene oxide	Internal explosion		?	56	Geismar, LA	Reactor
1976	Feed additivereaction mixture	Internal explosion		1		Kings Lynn	Reactor
1976	Isobutane	Vapour cloud explosion	13	7		Lake Charles, La	Refinery
1976	Ethylene	Vapour cloud explosion		1		Longview, Tex.	failure of mixing nozzle
1976	Gasoline	Fire		6	35	Los Angeles, CA	Pipeline
1976	Crude oil	Explosion		0		Los Angeles, CA	Terminal
1976	Pentanes	Vapour cloud fire		1		Puerto Rico	Storage
1976	Oil	Internal explosion		?		Plaquemine, LA	Surge tank
1976	Flammable liquid	Explosion		6		Sandefjord, Norway	-
1976	Trichlorphenol reaction mixture, including TCDD	Internal explosion	0.002	0		Seveso	Reactor
1976	Ethylene	Vapour cloud fire		1	15	Texas	Pipeline
1976	Petrol	Explosion		0	3	Westoning, UK	Road tanker
1976	Propylene	Fire	18	2	0	New Jersey	-
1977	Acrylonitrile	Explosion	400	0	0	Antwerp, Belgium	Storage tank
1977	Crude oil	Fire		0		Abqaiq, Saudi Arabia	Pipeline
1977	Fuel gas	Vapour cloud fire		?		Abqaiq, Saudi Arabia	NGL plant
1977	Oil	Explosion		?		Baton Rouge, LA	Preheat furnace
1977	Gasoline	Vapour cloud explosion	300	3		Baytown, TX	Tanker
1977	Gasoline	Fire		7	6	Beattyville, KY	Road tanker
1977	Sodium chlorate	Explosion	68	0	13	Braehead, Renfrew, UK	Warehouse
1977	Light HCs	Vapour cloud explosion		3	22	Brindisi, Italy	Ethylene plant
1977	LPG	Internal explosion		1	9	Cassino, Italy	-
1977	Isobutane	Vapour cloud explosion	68.2	0	1	Dallas, TX.	Rail tank car
1977	Crude oil	Fire		1		Fairbanks, Alaska	Pipeline
1977	Grain dust	Dust explosion		18	22	Galveston, TX.	Grain silo
1977	Ethylene oxide	Explosion		1	25	Gela, Italy	-
1977	LPG	Fire ball	70	2	9	Goldonna, LA	Rail tank car
1977	Hydrogen	Internal explosion		5	35	India	-
1977	LPG	Fire		0	0	Jacksonville, USA	storage
1977	Vinyl Chloride monomer	-	-	0	90	Mexico	-
1977	Propane	Vapour cloud explosion		4		Port Arthur, TX	Stabilizer unit
1977	-	Vapour cloud fire		?		Puebla, Mexico	-

1977	Gasoline	Fire		0		Romeoville, IL	Tank farm
1977	Propane	Vapour cloud fire		2		Ruff Creek, PA	Pipeline
1977	Vinyl Chloride monomer	Fire	-	6	10	Taiwan	-
1977	LPG	Fire	23,000	7	87	Umm Said, Qatar	LPG storage tank
1977	Grain dust	Dust explosion		36	10	Westwego, LA	Grain silo
1977	Natural gas	Fire & explosion		2	0	Kansas, USA	Pipeline
1977	Natural gas	Fire & explosion		2	23	Pennsylvania, USA	Pipeline, residential area
1977	Propane	BLEVE		1	9	Cassino, Italy	Gas tank
1978	LPG	Fire & Explosion	20.5	4	0	Abqaiq, Saudi Arabia	Gas pipeline
1978	LPG	Explosion		0		Conway, KS	Pumping station
1978	Propane	Vapour cloud explosion		3		Denver, CO	Cat polymerization unit
1978	LPG	Fire ball	435	3	2	Donnellson, IA	Pipeline
1978	Hydrogen	Vapour cloud explosion	0.25	0		Immingham, UK	heat reboiler
1978	Vinyl Chloride monomer	Fire ball	110	0	2	Lewisville, AR	Rail tank car
1978	Propylene	Fire	-	12		Mexico city, Mexico	Road tanker
1978	Gasoline	Fire & explosion		7		Oviedo Province, Spain	Rail tank car
1978	Propane	Vapour cloud explosion		0		Pitesti, Roumania	Gas concentration unit
1978	Natural gas	Vapour cloud explosion		40		Poblado Tres, Mexico	Pipeline
1978	Propylene	Vapour cloud fire	23.5	216	200	San Carlos, Spain	Road tanker
1978	LPG	BLEVE		7	10	Texas City, TX.	Storage vessel
1978	Butane	Explosion		12		Tula, Mexico	Road tanker
1978	Propane	BLEVE		16	43	Waverly, TN	Rail tank car
1978	Butane	Vapour cloud fire	36.4	100	220	Xilatopic, Mexico	Road tanker
1978	Butane	Explosion		6	14	Galveston Bay Texas, USA	Storage tank
1978	Natural gas	Explosion		7	19	Pennsylvania, USA	Pipeline
1978	Natural gas	Fire & explosion		6	41	Texas, USA	Pipeline
1978	Natural gas	Fire & explosion		2	2	Sayda, East Germany	Compression satation of pipeline
1979	Crude oil	Explosion	95,000	52		Istanbul, Turkey	Oil tanker
1979	Flour	Dust explosion		14	17	Bremen, FRG	Flour mill
1979	LNG	VEEB		1	1	Cove Point, MD	Pipeline
1979	Distillate	Explosion		?		Deer Park, TX	Tankship
1979	Crude oil	Explosion		32		Galveston Bay, TX	Oil tanker

1979	Oil	Fire		?		Geelong, Australia	Crude unit
1979	Butane	Fire ball		12	25	Good Hope, LA	Tank barge
1979	Grain dust	Dust explosion		?	2	Hamburge, FRG	Grain silo
1979	Grain dust	Dust explosion		7		Lerida, Spain	Grain silo
1979	LPG	Vapour cloud fire		0		Linden, NJ	Catalytic cracker
1979	LPG	Explosion		1	1	Orange, TX	Pipeline
1979	Chemicals	BLEVE		?	8	Paxton, TX	Rail tank car
1979	LNG	Vapour cloud fire		?		Pierre Port, LA	Pipeline
1979	LNG	Explosion		1	0	Maryland, USA	Pipeline
1979	HCs	Internal explosion		?		Ponce, Puerto Rico	Dimerizer vessel
1979	Crude oil	Explosion		0		Port Neches, TX	Oil tanker
1979	Reaction mixture	Internal explosion		?		Sauget, IL	Reactor
1979	Propane	Vapour cloud explosion	3.1	0		Texas City, TX.	Alkylation unit
1979	C3-C4 HCs	Vapour cloud explosion		?		Torrance, CA	Catalytic cracker
1979	Propane	Vapour cloud explosion		?		Ypsilanti, MI	Storage
1979	Crude oil	Fire	40,000	50		Banter Bay, Eire	Crude tanker
1979	Cumene	Fire		4	0	Italy	Cumene plant
1980	Sodium chlorate	Fire & explosion		?		Barking, UK	Warehouse
1980	Petrolum products	Explosion		1		Bayamon, Puerto Rico	Pipeline
1980	Light HCs	Vapour cloud explosion		0	41	Borger, TX	Alkylation unit
1980	Natural gas	Explosion		0		Brooks, Alberta	Compressor station
1980	HCs	Fire		?		Corpus Christi, TX	Hydrocracker
1980	-	Fire		?		Deer Park, TX	Phenolacetone plant
1980	Propane	Vapour cloud explosion	0.11	0		Enschede, Netherlands	propane tank
1980	Gasoline	Fire		7	6	Kenner, LA	Road tanker
1980	LPG	Fire & explosion		0	3	Longport, UK	Warehouse
1980	Gasoline	BLEVE		2	2	Los Angeles, CA	Road tanker
1980	Vinyl Chloride monomer	Fire	-	0	4	Muldraugh, KY	Rail tank car
1980	Grain dust	Dust explosion		?	8	Naples, Italy	Grain silo
1980	Hexane	Vapour cloud explosion	12.7	5	25	New castle, DE	Blow-out of plug valve
1980	Natural gas	Fire		0		New Orleans, LA	Pipeline
1980	Propane	Explosion		51		Ortuella, Spain	Storage vessel
1980	Crude oil	-		0		Rotterdam, Netherlands	Oil tanker

1980	Reaction mixture	Detonation		?		Seadrift, TX	Ethylene oxide reactor
1980	Oil	Explosion		?		Sydney, Australia	Refinery furnace
1981	Tank contents	VEEB		?		Chicago Heights, IL	Reactor weight tank
1981	Syngas	Vapour cloud explosion	12	6		Czechoslovakia	Ammonia plant
1981	Propane	Vapour cloud explosion	15	1	2	Gothenburge, Sweden	Pipeline
1981	Herbicide reaction mixture	Internal explosion		?		Greens Bavou, TX	Reactor
1981	LPG	Explosion		18	35	San Rafael, Venezuela	Pipeline
1981	Oil	Fire		1	1	Shuaiba, Kuwait	Tank farm
1981	Hexane	Explosion		?		Stalybridge, UK	Solvent recovery unit
1981	Cumene hydroperoxide	Fire & explosion		0	0	Taiwan	reactor
1982	Acrylonitrile	Fire & explosion		3	0	Mexico	process column
1982	Gasoline	Fire		7		Valdecott Tunnel, Oakland, CA	Road tanker
1982	Oil froth	Fire		150	> 500	Caracas, Venezuela	Storage tank
1982	Ethylene	Explosion	2.9	0	6	Edmonton, Alberta Canada	Compressor
1982	Propane	Explosion		5	30	Florence, Italy	Road tanker
1982	Hydrogen	Fire		0		Fort McMurray, Alaska USA	Compressor
1982	Oil	Fire		?		Freeport, TX	Transformer
1982	Natural gas	Explosion		5	0	Hudson, Iowa, USA	Pipeline
1982	HCs	Fire		?		Kashima, Japan	Desulphurization
1982	Cumene hydroperoxide	Fire & explosion		0	18	Philadelphia, PA	Phenol plant (boiler)
1982	Natural gas	Vapour cloud fire		0		Pine Bluff, AR	Pipeline
1982	Natural gas	Fire & explosion		6	0	Portales, NM, USA	Pipeline
1982	Sodium chlorate	Explosion	11	?	60	Salford, UK	Warehouse
1983	Recycle slurry	Fire		?		Avon, CA	Catalytic cracker
1983	Vinyl Chloride monomer	Fire	-	0		Baton Rouge, LA	Rail tank car
1983	Natural gas	VEEB		0	2	Bloomfield, NM	Compressor station
1983	LNG	Internal explosion		?		Bontang, India	LNG plant
1983	Kerosene	Explosion		47		Dhurabar, India	Rail tank car
1983	light Crude oil	Fire	25000	0	20	Milford Haven, UK	Storage tank
1983	Polyethylene	Fire		?		Port Arthur, TX	Polyethylene bead plant

1983	Acrylonitrile/methyle isoketone/ethyle acetate	Explosion		0	0	North Carolina, USA	reactor
1983	Gasoline	Vapour cloud explosion		1		Port Newark, NJ	Storage tank
1983	NGL	Fire		?		Prudhoe Bay, AK	NGL surge drum
1983	LPG	Fire & Explosion		6		West Odessa, TX	Pipeline
1983	HCs	Vapour cloud fire		?		Basile, LA	Gas plant
1983	Methane	Fire	-	1	2	Awali, Bahrain	Hydrogen desulphurising unit
1983	Natural gas	Fire & explosion		1	0	Virginia, USA	Pipeline
1983	Natural gas	Fire & explosion		13	32	Off Ivory Coast, West Africa	Pipeline
1983	Cumene hydroperoxide	Explosion		2	5	USA	transfer pump
1984	Methane	Explosion	-	16	28	Abbeystead, UK	Valve house
1984	Gasoline	Fire & Explosion		508	221	Cubatao, Brazil	Pipeline
1984	HCs	Vapour cloud fire		?		Fort McMurray, Alberta	Coking unit
1984	LNG	Explosion		60	11	Ghari Dhoda, Pakistan	Pipeline
1984	HCs	Explosion		0		Kerala, India	Cooling tower
1984	Oil	Fire		?		Las Piedras, Venezuela	Hydrodesulphurizer
1984	LPG	Vapour cloud fire	6000	650	6400	Mexico city, Mexico	Storage
1984	Natural gas	Fire & explosion		5	7	Phoenix, Arizona, USA	Pipeline in a building
1984	Propane	Explosion		15	76	Romeville, IL	Absorption column
1984	Hydrogen	Vapour cloud explosion	0.03	2		Sarnia, Ont.	Benzene plant
1984	Natural gas	Fire & explosion		9	41	Acachapan, Mexico	Pipeline, valve failure
1985	Styrene-butadiene, acrylonitrile	Fire & explosion		5	0	Arezona, USA	Pipeline, crack
1985	Naphtha	Fire & explosion		18	56	Algerais, Spain	-
1985	Natural gas	Fire		5	3	Beaumont, KY	Pipeline
1985	Syngas	VEEB		6		Clinton, IA	Ammonia plant
1985	Ethylene	Vapour cloud explosion	4.1	?		Cologne, FRG	Ethylene plant
1985	NGL	Vapour cloud explosion	4900 m^3	?		Edmonton, Alberta	Pipeline
1985	Naphtha	Explosion		7	12	Illinois, USA	-
1985	Aviation fuel	Explosion		1	6	Kaycee, WY	Pipeline
1985	Propane	Vapour cloud explosion		0		Lake Charles, LA	Reforming unit
1985	Ethane, propane	Vapour cloud explosion		0		Mont Belvieu	Salt dome storage
1985	Propane	Fire		4	13	Mont Belyieu, TX	-

1985	Gasoline, fuel oil	Fire		?		Naples, Italy	Terminal (tank overfilling)
1985	Acrylonitrile	Explosion		0	0	UK	Reactor
1985	HCs	Fire		23	11	Priola, Italy	Ethylene plant
1985	Natural gas	Fire & explosion		0		Sharpsville, PA	Pipeline
1985	HCs	internal explosion, VCE		?		Tioga, ND	Gas processing plant
1985	Propane	Vapour cloud fire		0	6	Wood River, IL	Deasphalting-dewaxing unit
1985	Methane	Explosion	-	1	2	Westfield, Fife, UK	Gas processing plant
1986	Hydrogen	Explosion		7	119	Kennedy Space center, FL USA	-
1986	Natural gas	Fire		3		Lancaster, KY	Pipeline
1986	Aniline	Explosion		3	76	Pascagoula, MS	Distillation column
1986	Pesticides, etc.	Fire, pollution	1200	0		Schweizerhalle, Basel, Switzerland	Warehouse
1986	Oil	Fire		?		Thessalonika, Greece	Oil terminal
1986	LNG	Fire & explosion		2	3	Edmonton, Canada	Pipeline
1987	Ethylene oxide	Explosion		5	20	Antwerp, Belgium	Distillation column
1987	Acrylonitrile, sulphuric acid, isopropyl alchol	Explosion		1	24	Bath, Pennsylvania USA	Reaction vessel
1987	HCs	Fire & explosion	-	1		Alberta	Oil refinery Oilwell site Progress
1987	Hydrogen	Fire		67	21	Grangemouth, UK	Separator vessel
1987	Gasoline	Fire		5		Lanzhhou, China	Rail tank car
1987	HCs	Fire & explosion		15	21	Louisiana, TX	-
1987	Hydrogen, HCs	Fire		0		Mississauga, Ont., Canada	Hydrotreater
1987	Acetic acid	Vapour cloud explosion		3	43	Pampa, TX	Acetic acid plant
1987	Hydrogen	Explosion		167	55	Piper Alpha	Drilling platform
1987	Oil	Fire		2	8	Port Herriot, France	Storage
1987	Propane	Vapour cloud explosion	300 m^3	0		Ras Tanura, Saudi Arabia	Gas plant
1987	HCs	Fire		?		Torrance, CA	Aklylation
1987	Acrylonitrile	Explosion		0	11	Kaohsiung, Taiwan	Polymerisation in column

1987	LPG	release/BLEVE	20	1	23	Queensland, Australia	Rail tanker
1988	Ethylene	Vapour cloud explosion		0		Beek, Netherlands	Polyethylene plant, reactor
1988	Acrylonitrile	Fire & explosion		0	0	Houston, USA	Holding tank
1988	Acrylonitrile	Fire		1	7	-	Acrylonitrile plant
1988	Naphtha	Fire		25	23	Maharastra, India	-
1988	Crude oil	Fire & explosion		12	80	Mexico city, Mexico	Pipeline
1988	Cyclohexane	Explosion	5	0	0	Melbourne, Australia	Terminal, unloading
1988	Propane	Vapour cloud explosion	9	7	48	Louisiana, USA	fluid catalytic cracking
1988	Propane	Fire		0		Port Arthur, TX	Storage tank (pipe failure)
1988	Naphtha	Fire		0		Pulau Merlimau, Singapore	Storage tank (mechanical failure)
1988	Ethylene dichloride, vinyl Chloride	Vapour cloud explosion	55	7	13	Rafnes, Norway	VC plant
1988	Propane	Explosion		6	6	Tennessee, USA	road tanker
1989	Ethylene oxide	Explosion		32	11	Antwerp, Belgium	Distillation column
1989	Natural gas	Explosion		2	24	Baker, Gulf of Mexico	-
1989	Ethane, propane	Vapour cloud explosion		4	12	Baton Rouge, LA	Refinery (pipeline)
1989	Ammonia	Fire & explosion	7000	7	55	Jonova, Lithuania	Ammonia storage
1989	Propane	Vapour cloud explosion		4		Minnebeavo, USSR	Gasoline plant
1989	Hydrogen, HCs	Fire or explosion		0		Martinez, CA	Hydrotreater
1989	Propylene	Vapour cloud fire	-	0	0	Morris, Illinios, USA	Distillation column
1989	LPG	Fire & explosion		462	290	Nizhnevartovsk, Russia	Pipeline
1989	Isobutane	Vapour cloud explosion	37.8	23	314	Pasadena, TX	Polyethylene plant
1989	Ethylene	Explosion		23	130	Phillips, USA	-
1989	Hydrogen	Fire		7		Richmond, CA	Refinery, hydrocraker
1989	Gasoline	Fire		2	3	San Bernadino, CA	Pipeline
1989	Acrylonitrilr-Butadiene -Styrene	Fire & explosion		13	23	South Korea	ABS compounding unit
1989	NGL	Vapour cloud explosion		645	500	Ufa, USSR	Pipeline
1989	Reaction mixture	Internal explosion		?		Urdingen, Germany	Paint plant
1989	Carbone dioxide	Explosion		3	25	Worms, Germany	-
1990	LPG	Vapour cloud fire	5.6	63	100	Bangkok, Thailand	Road tanker

1990	Gasoline	Explosion		1		Bay City, TX	Tankship
1990	HCs	Vapour cloud explosion		0		Chalmette, LA	Hydrocracker
1990	Hydrogen	Explosion		15	26	Czechoslovakia	-
1990	Waste oil	Explosion		5	13	Channelview, TX	Wastewater storage tank
1990	Xylene, solvent	VEEB		?		Cincinnati, OH	Acrylic resins plant
1990	Aviation fuel	Fire		?		Denver, CO	Storage
1990	Ethane, propane	Vapour cloud explosion		31		Nagothane, Bombay India	Ethylene, plant
1990	Propane	Fire and explosion	18	6		Candanos, Spain	Road tanker
1990	Propane	Vapour cloud fire		2	7	North Blenheim, NY	Pipeline
1990	Propane	Vapour cloud explosion		14	76	Porto de Leixhos Portugal	Deasphalting unit
1990	HCs	Fire		?		Ras Tanura, Saudi Arabia	Refinery
1990	HCs	Fire		3		Rio de Janeiro, Brazil	Boiler
1990	2-4 dichloronitrobenzene	Internal explosion		1	5	Stanlow, UK	Reactor
1990	Acrylonitril, sodium hydroxide	Explosion		0	2	Lima, USA	process equipment
1990	HCs	Fire & explosion		35	10	Thane, India	-
1990	Gas	Vapour cloud explosion		?	-	Tomsk, USSR	Ethylene plant
1990	LPG	Fire & explosion		0		Warren, PA	FCC, refinery
1990	Butadiene	Fire & explosion		0	0	South korea	Storage tanks
1991	Reaction mixture	Internal explosion		9		Charleston, SC	Reactor
1991	-	Explosion		?		Coatzacoala, Mexico	Chlorine plant
1991	Acrylonitrile	Internal explosion		0		Coode Island, Australia	Storage tank
1991	-	Explosion		?		Dhaka, Bangladesh	Stripping column
1991	Butadiene	Vapour cloud explosion		?		Kensington, GA	Synthetic rubber
1991	Propane	Vapour cloud explosion		3		Pajaritos, Mexico	Vinyl chloride plant
1991	Ethylene oxide	Vapour cloud explosion		1		Seadrift, TX	Ethylene oxide plant
1991	-	Explosion		8		Sterlington, LA	Nitroparaffin unit
1991	HCs	Explosion		?		Sweeny, TX	Reactor
1992	Ammonia	Fire & explosion		90	403	Dakar, Senegal	Storage tank, loading
1992	Ammonia	Explosion		11	9	Haryana, India	Pipeline
1992	Hydrogen	Vapour cloud explosion		10	7	Sodegaura, Japan	Refinery
1992	Propane, butane	Explosion	10	6	12	Marseilles, France	catalytic cracker
1993	LPG	-		3		Madas, India	-

1993	Ammonia	Explosion & toxic release		3	25	Panipat, India	-
1993	Naphtha	-		18		Thane, India	-
1994	Styrene, ethylene dibromide	Explosion	328	3	0	Belpre, Ohio	reaction vessel
1994	cyclohexane, buradiene	-	127	0		-	-
1994	Aviation fuel	Fire		410		Dronka, Egypt	Fuel storage
1995	Natural gas	Fire		0		Gujrat, India	-
1995	Gas	Fire		12	-	Ukhta, Russia	Gas pipeline
1996	HCs	Fire		2	45	Bombay, India	-
1997	LPG	Fire		3	4	Chennai, India	-
1997	Molten metal	Explosion		2	5	Chennai, India	-
1997	LPG	Fire		14	11	Kaoshiung, Taiwan	-
1997	HCs	Explosion		3	11	Gujrat, India	-
1997	LPG	Fire & explosion		60	30	Visag, India	-
1997	Phenolic resins	Explosion (runaway reaction)		1	4	Columbia, Ohio	Resins production unit
1998	LPG	Fire & explosion		4	43	Kaoshiung, Taiwan	-
1998	LNG	Fire	10	2		Longford, Victoria, Australia	-
1999	Oil	Fire		4	1	Avon, CA	Refinery, piping of fractionator tower
1999	Hydroxylamine	Explosion (decomposed)		5	13	Pennsylvania, USA	Process vessel
2000	Styrene, cyclohexane, butadiene	Fire & explosion		1	71	Pasadena, USA	Chemical plant
2000	Hydroxylamine	Explosion (decomposed)		4	25	Nissin chemical, japan	Chemical plant
tot. 512				tot. = 6663			

Table 2: Toxic Release Accidents

Date	Chemical	Type	Amount Released (Tonne)	Fatalities	Injuries	Location	Equipment
1914	chlorine	Toxic release	7	0		Chrome, N. J.	Rail tank car
1917	chlorine	Toxic release	17	1		Wyandotte, MI	Storage tank
1920	chlorine	Toxic release	0.066	3		Niagara Falls, N. Y.	Cylinder
1925	chlorine	Toxic release	0.066	2		De Noya, Oklahoma	Cylinder
1926	chlorine	Toxic release	25	19		St. Auban, France	Storage tank
1928	chlorine	Toxic release	2	0		Asbokan, N.Y.	Rail tank car
1928	Phosgen	Toxic release	10	10	200	Hamburge, Germany	Storage tank
1929	chlorine	Toxic release	22.5	1		Syracuse, N. Y.	Storage tank
1930	HF	Toxic release	-	63		Luttich, Belgium	Fuel plant
1934	chlorine	Toxic release	14.5	1		Niagara Falls, N.Y.	Rail tank car
1935	chlorine	Toxic release	27.5	0		Griffith, Ind.	Rail tank car
1936	chlorine	Toxic release	3	1		Johnsonburg, Pa.	Rail tank car
1939	chlorine	Toxic release	25	60		Zarnesti, Roumania	Storage tank
1940	chlorine	Toxic release	8	3		Mjodalen, Norway	Rail tank car
1944	chlorine	Toxic release	0.045	0	208	Brooklyn, NY	Cylinder
1947	chlorine	Toxic release	30	19		Rauma, Finland	Storage tank
1947	chlorine	Toxic release	16.3	0	0	Chicago, IL	Rail tank car
1947	chlorine	Toxic release	0.066	2	0	Natrium, West Va.	Cylinder
1949	chlorine	Toxic release	5	0		Freeport, Tex.	Pipeline
1949	TCDD	Toxic release	-	0	228	Nitro, WV.	Reactor
1950	chlorine	Toxic release	0.5	0		Billingham, U. K.	Rail tank car
1950	H2S	Toxic release	large quantities	22	320	Poza Rice, Mexico	Plant
1952	chlorine	Toxic release	15	7	0	Wilsum, Germany	Storage tank
1952	Ammonia	Toxic release	15	15	20	-	Storage tank
1953	TCDD	Toxic release	-	0	55	Ludwigschafen, Germany	Process
1954	chlorine	Toxic release	0.066	1		Montreal, Canada	Cylinder
1955	chlorine	Toxic release	-	?		Runcorn, UK	-
1956	chlorine	Toxic release	2.7	0		Lake Charles, La.	connecting pipework
1957	chlorine	Toxic release	2.50	0		Runcorn, U. K.	Rail tank car
1957	chlorine	Toxic release	-	8		Nitro, WV	Chlorination vessel

1961	chlorine	Toxic release	27.5	1	114	La Barre, Louisiana	Rail tank car
1961	chlorine	Toxic release	12	0		Billingham, U. K.	Pipeline
1961	chlorine	Toxic release	0	17		Morganza. LA	-
1962	chlorine	Toxic release	27.5	0	89	Cornwall, Ontario	Rail tank car
1962	H2S	Toxic release	-	1	1	USA	Plant
1963	chlorine	Toxic release	8	0	0	Brandtsville, Pa.	Rail tank car
1963	chlorine	Toxic release	-	0	430+	Philadelphia, PA	Rail tank car
1963	Ammonia	Toxic release	2	0	20	Liverpool, UK	road tanker
1963	TCDD	Toxic release	0.0002	8	14	Amesterdam, Holland	Process
1964	chlorine	Toxic release	-	1	0	Mobile, AL	Pipeline
1965	chlorine	Toxic release	-	-		Baton Rouge, LA	Tankship
1966	chlorine	Toxic release	7	0		La Spezia, Italy	Rail tank car
1966	chlorine	Toxic release	0.227	0	0	California, USA	Pipeline
1966	H2S	Toxic release	-	2	50	USA	Plant
1966	HCL	Toxic release	-	0	23	Deer Park, Tx.	-
1967	chlorine	Toxic release	50	0		Newton, Alabama	Rail tank car
1967	chlorine	Toxic release	-	-	5	Bankstown, Australia	-
1968	Ammonia	Toxic release	15	5	20	Lievin, France	Rail tank car
1968	H2S	Toxic release	-	1	60	Godorf, Germany	Plant
1968	TCDD	Toxic release	-	0	79	Bolsover, Derbyshire	Reactor
1968	SO2	Toxic release	-	3	2	Frankfurt, Germany	Process
1969	chlorine	Toxic release	1	2	0	Cleveland, Ohio	container
1969	Ammonia	Toxic release	64	9	53	Crete, Nebraska	Rail tank car
1969	Phosgen	Toxic release	-	0	2	La Porte, Tx	-
1969	H2S	Toxic release	-	3	6	Texas City, Tx.	-
1969	VCM	Toxic release	-		1	Glendora, MS	Rail tank car
1970	chlorine	Toxic release	2	0		Javle, Sweden	Pipeline
1970	Ammonia	Toxic release	145	0	3	Blair, Neb.	Storage tank
1970	Ammonia	Toxic release	75	0	1	Belle, W. Virginia	Rail tank car
1970	H2S	Toxic release	-	5	0	USA	-
1971	Ammonia	Toxic release	570	0	0	Floral, Ark.	Pipeline
1971	Cyclohexane	Toxic release	33.5	0	0	Pensacola, Fa.	Process
1971	Methyl promide	Toxic release	-	4		Gretna, FL	road tanker
1972	SO2	Toxic release	-	0	50	Hamburg, Germany	Process
1973	chlorine	Toxic release	15.5	0		Loos, B. C.	Rail tank car
1973	Ammonia	Toxic release	38	18	65	Potchefstroom, S.Africa	Storage tank

1973	Ammonia	Toxic release	210	0	2	McPherson, KS	Pipeline
1974	chlorine	Toxic release	-	-		Omaha, NE	Chlorine vaporizer
1974	Ammonia	Toxic release	350	0	4	Hutchinson, Kansas	Pipeline
1974	Phosgen	Toxic release	-	1	0	Krefeld, Germany	Process
1974	TCDD	Toxic release	-	0	6	Krefeld, Germany	-
1974	HCL	Toxic release	1.64	1		Chicago, Ill	Storage tank
1975	chlorine	Toxic release	30	4	176	Niagara Falls, NY	Rail tank car
1975	Ammonia	Toxic release	50	0	0	Texas City, TX	Pipeline
1975	H2S	Toxic release	-	1	2	Ingolstade, Germany	Repair
1976	chlorine	Toxic release	90	0	3	Baton Rouge, Louisiana	Storage tank
1976	chlorine	Toxic release	-	0	0	UK	Scrubber
1976	Ammonia	Toxic release	52	0	15	Glen Ellyn, Illinois	Rail tank car
1976	Ammonia	Toxic release	500	0	-	Enid, Oklahoma	Pipeline
1976	Ammonia	Toxic release	19	6	178	Houston, TX	road tanker
1976	Ammonia	Toxic release	-	21	30	Pasacabolo, Columbia	Fertiliser plant
1976	Ammonia	Toxic release	180	2	2	Landskrona, Sweden	Loading terminal
1976	TCDD	Toxic release	0.003	0		Seveso, Italy	Process
1976	CO2	Toxic release	-			Haltern, FRG	Storage tank
1976	Arsenic compounds	Toxic release	-		30	Manfredonia, Italy	Absorption column
1976	Acrylonitrile	Toxic release	10	0	0	Rijmond	-
1977	chlorine	Toxic release	-	-	10	Baton Rouge, LA	Chemical works
1977	Ammonia	Toxic release	40	2	46	Pensacola, FL	Rail tank car
1977	Ammonia	Toxic release	-	2	102	Cuernaveca, Mexico	Pipeline
1977	Ammonia	Toxic release	3	1	18	Thorganby, UK	Pipeline
1977	H2S	Toxic release	-	2	0	Alberta, Canada	Blow -out at well
1977	HF	Toxic release	18	0		Lunen, Germany	-
1978	chlorine	Toxic release	50	8	114	Youngstown, FL	Rail tank car
1978	H2S	Toxic release	-	8	29	Chicago, IL	Loading terminal
1978	SO2	Toxic release	30	0		Duisberg, Germany	-
1978	SO3	Toxic release	-	-	100	Baltimore, MD	-
1979	chlorine	Toxic release	-	-	-	Bayonne, NJ	Rail tank car
1979	chlorine	Toxic release	75	0		Mississauga, Ontario	Rail tank car
1979	chlorine	Toxic release	-	-		Rafnes, Norway	Chemical plant
1979	H2S	Toxic release	-	-		Burghausen, FRG	Chemical plant
1979	Acrylonitrile	Toxic release	-	1	0	Netherland	storage tank

1980	chlorine	Toxic release	-	17	280	Montana, Mexico	Rail tank car
1980	Ammonia	Toxic release	-	9	28	Mexico City, Mexico	Loading terminal
1981	chlorine	Toxic release	300	17	1000	San Luis Potosi, Mexico	Rail tank car
1981	Ammonia	Toxic release	50	0	30	Minnesota	Storage tank
1981	Ammonia	Toxic release	2	2		Enos, Indiana	Rail tank car
1982	chlorine	Toxic release	29	0	15	West Virginia, USA	Pipeline
1982	CO	Toxic release	-	5		Moselle River, France	Pipeline
1983	Cyclohexane	Toxic release	20000-30000 lb	0	0	Virginia, USA	cooler
1983	Nitric acid	Toxic release	-			Denver, CO	Rail tank car
1984	MIC	Toxic release	20	4000		Bhopal, India	Storage tank
1985	Ammonia	Toxic release	-	4	23	San Antonia, Texas	Storage tank
1987	chlorine	Toxic release	450	-		Kotka, Finland	Storage tank
1987	Ammonia	Toxic release	-	1	12	Teeside, UK	Stack
1987	H2S	Toxic release	-	4	7	Stuttgart, Germany	Repair
1987	Pyridine	Toxic release	0.015	0	0	Schweizerhalle, Switzerland	-
1989	Ammonia	Toxic release	1400	7		Jonova, Lithuania	Storage tank
1989	Ammonia	Toxic release	-	2	5	Billingham, UK	Pump
1990	Ammonia	Toxic release	-	3	374	Matanzas, Cuba	Rail tank car
tot. 119				tot. = 4449			

Table 3: Fire & explosion accidents with available mass of chemicals

Date	Chemical	Type	Amount Released (Tonne)	Fatalities	Injuries	Location	Equipment
1921	Hydrogen	Explosion	6.9	1		Hull, UK	Airship
1943	Butane	Vapour cloud fire	16.5	5	> 25	Los Angeles, Calif	-
1944	LNG	Fire & explosion	3000	128	300	Cleveland, OH	Storage tank
1948	Dimethyl ether	Vapour cloud explosion	33	245	2500	Ludwigshafen,Germany	Rail tank car
1949	Propane, butane	Vapour cloud explosion	1.6	5		Detroit, IL	Catalytic cracker
1950	Styrene, latex, butadiene	Explosion	1	0	0	Midland, MI	Reactor
1954	Acrolein	Internal explosion	19	0		Institute, WV	Rail tank car, polymerization
1955	Ethylene	Vapour cloud explosion	1	0		Freeport, TX	Polyethylene plant
1956	Butylene	Vapour cloud explosion	10	0		Baton Rouge, LA	Alkylation unit
1956	Ethylene	Vapour cloud explosion	2.5	0		North Tonawanda, NY	Polyethylene plant
1959	LPG	Vapour cloud explosion	18	23	78	Meldrin, GA	Rail tank car
1960	benzene,mononitrobenzene ,nitric acid, water	Detonation	6.6	15	60	Kingsport, TN	Nitrobenzene plant
1961	Cyclohexane	Vapour cloud explosion	18	1	5	Freeport, TX	Cyclohexane plant, valve failure
1962	Ethylene oxide	Internal explosion, VCE	16	1	19	Bradenburg, Kentucky	reactor
1962	LPG	Vapour cloud explosion	14.3	10	75	Berlin, NY	Road tanker
1962	Propane	Fire	1.1	1	115	Ras Tanura, Saudi Arabia	Storage vessel
1962	Organic peroxides	Explosion	20	4	4	Norwich, CT	Transport tank
1963	Ethylene	Vapour cloud explosion	0.9	0	7	Plaquemine, L.A	Ethylene plant
1964	Vinyl chloride monomer	VEEB	68	7	40	Attleboro, MA	Reactor
1964	Ethylene	Vapour cloud explosion	0.2	2		Orange, TX	HP Polyethylene line
1965	Ethyl chloride	Vapour cloud explosion	19.3	0	0	Baton Rouge, LA	Reactor
1966	Propane	BLEVE	200	18	6	Feyzin, France	Storage vessel
1966	Polystyrene	Explosion	32	11	10	LaSalle, Quebec	reactor
1966	Methane	Vapour cloud explosion	0.5	3	83	Raunheim, FRG	Ethylene unit
1966	Butadiene	Vapour cloud explosion	0.45	3		Scotts Bluff, LA	Reactor

1966	Ethylene	Explosion	0.3	3	83	Germany	Compressor, pipework
1967	Isobutylene	Vapour cloud explosion	46	7	13	Lake Charles, LA	Pipeline
1968	Light HCs	Vapour cloud explosion	140	2	85	Pernis, Netherlands	Slop tanks
1969	Hydrogen, naphtha	Vapour cloud explosion	23	0		Fawley, UK	Hydroformer
1969	Cyclohexane	Vapour cloud explosion	3.6	2	23	Wilton, UK	Oxidation plant
1969	LPG	BLEVE	63	2	976	Laurel, Mississipi	Rail tank car
1970	Propane	Fire	4	2		Hull, UK	-
1970	C10 HC	Vapour cloud explosion	114	0	40	Linden, N.J.	Refinery reactor
1970	Propane	Vapour cloud explosion	29	0	10	Port Hudson, MO, USA	Pipeline
1971	Ethylene	Vapour cloud explosion	3.6	0	21	Baton Rouge, LA	Rail tank car
1971	Vinyl Chloride monomer	BLEVE	165	1	50	Houston, TX	Rail tank car
1971	Butadiene	Vapour cloud explosion	12	1	6	Houston, TX	Butadiene plant
1971	Ethylene	Vapour cloud explosion	0.45	4	60	Longview, TX	Polyethylene plant
1971	Ethylene	Vapour cloud explosion	1	3	6	Texas, USA	Reactor
1972	Propylene	Vapour cloud explosion	53.5	1	230	East St. Louis, IL	Rail tank car
1972	Propane	Fire ball	9	2	5	Lynchburge, VA	Road tanker
1973	LNG	Fire	70	8	21	Austin, Tx.	Pipeline
1973	Hexane, propylene	Explosion	4	4		Goi, Japan	reactor
1973	Propane	BLEVE	45	13	95	Kingman, AZ	Rail tank car
1973	Vinyl Chloride monomer	Vapour cloud explosion	4.2	1	16	Noatsu, Japan	Vinyl chloride plant
1973	Propane	Vapour cloud explosion	19	9	37	St-Amand-les-Eaux, France	Road tanker
1973	Distillate	Explosion	0.61	3	29	Sheffield, UK	Tank
1974	Butane	Fire ball	2	0		Aberdeen, U. K.	Road tanker
1974	Isoprene	Vapour cloud explosion	7.6	2	10	Beaumont, TX	Isoprene plant
1974	Vinyl Chloride monomer	Vapour cloud explosion	110	7		Climax, TX	Rail tank car
1974	Isobutane	Vapour cloud explosion	69	7	152	Decatur, IL	Rail tank car
1974	Ethylene	Vapour cloud explosion	1.8	0		Fawley, UK	Polyethylene plant
1974	Cyclohexane	Vapour cloud explosion	25	28	104	Flixborough, UK	Caprolactam plant
1974	Butadiene	Vapour cloud explosion	75	1	235	Houston, TX	Rail tank car
1974	Butane	Vapour cloud explosion	2190	0	24	Petal, Mississippi USA	storage
1974	LPG	BLEVE	10	4	6	West St Paul, MN	Storage vessel
1975	Ethylene	Vapour cloud explosion	2.5	6	13	Antwerp, Belgium	Polyethylene plant
1975	Propylene	Vapour cloud explosion	5.5	14	107	Beek, Netherlands	Petrochemicals plant
1975	LPG	Fire ball	18.2	17	34	Eagle Pass, TX	Road tanker
1975	Gasoline	Vapour cloud explosion	37.5	2		Rosendaal, Netherlands	Line leak

1975	Hydrogen	Vapour cloud explosion	0.3	0		Watson, CA	Tank failure
1976	LPG	BLEVE	80	2	22	Belt, Mt	Rail tank car
1976	Isobutane	Vapour cloud explosion	13	7		Lake Charles, La	Refinery
1976	Trichlorphenol reaction mixture, including TCDD	Internal explosion	0.002	0		Seveso	Reactor
1976	Propylene	Fire	18	2	0	New Jersey	-
1977	Acrylonitrile	Explosion	400	0	0	Antwerp, Belgium	Storage tank
1977	Gasoline	Vapour cloud explosion	300	3		Baytown, TX	Tanker
1977	Sodium chlorate	Explosion	68	0	13	Braehead, Renfrew, UK	Warehouse
1977	Isobutane	Vapour cloud explosion	68.2	0	1	Dallas, TX.	Rail tank car
1977	LPG	Fire ball	70	2	9	Goldonna, LA	Rail tank car
1977	LPG	Fire	23,000	7	87	Umm Said, Qatar	LPG refrigrated tank
1978	LPG	Fire & Explosion	20.5	4	0	Abqaiq, Saudi Arabia	Gas pipeline
1978	LPG	Fire ball	435	3	2	Donnellson, IA	Pipeline
1978	Hydrogen	Vapour cloud explosion	0.25	0		Immingham, UK	heat reboiler
1978	Vinyl Chloride monomer	Fire ball	110	0	2	Lewisville, AR	Rail tank car
1978	Propylene	Vapour cloud fire	23.5	216	200	San Carlos, Spain	Road tanker
1978	Butane	Vapour cloud fire	36.4	100	220	Xilatopic, Mexico	Road tanker
1979	Crude oil	Explosion	95,000	52		Istanbul, Turkey	Oil tanker
1979	Propane	Vapour cloud explosion	3.1	0		Texas City, TX.	Alkylation unit
1979	Crude oil	Fire	40,000	50		Banter Bay, Eire	crude tanker
1980	Propane	Vapour cloud explosion	0.11	0		Enschede, Netherlands	propane tank
1980	Hexane, propylene (mix)	Vapour cloud explosion	12.7	5	25	New castle, DE	Polypropylene plant
1981	Syngas	Vapour cloud explosion	12	6		Czechoslovakia	Ammonia plant (catchpot)
1981	Propane	Vapour cloud explosion	15	1	2	Gothenburge, Sweden	Pipeline
1982	Ethylene	Explosion	2.9	0	6	Edmonton, Alberta, Canada	Compressor
1983	light Crude oil	Fire	25,000	0	20	Milford Haven, UK	Storage tank
1984	LPG	Vapour cloud fire	6000	650	6400	Mexico city, Mexico	LPG storage tank
1984	Hydrogen	Vapour cloud explosion	0.03	2		Sarnia, Ont.	Benzene plant
1986	Pesticides, etc.	Fire, pollution	1200	0		Schweizerhalle, Basel, Switzerland	Warehouse
1987	LPG	release/BLEVE	20	1	23	Queensland, Australia	Rail tanker
1988	Cyclohexane	Explosion	5	0	0	Melbourne, Australia	Terminal, unloading
1988	Propane	Vapour cloud explosion	9	7		Louisiana, USA	fluid catalytic

							cracking
1988	Ethylene dichloride, vinyl Chloride	Vapour cloud explosion	55	7	13	Rafnes, Norway	VC plant
1989	Ammonia	Fire & explosion	7000	7	55	Jonova, Lithuania	Ammonia storage
1989	Isobutane	Vapour cloud explosion	37.8	23	314	Pasadena, TX	Polyethylene plant
1990	LPG	Vapour cloud fire	5.6	63	100	Bangkok, Thailand	Road tanker
1990	Propane	Fire and explosion	18	6		Candanos, Spain	Road tanker
1992	Propane, butane	Explosion	10	6	12	Marseilles, France	catalytic cracker
1994	Styrene, ethylene dibromide,	Explosion	328	3	0	Belpre, Ohio	reaction vessel
1994	cyclohexane, butadiene	-	127	0		-	-
1998	LNG	Fire	10	2		Longford, Victoria, Australia	-
tot.101			206,386	1876			

Table 4: Process Fire and Explosion Accidents

Date	Chemical	Type	Amount Released (Tonne)	Fatalities	Injuries	Location	Equipment
1949	Propane, butane	Vapour cloud explosion	1.6	5		Detroit, IL	Catalytic cracker (refinery)
1950	Styrene, latex, butadiene	Explosion	1	0	0	Midland, MI	Reactor
1955	Ethylene	Vapour cloud explosion	1	0		Freeport, TX	Polyethylene plant
1956	Butylene	Vapour cloud explosion	10	0		Baton Rouge, LA	Alkylation unit
1956	Ethylene	Vapour cloud explosion	2.5	0		North Tonawanda, NY	Polyethylene plant
1960	benzene,mononitrobenzene,nitric acid, water	Detonation	6.6	15	60	Kingsport, TN	Nitrobenzene plant, process
1961	Cyclohexane	Vapour cloud explosion	18	1	5	Freeport, TX	Cyclohexane plant, valve failure
1962	Ethylene oxide	Internal explosion, VCE	16	1	19	Bradenburg, Kentucky	Reactor
1963	Ethylene	Vapour cloud explosion	0.9	0	7	Plaquemine, L.A	Ethylene plant
1964	Ethylene	Vapour cloud explosion	0.2	2		Orange, TX	HP Polyethylene line
1964	Vinyl chloride monomer	VEEB	68	7	40	Attleboro, MA	Reactor
1965	Ethyl chloride	Vapour cloud explosion	19.3	0		Baton Rouge, LA	Reactor
1966	Methane	Vapour cloud explosion	0.5	3	83	Raunheim, FRG	Ethylene unit
1966	Polystyrene	Explosion	32	11	10	LaSalle, Quebec	reactor
1966	Butadiene	Vapour cloud explosion	0.45	3		Scotts Bluff, LA	Reactor
1966	Ethylene	Explosion	0.3	3	83	Germany	Compressor, pipework
1969	Hydrogen, naphtha	Vapour cloud explosion	23	0		Fawley, UK	Hydroformer
1969	Cyclohexane	Vapour cloud explosion	3.6	2	23	Wilton, UK	Oxidation plant
1970	C10 HC	Vapour cloud explosion	114	0	40	Linden, N.J.	Refinery reactor
1971	Butadiene	Vapour cloud explosion	12	1	6	Houston, TX	Butadiene plant
1971	Ethylene	Vapour cloud explosion	0.45	4	60	Longview, TX	HP Polyethylene line
1971	Ethylene	Vapour cloud explosion	1	3	6	Texas, USA	reactor
1973	Hexane, propylene	Explosion	4	4		Goi, Japan	reactor
1973	Vinyl Chloride monomer	Vapour cloud explosion	4.2	1	16	Noatsu, Japan	Vinyl chloride plant
1974	Cyclohexane	Vapour cloud explosion	25	28	104	Flixborough, UK	Caprolactam plant
1974	Isoprene(>C5 HC)	Vapour cloud explosion	7.6	2	10	Beaumont, TX	Isoprene plant

1974	Ethylene	Vapour cloud explosion	1.8	0		Fawley, UK	Polyethylene plant
1975	Gasoline	Vapour cloud explosion	37.5	2		Rosendaal, Netherlands	Line leak
1975	Propylene	Vapour cloud explosion	5.5	14	107	Beek, Netherlands	Naphtha cracker column
1975	Ethylene	Vapour cloud explosion	2.5	6	13	Antwerp, Belgium	Polyethylene plant
1976	Trichlorphenol reaction mixture, including TCDD**	Internal explosion	0.002	0		Seveso	Reactor
1976	Isobutane	Vapour cloud explosion	13	7		Lake Charles, La	Refinery
1078	Hydrogen	Vapour cloud explosion	0.25	0		Immingham, UK	Heat reboiler
1979	Propane	Vapour cloud explosion	3.1	0		Texas City, TX.	Alkylation unit
1980	Hexane(propylene) erase propylene	Vapour cloud explosion	12.7	5	25	New castle, DE	Blow-out of plug valve
1981	Syngas	Vapour cloud explosion	12	6		Czechoslovakia	Ammonia plant
1982	Ethylene	Explosion	2.0	0		Alberta, Canada	Compressor
1984	Hydrogen	Vapour cloud explosion	0.03	2		Sarnia, Ont.	Benzene plant
1988	Propane	Vapour cloud explosion	9	7	48	Louisiana, USA	fluid catalytic cracking
1988	Ethylene dichloride, vinyl Chloride	Vapour cloud explosion	55	7	13	Rafnes, Norway	VC plant
1989	Isobutane	Vapour cloud explosion	37.8	23	314	Pasadena, TX	Polyethylene plant
1992	Propane, butane	Explosion	10	6	12	Marseilles, France	catalytic cracker
1994	Styrene, ethylene dibromide,	Explosion	328	3	0	Belpre, Ohio	reaction vessel
tot. 43				tot. = 184			

Table 5: Storage Fire and Explosion Accidents

Date	Chemical	Type	Amount Released (Tonne)	Fatalities	Injuries	Location	Equipment
1944	LNG	Fire & explosion	3000	128	300	Cleveland, OH	Storage tank
1962	Propane	Fire	1.1	1	115	Ras Tanura, Saudi Arabia	Storage vessel
1962	Organic peroxides	Explosion	20	4	4	Norwich, CT	Transport tank
1966	Propane	BLEVE	200	18	6	Feyzin, France	Storage vessel
1968	Light HCs (<C10)	Vapour cloud explosion	140	2	85	Pernis, Netherlands	Slop-oil tank, refinery
1973	Distillate	Explosion	0.61	3	29	Sheffield, UK	Tank
1974	Butane	Vapour cloud explosion	2190	0	24	Petal, Mississippi USA	storage
1974	LPG	BLEVE	10	4	6	West St Paul, MN	Storage vessel
1975	Hydrogen	Vapour cloud explosion	0.3	0		Watson, CA	Crack in tank
1977	Acrylonitrile	Explosion	400	0	0	Antwerp, Belgium	Storage tank
1977	Sodium chlorate	Explosion	68	0	13	Braehead, Renfrew, UK	Warehouse
1977	LPG	Fire	23,000	7	87	Umm Said, Qatar	LPG storage tank
1980	Propane	Vapour cloud explosion	0.11	0		Enschede, Netherlands	Propane tank
1983	light Crude oil	Fire	25,000	0	20	Milford Haven, UK	Storage tank
1984	LPG	Vapour cloud fire	6000	650	6400	Mexico city, Mexico	Storage
1986	Pesticides, etc.	Fire, pollution	1200	0		Schweizerhalle, Basel, Switzerland	Warehouse
1988	Cyclohexane	Explosion	5	0	0	Melbourne, Australia	Terminal, Unloading
1989	Ammonia	Fire & explosion	7000	7	55	Jonova, Lithuania	Ammonia storage
tot. 18				tot. =824			

Table 6: Fire and Explosion Transport Accidents

Date	Chemical	Type	Amount Released (Tonne)	Fatalities	Injuries	Location	Equipment
1948	Dimethyl ether	Vapour cloud explosion	33	245	2500	Ludwigshafen,Germany	Rail tank car
1954	Acrolein	Internal explosion	19	0		Institute, WV	Rail tank car, polymerization
1959	LPG	Vapour cloud explosion	18	23	78	Meldrin, GA	Rail tank car
1962	LPG	Vapour cloud explosion	14.3	10	75	Berlin, NY	Road tanker
1967	Isobutylene	Vapour cloud explosion	46	7	13	Lake Charles, LA	Pipeline
1969	LPG	BLEVE	63	2	33	Laurel, Missisipi	Rail tank car
1970	Propane	Vapour cloud explosion	29	0	10	Port Hudson, MO, USA	Pipeline
1970	Propane	BLEVE	75	0?	66	Crescent City, IL	Rail tank car
1971	Ethylene	Vapour cloud explosion	3.6	0	21	Baton Rouge, LA	Rail tank car
1971	Vinyl Chloride monomer	BLEVE	165	1	50	Houston, TX	Rail tank car
1972	Propylene	Vapour cloud explosion	53.5	1	230	East St. Louis, IL	Rail tank car
1972	Propane	Fire ball	9	2	5	Lynchburge, VA	Road tanker
1973	LNG	Fire	70	8	21	Austin, Tx.	Pipeline
1973	Propane	BLEVE	45	13	95	Kingman, AZ	Rail tank car
1973	Propane	Vapour cloud explosion	19	9	37	St-Amand-les-Eaux, France	Road tanker
1974	Vinyl Chloride monomer	Vapour cloud explosion	110	7		Climax, TX	Rail tank car
1974	Isobutane	Vapour cloud explosion	69	7	152	Decatur, IL	Rail tank car
1974	Butadiene	Vapour cloud explosion	75	1	235	Houston, TX	Rail tank car
1974	Butane	Fire ball	2	0		Aberdeen, U. K.	Road tanker
1975	LPG	Fire ball	18.2	17	34	Eagle Pass, TX	Road tanker
1976	LPG	BLEVE	80	2	22	Belt, Mt	Rail tank car
1977	Gasoline	Vapour cloud explosion	300	3		Baytown, TX	Oil tanker
1977	Isobutane	Vapour cloud explosion	68.2	0	1	Dallas, TX.	Rail tank car
1977	LPG	Fire ball	70	2	9	Goldonna, LA	Rail tank car
1978	LPG	Fire & Explosion	20.5)	4	0	Abqaiq, Saudi Arabia	Gas pipeline
1978	LPG	Fire ball	435	3	2	Donnellson, IA	Pipeline
1978	Vinyl Chloride monomer	Fire ball	110	0	2	Lewisville, AR	Rail tank car
1978	Propylene	Vapour cloud fire	23.5	216	200	San Carlos, Spain	Road tanker
1978	Butane	Vapour cloud fire	36.4	100	220	Xilatopic, Mexico	Road tanker
1979	Crude oil	Explosion	95,000	52		Istanbul, Turkey	Oil tanker

1979	Crude oil	Fire	40,000	50		Banter Bay, Eire	crude tanker
1981	Propane	Vapour cloud explosion	15	1	2	Gothenburge, Sweden	Pipeline
1987	LPG	release/BLEVE	20	1	23	Queensland, Australia	Rail tanker
1990	LPG	Vapour cloud fire	5.6	63	100	Bangkok, Thailand	Road tanker
1990	Propane	Fire and explosion	18	6		Candanos, Spain	Road tanker
tot. 134				tot. = 856			

Table7: Fire & explosion accidents (caused one or more fatalities)

Date	Chemical	Type	Amount Released (Tonne)	Fatalities	Injuries	Location	Equipment
1921	Hydrogen	Explosion	6.9	1		Hull, UK	Airship
1943	Butane	Vapour cloud fire	16.5	5	> 25	Los Angeles, Calif	-
1944	LNG	Fire & explosion	3000	128	300	Cleveland, OH	Storage tank
1948	Dimethyl ether	Vapour cloud explosion	33	245	2500	Ludwigshafen,Germany	Rail tank car
1949	Propane, butane	Vapour cloud explosion	1.6	5		Detroit, IL	Catalytic cracker
1959	LPG	Vapour cloud explosion	18	23	78	Meldrin, GA	Rail tank car
1960	benzene,mononitrobenzene, nitric acid, water	Detonation	6.6	15	60	Kingsport, TN	Nitrobenzene plant
1961	Cyclohexane	Vapour cloud explosion	18	1	5	Freeport, TX	Cyclohexane plant, valve failure
1962	Ethylene oxide	Internal explosion, VCE	16	1	19	Bradenburg, Kentucky	reactor
1962	LPG	Vapour cloud explosion	14.3	10	75	Berlin, NY	Road tanker
1962	Propane	Fire	1.1	1	115	Ras Tanura, Saudi Arabia	Storage vessel
1962	Organic peroxides	Explosion	20	4	4	Norwich, CT	Transport tank
1964	Vinyl chloride monomer	VEEB	68	7	40	Attleboro, MA	Reactor
1964	Ethylene	Vapour cloud explosion	0.2	2		Orange, TX	HP Polyethylene line
1966	Propane	BLEVE	200	18	6	Feyzin, France	Storage vessel
1966	Polystyrene	Explosion	32	11	10	LaSalle, Quebec	reactor
1966	Methane	Vapour cloud explosion	0.5	3	83	Raunheim, FRG	Ethylene unit
1966	Butadiene	Vapour cloud explosion	0.45	3		Scotts Bluff, LA	Reactor
1966	Ethylene	Explosion	0.3	3	83	Germany	Compressor, pipework
1967	Isobutylene	Vapour cloud explosion	46	7	13	Lake Charles, LA	Pipeline
1968	Light HCs	Vapour cloud explosion	140	2	85	Pernis, Netherlands	Slop tanks
1969	Cyclohexane	Vapour cloud explosion	3.6	2	23	Wilton, UK	Oxidation plant
1969	LPG	BLEVE	63	2	976	Laurel, Mississipi	Rail tank car
1970	Propane	Fire	4	2		Hull, UK	-
1971	Vinyl Chloride monomer	BLEVE	165	1	50	Houston, TX	Rail tank car
1971	Butadiene	Vapour cloud explosion	12	1	6	Houston, TX	Butadiene plant
1971	Ethylene	Vapour cloud explosion	0.45	4	60	Longview, TX	Polyethylene plant

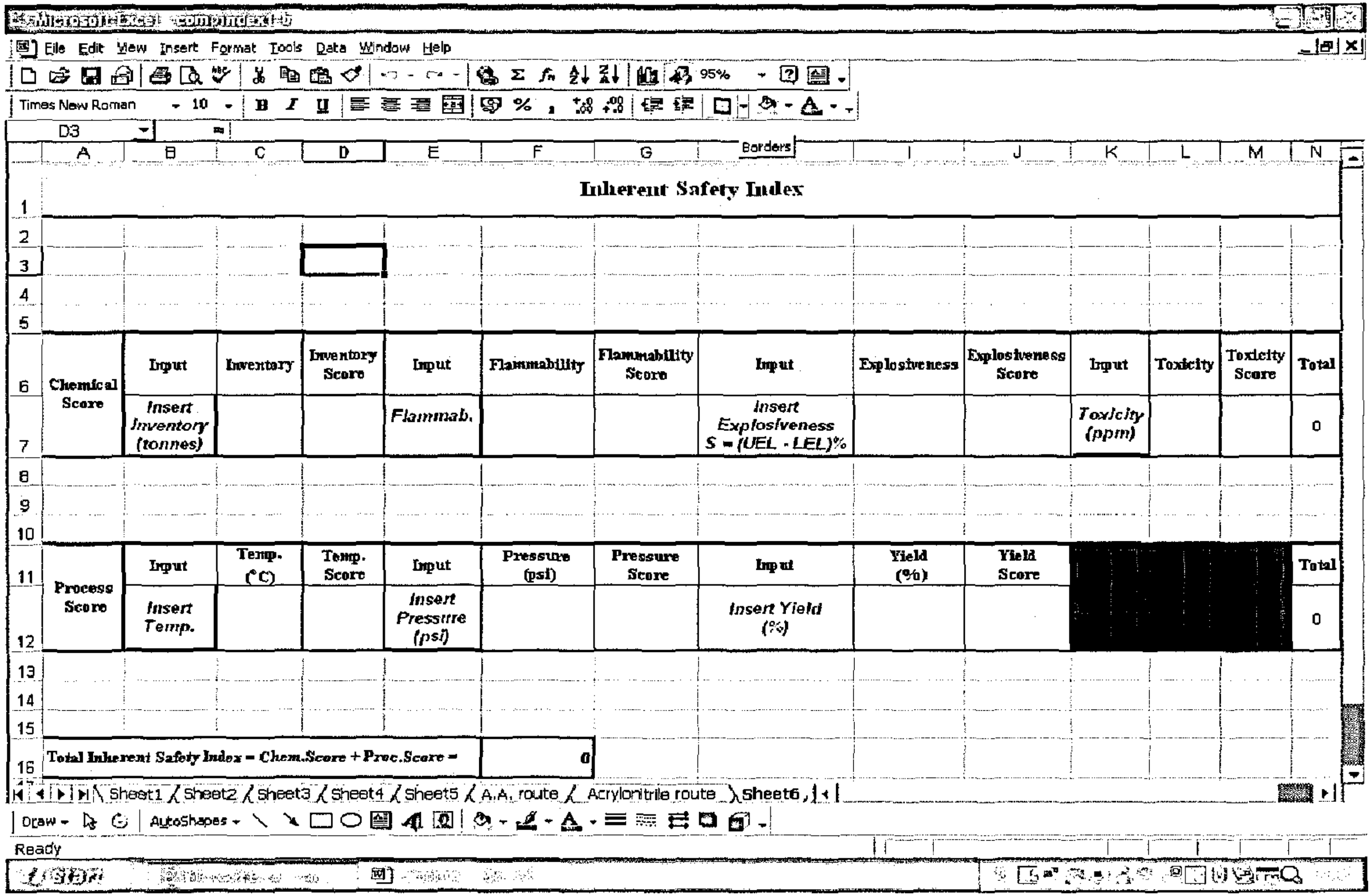
1971	Ethylene	Vapour cloud explosion	1	3	6	Texas, USA	Reactor
1972	Propylene	Vapour cloud explosion	53.5	1	230	East St. Louis, IL	Rail tank car
1972	Propane	Fire ball	9	2	5	Lynchburge, VA	Road tanker
1973	LNG	Fire	70	8	21	Austin, Tx.	Pipeline
1973	Hexane, propylene	Explosion	4	4		Goi, Japan	reactor
1973	Propane	BLEVE	45	13	95	Kingman, AZ	Rail tank car
1973	Vinyl Chloride monomer	Vapour cloud explosion	4.2	1	16	Noatsu, Japan	Vinyl chloride plant
1973	Propane	Vapour cloud explosion	19	9	37	St-Amand-les-Eaux, France	Road tanker
1973	Distillate	Explosion	0.61	3	29	Sheffield, UK	Tank
1974	Isoprene	Vapour cloud explosion	7.6	2	10	Beaumont, TX	Isoprene plant
1974	Vinyl Chloride monomer	Vapour cloud explosion	110	7		Climax, TX	Rail tank car
1974	Isobutane	Vapour cloud explosion	69	7	152	Decatur, IL	Rail tank car
1974	Cyclohexane	Vapour cloud explosion	25	28	104	Flixborough, UK	Caprolactam plant
1974	Butadiene	Vapour cloud explosion	75	1	235	Houston, TX	Rail tank car
1974	LPG	BLEVE	10	4	6	West St Paul, MN	Storage vessel
1975	Ethylene	Vapour cloud explosion	2.5	6	13	Antwerp, Belgium	Polyethylene plant
1975	Propylene	Vapour cloud explosion	5.5	14	107	Beek, Netherlands	Petrochemicals plant
1975	LPG	Fire ball	18.2	17	34	Eagle Pass, TX	Road tanker
1975	Gasoline	Vapour cloud explosion	37.5	2		Rosendaal, Netherlands	Line leak
1976	LPG	BLEVE	80	2	22	Belt, Mt	Rail tank car
1976	Isobutane	Vapour cloud explosion	13	7		Lake Charles, La	Refinery
1976	Propylene	Fire	18	2	0	New Jersey	-
1977	Gasoline	Vapour cloud explosion	300	3		Baytown, TX	Tanker
1977	LPG	Fire ball	70	2	9	Goldonna, LA	Rail tank car
1977	LPG	Fire	23,000	7	87	Umm Said, Qatar	LPG storage tank
1978	LPG	Fire & Explosion	20.5	4	0	Abqaiq, Saudi Arabia	Gas pipeline
1978	LPG	Fire ball	435	3	2	Donnellson, IA	Pipeline
1978	Propylene	Vapour cloud fire	23.5	216	200	San Carlos, Spain	Road tanker
1978	Butane	Vapour cloud fire	36.4	100	220	Xilatopic, Mexico	Road tanker
1979	Crude oil	Explosion	95,000	52		Istanbul, Turkey	Oil tanker
1979	Crude oil	Fire	40,000	50		Banter Bay, Eire	crude tanker
1980	Hexane, propylene	Vapour cloud explosion	12.7	5	25	New castle, DE	Polypropylene plant
1981	Syngas	Vapour cloud explosion	12	6		Czechoslovakia	Ammonia plant (catchpot)
1981	Propane	Vapour cloud explosion	15	1	2	Gothenburge, Sweden	Pipeline
1984	LPG	Vapour cloud fire	6000	650	6400	Mexico city, Mexico	Terminal (storage)
1984	Hydrogen	Vapour cloud explosion	0.03	2		Sarnia, Ont.	Benzene plant
1987	LPG	release/BLEVE	20	1	23	Queensland, Australia	Rail tanker

1988	Propane	Vapour cloud explosion	9	7		Louisiana, USA	fluid catalytic cracking
1988	Vinyl Chloride monomer	Vapour cloud explosion	55	7	13	Rafnes, Norway	VC plant
1989	Ammonia	Fire & explosion	7000	7	55	Jonova, Lithuania	Ammonia storage
1989	Isobutane	Vapour cloud explosion	37.8	23	314	Pasadena, TX	Polyethylene plant
1990	LPG	Vapour cloud fire	5.6	63	100	Bangkok, Thailand	Road tanker
1990	Propane	Fire and explosion	18	6		Candanos, Spain	Road tanker
1992	Propane, butane	Explosion	10	6	12	Marseilles, France	catalytic cracker
1994	Styrene, ethylene dibromide,	Explosion	328	3	0	Belpre, Ohio	reaction vessel
1998	LNG	Fire	10	2		Longford, Victoria, Australia	Report
tot. 73			177,111	1876			

Table 8: Hydrocarbons fire & explosion accidents (caused one or more fatalities)

Date	Chemical	Type	Amount	Fatalities	Injuries	Location	Equipment
1943	Butane	Vapour cloud fire	16.5	5	> 25	Los Angeles, Calif	-
1944	LNG	Fire & explosion	3,000	128	300	Cleveland, OH	Storage tank
1949	Propane, butane	Vapour cloud explosion	1.6	5		Detroit, IL	Catalytic cracker
1959	LPG	Vapour cloud explosion	18	23	78	Meldrin, GA	Rail tank car
1961	Cyclohexane	Vapour cloud explosion	18	1	5	Freeport, TX	Cyclohexane plant, valve failure
1962	LPG	Vapour cloud explosion	14.3	10	75	Berlin, NY	Road tanker
1962	Propane	Fire	1.1	1	115	Ras Tanura, Saudi Arabia	Storage vessel
1964	Ethylene	Vapour cloud explosion	0.2	2		Orange, TX	HP Polyethylene line
1966	Propane	BLEVE	200	18	6	Feyzin, France	Storage vessel
1966	Methane	Vapour cloud explosion	0.5	3	83	Raunheim, FRG	Ethylene unit
1966	Ethylene	Explosion	0.3	3	83	Germany	Compressor, pipework
1967	Isobutylene	Vapour cloud explosion	46	7	13	Lake Charles, LA	Pipeline
1968	Light HCs	Vapour cloud explosion	140	2	85	Pernis, Netherlands	Slop tanks
1969	Cyclohexane	Vapour cloud explosion	3.6	2	23	Wilton, UK	Oxidation plant
1969	LPG	BLEVE	63	2	976	Laurel, Mississipi	Rail tank car
1970	Propane	Fire	4	2		Hull, UK	-
1971	Ethylene	Vapour cloud explosion	0.45	4	60	Longview, TX	Polyethylene plant
1971	Ethylene	Vapour cloud explosion	1	3	6	Texas, USA	Reactor
1972	Propylene	Vapour cloud explosion	53.5	1	230	East St. Louis, IL	Rail tank car
1972	Propane	Fire ball	9	2	5	Lynchburge, VA	Road tanker
1973	LNG	Fire	70	8	21	Austin, Tx.	Pipeline
1973	Hexane, propylene	Explosion	4	4		Goi, Japan	reactor
1973	Propane	BLEVE	45	13	95	Kingman, AZ	Rail tank car
1973	Propane	Vapour cloud explosion	19	9	37	St-Amand-les-Eaux, France	Road tanker
1974	Isoprene	Vapour cloud explosion	7.6	2	10	Beaumont, TX	Isoprene plant
1974	Isobutane	Vapour cloud explosion	69	7	152	Decatur, IL	Rail tank car
1974	Cyclohexane	Vapour cloud explosion	25	28	104	Flixborough, UK	Caprolactam plant
1974	LPG	BLEVE	10	4	6	West St Paul, MN	Storage vessel
1975	Ethylene	Vapour cloud explosion	2.5	6	13	Antwerp, Belgium	Polyethylene plant

1975	Propylene	Vapour cloud explosion	5.5	14	107	Beek, Netherlands	Petrochemicals plant
1975	LPG	Fire ball	18.2	17	34	Eagle Pass, TX	Road tanker
1975	Gasoline	Vapour cloud explosion	37.5	2		Rosendaal, Netherlands	line leak
1976	LPG	BLEVE	80	2	22	Belt, Mt	Rail tank car
1976	Isobutane	Vapour cloud explosion	13	7		Lake Charles, La	Refinery
1976	Propylene	Fire	18	2	0	New Jersey	-
1977	Gasoline	Vapour cloud explosion	300	3		Baytown, TX	Tanker
1977	LPG	Fire ball	70	2	9	Goldonna, LA	Rail tank car
1977	LPG	Fire	23,000	7	87	Umm Said, Qatar	LPG storage tank
1978	LPG	Fire & Explosion	20.5	4	0	Abqaiq, Saudi Arabia	Gas pipeline
1978	LPG	Fire ball	435	3	2	Donnellson, IA	Pipeline
1978	Propylene	Vapour cloud fire	23.5	216	200	San Carlos, Spain	Road tanker
1978	Butane	Vapour cloud fire	36.4	100	220	Xilatopic, Mexico	Road tanker
1979	Crude oil	Explosion	95,000	52		Istanbul, Turkey	Oil tanker
1979	Crude oil	Fire	40,000	50		Bantry Bay, Eire	Crude tanker
1980	Hexane, propylene	Vapour cloud explosion	12.7	5	25	New castle, DE	Polypropylene plant
1981	Propane	Vapour cloud explosion	15	1	2	Gothenburge, Sweden	Pipeline
1984	LPG	Vapour cloud fire	6,000	650	6400	Mexico city, Mexico	LPG storage tank
1987	LPG	release/BLEVE	20	1	23	Queensland, Australia	Rail tanker
1988	Propane	Vapour cloud explosion	9	7		Louisiana, USA	fluid catalytic cracking
1989	Isobutane	Vapour cloud explosion	37.8	23	314	Pasadena, TX	Polyethylene plant
1990	LPG	Vapour cloud fire	5.6	63	100	Bangkok, Thailand	Road tanker
1990	Propane	Fire and explosion	18	6		Candanos, Spain	Road tanker
1992	Propane, butane	Explosion	10	6	12	Marseilles, France	catalytic cracker
1998	LNG	Fire	10	2		Longford, Victoria, Australia	Gas processing plant
tot. 54			169,039	1550			



	A	B	C	D	E	F	G		I	J	K	L	M	N
1	Inherent Safety Index													
2														
3														
4														
5														
6	Chemical Score	Input	Inventory	Inventory Score	Input	Flammability	Flammability Score	Input	Explosiveness	Explosiveness Score	Input	Toxicity	Toxicity Score	Total
7		Insert Inventory (tonnes)			Flammab.			Insert Explosiveness S = (UEL - LEL)%			Toxicity (ppm)			0
8														
9														
10														
11	Process Score	Input	Temp. (°C)	Temp. Score	Input	Pressure (psi)	Pressure Score	Input	Yield (%)	Yield Score				Total
12		Insert Temp.			Insert Pressure (psi)			Insert Yield (%)						0
13														
14														
15														
16	Total Inherent Safety Index = Chem.Score + Proc.Score =					0								

Figure 1: Display of Visual Basic Programme for Inherent Safety Index (Compindex)

Compindex VB code

The following is the Visual Basic Code used for the above programme.

```
Sub InsertInventory()
sInventory = InputBox("Please Enter Inventory Value")
Worksheets("sheet6").Cells(7, 3) = sInventory
sInventory = Workbooks("compindex1.xls").Worksheets("sheet6").range("C7")
    Select Case sInventory
    Case 0.1 To 250
      Score = 1
    Case 251 To 2500
      Score = 2
    Case 2501 To 7000
      Score = 3
    Case 7001 To 16000
      Score = 4
    Case 16001 To 26000
      Score = 5
    Case 26001 To 38000
      Score = 6
    Case 38001 To 50000
      Score = 7
    Case 50001 To 65000
      Score = 8
    Case 65001 To 80000
      Score = 9
    Case 80001 To 100000
      Score = 10
      End Select
      Worksheets("sheet6").Cells(7, 4) = Score
End Sub
```

```
    Sub InsertTemperature()
    sTemperature = InputBox("Please Enter Temperature")
    Worksheets("sheet6").Cells(12, 3) = sTemperature
    'This program calculate the Temperature score of chemical roots
    sTemperature =
Workbooks("compindex1.xls").Worksheets("sheet6").range("C12")
        Select Case sTemperature
        Case Is < -25
          Score = 10
        Case -25 To -9
          Score = 3
        Case -10 To 9
          Score = 1
        Case 10 To 29
          Score = 0
        Case 30 To 99
          Score = 1
        Case 100 To 199
          Score = 2
        Case 200 To 299
          Score = 3
        Case 300 To 399
          Score = 4
        Case 400 To 499
          Score = 5
        Case 500 To 599
          Score = 6
        Case 600 To 699
          Score = 7
        Case 700 To 799
          Score = 8
        Case 800 To 899
          Score = 9
        Case Is >= 900
          Score = 10
```

```
  End Select
  Worksheets("sheet6").Cells(12, 4) = Score
End Sub



Sub InsertPressure()
sPressure = InputBox("Please Enter Pressure Value")
Worksheets("sheet6").Cells(12, 6) = sPressure
sPressure = Workbooks("compindex1.xls").Worksheets("sheet6").range("F12")
    Select Case sPressure
    Case 0 To 90
      Score = 1
    Case 91 To 140
      Score = 2
    Case 141 To 250
      Score = 3
    Case 251 To 420
      Score = 4
    Case 421 To 700
      Score = 5
    Case 701 To 1400
      Score = 6
    Case 1401 To 3400
      Score = 7
    Case 3401 To 4800
      Score = 8
    Case 4801 To 6000
      Score = 9
    Case 6001 To 8000
      Score = 10
  End Select
  Worksheets("sheet6").Cells(12, 7) = Score
End Sub
```

```
Sub InsertYield()
syield = InputBox("Please Enter yield percentage")
Worksheets("sheet6").Cells(12, 9) = syield
syield = Workbooks("compindex1.xls").Worksheets("sheet6").range("I12")
    Select Case syield
    Case Is = 100
      Score = 0
    Case 90 To 99
      Score = 1
    Case 80 To 89
      Score = 2
    Case 70 To 79
      Score = 3
    Case 60 To 69
      Score = 4
    Case 50 To 59
      Score = 5
    Case 40 To 49
      Score = 6
    Case 30 To 39
      Score = 7
    Case 20 To 29
      Score = 8
    Case 10 To 19
      Score = 9
    Case 0 To 10
      Score = 10
    End Select
    Worksheets("sheet6").Cells(12, 10) = Score
End Sub
```

```
Sub InsertExplosiveness()
 sExplosiveness = InputBox("Please Enter Explosiveness (S)")
Worksheets("sheet6").Cells(7, 9) = sExplosiveness
  sExplosiveness =
Workbooks("compindex1.xls").Worksheets("sheet6").range("I7")
      Select Case sExplosiveness
      Case 0 To 9
         Score = 1
      Case 10 To 19
         Score = 2
      Case 20 To 29
         Score = 3
      Case 30 To 39
         Score = 4
      Case 40 To 49
         Score = 5
      Case 50 To 59
         Score = 6
      Case 60 To 69
         Score = 7
      Case 70 To 79
         Score = 8
      Case 80 To 89
         Score = 9
      Case 90 To 100
         Score = 10
   End Select
   Worksheets("sheet6").Cells(7, 10) = Score
End Sub
```

```
Sub InsertToxicity()
STLV = InputBox("Please Enter TLV Value (ppm)")
Worksheets("sheet6").Cells(7, 12) = STLV
STLV = Workbooks("compindex1.xls").Worksheets("sheet6").range("L7")
      Select Case STLV
     Case Is < 0.001
        Score = 8
     Case 0.001 To 0.009
        Score = 7
     Case 0.01 To 0.09
        Score = 6
     Case 0.1 To 0.9
        Score = 5
     Case 1 To 9
        Score = 4
     Case 10 To 99
        Score = 3
     Case 100 To 999
        Score = 2
     Case 1000 To 9999
        Score = 1
     Case Is >= 10000
        Score = 0
     End Select
     Worksheets("sheet6").Cells(7, 13) = Score
End Sub
```