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Thermal Safety of Chemical Processes

Risk Assessment and Process Design

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To Michèle,
Sébastien, Claire-Lise and Anne-Florence

Contents

Preface

Often, chemical incidents are due to loss of control, resulting in runaway reactions. Many of these incidents can be foreseen and avoided, if an appropriate analysis of thermal process data is performed in the proper way and in due time. Chemical process safety is seldom part of university curricula and many professionals do not have the appropriate knowledge to interpret thermal data in terms of risks. As a result, even though responsible for the safety of the process, they do not have easy access to the knowledge. Process safety is often considered a specialist matter, thus most large companies employ specialists in their safety departments. However, this safety knowledge is also required at the front, where processes are developed or performed, that is in process development departments and production. To achieve this objective of providing professionals with the required knowledge on the thermal aspects of their processes, the methods must be made accessible to non-specialists. Such systematic and easy-to-use methods represent the backbone of this book, in which the methods used for the assessment of thermal risks are presented in a logical and understandable way, with a strong link to industrial practice.

The present book is rooted in a lecture on chemical process safety at graduate level (Masters) at the Swiss Federal Institute of Technology in Lausanne. It is also based on experience gained in numerous training courses for professionals held at the Swiss Institute for the Promotion of Safety & Security, as well as in a number of major chemical and pharmaceutical companies. Thus it has the character of a textbook and addresses students, but also addresses professional chemists, chemical engineers or engineers in process development and production of fine chemicals and pharmaceutical industries, as support for their practice of process safety.

The objective of the book is not to turn the reader into a specialist in thermal safety. It is to guide those who perform risk analysis of chemical processes, develop new processes, or are responsible for chemical production, to understand the thermal aspects of processes and to perform a scientifically founded – but practically oriented – assessment of chemical process safety. This assessment may serve as a basis for the optimization or the development of thermally safe processes. The methods presented are based on the author's long years of experience in the practice of safety assessment in industry and teaching students and professionals in this matter. It is also intended to develop a common and understandable language between specialists and non-specialists.

The book is structured in three parts:

Part I gives a general introduction and presents the theoretical, methodological and experimental aspects of thermal risk assessment. The first chapter gives a general introduction on the risks linked to the industrial practice of chemical reactions. The second chapter reviews the theoretical background required for a fundamental understanding of runaway reactions and reviews the thermodynamic and kinetic aspects of chemical reactions. An important part of Chapter 2 is dedicated to the heat balance of reactors. In Chapter 3, a systematic evaluation procedure developed for the evaluation of thermal risks is presented. Since such evaluations are based on data, Chapter 4 is devoted to the most common calorimetric methods used in safety laboratories.

Part II is dedicated to desired reactions and techniques allowing reactions to be mastered on an industrial scale. Chapter 5 introduces the dynamic stability of chemical reactors and criteria commonly used for the assessment of such stability. The behavior of reactors under normal operating conditions is a prerequisite for safe operation, but is not sufficient by itself. Therefore the different reactor types are reviewed with their specific safety problems, particularly in the case of deviations from normal operating conditions. This requires a specific approach for each reactor type, including a study of the heat balance, which is the basis of safe temperature control, and also includes a study of the behavior in cases where the temperature control system fails. The analysis of the different reactor types and the general principles used in their design and optimization is presented in Chapters 6 to 8. Chapter 6 presents the safety aspects of batch reactors with a strong emphasis on the temperature control strategies allowing safe processes. In Chapter 7, the semi-batch reactor is analysed with the different temperature control strategies, but also with the feed control strategies reducing the accumulation of non-converted reactants. In Chapter 8, the use of continuous reactors for mastering exothermal reactions is introduced. The temperature control requires technical means that may strongly influence operation safety. Therefore Chapter 9 is dedicated to the technical aspects of heat transfer, and the estimation of heat transfer coefficients. Since risk reducing measures are often required to maintain safe operation, such as in the failure of the process control system, Chapter 10 is specifically dedicated to the evaluation of the control of a runaway reaction and the definition and design of appropriate risk reducing measures.

Part III deals with secondary reactions, their characterization, and techniques to avoid triggering them. Chapter 11 reviews the general aspects of secondary reactions, determination of the consequences of loss of control and the risk assessment. Chapter 12 is dedicated to the important category of self-accelerating reactions, their characteristics, and techniques allowing their control. The problem of heat confinement, in situations where heat transfer is reduced, is studied in Chapter 13. The different industrial situations where heat confinement may occur are reviewed and a systematic procedure for their assessment is presented together with techniques that may be used for the design of safe processes.

Each chapter begins with a case history illustrating the topic of the chapter and presenting lessons learned from the incident. Within the chapters, numerous examples stemming from industrial practice are analysed. At the end of each chapter, a series of exercises or case studies are proposed, allowing the reader to check their understanding of the subject matter.

Acknowledgements

The methodology presented in this book is the result of long-term experience and concerns with the assessment of thermal risks in the chemical process industry gained in the Central Safety Research Laboratories of Ciba. Therefore the author would like to thank his colleagues: K. Eigenmann, F. Brogli, R. Gygax, H. Fierz, B. Urwyler, P. Lerena, and W. Regenass, who all participated in the development of the methodology and techniques covered in this book. He would also like to thank the management of the Swiss Institute for the Promotion of Safety & Security, M. Glor and H. Rüegg, who encouraged him to persevere in the project.

Many applications and methods were developed by students or young colleagues during diploma works, PhD-thesis or development projects. Among others, the author is grateful to J.M. Dien, O. Ubrich, M.A. Schneider, B. Zufferey, P. Reuse and B. Roduit.

Writing a book like this is a long-term project, which cannot be brought to its end without some sacrifices. Thus my last thoughts go to my family, especially my wife Michèle, who not only accepted neglect during the course of writing, but also encouraged and supported me and the work.

Part I
General Aspects of Thermal Process Safety

1
Introduction to Risk Analysis of Fine Chemical Processes

Case History

A multi-purpose reactor was protected against overpressure by a rupture disk, which lead directly to the outside through the roof of the plant. During a maintenance operation, it was discovered that this disk was corroded. Although it was decided to replace it, there was no spare part available. Since the next task to be carried out was a sulfonation reaction, it was decided to leave the relief pipe open without the rupture disk in place. In fact, a sulfonation reaction cannot lead to overpressure (sulfuric acid only starts to boil above 300 °C), so such a protection device should not be required. During the first batch a plug of sublimate formed in the relief line. This went unnoticed and production continued. After heavy rain, water entered the relief tube and accumulated above the sublimate plug. As the next batch began, the plug heated and suddenly ruptured, allowing the accumulated water to enter the reactor. This led to a sudden exothermal effect, due to the dilution of concentrated sulfuric acid. The increase in temperature triggered sudden decomposition of the reaction mass, causing the reactor to burst, resulting in huge damage.

Lessons drawn

This type of incident is difficult to predict. Nevertheless, by using a systematic approach to hazard identification it should become clear that any water entering the reactor could lead to an explosion. Therefore when changing some parts of the equipment, even if they are not directly involved in a given process, especially in multi-purpose plants, one should at least consider possible consequences on the safety parameters of the process.

1.1
Introduction

Systematic searches for hazard, assessment of risk, and identification of possible remediation are the basic steps of risk analysis methods reviewed in this chapter.

After an introduction that considers the place of chemical industry in society, the basic concepts related to risk analysis are presented. The second section reviews the steps of the risk analysis of chemical processes discussed. Safety data are presented in the third section and the methods of hazard identification in the section after that. The chapter closes with a section devoted to the practice of risk analysis.

1.2
Chemical Industry and Safety

The chemical industry, more than any other industry, is perceived as a threat to humans, society, and the environment. Nevertheless, the benefits resulting from this activity cannot be negated: health, crop protection, new material, colors, textiles, and so on. This negative perception is more enhanced after major accidents, such as those at Seveso and Bhopal. Even though such catastrophic incidents are rare, they are spectacular and retain public attention. Thus, a fundamental question is raised: “What risk does society accept regarding the benefits of an activity, of a product?” Such a question assumes that one is able—a priori—to assess the corresponding risk.

In the present chapter, we focus on the methods of risk analysis as they are performed in the chemical industry, and especially in fine chemicals and pharmaceutical industries.

1.2.1
Chemical Industry and Society

The aim of the chemical industry is to provide industry and people in general with functional products, which have a precise use in different activities such as pharmaceuticals, mechanics, electricity, electronics, textile, food, and so on.

Thus, on one hand, safety in the chemical industry is concerned with product safety, that is, the risks linked with the use of a product. On the other hand, it is concerned with process safety, that is, the risks linked with manufacturing the product. In this book, the focus is on process safety.

1.2.1.1 Product Safety

Every product between its discovery and its elimination passes through many different steps throughout its history: conception, design, feasibility studies, market studies, manufacturing, distribution, use, and elimination, the ultimate step, where from functional product, it becomes a waste product [1].

During these steps, risks exist linked to handling or using the product. This enters the negative side of the balance between benefits and adverse effects of the product. Even if the public is essentially concerned with the product risks during its use, risks are also present during other stages, that is, manufacture, transportation, and storage. For pharmaceutical products, the major concerns are secondary effects. For other products, adverse effects are toxicity for people and/or for the environment, as well as fire and explosion. Whatever its form, once a product is no longer functional, it becomes a waste product and thus represents a potential source of harm.

Therefore, during product design, important decision have to be made in order to maximize the benefits that are expected from the product and to minimize the negative effects that it may induce. These decisions are crucial and often taken after a systematic evaluation of the risks. Commercialization is strictly regulated by law and each new product must be registered with the appropriate authorities. The aim of the registration is to ensure that the manufacturer knows of any properties of its product that may endanger people or the environment and is familiar with the conditions allowing its safe handling and use, and finally safe disposal at the end of the product's life. Thus products are accompanied by a Material Safety Data Sheet (MSDS) that summarizes the essential safety information as product identity, properties (toxicity, eco-toxicity, physical chemical properties), information concerning its life cycle (use, technology, exposure), specific risks, protection measures, classification (handling, storage, transportation), and labeling.

1.2.1.2 **Process Safety**

The chemical industry uses numerous and often complex equipment and processes. In the fine chemical industries (including pharmaceuticals), the plants often have a multi-purpose character, that is, a given plant may be used for different products. When we consider a chemical process, we must do it in an extensive way, including not only the production itself but also storage and transportation. This includes not only the product, but also the raw material.

Risks linked with chemical processes are diverse. As already discussed, product risks include toxicity, flammability, explosion, corrosion, etc. but also include additional risks due to chemical reactivity. A process often uses conditions (temperature, pressure) that by themselves may present a risk and may lead to deviations that can generate critical effects. The plant equipment, including its control equipment, may also fail. Finally, since fine chemical processes are work-intensive, they may be subject to human error. All of these elements, that is, chemistry, energy, equipment, and operators and their interactions, constitute what we call process safety.

1.2.1.3 **Accidents in Chemical Industry**

Despite some incidents, the chemical industry presents good accident statistics. A statistical survey of work accidents shows that chemistry is positioned close to the end of the list, classified by order of decreasing lost work days [2] (Table 1.1). Further, these accidents only constitute a minor part due to chemical accidents, the greatest part consisting of common accidents such as falls, cuts, and so on that can happen in any other activity.

1.2.1.4 **Risk Perception**

Another instructive comparison can be made by comparing fatalities in different activities. Here we use the Fatal Accident Rate index (FAR) that gives the number of fatalities for 10^8 hours of exposure to the hazard [3, 4]. Some activities are compared in Table 1.2. This shows that even with better statistics in terms of fatali-

Table 1.1 Accidents at work in different industries in Switzerland, from the statistics of the Swiss National Accident Insurance (2005).

Activity	Work accidents for 1000 insured
Construction	185
Wood	183
Mining	160
Metallurgy	147
Cement, glass, ceramics	130
Food	113
Rubber, plastics	95
Machinery	72
Transport	66
Energy	59
Textile, clothes	50
Offices, administration	46
Paper, graphics	45
Chemistry	**37**
Electricity, fine mechanics	33

Table 1.2 Some values of the FAR index for different activities.

Industrial activities	FAR	Non industrial activities	FAR
Coal mining	7.3	Alpinism	4000
Construction	5	Canoe	1000
Agriculture	3.7	Motor bike	660
Chemistry	**1.2**	Travel by air	240
Vehicle manufacturing	0.6	Travel by car	57
Clothing manufacturing	0.05	Travel by railway	5

ties, industrial activities are perceived as presenting higher risks. This may essentially be due to the risk perception. The difference in perception is that for traveling or sporting activities, the person has the choice as to whether to be exposed or not, whereas for industrial activities exposure to risk may be imposed. Industrial risks may also impinge on people who are not directly concerned with the activity. Moreover, the lack of information on these risks biases the perception [5].

1.2.2 Responsibility

In industrial countries, employers are responsible for the safety of their employees. On the other hand, legal texts often force the employees to apply the safety rules prepared by employers. In this sense, the responsibility is shared. Environment protection is also regulated by law. Authorities publish threshold limits for pollutants and impose penalties in cases where these limits are surpassed. In the European Union, the Seveso directive regulates the prevention of major accidents: if dangerous substances are used in amounts above prescribed limits, industries have to prepare a risk analysis that describes quantitatively possible emissions and their effect on the neighboring population. They also have to provide emergency plans in order to protect that population.

In what concerns process safety, the responsibility is shared within the company by the management at different levels. The Health Safety and Environment staff plays an essential role in this frame, thus during process design, safety should have priority.

1.2.3 Definitions and Concepts

1.2.3.1 Hazard

Definition of the European Federation of Chemical Engineering (EFCE) [6]:

> A situation that has the potential to cause harm to human, environment and property.

Thus, hazard is the antonym of safety. For the chemical industry, the hazard results from the simultaneous presence of three elements:

1. A threat stemming from the properties of processed substances, chemical reactions, uncontrolled energy release, or from equipment.
2. A failure that may be of technical origin or stem from human error, either during the operation or during process design. External events, such as weather conditions or natural catastrophe may also be at the origin of a failure.
3. An undetected failure in a system as non-identified hazards during risk analysis, or if insufficient measures are taken, or if an initially well-designed process gradually deviates from its design due to changes or lack of maintenance.

1.2.3.2 Risk

The EFCE defines risk as a measure of loss potential, and damage to the environment or persons in terms of probability and severity. An often-used definition is that risk is the product of severity time probability:

$$Risk = Severity \times Probability \tag{1.1}$$

In fact, considering risk as a product is somewhat restrictive: it is more general to consider it as a combination of the terms, severity and probability, that characterize the effects, that is, consequences and impact of a potential accident and its probability of occurrence. This also means that the risk is linked to a defined incident scenario. In other words, the risk analysis will be based on scenarios that must first be identified and described with the required accuracy, in order to be evaluated in terms of severity and probability of occurrence.

1.2.3.3 Safety

Safety is a quiet situation resulting from the real absence of any hazard [7].

Absolute safety (or zero risk) does not exist for several reasons: first, it is possible that several protection measures or safety elements can fail simultaneously; second, the human factor is a source of error and a person can misjudge a situation or have a wrong perception of indices, or may even make an error due to a moment's inattention.

1.2.3.4 Security

In common language, security is a synonym of safety. In the context of this book, security is devoted to the field of property protection against theft or incursion.

1.2.3.5 Accepted Risk

The accepted risk is a risk inferior to a level defined in advance either by law, technical, economical, or ethical considerations. The risk analysis, as it will be described in the following sections, has essentially a technical orientation. The minimal requirement is that the process fulfils requirements by the local laws and that the risk analysis is carried out by an experienced team using recognized methods and risk-reducing measures that conform to the state of the art. It is obvious that non-technical aspects may also be involved in the risk acceptation criteria. These aspects should also cover societal aspects, that is, a risk–benefit analysis should be performed

1.3 Risk Analysis

A risk analysis is not an objective by itself, but is one of the elements of the design of a technically and economically efficient chemical process [1]. In fact, risk analysis reveals the process inherent weaknesses and provides means to correct them. Thus, risk analysis should not be considered as a "police action," in the sense that, at the last minute, one wants to ensure that the process will work as intended. Risk analysis rather plays an important role during process design. Therefore, it is a key element in process development, especially in the definition of process control strategies to be implemented. A well-driven risk analysis not only leads to a safe process, but also to an economic process, since the process will be more reliable and give rise to less productivity loss.

1.3.1 Steps of Risk Analysis

There are many risk analysis methods, but all have three steps in common:

1. search for hazards,
2. risk assessment, and
3. definition of risk-reducing measures.