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A Hierarchical Approach for Assessment of Principal Hazards in Early Stages of Chemical Process Design

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TO MY PARENTS
AND SISTERS

"We owe a lot to the Indians, who taught us how to count, without which no worthwhile scientific discovery could have been made."

ALBERT EINSTEIN

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Abstract

In recent years the importance of safety and environmental issues in chemical process design has increased. The idea of inherent safe and 'green' processes has arisen. From this perspective the final goal is to design ideal chemical processes that need only the minimum amounts of raw materials and energy and that do not require elaborate safety measures and end of pipe technologies. While chemical processes are continuously improving in this direction, nowadays safety and end of pipe technologies are still indispensable. This thesis presents a concept that in a hierarchical approach reveals the degree of non-ideality of chemical processes with regard to SHE (Safety, Health and Environment) aspects at different layers: the properties of the chemical substances involved (Substance Assessment Layer), possible interactions between the substances (Reactivity Assessment Layer), possible hazard scenarios resulting from the combination of substances and operating conditions in the various equipments involved (Equipment Assessment Layer), and the safety technologies that are required to run a process safely and in accordance with legal regulations (Safety-Technology Assessment Layer).

The developed method called SREST (Substance, Reactivity, Equipment, Safety-Technology) Layer-Assessment method is suited for the early stages of chemical process design. Substance Assessment Layer (SAL) and Reactivity Assessment Layer (RAL) are adequate for process research stage while Equipment Assessment Layer (EAL) and Safety-Technology Assessment Layer (STAL) are suitable for process development stage. In SAL, EHS method (Koller, 2000), which is slightly modified in the SREST method, is used to assess all the substances present in the process under environmental, health and primarily safety aspects. In RAL, reactivity of different substances present in the process is crosschecked with air, water, trace impurities, material of construction and other substances present in the process and the surroundings. In EAL, possible worst-case scenarios in different equipment units (batch/semi-batch reactor, storage tank, distillation column and dryer) are assessed with the help of unit-operation models. In STAL, safety technologies are predicted to prevent and to mitigate worst-case scenarios in different equipment units. In each layer, the

assessment results are presented as indices, for example, substance indices in 11 effect categories under safety, health and environmental aspects in SAL, reactivity indices in RAL, runaway hazard indices in EAL and reduction factors in STAL. In each layer, the acceptability decisions are to be taken with the help of these indices and the acceptable limits (defined for each layer). One can use inherent-safety-principles, (e.g., minimization and substitution of critical substances) after the assessment of any layer or after the assessment of the whole process if hazard potentials are not acceptable. If the overall assessment of all hazard potentials resulting from the four layers concludes an unacceptable process, even after using the inherent-safety principles and applying appropriate safety technologies, then an alternative i.e., a different synthesis route, should be assessed and investigated again using the SREST method.

Several case studies were used to demonstrate the applicability of method. These case studies are: production of an azo dye intermediate; sulfonation of nitro-aromatic compound; production of mono-nitro-toluene; production of poly-acrylonitrile; production of acrylic resins; storage of methyl-ethyl-ketone-peroxide; separation of hydroxylamine and water in distillation column; and drying of hydroxyurea. With the help of results obtained, it is shown how the method reveals the degree of non-ideality of different chemical process aspects with regard to inherent and process safety. Furthermore, the method helps in identifying those technical measures that have to be taken in order to run the process nonetheless. Overall it is concluded that the method can be used as a systematic tool to support chemical engineers and chemists in evaluating chemical process safety in early process development stages.

Zusammenfassung

Sicherheits- und Umweltschutzaspekte gewinnen im Rahmen der chemischen Prozessentwicklung zunehmend an Bedeutung. Dieser Trend drückt sich in der in den letzten Jahren formulierten Zielsetzung inhärent sicherer und "grüner" Prozesse aus. Aus dieser Sichtweise ergibt sich das Ziel der Entwicklung von chemischen Prozessen, die lediglich ein Minimum an Rohmaterialien und Energie gebrauchen und die keine aufwändigen Sicherheits- und Entsorgungsmassnahmen benötigen. Während sich chemische Prozesse kontinuierlich in die Richtung dieser Zielsetzung entwickeln, so sind heute Sicherheits- und Entsorgungsmassnahmen noch unverzichtbar. Diese Arbeit präsentiert ein Konzept, das in einem hierarchischen Ansatz mit verschiedenen Ebenen den Grad der Nicht-Idealität chemischer Prozesse in Hinsicht auf Sicherheits-, Arbeitsschutz- und Umweltzschutzaspekte (Environment, Health and Safety, EHS) aufdeckt. Der hierarchische Ansatz beinhaltet die folgenden vier Ebenen: die Eigenschaften der chemischen Substanzen (Substance Assessment Layer, SAL); potentielle Wechselwirkungen zwischen den chemischen Substanzen (Reactivity Assessment Layer, RAL); mögliche Gefahrenszenarien die sich aus der Kombination von Substanzen und Betriebsbedingungen in verschiedenen Apparaten ergeben können (Equipment Assessment Layer, EAL); Sicherheitstechnologien die benötigt werden, um den Prozess sicher und in Übereinstimmung mit gesetzlichen Regelungen durchzuführen (Safety-Technology Assessment Layer, STAL).

Die in dieser Arbeit vorgestellte Methode mit der Abkürzung SREST (Substance, Reactivity, Equipment, Safety-Technology) eignet sich für die frühen Stufen der chemischen Prozessentwicklung. SAL und RAL können auf der Stufe der Prozessforschung eingesetzt werden und EAL und STAL in der Prozessentwicklungstufe. Auf der SAL-Ebene wird in leicht modifizierter Form die sogenannte EHS-Methode (Koller, 2000) verwendet, um die chemischen Substanzen in einem Prozess im Hinblick auf Sicherheits-, aber auch Arbeitsschutz- und Umweltschutzaspekte zu bewerten. Auf RAL-Ebene werden mögliche Wechselwirkungen zwischen den im Prozess vorhandenen Chemikalien sowie mit Luft, Wasser, Verunreinigungen, den Konstruktionsmaterialien der Apparate und den in

benachbarten Prozessen gebrauchten Verbindungen untersucht. Auf EAL-Ebene werden mögliche Worst-Case Szenarien in verschiedenen Apparaten (Batch/Semi-Batch Reaktor, Tank, Rektifikationskolonne und Trockner) anhand von Einheitsoperationsmodellen untersucht. Auf STAL-Ebene wird vorausgesagt, welche Sicherheitsmassnahmen vermutlich benötigt werden, um die möglichen Worst-Case Szenarien zu verhindern oder zu entschärfen. Auf jeder Ebene wird das Resultat der Bewertung in Form von Indizes festgehalten, z.B. den Indizes für die Substanzbewertung auf SAL-Ebene, den Reaktivitätsindizes, oder den Runaway-Indizes für das entsprechende Worst-Case Szenario in einem Batch-Reaktor. Die berechneten Indizes können mit entsprechenden Limiten verglichen werden. Aus diesem Vergleich kann z.B. ersehen werden, ob Prinzipen der inhärenten Sicherheit zur Anwendung kommen sollten, um z.B. kritische Substanzen zu ersetzen oder ihre Menge zu minimieren. Wenn auch die Anwendung derartiger Prinzipen nicht zu einem akzeptablem Risikoniveau führt, dann muss nach einer alternativen Synthese-Route gesucht werden, die wiederum mit der SREST-Methode untersucht werden kann.

Mehrere Fallbeispiele wurden untersucht, um die Anwendbarkeit der Methode zu demonstrieren: die Produktion einer Zwischenstufe eines Azo-Farbstoffes; die Sulfonierung eines Nitro-Aromaten; die Produktion von Nitro-Toluol; die Produktion von Poly-Acrylnitril; die Produktion von Acryl-Harzen; die Lagerung von Methyl-Ethyl-Keton-Peroxid; die Trennung von Hydroxyl-Amin und Wasser in einer Rektifikationskolonne; sowie die Trocknung von Hydroxyl-Harnstoff. Anhand der mittels der SREST-Methode erhaltenen Resultate wird gezeigt, wie die Methode den Grad der Nicht-Idealität von chemischen Prozessen im Hinblick auf Sicherheitsaspekte aufdeckt. Desweiteren unterstützt die Methode die Benennung derjenigen Sicherheitsmassnahmen, die getroffen werden müssen, um einen nicht vollständig inhärenten Prozess trotzdem durchzuführen. Insgesamt wird die Schlussfolgerung gezogen, dass die SREST-Methode Chemiker und Chemieingenieure dabei unterstützen kann, auf systematische Weise Aspekte der chemischen Prozesssicherheit in verschiedenen Stufen der Prozessentwicklung zu bewerten.

1. Introduction

Chemical industries play an important role in human life. They contribute in many parts of human life to make it easy to live and to increase the standard of living by producing a variety of products. For example, they produce medicines to recover from diseases, produce fertilizers to keep land fertile, refine natural oil to use for different purposes, and produce preservatives for food products. As every part has some advantages and disadvantages, chemical industries also have some negative consequences to human and environment, for example, toxic substances which affect human health; unsafe reactions which cause accidents; and release of green house gases which cause global warming. Due to increasing production volumes and a higher knowledge about the hazard potential of chemical substances and processes, environmental and safety issues came into public, regulatory as well as industrial focus during the 60's.

Stringent environmental regulations and the hard competition on the global market forced industry to adjust its approach towards safety and the environment. An increase in the number of accidents in chemical industries and growing environmental concerns have caused many governments to ask industries to study worst-case scenarios, to control the risk of accidents and to handle produced hazardous wastes and emissions. As a consequence, academia as well as industries put an increased effort in the development of alternative synthesis routes that are inherently safer i.e. result in reduced environmental, health and safety hazards. A system is inherently safe if it remains in a non-hazardous situation after the occurrence of all expected deviations from normal operating conditions. Avoiding problems rather than handling them, solving problems at their roots rather than managing the consequences, was the new goal in the centre of industrial and government attention. The concept of integrated process development (Hungerbühler et al., 1998) stresses the importance of considering all economic as well as environmental, health and safety aspects starting from the early stages of developing a new chemical process.

Before performing risk or EHS (Environment, Health and Safety) assessment, a clear definition of hazard and risk is necessary for better understanding. The sciences

analyzing and describing risks are relatively new and developing, and the associated terminologies are developing as well. This has led to ambiguity in the use of terms, both between different risk sciences and between the different parties involved in risk debates. Christensen et al. (2003) have examined and explained these vocabularies or terminologies based on a division into fundamental and action oriented risk terms. The paper, which is a complementary to a recent work prepared by WHO, covers mainly terminology applied within engineering risk analysis and toxicological risk assessment for characterization and management of risks towards humans, the environment and physical installations caused by physical forces or chemical agents. They have used core references, for example, EU, UN/OECD, US-EPA, Seveso II-directive for comparison and discussion. *They have defined hazard as "The inherent property/properties of a risk source potentially causing consequences/effects." and risk as "A combination of the probability of consequence/effect on the considered object(s), severity and extent of the consequence/effect under given specified circumstances".* A number of definitions, for example, event, exposure, cause-effect relationship, severity and probability etc. from different core sources have been discussed and presented for better understanding.

In order to assess environmental, health and safety hazards of chemical processes, various methods were developed by academia (e.g., EHS method by Koller et al. (2000), HIRA, HIRA-TDI and HIRA-FEDI by Khan and Abbasi (1998a)) and industries (e.g., Dow F&EI by Dow Chemicals (1994)) for different stages of process design. There are a large number of methods of hazard identification and techniques available preliminary to hazard and risk analysis (McCoy et al., 1999a). They include:

1. Checklists.
2. What if? analysis.
3. Failure mode effects analysis.
4. Coarse hazard study.
5. HAZOP.
6. Event tree analysis.
7. Fault tree analysis.
8. Cause-consequence analysis.

9. Sneak analysis.

10. Task analysis.

11. Scenario development.

12. Preliminary hazard analysis.

13. Preliminary safety analysis.

14. EHS assessment.

15. Inherent hazard indices, etc.

Overviews of these and other methods of hazard identification have been given by the Center for Chemical Process Safety (1985, 1992) and Lees (1996). Khan and Abbasi (1998b) also presented a brief overview of different risk assessment methods, for example, HAZOP, Fault tree analysis, Failure mode effect analysis etc. with their salient features and important drawbacks. Each method has its advantages, limitations and applicability for different scenarios and processes. Some methods are quite detailed (e.g., HAZOP, Fault tree analysis (FTA), Failure mode effect analysis (FMEA)) and therefore only applicable for well-defined plant systems and some are qualitative index methods (e.g., EHS method by Koller et al. (2000), Inherent Safety Index (ISI) by Edward and Lawrence (1995)) meant for the early stages of process design. A number of textbooks and reviews are available describing hazard evaluation methods (e.g., Crowl and Louvar (1990), Khan and Abbasi (1998b)) and providing comparison of different methods (Koller et al., (2001), Khan and Abbasi (1998a), Steinbach et. al (1998)). Recently, Tixier et al. (2002) reviewed 62 different risk analysis methodologies of industrial plants and dealt with the application fields and the main limitations of these methodologies. They classified the methods into qualitative and quantitative ones and analysed the relationships between the methodologies, input data and the results delivered. They concluded that there is not a single general method to deal with the problems of industrial risks. The complexity of chemical processes together with social and legal pressures emphasizes the strong need of more effective solutions for the safety and environmental issues in the design and operation of chemical plants.

This thesis presents a new concept for environmental, health and primarily safety assessment of chemical processes in early design stages. The new method is based on the following concepts that are discussed in detail below:

a) EHS assessment in early stages of process design

b) Focus on inherent safety,

c) Assessment of major unit operations and major worst-case scenarios,

d) Incorporation of safety technologies in risk assessment, i.e., multilayer approach including the layer of safety technologies, and

e) Different existing software tools, i.e., high degree of automation of the methodology.

a) EHS assessment in early stages of process design

A new approach to assess environmental, health and safety aspects in early stages of design was considered by Koller et al. (2000) in their EHS method. A flexible structure combining best available practices from risk analysis and environmental assessment is proposed. EHS aspects are assessed in 11 effect categories. For each substance of a given chemical process and each EHS effect, the most reliable data are selected out of a set of possible parameters depending on the substance data availability. The EHS method is flexible enough to incorporate all available information with the help of using different priority levels and is also applicable in the case that some substance data are missing.

The EHS method has been compared with other methods for assessing the hazard potential of chemical processes during early design stages (e.g., ISI, ISI2, INSET, RPE, Metrik, Dow F&EI, Dow CEI, HIRA-FEDI, HIRA-TDI) and advantages and limitations of the different methods have been discussed (Koller et al., 2001). The selected methods are applied to nine different processes and the results show that if two different assessment methods are used for comparing two processes in order to identify the more dangerous one, in 75% of the cases both methods deliver the same result. The comparison (Koller et al., 2001) shows the high dependence of the results on the selected assessment method. Thus, the selection of a method for a given purpose has to

be made carefully and the user should be aware of its characteristics and their influence on the results obtained.

b) Focus on inherent safety

It is well accepted that achieving increased inherent safety by the consideration of EHS aspects in the initial stages of chemical process design, not only leads to plants that are safer, more health friendly and environmentally benign but also results in reduced overall costs. Therefore chemical industries are moving towards the concept of inherent safety in early stages of design in which the goal is to avoid possible sources of dangers and to minimize the potential risk. 'Inherent safety' (Kletz, 1976) was introduced as a different concept of risk management and a number of qualitative index methods for assessing the degree of inherent safety (e.g., Koller et al. (2000), Edwards and Lawrence (1995)) were developed. Edwards and Lawrence (1995) developed an index method for ranking the inherent safety of different possible synthesis routes, which is the key decision in early design that fixes the major extent of inherent safety of the plant.

One overall inherent safety index for process synthesis was developed by Heikkila et al. (1996). This index method can be applied in the earlier stages of a process development. This inherent safety index is divided into two main categories, the Chemical Inherent Safety Index and the Process Inherent Safety Index. Different sub-indices further depict specific aspects affecting inherent safety e.g. flammability and side reaction hazards. These sub-indices are based on Boolean mathematics, and each sub-range can be seen as a set with sharp boundaries. This behaviour produces two significant effects i.e. excessive sensitivity in regions close to the limits of each sub-range and insufficient sensitivity within each sub-range. For solving these two problems, Gentile et al. (2003) used fuzzy logic theory that is an extension of the Boolean theory, and compared their results to those from the Heikkila index.

Khan and Abbasi (1998c) proposed, "Rapid Risk Analysis based Inherently Safer Design" in which they define a set of accident scenarios, acceptance criteria and propose a design solution. Deterministic calculations are performed on these design solutions and results are evaluated against acceptance criteria until an acceptable design

is reached. Palaniappan et al. (2002a, 2002b) developed an automated expert system for the design of inherently safer processes in the route selection and flow-sheet development stages of process design. They have presented a new inherent safety index for ranking of process routes and a graphical method for analyzing reaction networks. Gupta and Edwards (2003) worked to solve the question about how to measure inherently safer design characteristics of a process and they proposed a graphical method where each of the important parameters affecting the safety (e.g., temperature, pressure, toxicity, etc.) are considered and plotted with the range of possible values these parameters can have for all the process routes under consideration for an end product and then are compared with each other. They noted that the experts, when they looked at the reaction steps, were not looking at the tables of scores but at each step individually as to how it measured up to their idea of the hazard potential. By this way, they confirmed that consideration of each step is important instead of the tables of scores and their subsequent addition that will get biased by the number of steps. This concept is also used in EHS method by Koller et al. (2000) by presenting 11 different categories separately instead of making one overall index to highlight the problems.

c) Assessment of major unit operations and major worst-case scenarios

In order to focus the limited resources available for hazard evaluation on the major problems of a plant (e.g., the most dangerous units in a large process, or the most dangerous process in a high number of processes), some kind of hazard evaluation method has to be applied (e.g., HIRA-FEDI, HIRA-TDI, Dow F&EI, Dow CEI). Such methods and tools can be applied quickly and result in a ranking showing whether a process or a unit operation has a high potential of danger and needs further investigation or not. These methods are developed for existing processes and require a varying amount of information about the plant (Koller et al., 2001). Khan and Abbasi (2002a) have developed a criterion for developing credible accident scenarios for risk assessment. With the help of this criterion, credible accident scenarios may be identified from among a large number of possibilities and may then be processed for detailed consequence analysis. This proposal of a maximum credible accident analysis with a maximum credible accident scenario approach, scores over a worst-case scenario approach for being realistic and reliable. Some methods, for example, scenario

development and maximum credible accident analysis use worst-case or credible accident scenario analysis for presenting the risk hazards. Leggett (2001) used worst-case scenario analysis in his paper about the 'safe process development from reaction hazards testing'. He presented that the *basis of safety* is derived from the WCS (Worst Case Scenario) analysis which defines specific operating conditions that must be adhered to in order to ensure that the WCS is not realized. The OSHA-PSM (Occupational Safety and Health Administration-Process Safety Management in USA) standard also evaluates the chemical process hazards by establishing the worst-case scenario(s) and by defining the most severe credible worst-case scenario(s).

d) Incorporation of safety technologies in risk assessment

Zwetsloot et al. (2002) concluded that the concept of inherently safer production is feasible and that it has great potential for simultaneous improvement of safety and economic performance. However, the complexity of modern plants and economic factors render it difficult to replace instantaneously or avoid all possible sources of danger from the processes. According to the well-known Murphy's Law (Hendershot, 2000), "If anything can go wrong, it will and nature always sides with the hidden flaw.", the existing non-idealities of processes make safety and end-of-pipe technologies still indispensable. Khan et al. (2001) pointed out that Dow (Dow chemicals, 1994) and Mond (Lewis, 1979) indices do consider some factors to account for the safety measures existing or planned in the unit, but much greater rigour, accuracy and precision are needed. In this context, Khan et al. (2001) have developed the Safety Weighted Hazard Index (SWeHI) for assessing hazards in chemical process industries, which incorporates the contribution of safety measures in its final hazard assessment score. Furthermore, Khan and Abbasi combined two approaches, maximum credible accident analysis (Khan and Abbasi, 2002) and probability fault tree analysis (Khan and Abbasi, 2000) for a more realistic, reliable and efficient safety evaluation and the design of risk control measures, which resulted in a methodology called SCAP (Khan et al., 2002). In this methodology, they use SWeHI method, which takes the credit of control measures and safety arrangement, to identify and rank the hazards. Gupta et al. (2003) have extended Dow Fire and Explosion Index by taking the effects of the LCMs (Loss Control Measures) into account in the F&EI value because without LCMs

consideration, it makes the plant look more hazardous, makes it more spread out, requires more elaborate emergency measures and alarms the public and the civil administration more than is necessary. It also affects the insurance premium.

e) Different existing software tools

A number of software tools exist to apply EHS assessment and hazard evaluation methods in different stages of process development. Due to the automation, the assessment process becomes faster. Using different design algorithms or mathematical optimization techniques one can make decisions quickly and efficiently. The Dow fire and explosion index (F&EI) and chemical exposure index (CEI) have been successfully implemented in a Visual Basic environment as a tool for the inherent safety assessment of chemical processes (Etowa et al., 2002). The paper-based INSET toolkit was developed by the INSIDE Project, an European Community project, to review the status of inherently safer process and plant design in European process industries and to develop tools and methodologies for systematic application of inherent safety. The INSET toolkit provides a number of tools, which vary in their level of detail and scope to suit different types of projects and the different stages in a project. The Toolkit uses 4 project stages that represent some of the main decision points and that have been derived from a study of design and development projects practices across Europe. Schabel (1997) has presented stages I and II and Mansfield (1997) has presented stages III and IV in their papers regarding INSET toolkit. Also the EHS method is presented in the form of a software tool (Koller et al., 1999 and Koller, 2000). McCoy et al. (1999a, 1999b, 1999c) presented the HAZID or HAZOP emulator, which is a computer aid for hazard identification in the style of HAZOP for an existing plant. Khan and Abbasi have also presented their different risk assessment methods with automatic tools, for example, SCAP (Safety, Credible Accident, Probabilistic fault tree analysis) etc. to speed up the evaluation process.

Successful management of health and safety aspects in industry requires a systematic approach. This must include a decision-making process that is appropriate, soundly based, open and transparent, so that all interested parties can participate and see that the objectives are achieved (HSE, 1997). For all installations with the potential to cause a

major accident, a risk assessment is necessary where all significant hazards must be addressed, and suitable controls provided (HSE, 1999). The different concepts can be used in one single framework or in a hierarchical approach with an automatic software tool to scrutinize different synthesis routes of the process in early development stage with the help of database available and to help chemists and chemical engineers in laboratory to speed up the procedure. This single framework can be developed for efficient, economic and fast assessment of the chemical process.

1.1 Motivation for developing a new concept

The goal of the thesis is to make chemical processes safe, health friendly and environmentally benign already in early stages of process development by identifying different hazards related with substances and unit operations in the plant, by using inherent safety principles and by predicting and proposing different safety technologies to reduce the probability of accidents. For this purpose a new approach has to be developed.

There are different stages of chemical process design as shown in Figure 1.1. The selection of synthesis routes, reaction chemistry etc. is done in process research, i.e. laboratory stage. The process conditions are decided, major unit-operations are selected and the reaction route is developed further in the process development i.e. bench/pilot stage. Finally, a detailed pipe and instrumentation diagram (PID) is prepared and the selected process is scaled up to the manufacturing level in production stage. In the early stages of design, detailed information for example, reaction kinetics, pipe and instrumentation diagram (PID) is not available. Therefore detailed risk assessment methods, which use all the particulars and specifications in the process, cannot be used in process research stage.

A lot of research work is done to assess the EHS aspects in early stages of chemical process design but still there are some vital points to be considered carefully in the assessment:

1.   In early stages of process design, generally no information about technical details (e.g., safety measures) or sometimes even about the flow-sheet itself

is available. Therefore thorough concepts cannot be used for assessing EHS aspects.

2. In early stages of process design, the assessment should incorporate as much information as available. Nevertheless, the limitations of the available data should be considered.

3. High time pressure on process development teams can generate flaws in the assessment and can be a cause of a problem. Therefore as many tasks as possible should be automated (e.g., by using computer programs that provide required data and conduct hazard assessments).

4. The automated tool should have a systematic procedure to educate chemists, chemical engineers and technicians.

5. The methodology should cover the concept of inherent safety to remove or avoid possible sources of danger.

6. The methodology should consider the assessment of possible worst-case scenarios in the case of moderate or highly hazardous chemicals or reactions present in the process.

7. The methodology should use screening methods requiring as few data as possible to remove undesired or highly hazardous options from the list.

8. In the case of non-idealities of the process, prevention and protective measures should be predicted and recommended in order to show realistic hazards.

There is a need of a method that can be used in early stages of design and that uses all available information and data in this stage, screens different reactions and reaction routes, helps in designing the process flow-sheet, identifies and assesses different possible or credible worst-case scenarios with limited data constraint, avoids undesirable process conditions, predicts safety technologies and provides options to make a plant inherently safe.

There is also a need of a software tool that uses this method to assess and design the chemical process under safety, environment and health constraints in rather short time with the help of expert's decisions, has different databases of substance properties and

reactivity information integrated with it and incorporates a simulation code to perform the method efficiently.

These points emphasize the need for a single framework for the comprehensive view of EHS aspects in chemical processes. An automated assessment system (i.e. a systematic methodology and software tool) for analyzing inherent safety, revealing non-idealities by assessing environmental, health and safety aspects in the early stages of design can save time and effort, can highlight the possible dangers and can minimize human errors. It has to be emphasized that such an automated assessment is not meant to replace rather support a detailed risk analysis conducted by a panel of experts. The thesis presents a new Substance-Reactivity-Equipment and Safety-Technology (SREST)-Layer-Assessment method to assess environmental, health and primarily safety aspects.
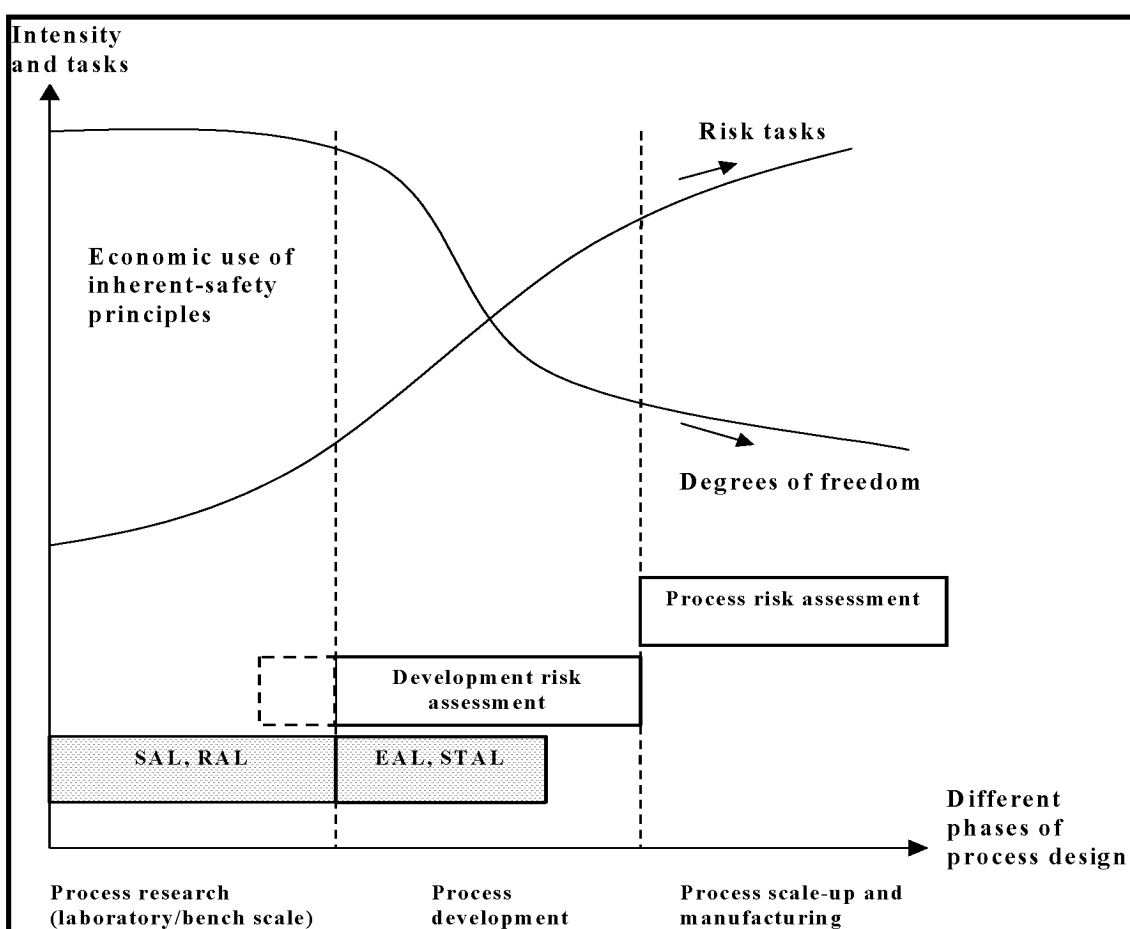
Figure 1.1:   Use of SREST-Layer-Assessment method in different process design stages. SAL, RAL, EAL and STAL are Substance, Reactivity, Equipment and Safety-Technology Assessment Layers in SREST method (Chapter 2).

1.2 Contents of the thesis

The thesis presents a new Substance-Reactivity-Equipment and Safety-Technology (SREST) Layer-Assessment method to assess environmental, health and safety aspects with the help of an integrated assessment tool. This method helps in making decisions with the help of inherent-safety-principles in process design.

Chapter 2 proposes a hierarchical approach in which a chemical process is divided into different layers (substance, reactivity, equipment and safety-technology) each representing a different level of analysis. All the layers are explained in detail in subsequent subchapters. These layers are successively assessed for non-idealities of the process with regard to inherent safety. In the case of non-idealities, a worst-case scenario is defined and analyzed with the help of available data and recommendations are made for possible preventive and protective measures. The details of decision-making with the help of inherent safety principles are presented in Chapter 3. The chapter also presents a flow-chart to use the method efficiently and to make the decisions about inherent safety in each layer after judging the results obtained.

The overall concept is demonstrated with the help of various case studies in Chapter 4 and it is shown how the method reveals the degree of non-ideality of different chemical process aspects with regard to inherent safety. Chapter 5 draws some final conclusions on (i) explaining the application of the proposed method during process design; (ii) the use of different layers of the method; and (iii) the use of the assessment tool for decision making in the design of a chemical plant. The appendices give further details about the methodology and the tool developed in this project. The tool contains interfaces with various databases of substance properties and reactivity/incompatibility information, simulation code to assess possible worst-case scenarios and user-friendly interface to perform the assessment step by step.

2. Developing a hierarchical methodology for safety, environmental and health assessment in early stages of process development

One can use detailed risk assessment methods to assess environmental, health and safety aspects in an existing plant but considering these aspects in *early stages* makes it economically viable because it is easier and more economical to adapt process design in early stage than in an already existing process. In a similar way, reducing inherent hazards in the plant rather than handling them with the help of safety technologies, i.e., *inherent safety concept* can make plant safer and more profitable. Inherent safety concept is also becoming popular and useful because of recent terrorist activities. If there is no inherent hazard, there will be no severe or catastrophic accidents by any means. There is a lack of a single framework, which can accept the challenge to perform safety, environmental, and health assessment and to use inherent safety principles in early stages of chemical process design when there is lack of data and information about the process. It is efficient for a chemical industry to use a systematic approach, which can assess inherent hazards of substances, can evaluate major worst-case scenarios in equipment units, can predict safety technologies and can use inherent safety principles in early research stage of a process.

2.1 Overview of SREST-Layer-Assessment method

A single framework, i.e., a hierarchical approach called SREST (Substance, Reactivity, Equipment and Safety-Technology)-Layer-Assessment method, with automated software tool has been developed which helps chemists and chemical engineers in the laboratory and in the conceptual flow-sheet stage:

1. To collect the property data (for example, environmental, toxicity, physical and chemical properties etc.),
2. To assess the substances for environmental, health and safety aspects with the help of collected properties,
3. To acquire reactivity/incompatibility information from databases,
4. To predict reactivity/incompatibility with the help of incompatibility charts,

5. To identify different possible worst-cases in various unit-operations involved,

6. To evaluate these possible worst-cases,

7. To predict and recommend safety technologies to prevent and protect the plant,

8. Finally to use the inherent safety principles for selecting process conditions or different reaction routes or the process design.

The most rigorous approach to cover all details in EHS assessment is to divide the problem into small parts and assess them carefully. Since these small parts are related with each other and consequences in one part can influence other parts, a layer system is suitable for the complete assessment. In the SREST method, the chemical plant is considered as an onion consisting of layers. Assessment is started from the inner layer to the direction of the outer layer (Figure 2.1.1). The division of a plant into layers helps to highlight the problems in different parts and locations by pointing towards all possible potentials of danger. ***The method runs step by step as shown in Figure 2.1.2 with the decisions about inherent safety made by the user in each layer after judging the results obtained.*** The method tries to recognize all the problems related with substances, incompatibility of substances and procedures in equipment. The method consists of four layers for assessing substances, reactivity, equipments and safety technologies. In the first layer, i.e. Substance Assessment Layer (SAL), all substances present in the process are assessed with the help of the EHS method (which is slightly modified in SREST method, see SAL for detail) proposed by Koller et al. (2000) using 11 categories of EHS aspects. The result in each category, i.e. potential of danger, is obtained in the form of index in the range between 0 and 1 and physical value. Decisions for the replacement or appropriate mass of substances for the reasons of inherent safety can be taken on the basis of the results generated by the EHS method and acceptability limit proposed for different categories. In the case of replacement, the assessment can be repeated for new substances. The high indices (above the acceptable limit) can be helpful in identifying the possible worst-case scenarios in the process. The second layer, i.e. Reactivity Assessment Layer (RAL) assesses the intended reaction, unintended reactions and the reactivity of substances with air, water, cooling/heating media, material of construction and with other reactive substances present in the equipment or in the surroundings where contact might be possible. The assessment is

based on data available in Bretherick's database (Urben, 1999) and Chemical Reactivity Worksheet (NOAA, 2000). If reactivity between substances exists or reactivity indices are higher than acceptable limit, appropriate measures can be taken, for example, avoid contact by proper design and substitution or less amount of substance. The third layer, i.e. Equipment Assessment Layer (EAL) assesses possible worst-case scenarios in equipment units using appropriate models. The result is obtained in the form of hazard indices and decisions about the acceptability are made with the help of acceptable limit proposed. In case of unacceptable risks the operating conditions or the unit operations used can be changed and the assessment can be repeated. Finally, safety technologies are recommended in the fourth layer, i.e. Safety-Technology Assessment Layer (STAL) to mitigate all possible dangers identified with the help of results generated from SAL, RAL and EAL. The hazard indices from the inner layers are reduced by reduction factors from safety technologies. The result is obtained in the form of a remaining hazard index in the range from 0 to 1 and acceptability decision is made with the help of acceptable limit proposed. The selection of safety technologies can be varied until an acceptable risk potential remains. If this cannot be obtained or if the overall assessment of all hazard potentials resulting from the four layers concludes an unacceptable process, then an alternative i.e., a different synthesis route has to be investigated again using the SREST framework (Figure 2.1.2). All the indices and acceptable limits in this method are defined with the help of case studies and the discussion with experts.

SAL: Substance Assessment Layer
RAL: Reactivity Assessment Layer
EAL: Equipment Assessment Layer
STAL: Safety Technology Assessment Layer

Figure 2.1.1: Concept of SREST-Layer-Assessment method.

Automated EHS Tool

Interface with databases/ Simulation	SREST Layer Assessment Method	User's Actions

Start

Investigation of available options or other alternatives, e.g., different synthesis route

R e c i p e

Substance data from databases (e.g., IGS, IUCLID, CHRIS)

Substance Assessment Layer Calculation of EHS indexes in 11 categories

Are EHS indexes acceptable?

No → Substitution of critical substances or decreasing amount of hazardous substances

Yes

Bretherick's reactivity database and Chemical Reactivity Worksheet

Reactivity Assessment Layer Generation of matrix and reactivity indexes

Are reactivity indexes acceptable?

No

Yes

Simulation of equipment related worst-case scenarios

Equipment Assessment Layer Characterization of possible worst-case scenarios (e.g., criticality class for runaway)

Are worst-case hazards acceptable?

No → Change of operating procedures or unit operations

Yes

MS-Excel or Batch Plus™

Safety Technology Assessment Layer Recommendation of safety technologies (e.g., pressure relief system in runaway scenario)

Are remaining worst-case hazards acceptable?

No → Selection of other safety technologies

Yes

Is overall potential of danger acceptable?

No

Yes

Assessment finished

Figure 2.1.2: Flow chart for taking decisions in process design using the SREST-Layer-Assessment method.

The Figure 2.1.3 shows the applicability of SREST method in identifying different process risk hazards in Substance and Reactivity Assessment Layers, in assessing these risk hazards or possible worst-case scenarios in Equipment Assessment Layer and in predicting various safety technologies in Safety-Technology Assessment Layer. The decision to make detail assessment of any worst-case scenario or to use inherent-safety-principles or to predict safety technologies can be made with the help of indices generated in SAL and RAL for each category and the acceptability limits proposed. The four SREST layers are discussed in detail below.
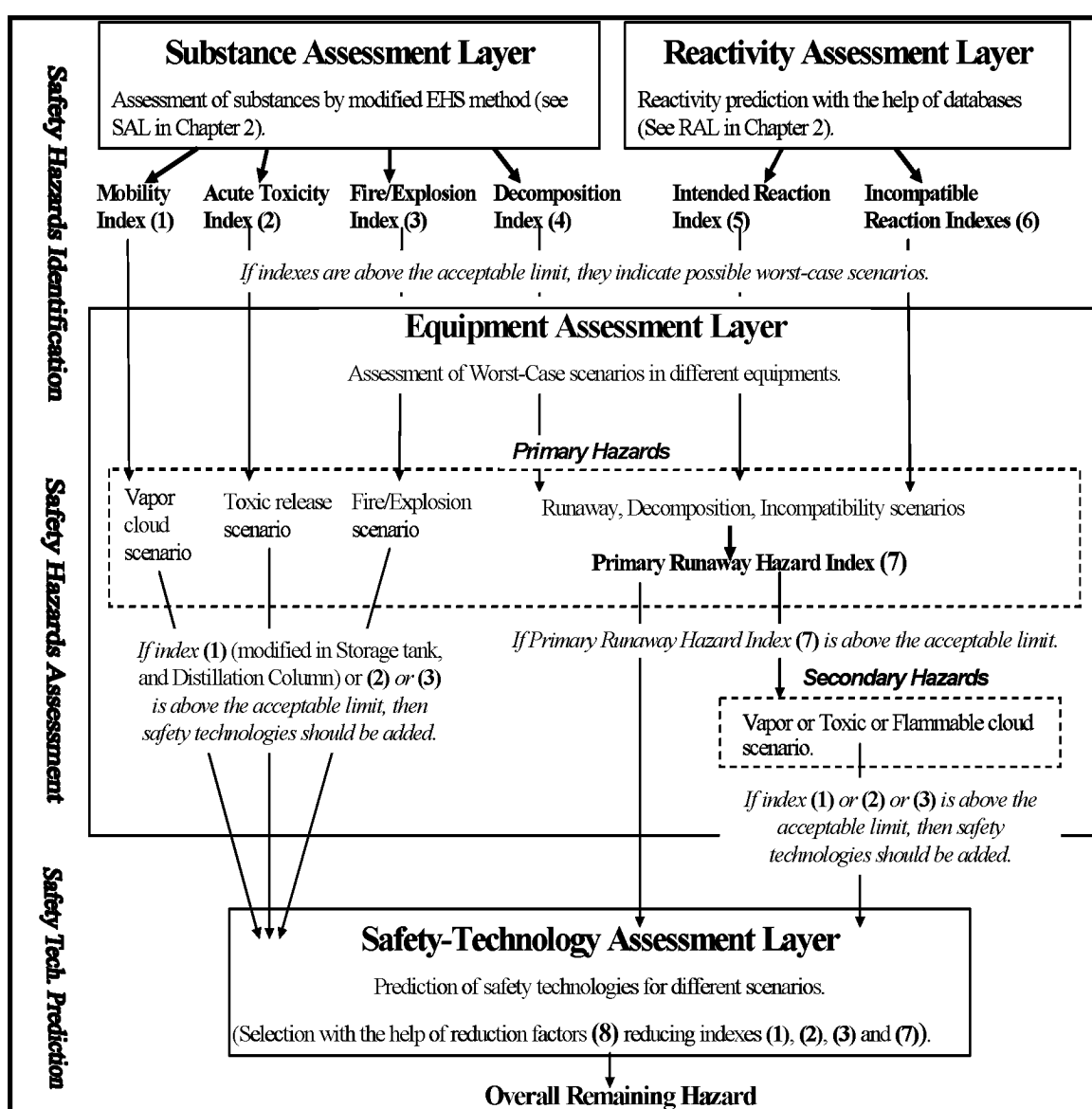
Figure 2.1.3:   Principal application of SREST method in identifying and assessing principal hazards and in predicting safety technologies.

2.2 Substance Assessment Layer (SAL)

Substance hazards identification and assessment is very important in making decisions about inherent safety and predicting safety-technologies to reduce hazards related with environment, health and safety. Selection of substances plays an important role in the design of inherently safer processes. The goal of inherently safer design is to remove hazards by using less of a hazardous material or by using a hazardous material in a less hazardous form or by substituting a hazardous material with a safer material. Substance hazard identification is also helpful in predicting and identifying worst-case scenarios in major unit operations in early stages of design.

In this layer, for assessing substance hazards, a list is compiled of all the substances present in the process. Physical and chemical properties, toxicity, environmental and safety data of these substances are collected from different databases (e.g., IGS (Nationale Alarmzentrale, 1997), IUCLID (European Chemicals Bureau, 1998)) automatically by EHS tool (Koller, 2000) with the help of an interface between tool and databases. In the EHS method (Koller et al., 2000), substances are assessed in 11 effect categories (Mobility, Fire/Explosion, Reaction/Decomposition, Acute Toxicity, Chronic Toxicity, Irritation, Air Mediated Effects, Water Mediated Effects, Solid Waste, Accumulation and Degradation). Depending on the substance information available, different measures or properties can be used to calculate an index value (see Appendix A for details of indices for 11 effect categories). The index for Mobility for instance can be calculated using the VP (vapour pressure data) or BP (boiling point) or MP (melting point) etc. This index representing a Dangerous Property (DP) of a substance can vary between 0 and 1 depending on the size of the EHS-effect. In the next step, this index is modified by the fate factors, i.e., Mobility, Degradability or Accumulation potential of the substance. Toxic substances that are solid or degradable are considered less dangerous in safety respectively environmental assessment. This modified value indicates the Effective Dangerous Property (EDP) of a substance and can be used to evaluate which EHS-problems exist in a process and which substances are responsible for it (which problem?). For estimating the magnitude of the EHS-problem, the index value for the EDP is combined with the relevant mass and converted into a physical

unit, i.e. the Potential of Danger (PoD) that represents the magnitude of EHS-problem
(how serious?) (Figure 2.2.1 and Koller et. al, 1999).

The main problem of early EHS assessment is the lack of substance data (e.g.,
intermediates, products) and process information. The EHS method closes this gap
considerably. For each substance of a given chemical process and each effect category,
the most reliable data can be selected out of a variety of different substance databases or
property estimation methods (e.g., quantitative-structure-activity-relationships
(QSAR)). For each effect category, one index is generated. These indices can be used
for selecting the materials or the maximum limit of mass used in the chemical process
and further for deciding the safety technologies for mitigating the hazard impact of
these substances.
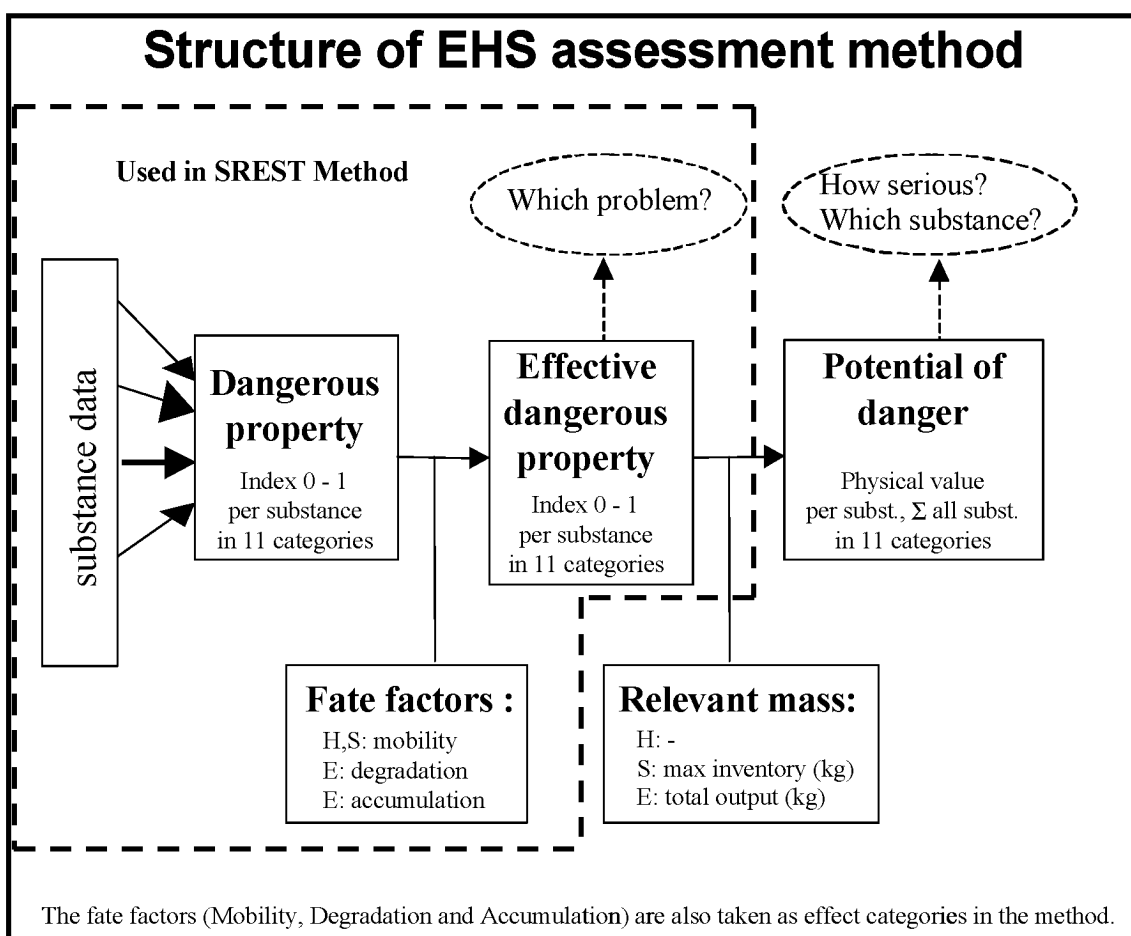
Figure 2.2.1: Representation of EHS method for substance assessment.

Within the SREST method one modification of the original EHS method (Koller, 2000) has been defined. *The effect category Reaction/Decomposition is changed into effect category Decomposition (see Figure 2.2.2 and Appendix A) in which only the instability of single substances is considered while the intended reaction and the interactions between substances, water, trace impurities and material of construction are the subject of Reactivity Assessment Layer (RAL, defined in next sub-chapter).* In the SREST method, Effective Dangerous Property indices are used for each effect categories and for each substance to present the results.

The substance index for each category and the table of acceptable limit (see Table 2.2.1) can be used for selecting the materials or the maximum limit of mass used in the chemical process, for deciding to make the detailed assessment for possible worst-case scenarios and further for deciding the safety technologies for mitigating the hazard impact of these substances.

Decomposition

Index value	Priority	0	0.5	1	
considered aspects	A1.	0	100	400	$-\Delta H$ decomp, meas. (kJ/kg)
A: thermal stability	A1.	0	100	400	$-\Delta H$ decomp, est. (kJ/kg)
	A2.	200	100	0	ΔT decomp. (°C)
	A3.	-240 +160	-180 +120	-120 +80	Oxygen balance (%)
	A4.			5,19, 44 | 1,2,3, 6,17	R-codes (EC)
	A5.	no instable group found	azo, cyanat	nitro,ether peroxo, | dinitro	Substance types
	A6.			gaseous | toxic flammable	Decomp. products

ΔH decomp, meas.	Decomposition enthalpy (measured)
ΔH decomp, est.	Decomposition enthalpy (estimated)
Oxygen balance	% (wt/wt) external oxygen required for complete combustion (not bound within molecule)
Decomp. products	Decomposition products produced
ΔT decomp. (°C)	Difference between decomposition (e.g., T_{onset} from DSC) and process temperature

Figure 2.2.2: Representation of Decomposition category for substance assessment.

Table 2.2.1: Acceptable region for EHS effect categories in Substance Assessment Layer.

EHS effect category	Acceptable region for EHS substance-indices
Mobility	≤ 0.6
Fire/Explosion	≤ 0.6
Acute Toxicity	≤ 0.5
Decomposition	≤ 0.5
Irritation	≤ 0.5
Chronic Toxicity	≤ 0.6
Water Mediated Effects	≤ 0.5
Air Mediated Effects	≤ 0.6
Accumulation	≤ 0.5
Degradation	≤ 0.5
Solid Waste	< 1

2.3 Reactivity Assessment Layer (RAL)

The chemical and pharmaceutical industries use many exothermic reactions where loss of control can lead to runaway. Many of the thermal runaway accidents in the chemical industries are due to secondary exothermic reactions. Sometimes these reactions are known but reasons for undesired events may be loss of control or mishandling of substances among others. Sometimes incompatibility of substances is not known beforehand and undesired mixing of these substances by any means can cause heat generation or can trigger decomposition of substances with a high heat or gas release and can lead to a thermal explosion. The influence of trace impurities is also frequently mentioned as a possible or probable cause of accidents in the chemical industry. In process conditions where there is a potential of a fast exothermic decomposition or polymerization reaction, the contamination of pure chemicals by trace impurities may cause problems. Typical examples of this situation (decomposition because of trace impurities) are described concerning the processing of organic nitro-compounds and the

storage of reactive monomers, i.e. vinyl-acetate and ethylene-oxide. One of the notorious disasters due to reactivity or incompatibility of substance with water is Bhopal accident (Willey, 1998). Therefore the knowledge of reactivity of substances with air, water and other reactive substances is extremely important to assess runaway scenarios, to control the exothermic reactions and to design the mitigation systems.

In 1996, AIChE announced the availability of the computer package CHEMPAT that provides a straightforward method of documenting the interaction matrix, or compatibility chart. CHEMPAT was developed and used internally, by the Dow Chemical Company since 1987 and was donated by Dow to AIChE in 1995 (Leggett, 1997). The systematic approach to assess reactivity and avoiding accidents leads to literature searches, laboratory experiments and an operating procedure to handle these problems. Mosley et al. (2000) have presented an effective procedure to screen reactive chemical hazards early in process development by developing an interaction matrix of substances. The interaction matrix is a useful tool for understanding possible reactions, both intended and unintended, among the various materials used in a chemical process. The matrix can be applied at any stage in the process life cycle, from early research through commercial plant operation, and it can even be used to help understand the hazards associated with plant decommissioning and demolition (Mosley et al., 2000). The generation of the interaction matrix with the help of software can save time in literature search and can be helpful in getting a more systematic search. The matrix can be used to select inherently safer alternatives out of a list of possible process routes and to take decisions for laboratory work in the early process development.

In the RAL, reactivity information is divided into two categories, i.e. Intended Reactions category and Incompatible or Unintended Reactions category. The indices for both categories are defined as shown in the Figures 2.3.1 and 2.3.2, for example, high heat of reaction or toxic and flammable gas generation accounts for high reactivity indices. In this layer, all substances that possibly can come into contact are also crosschecked automatically for the reactivity with air, water, heating\cooling media, material of construction, trace impurities and with all the other substances. An interaction matrix (see Table 2.3.1) is generated and information present in Bretherick's

database (Urben, 1999) and Chemical Reactivity Worksheet (NOAA, 2000) is compiled in a text file as a result by EHS tool with the help of interface between tool and databases. All the intended and incompatible reactions should be assessed and indices should be given to each reaction. There are lists of reactions (Tables B1, B2 and B3 in Appendix B) stored in EHS tool (see Appendix D) to predict hazards of desired or undesired reactions. In a similar way, incompatibility chart (Figure B1 in Appendix B) is used in EHS tool to recognize incompatibilities or reactivity between different chemical groups. Incompatibility chart is useful to fill up the gap in reactivity information and provides initial information about the reactivity between two chemical groups.
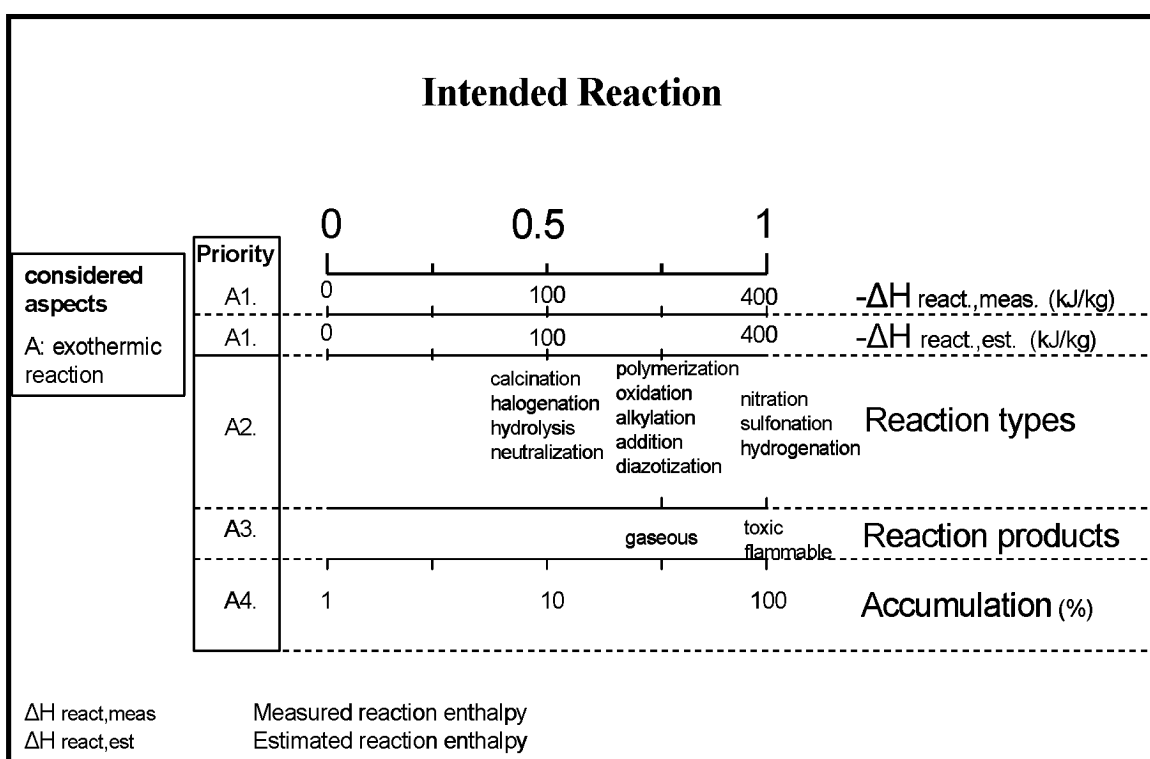
Figure 2.3.1: Representation of Intended Reaction category for reactivity assessment.

Table 2.3.1: Representation of reactivity matrix generated in Reactivity Assessment Layer (RAL). An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substances	1	2	3	water	air	material of construction
1	SI		X	X		
2		SI				X
3			SI		X	
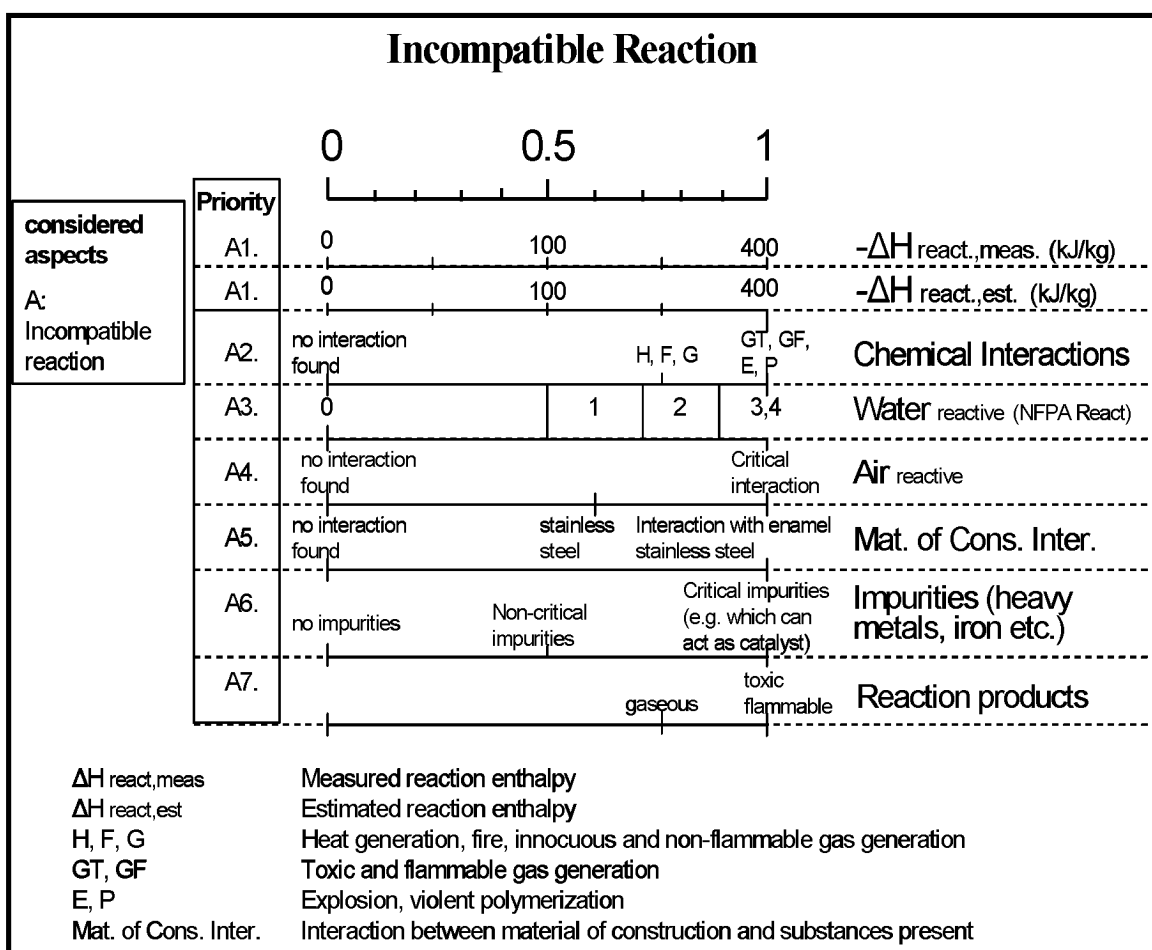
Figure 2.3.2: Representation of Incompatible Reaction category for reactivity assessment.

The reactivity indices of Intended Reactions category (see Figure 2.3.1) and Incompatible Reactions category (see Figure 2.3.2) together with the table of acceptable limits (see Table 2.3.2) can be helpful in making decisions about drawing pipe and instrumentation diagram to avoid the unintended contacts, about selecting substances and in making decision of performing detailed runaway assessment.

Table 2.3.2: Acceptable region for reactivity indices in Reactivity Assessment Layer (RAL).

Reactivity category	Acceptable region for reactivity-indices
Intended Reaction	≤ 0.5
Incompatible Reaction	≤ 0.5

2.4 Equipment Assessment Layer (EAL)

In the process assessment not only the substances but also equipment or unit operations play an important role. Most of the times, accidents occur because of failure of one or the other part of equipment. The accidental risk is a function of consequence severity and frequency. To reduce risk, one can reduce the severity of the consequence or reduce the frequency of occurrence of the consequence. Indeed, the application of inherently safer design is to reduce the hazard inherent in (or characteristic of) the material or chemistry of the process. For example, we can reduce the hazard by choosing less toxic or less flammable materials, or by changing the chemistry of the process. Such changes reduce the severity of the consequence. On the other hand, reducing the inherent hazard in the process may not be sufficient to meet the risk criteria. Consequently, a second application of safe design is to create prevention and protection measures. This reduces the frequency of the consequence. Both applications of safer design should be considered in early process design and in process modifications.

The worst-case scenario analysis is a widely used concept in risk assessment. Khan and Abbasi (1998c) have used accident scenario generation in Rapid Risk Analysis Based Design (RRABD) and maximum credible accident analysis in SCAP risk assessment method. The Control of Major Accident Hazard Regulations 1999 (COMAH) in the UK, requires operators of qualifying establishments to submit a safety report, which demonstrates that all necessary measures have been taken to prevent major accidents, and to limit the consequences to people and the environment of any that do occur (Carter et al., 2003). The possible worst-case scenario generation and assessment in early development stage helps to predict these scenarios; and to avoid, to prevent and to protect chemical plants from them.

In the EAL, possible worst-case scenarios related with equipment units are identified and characterized by using unit-operation models, and process conditions are evaluated for improving safety. The possible worst-case scenarios are identified with the help of process conditions (for example, process temperature, pressure etc.) and results coming from SAL (hazard indices of substances present in the equipment) and RAL (reactivity/incompatibility information). Four major equipment units are assessed in this

layer with possible worst-case scenario identification and hazards are presented in the form of qualitative indices. These equipments are:

1. Batch/semi-batch reactor
2. Storage tank
3. Distillation column
4. Dryer

These different equipment units with possible worst-case scenarios are explained in detail below.

2.4.1 Batch/semi-batch reactor

Pharmaceutical and fine chemical industries are leadingly involved in multi-purpose and multi-product batch processes. In the batch processes, batch and semi-batch reactors are predominantly used. There are different worst-case scenarios possible, for example, fire/explosion, toxic and vapour cloud scenario due to flammable, toxic and volatile substances present; runaway scenarios due to exothermic reactions; decomposition of reaction mixture or any substance in reaction mixture with heat evolution; reactivity/incompatibility due to undesired substances etc. The assessment of these scenarios is explained in detail here:

Fire/explosion, toxic and vapour cloud scenario as primary hazards

Flammable, toxic and vapour clouds could be formed via the release of the chemicals from equipment unit by any means. Some of common causes of release from the equipment unit are leakage, overpressure, corrosion, human failure or auxiliary failure etc. One can identify these hazards by the inherent properties of the substances in very early development stages. This can be useful in deciding preventive and protective measures. In the SAL, modified EHS method is used to identify and assess these substance hazards (e.g., Fire/Explosion, Mobility and Acute Toxicity categories) and result is obtained in the form of index value between 0 and 1 for each category and for each substance. Different priorities (for example, flash point, R-codes, NFPA-Flammability, EC classification, Auto Ignition Temperature (AIT) etc. for Fire/Explosion category; boiling point, vapour pressure, melting point etc. for Mobility category; and Immediate Danger to Life and Health (IDLH), GK (Gift Klasse) values

for Acute Toxicity) are used to identify and assess the inherent properties of the substances (see Figure A1 in Appendix A). If the index is not in the acceptable limit (Table 2.2.1), there is high possibility of severe consequences in the case of accidents. Flammable and toxic cloud scenario can also be considered as secondary hazards in reaction runaway, which is discussed in more detail in runaway scenario.

Runaway scenario

Some of the reactions performed in batch/semi-batch reactors are highly exothermic i.e. heat is evolved in the process, and therefore need a scrutiny in the risk assessment to avoid severe consequences. There have been a number of accidents in chemical industries related with exothermic reactions. Uncontrolled reactions can cause severe fires, explosions and toxic emissions.

Different criteria presented in literature for runaway assessment: Gygax (1988) has presented in his paper how risk assessment can be performed by extending Chemical Engineering Principles to the study of potential runaway reactions. He has distinguished a number of cases of thermal runaway scenarios in which the heat generation of an ongoing reaction exceeds the heat dissipation capacity of the process equipment, for example, in the long run, even weakly active undesired reactions run away; loss of control of the desired reaction; secondary or side reaction events; undesired reactions because of mixing incompatible substance accidentally.

Experienced chemists are often aware of potential problems because of their knowledge of the chemical species involved; but frequently this knowledge alone is insufficient to ensure safe operation of the process facilities. It is now widely accepted that the chemist's experience must be supplemented by bench scale testing, using suitable test procedures, to evaluate all steps in a chemical process for their potential hazard and to test the various feeds, products and intermediates (CCPS, 1995).

Different criteria are used to determine a substance or a mixture of substances or a reaction/reactions as highly or moderate hazardous due to chemical reactivity, for example, NFPA classification, oxygen balance, heat of reaction, onset temperatures,

Adiabatic Temperature Rise (ΔT_{ad}), Time to Maximum Rate at adiabatic conditions (TMR_{ad}), Adiabatic Decomposition Temperature which will lead to runaway in 24 hours (ADT_{24} or $T_{0,24}$) etc. Some data can be collected from databases but most of the data are obtained via experimental work or they are dependent on the parameters that are obtained from calorimeters (DSC, ARC etc.) in the laboratory. Risk evaluation can be done with the help of some of these criteria but detail risk assessment should be done considering as many criteria and classifications as possible. Different screening methods can also be used in early stages to eliminate hazardous reactions from the list.

The complete understanding of all criteria and the sensitivity of calorimeters is a must for detailed and proper runaway assessment. Hofelich and LaBarge (2002) presented in their work the use and misuse of detected onset temperatures of calorimetric experiments for reactive chemicals. They summarized that one needs to heed rules of thumb and understand that their use is often more limited than is typically recognized. Calorimeters are instruments with finite sensitivities and the detection of a thermal event is a strong function of the thermo-kinetics and the intrinsic sensitivity of the calorimeter used.

To assess runaway scenarios due to exothermic reactions, plenty of literature is available. However, runaway accidents still occur due to improper runaway assessment, time pressure to perform literature search and proper safety assessment in the developing stage. There is a need of systematic procedure with a software tool that can collect the substance data (decomposition, instability, flammability, toxicity etc.) from different databases, check the reactivity/incompatibility, perform the runaway assessment with the help of data available from databases and laboratory. This tool can provide the desired or feasible range of process conditions and can avoid possible worst-case scenario by showing inherent hazards involved.

Runaway assessment in SREST method: In SREST method, runaway hazards in batch/semi-batch reactors are divided into two types i.e. primary runaway hazard due to desired and undesired exothermic reactions and secondary runaway hazard due to volatility, flammability and toxicity of substances present. These hazards are recognized

by the results from SAL for substance decomposition or instability information in the form of Decomposition index, volatility as Mobility index etc. and from RAL in the form of incompatibility matrix, Intended and Incompatibility Reaction Index. In our methodology, we use probability and severity characteristics as well as Stoessel's classification system (Stoessel, 1993) to highlight the primary hazards related with runaway scenarios and as indicators to design safety measures (see next sub-chapter (STAL)). Stoessel (1993) has developed a criticality classification of runaway scenarios to simplify the part of the risk analysis concerning the thermal process safety (Figure 2.4.1.1). Probability and severity calculation of runaway scenario is also helpful in taking safety measures (Figure 2.4.1.1). Keller et al. (1997) presented a screening method, which is used in SREST method, based on Dynamic Differential Scanning Calorimetry (DSC) measurements for estimating the time to maximum rate at adiabatic conditions (TMR_{ad}) which is an indicator for the probability of thermal risk due to exothermic reactions. This estimation method is a good tool for preliminary screening and may be applied at the early stages in process design to save both time and money without loss of safety (Keller et al., 1997). Pastré et al. (2000) concluded in their paper that this estimation method is more on the safe side than other common and often applied estimation methods like the so-called 50 or 100-degree rule.

The flow-chart in Figure 2.4.1 shows the procedure of runaway assessment. The procedure of runaway assessment is followed if severity (Adiabatic Temperature Rise, ΔT_{ad}) is medium or high otherwise runaway hazards are considered low or negligible. In the similar way, secondary hazards, i.e., toxic or flammable vapour cloud, are considered only if primary runaway hazards are considerable.

Runaway Scenario

Primary Runaway Hazards

Is severity low? — Yes → No primary runaway hazards present

No ↓

Define probability and criticality class

↓

Select proper measures for primary runaway hazards

↓

Is primary runaway hazard present? (If index > 0.2) — No → STOP (If no primary runaway hazards, then no secondary hazards)

Yes ↓

Select proper measures for secondary runaway hazards (fire, explosion, toxic release etc.) (If index > 0.5)

Figure 2.4.1: Representation of the procedure to perform runaway assessment.

The procedure to calculate Primary and Secondary Runaway Hazard Indices is presented here in detail.

Primary Runaway Hazard Index (PRHI): In the following, the step-by-step procedure to assess primary hazards in a runaway scenario is explained:

- *Collection of data:* The reaction recipe, substance inventory, physical and chemical properties of substances, reaction enthalpies and activation energies, q_{onset} (heat release rate at the onset temperature in a dynamic DSC run), T_{onset} (onset temperature, the temperature at which the heat rate signal can first be differentiated from the baseline temperature reading in a dynamic DSC run),

decomposition enthalpies, gas development and other data are collected from databases (e.g., boiling points, heat capacities) or laboratory experiments (e.g., T_{onset} and q_{onset} from DSC runs, reaction enthalpies). For some substances T_{onset} and q_{onset} data can also be obtained from Grewer's Safety-Relevant Properties Table (Grewer, 1994) for primary screening purposes.

- *Calculation of Primary Adiabatic Temperature Rise (ΔT_{ad}):* The adiabatic temperature rise of the desired reaction is calculated by dividing the energy of the desired reaction by the specific heat capacity. In the case of semi-batch reactor, maximum accumulation is taken into consideration for calculating the adiabatic temperature rise.

$$\Delta T_{ad} = X_{acc} \frac{-\Delta H_R}{c_p} \qquad (2.4.1.1)$$

- *Calculation of Maximum Temperature of Synthesis Reaction (MTSR):* MTSR is calculated by adding the process temperature to the adiabatic temperature rise of the desired synthesis reaction.

- *Determination of the maximal allowed process temperature ($T_{0,24}$) or ADT_{24} where TMR_{ad} is 24 hours:* The estimation method to calculate $T_{0,24}$ is given by Keller et al. (1997) who used T_{onset} and q_{onset} data of reaction mixture from a dynamic DSC run. For a zero order reaction, $T_{0,24}$ can be estimated by solving the following equation:

$$T_{0,24} = \left(\frac{1}{T_{onset}} - \frac{R}{E_a} * \ln\left(\frac{T_{0,24}^2 * R * c_p}{E_a * TMR_{ad} * q_{onset}} \right) \right)^{-1} \qquad (2.4.1.2)$$

In the case of unknown activation energy, as a rule of thumb, an activation energy as low as 50 kJ/mol can be taken for screening purposes. Depending on the sensitivity of the instrument and the curvature of the baseline, the minimal detectable heat release rate q_{onset} can be assumed equal to 20 W/kg. Equation (2.4.1.2) may be solved by iteration and inserting the estimation values ($E_a = 50$ kJ/mol, $q_{onset} = 20$ W/kg and the limiting value of 24 hours for TMR_{ad}). Based on

linear regression of the solution of Equation (2.4.1.2) and with a correlation factor of 0.9998, Equation (2.4.1.3) can be obtained (Keller et al., 1997), which can be used for the screening of safe processes.

$$T_{0,24}[K] = 0.65 * T_{onset}[K] + 50 \tag{2.4.1.3}$$

- *Criticality Classes of runaway scenarios:* Stoessel's Criticality Classes (Stoessel, 1993) are assigned as shown in the Figure 2.4.1.1 with the help of process temperature (Step 1), MTSR (Step 3), boiling point of reaction mass (Step 1) and maximal allowed process temperature ($T_{0,24}$) or ADT_{24} (Step 4). This classification helps in judging thermal potential and in identifying different safety technologies.

- *Probability:* The probability can be evaluated using TMR_{ad}, i.e. the time to maximum rate under adiabatic conditions as shown in Figure 2.4.1.1. At least in principle, the best way to obtain a TMR_{ad} value would be to perform an adiabatic experiment (Barton and Rogers, 1993). By assuming zeroth order model reactions, TMR_{ad} for a start temperature T_0 can be estimated by the following formula:

$$TMR_{ad} = \frac{c_p R T_0^2}{q(T_0) * E_a} \tag{2.4.1.4}$$

This formula can also be used for other reaction types, if the influence of concentration on reaction rate can be neglected. This approximation is particularly valid for fast and highly exothermic reactions (Barton and Rogers, 1993).

- *Severity:* The severity of the runaway can be evaluated by means of the temperature rise attained if the desired reaction and the decomposition reaction proceed under adiabatic conditions (Stoessel, 1993) (Figure 2.4.1.1).
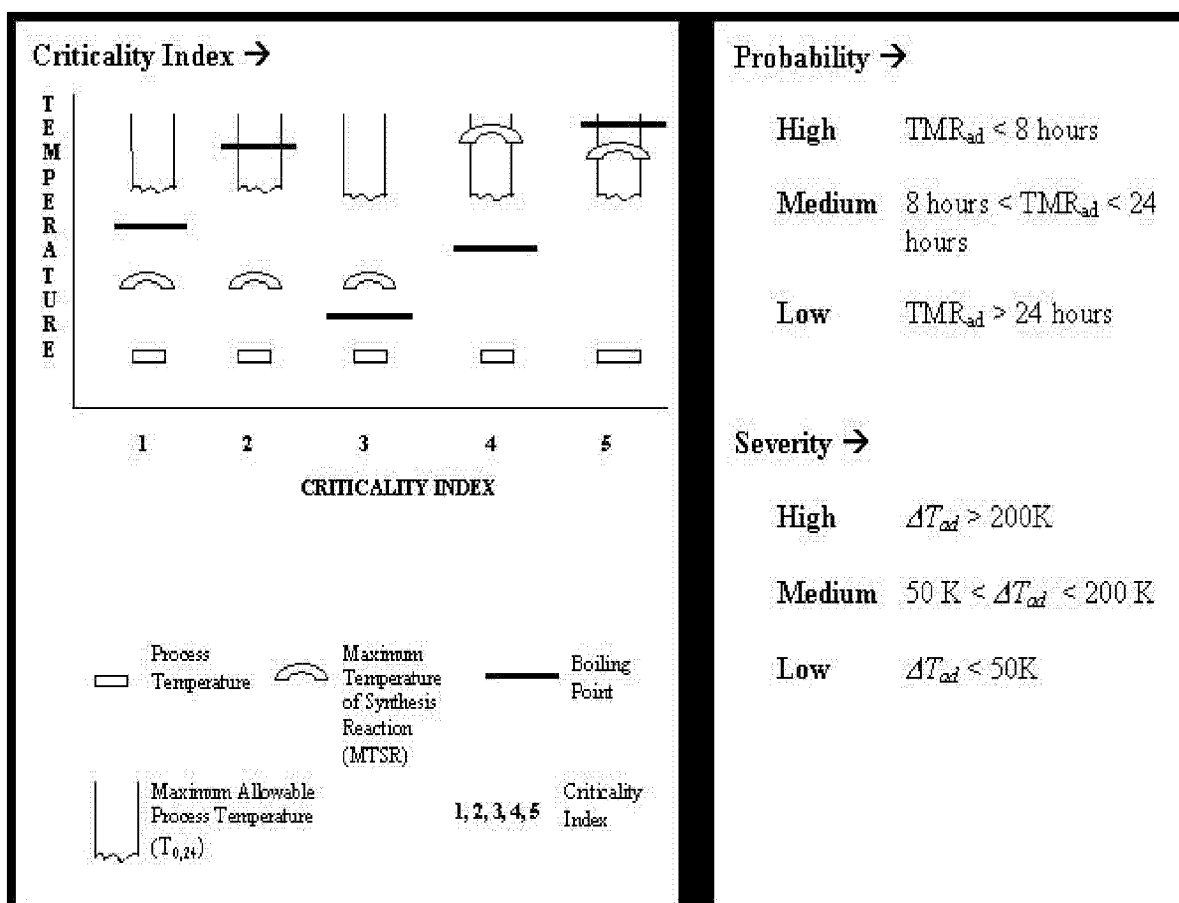
Figure 2.4.1.1: Evaluation of probability, severity and criticality index for runaway scenario in batch/semi-batch reactor.

Table 2.4.1.1: Different categories of criticality-class, probability and severity to define Primary-Runaway-Hazard-Index (PRHI).

Criticality Class	Probability	Severity	Primary Runaway Hazard Index	
1	Low	Low	0.2	Low
1	Low	Medium	0.2	
2	Low	Low	0.2	
2	Low	Medium	0.2	
3	Low	Low	0.2	
4	Medium	Low	0.2	
4	High	Low	0.2	
5	Medium	Low	0.2	
5	High	Low	0.2	
1	Low	High	0.4	Moderate
2	Low	High	0.4	
3	Low	Medium	0.7	
3	Low	High	0.7	
4	Medium	Medium	0.9	
	High	Medium		Critical
4	Medium	High	0.9	
	High	High		
5	Medium	Medium	1.0	Highly Critical
	High	Medium		
5	Medium	High	1.0	
	High	High		

(Left vertical label: **Hazards** with downward arrow)

In the method, the primary runaway hazard is classified into different possible categories with the help of criticality class, probability and severity of desired and undesired exothermic reactions as shown in Table 2.4.1.1, in order to consider as many criteria in the assessment as possible. For example, in the case of criticality classes 1, 2 and 3, only low probability is feasible while for criticality classes 4 and 5, it can be medium and high (see Figure 2.4.1.1). To each category, a hazard index (Table 2.4.1.1) is assigned according to the possibility of accidents and the resulting requirements of safety technologies. *The acceptable region for Primary Runaway Hazard Index is less than or equal to 0.2.* In the case of high index value, inherent-safety-principles or proper measures should be considered (see STAL in next subchapter).

Secondary Runaway Hazard Index (SRHI): The presence of flammable, toxic and volatile substances in the reactor can increase the severity of the accident due to runaway scenario as happened, for example, in Seveso case after the release of these substances into the environment. When a plant is built, determining a safe location for a

vent is just as important as proper sizing. The accidents in Seveso and Bhopal show what happens when it is not done properly. The plant may be undamaged but a lot of harm is done to the environment and the people within the hazardous zone of the plant (Braken, 2002). The estimation of secondary hazards due to runaway can help in deciding the vent location in the plant and measures for handling toxic and flammable substances. In SREST method, the secondary runaway hazards are considered only if there is primary runaway hazard present (see Figure 2.4.1). The Secondary Runaway Hazard Index corresponds to the maximum of Effective Dangerous Property (EDP) index values of Mobility, Fire/Explosion and Toxicity categories generated in Substance Assessment Layer (SAL) for all substances present. *The acceptable region for Secondary Runaway Hazard Index is less than or equal to 0.5.*

2.4.2 Storage tank

There have been a number of accidents recorded in storage tanks due to unstable chemical compound decomposition or reactivity/incompatibility of chemicals with impurity or water or air. An example of notorious disaster due to ignorance of unsafe part and incompatibility of chemical with water in the plant is the Bhopal gas disaster (Willey, 1998) in which management suspended some of the safety systems near to the storage tank of methyl-isocyanates, a highly poisonous substance, without knowing the consequences of the action. On 2nd Dec. 1984, slightly more than 500 kg of water entered into a storage tank containing 41 metric tons of methyl-isocyanates (MIC) at a pesticide plant located in Bhopal, India. The entry of water initiated a number of exothermic reactions. The reaction of methyl-isocyanates with water produces methylamine and carbon dioxide, along with heat.

$$H_3C-N=C=O \;+\; H_2O \;\longrightarrow\; H_3C-NH_2 \;+\; CO_2$$
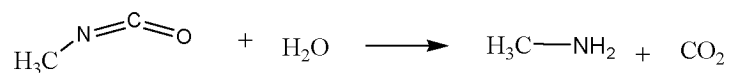
Methylamine and carbon dioxide are both gases at room temperature. The production of gas by the reaction raised the pressure in the container. The pressure inside the tank exceeded the pressure setting on the relief valve. The release followed the relief valve vent header to a vent gas scrubber system and flare stack. Regrettably, both of these safety control systems were not operational and suspended by management.

Consequently, the release from the relief valve entered the environment and followed the prevailing winds that carried the extreme toxic MIC into the slums and shantytowns resulting in more than 2,000 fatalities.

Different worst-case scenarios are possible in a storage tank:

1. Decomposition of substance with large amount of heat evolution in the tank;

2. Reactivity with water, cooling/heating media, material of construction and impurities etc.

3. Release of flammable, toxic and volatile substances from the tank because of different causes (leakage, overpressure etc.)

4. Release of hot liquids with high pressure and causing fatalities or triggering other events in neighbourhood (domino effects) etc.

Various inherent properties and storage parameters are considered to assess possible worst-case scenarios. These scenarios are presented here in detail:

- *Mass:* Mass of the substance stored in the tank is assessed according to the recommendations made in the "Seveso II Directive [96/82/EC]" and "Handbuch I zur Störfallverordnung StFV" (BUWAL, 1991). The mass limits in the tank have been defined with the help of these recommendations that consider the index value of Fire/Explosion and Acute Toxicity effect categories as shown in Table 2.4.2.1.

  All indices of safety categories obtained from SAL via modified EHS method and recommendations made by "Seveso II Directive [96/82/EC]" and "Handbuch I zur Störfallverordnung StFV" (BUWAL, 1991) are helpful to show if mass is in the acceptable limit (see Table 2.4.2.1). In the case of higher amount than acceptable limit, one should take proper measures or use inherent-safety-principles to reduce high hazards contained in the tank.

Table 2.4.2.1:   Relation between mass of substance and substance-index (results from SAL) according to "Seveso II Directive [96/82/EC]" and "Handbuch I zur Störfallverordnung StFV" (BUWAL, 1991).

Mass of Substance	< 200 kg	< 2000 kg	< 20000 kg	< 200000 kg
Acute Toxicity (index from SAL)	1	>= 0.75 but < 1	>= 0.5 but < 0.75	< 0.5
Fire/Explosion (index from SAL)		1	>= 0.75 but < 1	< 0.75

- *Decomposition:* Instability or decomposition data of the substance is assessed in SAL via modified EHS method in Decomposition category. The result is obtained in the form of index between 0 and 1. After collecting the information about decomposition, one can identify runaway or decomposition hazards and can assess them by decomposition-runaway model. In this model, decomposition hazards are divided into two categories i.e., primary decomposition hazards and secondary decomposition hazards, in a similar way as in batch/semi-batch reactor runaway model. The primary decomposition scenario is when a stored substance will decompose and generate a large amount of heat evolution that could not be controlled in the vessel itself. *This scenario should be considered for temporary storage vessels in which reaction mixture or reaction products are stored temporarily for some time or for weekend.* The primary decomposition hazard is assessed with the help of probability (TMR_{ad}) and severity (ΔT_{ad}) and an index is obtained as shown in Table 2.4.2.2 and Figure 2.4.2.1. Different possible critical scenarios due to decomposition are presented in the Figure 2.4.2.1 and are based on process temperature and Adiabatic Decomposition Temperature at 24 hours ($T_{0.24}$ or ADT_{24}) and 64 hours ($T_{0.64}$ or ADT_{64}) [which is obtained by taking TMR_{ad} = 64 hours in equation 2.4.1.2]. Since there have been many accidents in weekend time (from Friday evening till Monday morning) because of less personal present in the plant and less checking of process conditions, we have chosen 64 hours (from Friday 4PM to Monday 8AM), as a time parameter to show decomposition hazard. If 64 hours are available to control the scenario or to store the substance temporarily, hazard is considered moderate because substance could be stored for weekend. Attention should be given to storage time. If storage time in vessel is more than the time in

which temperature reaches beyond the limit of ADT_{24}, there can be severe accident. Secondary decomposition hazards are calculated by substance-indices from SAL, as it is in batch/semi-batch reactor runaway model, in the case of primary decomposition hazards present. *The acceptable limits for Primary and Secondary Hazard Indices are less than or equal to 0.2 and 0.5 respectively.*
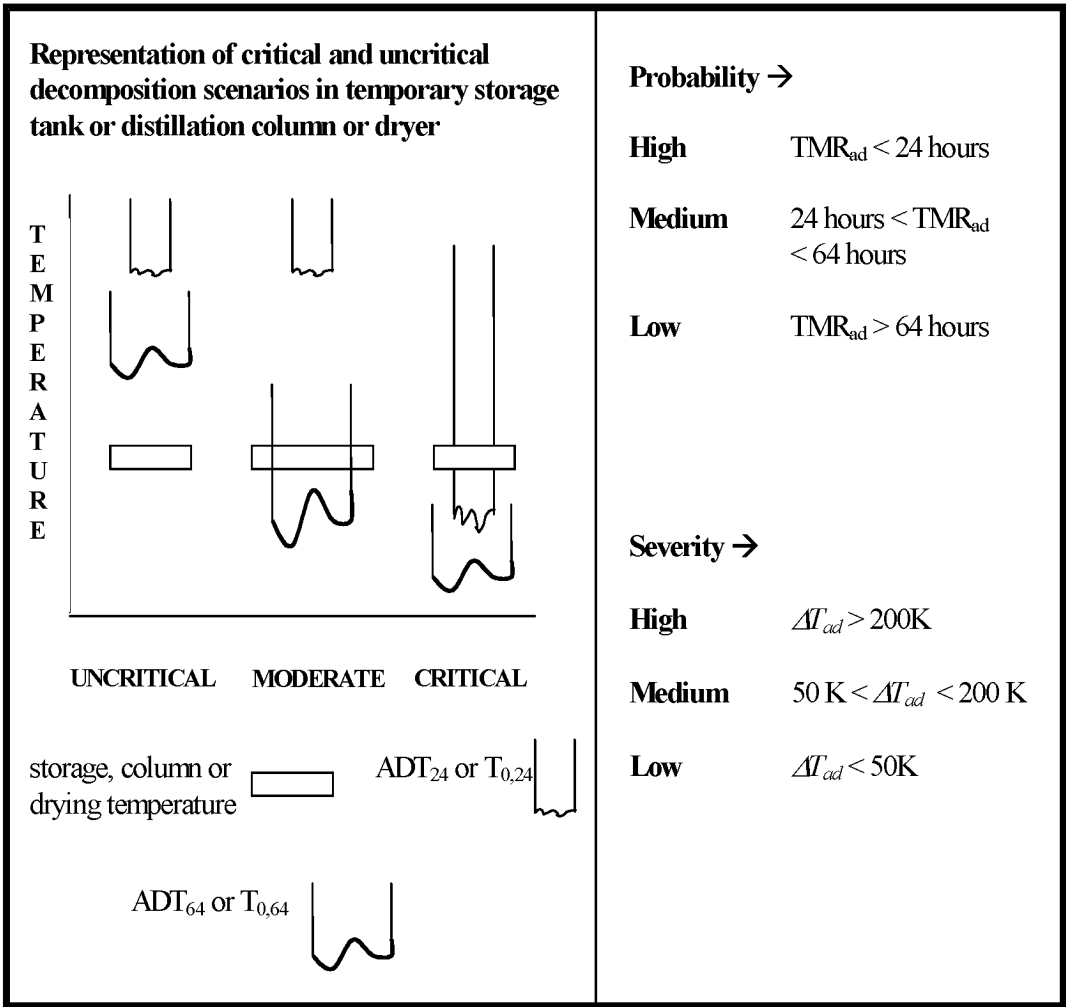
Figure 2.4.2.1: Evaluation of probability and severity for decomposition-runaway scenario in storage tank, distillation column and dryer.

Table 2.4.2.2: Different categories of probability and severity to define Primary Decomposition/Incompatibility-Hazard-Index (PDHI or PIHI) for decomposition and incompatibility scenarios.

	Probability	Severity	Primary Hazard Index	
Low	Low	Low	0.2	
	Low	Medium	0.2	
	Medium	Low	0.2	
	High	Low	0.2	
Moderate	Low	High	0.7	**H**
	Medium	Medium	0.7	**a**
Critical	High	Medium	0.9	**z a**
	Medium	High	0.9	**r**
Highly Critical	High	High	1.0	**d s**

- *Incompatibility:* Reactivity or incompatibility information is collected from RAL in the form of matrix and reactivity indices. After collecting the information about reactivity/incompatibility, one can identify runaway hazards and can assess them by incompatibility-runaway model (see Figure 2.4.2.2). Primary and Secondary Incompatibility Hazard Indices (PIHI or SIHI) are calculated as presented in decomposition-runaway model and shown in Table 2.4.2.2. ***The acceptable regions for Primary and Secondary Hazard Indices are less than or equal to 0.2 and 0.5 respectively.*** Different critical scenarios are shown in Figure 2.4.2.2 and are based on process temperature, ADT_{64}, Maximum Temperature of Incompatible Reaction (MTIR) and design or set temperature of equipment unit. One can note that if design temperature of vessel or decomposition temperature of substance comes in the range of MTIR, the scenario will be critical. This assessment could be measured with the help of incompatible reaction data, probability (TMR_{ad}) and severity (ΔT_{ad}).

Representation of critical and uncritical reactivity/incompatibility scenarios in storage tank or distillation column or dryer	Probability →	
	High	$TMR_{ad} < 24$ hours
	Medium	24 hours $< TMR_{ad} < 64$ hours
	Low	$TMR_{ad} > 64$ hours
	Severity →	
	High	$\Delta T_{ad} > 200K$
	Medium	$50 K < \Delta T_{ad} < 200 K$
	Low	$\Delta T_{ad} < 50K$
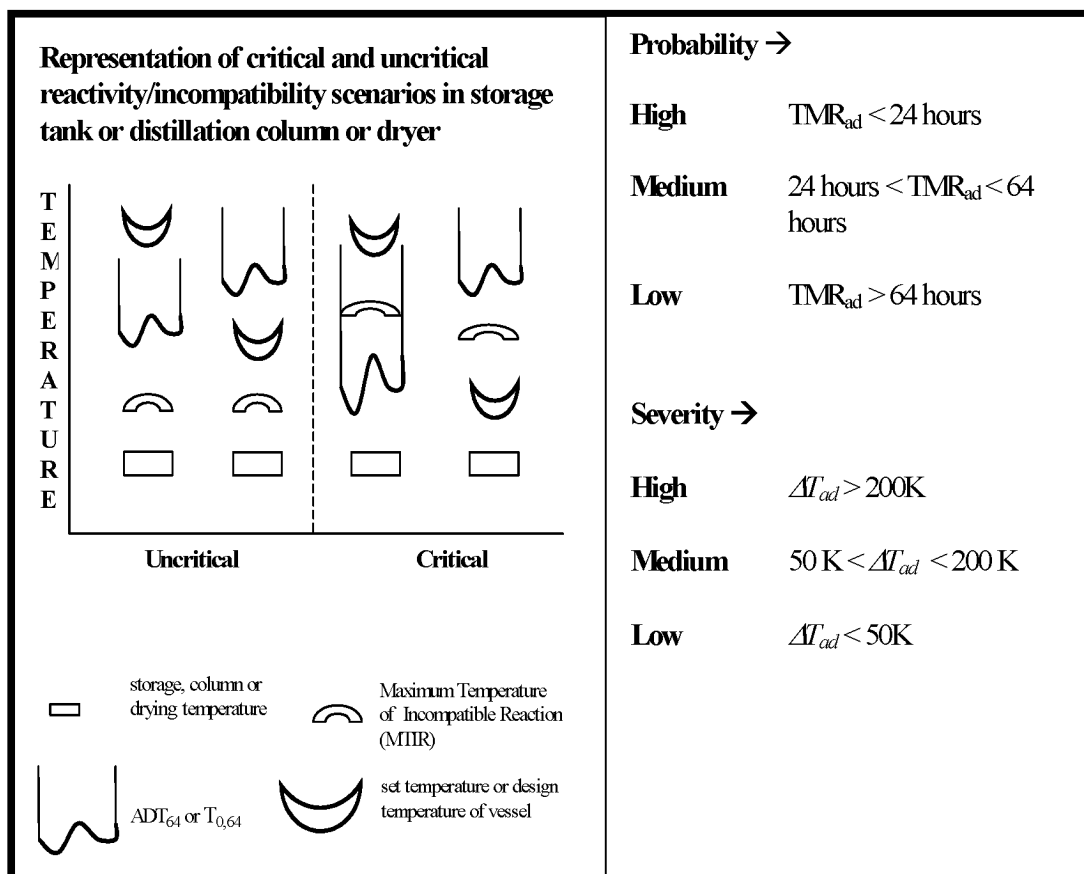
Figure 2.4.2.2: Evaluation of probability and severity for incompatibility-runaway scenario in storage tank, distillation column and dryer.

▪ *Storage conditions:* Storage pressure and temperature data can be collected from user and compared with boiling point, ambient temperature and ambient pressure. These parameters are considered in modifying Mobility index as following:

   a. $\Delta T_{storage}$ = storage temperature – ambient temperature (similar to Δbp (°C) priority in Mobility category in EHS method (see Figure A1 in Appendix A))

   b. ΔT_{bp} = boiling point (at storage pressure) – storage temperature (similar to Δbp (°C) priority in Mobility category in EHS method (see Figure A1 in Appendix A))

   c. $\Delta P_{storage}$ = storage pressure – ambient pressure (similar to pi° (bar) priority in Mobility category in EHS method (see Figure A1 in Appendix A))

Modified Mobility Index = Max (Considered aspects in Mobility category in EHS method (see Figure A1 in Appendix A), ΔT_{bp}, $\Delta T_{storage}$ and $\Delta P_{storage}$).

▪ *Flammability and toxicity:* Fire/Explosion, Acute Toxicity and Mobility indices from SAL (see Figure A1 in Appendix A) are used to identify and assess the severity of primary hazards as fire, explosion and toxicity scenarios.

2.4.3 Distillation column

Distillation columns are commonly used in chemical plants for separation purposes. Petroleum industries and refineries use predominantly distillation columns for separating mixed feed into pure components. Since the process requires energy (mainly in the form of steam), it is referred to as thermal separation. A distillation system in itself contains different units, for example, condenser, reboiler and pump etc. These units can cause different problems in the operation of distillation column. Some of the causes that can lead to an accident are:

1. Loss of cooling media in condenser
2. Loss of vacuum in the case of vacuum distillation
3. Loss of electricity etc.

Loss of cooling media in condenser can cause pressure and temperature rise in distillation column, which can trigger decomposition of substances. The pressure rise can cross the maximum pressure limit of distillation column and can be a reason of rupture of column. In the similar way, loss of vacuum in column can increase boiling point of mixture and can trigger decomposition of any substance or mixture.

Some other causes related with substances that can lead to an accident are:

1. Flammable, toxic and volatile solvents or substances present,
2. Reactivity/incompatibility with impurity or other substances present in connecting units,
3. Decomposition of mixture substances,
4. Release of hot and pressurized fluid in the surroundings etc.

Various inherent properties and column parameters are considered to assess possible worst-case scenarios. These possible worst-case scenarios are explained in detail here:

- *Decomposition:* Instability or decomposition data of the substance is assessed in SAL via modified EHS method (see Sub-chapter SAL) using Decomposition category. The result is obtained in the form of index between 0 and 1. After collecting the information about decomposition, one can identify runaway/decomposition hazards and can assess them by decomposition-runaway model (see Figure 2.4.2.1) explained in storage tank assessment.

- *Incompatibility:* Reactivity/incompatibility information is collected from RAL in the form of matrix and reactivity indices. After collecting the information about reactivity/incompatibility, one can identify runaway/incompatibility hazards with the help of acceptability limits given and can assess them by incompatibility-runaway model (see Figure 2.4.2.2) as explained in storage tank assessment.

- *Column conditions:* Column pressure and temperature data are collected via user interface from user and compared with boiling point, ambient temperature and ambient pressure. These parameters are considered in Mobility index as following:

  a. ΔT_{bp} = boiling point (at column pressure) – column temperature (similar to Δbp (°C) priority in Mobility category in EHS method (see Figure A1 in Appendix A))

  b. ΔT_{column} = column temperature – ambient temperature (similar to Δbp (°C) priority in Mobility category in EHS method (see Figure A1 in Appendix A))

  c. ΔP_{column} = column pressure – ambient pressure (similar to pi° (bar) priority in Mobility category in EHS method (see Figure A1 in Appendix A))

  Modified Mobility Index = Max (Considered aspects in Mobility category in EHS method (see Figure A1 in Appendix A), ΔT_{bp}, ΔT_{column} and ΔP_{column})

- *Flammability and toxicity of solvents and other substance assessment:* Assessment of properties of solvents is very important to avoid fire/explosion scenario. Fire/Explosion, Acute Toxicity and Mobility indices (see Figure A1 in Appendix A) from SAL are used to identify and assess the severity of fire, explosion and toxicity consequences as primary hazards.

2.4.4 Dryer

Drying is understood as the separation of liquid from a wet solid by vaporizing the liquid and removing the vapour. Since this process requires energy (mainly in the form of heat), it is referred to as thermal drying. Depending on the temperature, the drying process takes place either below the boiling point of the liquid being removed, or at its boiling point. Wherever chemicals are processed on an industrial scale, frequent use is made of drying processes. When drying takes place, the substance being dried is subjected to physical stresses that can lead to hazardous situations and possibly accidents (ESCIS, 2001). Therefore process conditions, i.e. drying temperature, should be selected carefully after safety assessment. Different worst-case scenarios are possible in the dryer:

1. Exothermic decomposition
2. Reactivity/incompatibility
3. Fire/explosion hazards
4. Spontaneous decomposition
5. Hot discharging

Various inherent properties and drying parameters are considered to assess possible worst-case scenarios. These scenarios are presented here in detail.

- *Decomposition:* Instability or decomposition data of the substance is assessed in SAL via modified EHS method (see Sub-chapter SAL) in Decomposition category. The result is obtained in the form of index between 0 and 1 and also in the form of information. The hazard can be represented by indices as shown in decomposition-runaway model (see Figure 2.4.2.1) in storage tank assessment. The starting temperature of the decomposition (for example, t_{onset} for decomposition in DSC) is collected via databases or from user and ADT_{64} and TMR_{ad} values are calculated to predict, propose or assess drying temperature. TMR_{ad} values are important to prevent the decomposition scenario.

- *Incompatibility:* Reactivity or incompatibility information is collected from RAL in the form of matrix and reactivity indices. Similar assessment, as presented in decomposition step for primary and secondary hazards, of starting

temperature of reaction regarding reactivity/incompatibility could be done to define safe drying temperature and to avoid contact with undesired substances.

- *Substance flammability and toxicity:* Fire/Explosion (which incorporates flash point, auto-ignition temperature etc.) and Acute Toxicity from SAL are used to identify and assess the severity of fire, explosion and toxicity consequences as primary hazards.

2.5 Safety-Technology Assessment Layer (STAL)

It is important to consider control measures in the risk assessment in order to show realistic hazards. If a plant and its emissions are not completely inherently safe, safety and/or end of pipe technologies are needed to control the hazard and to reduce the risk. Especially in the fine and speciality chemical industries where multi-purpose units are used and processes are frequently changed, the assessment and prediction of safety measures in the early stage of design are required. In this layer, the selection of safety technologies around the equipments is considered as a function of results available from the other layers (11 effect categories from SAL, reactivity indices and detailed information from RAL and worst case scenarios assessment from EAL).

The basic set of safety technologies that are recommended for all equipment units for handling flammable, volatile and toxic substances (as primary hazards) are given in Tables 2.5.1, 2.5.2 and 2.5.3. The safety technologies are selected for reducing primary hazard indices (for example, Mobility, Fire/Explosion and Toxicity) to acceptable region for each substance, if substance index is above the acceptable limit.

New allocation of safety technologies and corresponding hazard reduction factors based on results from EAL for the case of runaway scenario due to undesired secondary reaction or decomposition or incompatibility in different equipment units has been developed. In the Safety-Technology Assessment Layer (STAL), all possible safety technologies for this scenario are categorized into three lists. These lists are shown in Tables 2.5.4, Table 2.5.5 and Table 2.5.6. *The first list (Table 2.5.4) shows the process factors to be checked before predicting any specific safety technology with regard to the prevention of runaway hazards. One can avoid instrumental and human errors by*

checking these factors before starting a process. Several steps (for example, redundant safety control and instrumented systems, programmable electronic systems, redundant interlocks (IEC 61508 and IEC 61511, 1987)) can be taken to prevent major scenarios. The second list (Table 2.5.5) contains sets of safety technologies in the case of emergencies to prevent severe accidents by mitigating primary runaway hazards. The third list (Table 2.5.6) comprises a number of technologies to mitigate secondary hazards, i.e., safety, health and environmental hazards posed by chemicals. It should be noted that safety technologies for handling secondary hazards are considered only if there are primary runaway hazards present. *The inherent safety concepts, i.e., avoid accumulation with the help of dosing control or by increasing temperature of reaction (with safety constraint), change the mode by using continuous reactor instead of batch, can also be used, in case, safety technologies are not sufficient or hazard indices are in highly critical region (see Chapter 3).*

The design, costing and selection of some of the safety technologies for example, safety valves, bursting discs, dump and quench tanks, cyclone separators, gas absorbers and flares, for mitigating primary and secondary runaway hazards can be done with the help of methodologies and tool explained in Appendix E. The design and cost of different safety technologies can be factors in deciding the feasibility or applicability of their use for different runaway scenarios. The advantages and disadvantages of using different safety technologies are given in Tripuraneni (2002), which can be useful in making decisions for selecting safety technologies.

Table 2.5.1: Safety technologies for handling volatile substances as primary hazards.

Set #	Substances are volatile (vapour-cloud scenario) (If Mobility index in SAL $\geq$ 0.6)	Proposed reduction factors
P_1	Pressure measurement system with alarm.	0.2
P_2	Avoid release of gas e.g., by pH control, operating instructions.	0.2
P_3	Drainage.	0.2
P_4	Sufficient cooling capacity to avoid undesired volatility.	0.2
P_5	Working under reflux e.g., evaporative cooling.	0.3
P_6	Single containment.	0.3
P_7	Reduce dust by e.g., ventilation, dust filter.	0.4
P_8	Double containment.	0.4

Table 2.5.2: Safety technologies for handling flammable substances as primary hazards.

Set #	Substances are flammable (fire or explosion scenario) (If Fire/Explosion index in SAL $\geq$ 0.6)	Proposed reduction factors
P_1	Reduce explosion consequences by using explosion protection technologies e.g., suppressers and water sprinklers, water curtains, foam, hand extinguishers, cable protection.	0.1
P_2	Leak detection.	0.1
P_3	Emergency power and emergency shutdown system.	0.1
P_4	Equipment protected with fixed water spray.	0.1
P_5	Fire water and foam monitors.	0.1
P_6	Fireproof cable tray, steel supports (fire resistant wiring, flame shields, etc.)	0.1
P_7	Fire protection measures e.g., fire compartments, extinguishers, and drainage for water in fire fighting.	0.1
P_8	Pressure and temperature control, alarm and adequate cooling capacity.	0.2
P_9	No storage of other flammable materials nearby.	0.2
P_{10}	No ignition sources in the surrounding by making explosion zones.	0.2
P_{11}	Low oxygen content by partly inertization, ventilations and concentration control.	0.2
P_{12}	Explosion zone 2 (outside the vessel) and Explosion zone 0 (inside the vessel)	0.2
P_{13}	Inertization.	0.3
P_{14}	Blow-off tank.	0.3
P_{15}	Single containment.	0.3
P_{16}	Double containment.	0.4

Table 2.5.3: Safety technologies for handling toxic substances as primary hazards.

Set #	Substances are toxic (toxic-release scenario) (If Acute Toxicity index $\geq$ 0.5)	Proposed reduction factors
P_1	Leak detection.	0.1
P_2	Emergency power and emergency shutdown system.	0.1
P_3	Interlocks, remote control valves etc.	0.1
P_4	No manual handling of toxic substances e.g., use of gloves, masks.	0.1
P_5	Procedures for service and maintenance e.g., standard manuals for handling toxic substances.	0.1
P_6	Fresh air ventilation for working areas.	0.3
P_7	Blow-off tank.	0.3
P_8	No escaping of toxic substances e.g., single containment.	0.3
P_9	No escaping of toxic substances e.g., double containment.	0.5

Table 2.5.4: Process factors required to be checked for runaway hazards before predicting specific safety technologies. The redundant safety control or instrumentation systems should be used to prevent any hazard scenario.

Factors required to be checked for prevention of runaway/incompatibility/decomposition hazards (if primary hazards > 0.2):	Equipment units
Mixing assured (reliable stirring system).	Batch/semi-batch reactor
Sufficient cooling capacity (reliable cooling system).	Batch/semi-batch reactor, storage tank
Isothermal and controlled by dosing.	Batch/semi-batch reactor
Start of desired/undesired reaction detectable.	Batch/semi-batch reactor, storage tank, dryer, distillation column
Avoid wrong dosing (wrong chemicals, wrong sequence etc.).	Batch/semi-batch reactor, storage tank, dryer, distillation column
No water, metal, acid, oxidizable material, incompatibilities.	Batch/semi-batch reactor, storage tank, dryer, distillation column
Pressure and temperature control, alarm, interlocks, avoiding undesired heating.	Batch/semi-batch reactor, storage tank, dryer, distillation column
Exact knowledge of decomposition.	Batch/semi-batch reactor, storage tank, dryer, distillation column

Table 2.5.5: Safety technologies for mitigating primary runaway hazards.

Set #	Safety technologies for primary runaway hazards/ decomposition/incompatibility (If primary hazards > 0.2)	Equipment units	Proposed reduction factors
P_1	Back up cooling system (for emergency cooling) Or parallel cooling pump system Or design of alarm at cooling/heating water tank	Batch/semi-batch reactor, storage tank, distillation column	0.1
P_2	Evaporative cooling with sufficient condenser capacity	Batch/semi-batch reactor	0.3
P_3	Pressure relief device (safety valve or rupture disc)	Batch/semi-batch reactor, storage tank, distillation column	0.3
P_4	Quenching or inhibition in the process vessel itself	Batch/semi-batch reactor, storage tank	0.5
P_5	Special vessel design with bottom outlet for sudden pressure rise	Batch/semi-batch reactor, storage tank	0.8

Table 2.5.6: Safety technologies for mitigating secondary runaway hazards.

Set #	Safety technologies for handling secondary runaway hazards (If primary hazards present and secondary hazards > 0.5)	Equipment units	Proposed reduction factors
S_1	Explosion zone 2, (ignition source improbable) [outside the vessel]	Batch/semi-batch reactor, storage tank, dryer, distillation column	0.2
S_2	Catch tank [with collection balloon]	Batch/semi-batch reactor, storage tank, dryer, distillation column	0.3
S_3	Dump/catch tank with scrubber/flare and vent	Batch/semi-batch reactor, storage tank, dryer, distillation column	0.3
S_4	Quench tank with scrubber/flare and vent	Batch/semi-batch reactor, storage tank, dryer, distillation column	0.3
S_5	Cyclone separator with catch tank, scrubber/flare and vent	Batch/semi-batch reactor, storage tank, dryer, distillation column	0.5
S_6	Full containment system (first and second containment) [(set #S_1 Or #S_2 Or #S_3 Or #S_4) + containment walls + drainage system Or full containment walls around the reactor]	Batch/semi-batch reactor, storage tank, dryer, distillation column	0.5

A hazard reduction factor has been assigned to each set of safety-technologies as shown in Tables 2.5.1, 2.5.2, 2.5.3, 2.5.5 and 2.5.6 after collecting feedback from experts and testing on several runaway case studies. The hazards from SAL, RAL and EAL are reduced with the help of these hazard reduction factors related to the application of safety technologies. The acceptable regions for remaining hazard indices for Mobility (vapour-cloud scenario), Fire/Explosion (fire or explosion scenario) and Acute Toxicity (toxic-release scenario) are given in Table 2.2.1.

For a set of selected safety technologies, the Remaining Primary and Secondary Hazard Indices (RPHI and RSHI) are defined with the help of following equations.

Remaining Primary Hazard Index (RPHI) = [Primary Hazard Index (PHI) − ΣSafety Technology Reduction Factor (STRF)]   *2.5.1)*

Remaining Secondary Hazard Index (RSHI) = [Secondary Hazard Index (SHI) − ΣSafety Technology Reduction Factor (STRF)]   *(2.5.2)*

The above-mentioned equations can be applied for all primary and secondary hazards, for example, runaway or decomposition or incompatibility or fire/explosion or toxic release scenario. *The acceptable region defined here is below 0.2 for the Remaining Primary Hazard Index (RPHI) and is below 0.5 for the Remaining Secondary Hazard Index (RSHI). The secondary hazards should be handled only if there are primary hazards present.* The decision about selecting different safety technologies can be taken to bring the remaining primary and secondary hazards to an acceptable level.

3. Decision-making with the help of inherent-safety-principles

In the multi-purpose and multi-product plants (for example, fine chemicals and pharmaceutical industries), processes are changed and developed quite frequently to release a new or changed product or to meet the demand of the product in the competitive market. To lead in the market, to meet the demand speedily and to fulfil the environmental, health and safety rules and regulations efficiently, one should consider EHS aspects, and inherent safety principles in early stage of development. Deliberating EHS aspects in early stages of design, on one side, can improve technologies in the plant that can lead to an economic process, on the other side, can make the process more environmental benign, health friendly and safe.

Exploring inherently safer alternatives may require more resources during the early stages of development than is otherwise the case. However, the resulting understanding will, in many cases, minimize or eliminate the need for appended safety mitigation devices and the costs of maintaining them as well as reduce the possibility of incidents. The economic benefits to be derived from inherently safer thinking will increase by application early in the process. However, it is never too late to start using inherently safer concepts for existing facilities (CCPS, 1996). Inherent safety as a way of thinking involves a holistic approach to consider the process as a system with interacting concerns such as toxicity, flammability, reactivity, stability, quality, process conditions etc.

This chapter presents how to make decisions regarding process hazards and safety of the plant with the help of SREST-Layer-Assessment method and inherent-safety-principles (ISP) in early development stage under the expert's supervision. Process hazards come from two sources, hazards that are characteristic of the materials and chemistry used, and hazards that are characteristic of the process variables – the way the chemistry works in the process (CCPS, 1996). In SREST method, both the hazard sources are recognized and assessed. SAL and RAL identify and assess hazards related with materials, reactivity, and incompatibility while EAL assesses the process variables and chemistry used i.e. different process conditions in various equipment units. Each layer

gives the assessment results in the form of indices or detailed information that can be judged to make decisions about inherent safety as shown in Figure 2.1.2. It provides the possibilities to use inherent-safety-principles (for example, minimization or substitution of mass, changing process conditions or changing reaction routes etc.) after assessment in each layer and also at the end of SREST concept as shown in Figures 2.1.2 and 3.1. STAL can be used to predict safety technologies in early stages to prevent and protect the environment, human and plant from the hazard.
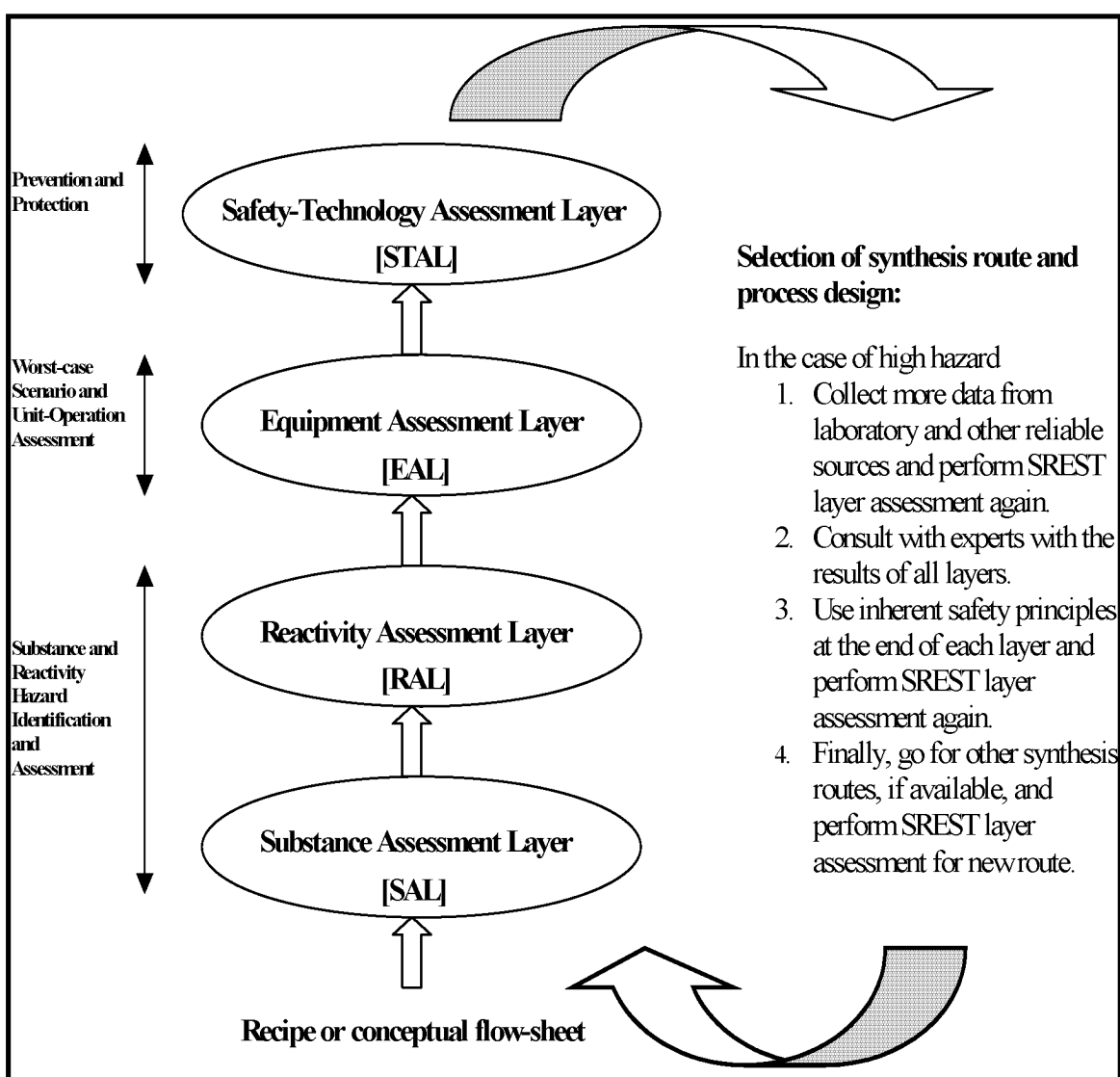
Figure 3.1: SREST-Layer-Assessment method with use of inherent-safety-principles.

3.1 Substance Assessment Layer

The EHS method (which is slightly modified, see SAL in Chapter 2) developed by Koller et. al (2000) is used to assess the substances in this layer. The details are given in Appendix A and in Koller et. al (1999). The results can be shown in different degrees of detail ranging from simple overall indices of the whole process to detailed studies of selected effects of a specific stage. Consequently, the user is able to see the EHS-problems of a process at one sight using simple graphs but can also go into further detail to understand the reasons of the EHS-problem. After assessing all the substances in SAL for their inherent hazards, for example, flammability, toxicity, decomposition etc., one can imply the following inherent safety principles as shown in Figure 3.1.1 if indices are not in the acceptable limit:

1. Minimize critical substances
2. Substitute critical substances

Minimization is the reduction in the quantity of substances in any equipment unit. "Handbuch I zur Störfallverordnung StFV" (BUWAL, 1991) recommendations can be used to improve inherent safety in the plant by a user to reduce the quantity of the hazardous chemicals up to the acceptable level as shown in Table 2.4.2.1. These recommendations have been used in storage tank in EAL to propose the desired mass of the chemical stored in the tank.

Substitution is to replace the hazardous substance by less hazardous or non-hazardous one. This principle is used predominantly in reaction chemistry and solvent usage.

START

Substance Import from different databases by interfaces:
    1. IUCLID
    2. IGS
    3. CHRIS
    4. EPIWIN
    5. BIODEG
    6. CHEMFATE
    7. MS-EXCEL connection to import lab or other data

Substance Data Analysis:
    1. Combining data from different databases.
    2. Standard deviation calculation.
    3. Comparison of different databases.
    4. Possibility to choose user's own data.

Missing Property Data Calculation:
    QSAR
    Different models

Substance Assessment by EHS Method (With minor changes in EHS method in Reaction/Decomposition Category):

Potential of Danger
        For each substance &
                For each category
(Result is in the form of Effective Dangerous Property (EDP) Index value [0-1] and Physical value (see SAL in Chapter 2))

Safety:
    1. Mobility
    2. Decomposition
    3. Fire/Explosion
    4. Acute Toxicity
Health:
    1. Irritation
    2. Chronic Toxicity
Environment:
    1. Water Mediated Effects
    2. Air Mediated Effects
    3. Solid Waste
    4. Degradation
    5. Accumulation

Substance Assessment Layer:

Result is in the form of Effective Dangerous Property (EDP) Index (see SAL in Chapter 2):
        For each substance
                For each category

Use of Inherent Safety Principles:

Acceptable limit is proposed for each category in EHS method
If substance index for any category >= Acceptable limit Then
    1. Use inherent safety principles (for example, substitution, minimization etc.)
    2. Proceed with other layers to check final potential of danger.

Data Collection, Analysis and Calculation

Substance Assessment by EHS Method

Result in the SAL and Use of Inherent Safety Principles

Figure 3.1.1: Substance Assessment Layer (SAL) and use of inherent-safety-principles.

3.2 Reactivity Assessment Layer

After assessing all the substances in RAL for their inherent hazards, for example, reactivity and incompatibility etc., one can imply the following inherent-safety-principles as shown in Figure 3.2.1 if hazards are not acceptable:

    1. Minimize critical substance

    2. Substitute critical substance

    3. Avoid contact with the help of proper design

```
┌─────────────────────────────────────────────────────────────────────────────┐
│  ⬙  START                                                                     │
│                                                                               │
│  ┌───────────────────────┐                          ╱─────────────────╲      │
│  │ Reactivity/Incompatibility │   ┌──────────────────┐  │ Reactivity Assessment Layer: │
│  │ data Import from different │   │ Reactivity Assessment by │ │ Result is in the form of │
│  │ databases by interfaces:   │   │ crosschecking all the    │ │ reactivity/incompatibility matrix and │
│  │  1. Bretherick's chemical  │   │ substances present in the │ │ reactivity indexes │
│  │     reactivity database    │   │ plant with the help of   │  ╲─────────────────╱     │
│  │  2. Chemical Reactivity    │   │ visual basic code        │                          │
│  │     Worksheet              │   │ Crosscheck with          │                          │
│  │  3. MS-EXCEL connection    │   │     Water                │                          │
│  │     to import lab or other data │ │   Air                  │   Use of Inherent Safety  │
│  │                            │   │     Cooling/Heating media │   Principles:            │
│  │         ⬇                  │   │     Material of Construction │                       │
│  │                            │   │     Impurities known     │  If there is incompatibility or │
│  │ Reactivity prediction with │   │     Other substances present │ undesired reactivity indication then │
│  │ the help of:               │   └──────────────────┘     │    1. Use inherent safety │
│  │  1. Group incompatibility  │                             │       principles (for example, │
│  │     chart (see Figure B1 in │                            │       avoid contact by designing │
│  │     Appendix B) with the    │                            │       better flow-sheet etc.) │
│  │     information about hazards. │                          │    2. Proceed with other layers to │
│  │  2. List of hazardous reactions │                        │       see final potential of danger. │
│  │  3. Possibility to choose   │                            │                          │
│  │     user's own data.        │                            │                          │
│  └───────────────────────┘                                  │                          │
│                                                              │                          │
│                                                       Result in the RAL                 │
│     Data Collection          Reactivity Assessment    and Use of                        │
│     & Prediction                                      Inherent Safety                   │
│                                                       Principles                        │
└─────────────────────────────────────────────────────────────────────────────┘
```

Figure 3.2.1: Reactivity Assessment Layer (RAL) and use of inherent-safety-principles.

"Handbuch I zur Störfallverordnung StFV" (BUWAL, 1991) recommendations can be used to improve inherent safety in the plant by a user to reduce the quantity of the hazardous chemicals up to the acceptable level as shown in Table 2.4.2.1. These recommendations have been used in storage tank in EAL to propose the desired mass of the chemical stored in the tank. Substitution is to replace the hazardous substance by a less hazardous or non-hazardous one. This principle can be used in replacing heating/cooling media or reactive solvent to avoid reactivity hazards. Proper design steps can be taken to avoid contacts between incompatible substances.

3.3 Equipment Assessment Layer

The prediction, identification and assessment of possible worst-case scenarios in major unit-operations can be helpful in defining process conditions, can improve safety in equipment units and can prevent accidents to occur. After identifying and assessing different possible worst-case scenarios in each equipment unit, results can be analyzed

by using acceptable limit (see Chapter 2.4) and inherent-safety-principles, as shown in Figure 3.3.1, can be used to reduce hazards. One can use the following inherent-safety-principles:

1. Moderate
2. Simplify

Moderate means using materials under less hazardous conditions, also called attenuation. Moderation of conditions can be accomplished by strategies that are either physical (lower temperatures, dilution) or chemical (development of a reaction chemistry which operates at less severe conditions). Dilution, refrigeration and less severe process conditions are some examples to increase inherent safety in the plant.

START

Reaction and major unit-operation data collection
1. Laboratory data (for example, DSC data, reaction enthalpies etc.),
2. Process conditions in unit-operations via user-interface,
3. Connection to Batch-Plus™ for mass and process conditions.

Possible Worst-case scenario Identification

With the help of
1. Hazards related with substances (toxicity, flammability etc.) and mass of substances present,
2. Reactivity/incompatibility information and
3. Process conditions in unit-operations.

Possible Worst-case scenario assessment

Simulation code for assessing different worst-case scenarios
1. Runaway,
2. Decomposition,
3. Fire/explosion etc.
In major unit-operations
1. Batch/semi-batch reactor
2. Storage tank
3. Distillation Column
4. Dryer

Equipment Assessment Layer:

Result is in the form of hazard indexes
For each unit operation
For each worst-case

Use of Inherent Safety Principles:

Acceptable limit is proposed for each worst-case in each unit-operation

If hazard index is >= acceptable limit then
1. Use inherent safety principles (for example, change process conditions, concentrations, accumulations etc.)
2. Proceed with other layers to check final potential of danger.

Process and unit-operation Data Collection

Major unit-operation Assessment

Result in the EAL and Use of Inherent Safety Principles

Figure 3.3.1: Equipment Assessment Layer (EAL) and use of inherent-safety-principles.

Simplify means designing to eliminate unnecessary complexity, reducing the opportunities for error and misoperation. A simpler plant is generally safer and more cost effective than a complex one. For example, it is often cheaper to spend a relatively small amount of money to build a higher-pressure reactor, rather than a large amount of money for an elaborate system to collect and treat the discharge from the emergency relief system of a reactor designed for a lower maximum pressure (CCPS, 1996).

3.4 Safety-Technology Assessment Layer

Prediction of safety technologies for reducing the hazards related with substances, reactivity and possible worst-case scenarios in equipment units in early design stage is important because it can be helpful in deciding economic safety technologies and using inherent safety principles to make plant safer. After reducing the inherent hazards in substance, reactivity and equipment assessment layer, remaining hazards should be handled carefully with the help of safety technologies. Introducing safety technologies, for example, secondary containment etc. can increase process safety. Secondary containment systems do not eliminate or prevent a spill or leak, but they can significantly moderate the impact without the need for any active device. In this way, Safety-Technology Assessment Layer can be used to increase process safety with the help of inherent-safety-principles (for example, simplification of design) as shown in Figure 3.4.1.

3.5 SREST-Layer-Assessment method and decision-making

After assessing all four layers, results are available in the form of substance hazards or remaining hazards of any worst-case scenario in any equipment unit. If the hazards are above the acceptable limit, the following steps should be performed as shown in Figures 2.1.2 and 3.1:

- One can collect more data from experiments in the laboratory or from other reliable sources and can perform SREST layer assessment again to rely on decisions.
- After performing SREST layer assessment with reliable data and synthesis route, experts can be consulted with available results for detailed assessment.

▪ Inherent-safety-principles, for example, changing the synthesis route or process chemistry, can be used and complete assessment can be repeated.

START

Prediction of Safety Technologies:

Different safety technologies are proposed for preventing and protecting plant from major worst-case scenarios. The lists of safety technologies exist for
1. Runaway scenario
2. Decomposition/reacti-vity/incompatibility scenario
3. Fire/explosion scenario
4. Handling flammable, toxic and volatile substances in unit-operations.

Safety-Technology Assessment Layer:

Result is in the form of list of safety technologies with qualitative indexes
For each unit-operation
For each worst-case scenario

Use of Inherent Safety Principles:

Acceptable limit is proposed for each worst-case in each unit-operation

If remaining hazard index is >= acceptable limit then
1. Use other safety technologies from the list Or
2. Use inherent safety principles (for example, change process conditions, concentrations, accumulations etc.) Or
3. Change unit operations (for example, from batch to semi-batch reactor)

List of Safety Technologies

Result in the STAL and Use of Inherent Safety Principles

Figure 3.4.1: Safety-Technology Assessment Layer (STAL) and use of inherent-safety-principles.

Development Stages	Different Tasks	Use of SREST-Layer-Assessment-Method & Tool	Inherent Safety Principles
R&D (Research and Development) Laboratory and Bench scale	▪ Market search, ▪ Demand of the products, ▪ New discovery in the research, etc.		**Use of inherent-safety-principles with the help of SREST-Layer-Assessment method**
	▪ Synthesis route development ▪ Route screening	**Substance Assessment Layer** 1.Collection of data	
	▪ List of reactants, intermediates, products etc., ▪ Collection of substance properties (for example, physical and chemical properties, safety, environment, health related data etc.), ▪ Collection of reactivity/incompatibility data, etc. ▪ Substance and reactivity assessment	2.Substance Assessment **&** **Reactivity Assessment Layer** 1.Collection of data 2.Reactivity assessment **Or** **Complete SREST-Layer-Assessment method**	
R&D (Research and Development) Pilot/trial	▪ Conceptual flow sheet diagram, ▪ Contacting scheme, batch or continuous design selection, ▪ Selection of major unit-operations, ▪ Selection of process conditions, etc. ▪ Scale up	**Equipment Assessment Layer** 1.Identification of worst-case scenarios 2.Unit-operation assessment 3.Worst-case assessment **&** **Safety Technology Assessment Layer** 1.Prediction of safety technologies **Or** **Complete SREST-Layer-Assessment method**	
Engineering section	▪ Detailed flow sheet diagram, ▪ Piping and Instrumentation Diagram, ▪ Equipment design, scale up, etc.		
Full Manufacturing (Production) Scale	▪ Detail risk assessment, ▪ Environmental assessment, ▪ Handling, ▪ Maintenance, etc.	Education, training, preparation of safety manual, preparation of operating instructions etc.	

Figure 3.6.1: Use and timings of SREST-Layer-Assessment method.

3.6 Use and timing of SREST-Layer-Assessment method

The chemical processes in industries are developed step by step in different stages as shown in Figures 1.1 and 3.6.1. SREST-Layer-Assessment method can be used efficiently and quickly in laboratory where substance data and reaction recipe is defined and in conceptual flow-sheet stage where a rough sketch of flow-sheet is prepared with the list of major unit-operations involved. The Substance Assessment Layer (SAL) and Reactivity Assessment Layer (RAL) are mostly adequate in process research stage where synthesis route is developed. The Equipment Assessment Layer (EAL) and Safety-Technology Assessment Layer (STAL) are mostly suitable in process development stage where selection of major unit operations and process condition is done. The method with tool can be useful for chemists and chemical engineers in getting property data of chemicals, in knowing incompatibility/reactivity matrix of different substances present and in educating technicians and workers in the plant. Information about reactivity/incompatibility and safety technologies can be used in drawing Piping and Instrumentation Diagram (PID) for avoiding the contact or connection between incompatible substances.

4. Case studies

The SREST method as described in Chapter 2 can be used to analyse the hazards in a chemical process, to identify better alternatives in the direction of inherent safety and to propose safety technologies to handle the risk potential. In this chapter, different case studies are presented for different equipment units and processes to highlight the usefulness of SREST-Layer-Assessment method in assessing EHS aspects and in making decisions with the help of inherent-safety-principles (see Chapter 3).

4.1 Single equipment units

Different case studies are presented here to show possible worst-case scenarios in single major unit operations.

4.1.1 Batch/semi-batch reactor

Many basic synthesis steps, such as halogenation, oxidation, alkylation, nitration, diazotization and sulfonation are common to a large number of organic chemical manufacture in different industry sectors (Sikdar and Howell, 1998). These processes on one hand might lead to runaway accidents due to exothermicity and on the other hand might be harmful to human health and the environment by using toxic or flammable chemicals. Here four case studies are presented to demonstrate use of the method:

1. Production of an azo dye intermediate (Partington and Waldram, 2002),
2. Sulfonation of a nitro-aromatic compound (Keller, 1998),
3. Production of mono-nitro-toluene (Chen and Wu, 1996 and Chen et al., 1998),
4. Production of poly-acrylonitrile (Surinarayanan et al., 1998).

Case study 1: Production of an azo dye intermediate

Partington and Waldram, (2002) studied an accident that occurred due to runaway in a diazotization reaction and performed a risk analysis with the data obtained from laboratory experiments. This scenario is reconsidered here to highlight the capabilities of the methodology.

Substances present: Raw materials used in this case study are aromatic-amine (25 wt%), nitrosyl-sulfuric-acid (36.5 wt%) and sulfuric-acid (38.5 wt%).

Reaction recipe: A given quantity of the amine to be diazotized is added into 100% sulfuric-acid to give a solution in a semi-batch reactor. Nitrosyl-sulfuric-acid (NSA) is added over 5 hours whilst maintaining the temperature between 30 and 40 °C. At the end of the addition, diazotization is complete.
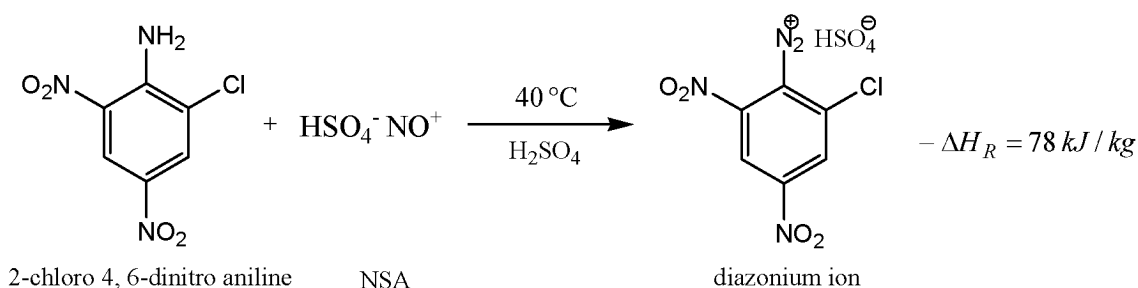
2-chloro 4, 6-dinitro aniline   NSA   diazonium ion

$-\Delta H_R = 78\,kJ\,/\,kg$

Substance Assessment Layer: **Results from SAL with acceptable limit line are shown in Figure 4.1.1.1 and in Table A2 in Appendix A.** For each category in modified EHS method (Koller et al., 2000), Dangerous Property indices are calculated for different priorities with the help of available data. These indices are modified by fate indices because the potential of dangerous properties are affected by, for example, volatility and degradability. The resulting indices i.e., Effective Dangerous Property (Koller et al., 2000) indices, are selected here to show the hazards. The data for Effective Dangerous Property Index (with the priority data) and fate indices are given in the Table A2 in Appendix A. Both sulfuric-acid and NSA show high health and environmental effects therefore measures for handling these substances are required. **The safety problems are the high Decomposition category index for diazonium-salt and high Acute Toxicity index values for sulfuric-acid and NSA.** Diazonium-salts are unstable in the solution and some are in the solid state. They are noted as being explosive (because of high heat

evolution in decomposition), and sensitive to friction, heat, shock and radiation. In view of their technical importance, diazonium-salts are often isolated as their zinc chloride (or other) double salts. High Decomposition category index for diazonium-salt indicates that there can be *decomposition* of this substance in any equipment in the case of high temperature or cooling failure. In the similar way, high Acute Toxicity index for sulfuric-acid and NSA predicts *toxic release scenario* in any equipment in the case of leakage as primary hazard or in the case of runaway as secondary hazard. *To handle these scenarios, i.e., toxic release or decomposition as primary hazard or toxic release as secondary hazard, detail assessment for runaway (decomposition of diazonium-salt) is performed in EAL and safety technologies are proposed with reduction factors in STAL in this case study.* The major problem of the aromatic-amine is its low degradability, which might lead to accumulation in the environment or in the food chain. The Chronic Toxicity index is taken as an Air Mediated Effects in EHS method to show the influence of substances in air. Sulfuric-acid and NSA show high index values for Air Mediated Effects. Sulfuric-acid and NSA can produce salt as a solid waste. This is indicated by high index value of Solid Waste. The Solid Waste category index is 0.0 for water, gases and organics and 1.0 for other chemicals.

Figure 4.1.1.1: Production of an azo dye intermediate: Substance Assessment Layer (SAL) results in the form of Effective Dangerous Property index (as defined in EHS method).

Reactivity Assessment Layer: The reactivity matrix based on information available in **Bretherick's database (Urben, 1999)** and **Chemical Reactivity Worksheet (NOAA, 2000)** is shown in Table 4.1.1.1. With the help of information available about intended and incompatible reactions, the reactivity indices are defined for these reactions and are presented in Table 4.1.1.2. **There can be violent reaction in the case of undesired mixing of water in sulfuric-acid.** The information on reactivity of sulfuric-acid with water and high incompatibility index is helpful in making decisions about detail assessment and in taking measures to prevent contact with water. **Steel is normally considered a safe material for contact with (reasonably pure) sulfuric-acid. However, there has been a case of a fatal explosion when working on a sulfuric-acid tank with cutting torches, attributed to hydrogen in the headspace arising from corrosion of the metal ascribed to poor maintenance (Bretherick's database, (Urben, 1999)).** The knowledge of intended **exothermic reaction of aromatic-amine with nitrosyl-sulfuric-acid** is available and high index indicates **runaway scenario** and should be assessed in detail (the detail assessment is done in EAL in this case study). By this way, literature search is helpful in highlighting commonly known problems by providing available information regarding desired and undesired reactions.

Table 4.1.1.1: Results from RAL obtained for azo dye intermediate case study. An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	aromatic-amine	nitrosyl-sulfuric-acid	sulfuric-acid	diazonium-salt	air	water	stainless-steel
aromatic-amine	SI	X	X				
nitrosyl-sulfuric-acid		SI					
sulfuric-acid			SI			X	X
diazonium-salt				SI			

Table 4.1.1.2: Results from RAL obtained for azo dye intermediate case study. The reactivity indices are defined for intended and incompatible reactions.

Reactivity Indices (acceptable limit ≤ 0.5)	Index values (defined in Figures 2.3.1 and 2.3.2 in Chapter 2)
Intended reaction (aromatic-amine diazotization)	0.75 (because of diazotization reaction)
Incompatible reaction (sulfuric-acid/water)	0.8 (NFPA = 2 and heat evolution)
Incompatible reaction (sulfuric-acid/steel)	0.6

Equipment Assessment Layer: The results from SAL (Figure 4.1.1.1) show that there can be ***toxic release scenario (release of sulfuric-acid and nitrosyl-sulfuric-acid)*** in the vessel due to leakage or spillage. This scenario as primary hazard should be considered carefully. The safety technologies are proposed in STAL in this case study.

The results from SAL (Figure 4.1.1.1) and RAL (Tables 4.1.1.1 and 4.1.1.2) indicate that detail assessment should be performed for the case of ***decomposition of diazonium-salt and intended exothermic reaction (diazotization)***. Therefore, ***the scenarios in batch and semi-batch reactors are compared and runaway assessment is performed.*** In the case of cooling failure, the maximum temperature attained by the desired reaction (MTSR) in a batch reactor where 100% reactants are charged at once, exceeds ADT_{24} as shown in Table 4.1.1.9. This shows that decomposition of the final reaction mixture can be triggered in the cooling failure scenario. Accordingly the investigated scenario results in criticality class 5. If reaction is performed in the semi-batch reactor as mentioned in the reaction recipe, the maximum accumulation (Partington and Waldram, 2002) of NSA will be 25% and MTSR will be lower than ADT_{24}. This decreases criticality class from 5 to 2 (see Table 4.1.1.9). The time to maximum rate at adiabatic conditions (TMR_{ad}) will increase from 0.6 hours in the batch reactor to 64 hours in semi-batch reactor (25% accumulation) and will provide enough time to take safety measures in the case of cooling failure. Nevertheless it should be noted that any additional heat input to the reactor could cause an accident as happened in the diazotization reactor at Holidays Dyes and Chemicals (Partington and Waldram, 2002). Since criticality class is 2, probability is low and severity is high, primary runaway hazard is moderate and ***Primary Runaway Hazard Index (PRHI) is 0.4*** (see Table 2.4.1.1 in Chapter 2). Substances present in the reactor are toxic as shown in Figure 4.1.1.1 and ***Secondary Runaway Hazard Index is 0.7.***

Safety-Technology Assessment Layer: The results from SAL (high Acute Toxicity index for sulfuric-acid and NSA) show that there can be toxic release scenario in the case of leakage or crack in the vessel. Therefore these substances should be handled carefully in the vessel. The safety technologies to handle these substances and to prevent primary hazard as toxic release scenario are: a) set $\#P_1$ (leak detection (-0.1)), set $\#P_2$

(emergency shutdown system (-0.1)) and set #P$_3$ (interlocks, remote control valves (-0.1)) or b) set #P$_8$ (single containment (-0.3)) from Table 2.5.3 in Chapter 2 and presented in Figure 4.1.1.2b and Table C1 in Appendix C. The safety category indices are reduced to the acceptable region as shown in Figure 4.1.1.2b.

The results from EAL (moderate Primary Runaway Hazard Index and high Secondary Runaway Hazard Index) show that safety technologies should be used to prevent these hazards. Since the criticality class is 5 in the case of batch reactor, reaction should not be performed in a batch mode. The criticality class 2 in the case of semi-batch reactor (maximum 25% accumulation) shows that the reaction can be carried out in the semi-batch mode but precaution should be taken in the case of cooling failure not to keep reacted material uncontrolled for a long time in the reactor. If external deviations, for example, heating of reactor due to instrumentation failure or due to human errors, are excluded, one can predict safety technologies, i.e. set #P$_1$ (back-up cooling system (-0.1)) and set #P$_3$ (pressure relief device (-0.3)) in Table 2.5.5 to run this reaction in the plant. The list of process factors is given in Table 2.5.4, which should be checked before applying any safety technologies.

In the case of a variation in process conditions or cooling due to any error, the degree of non-ideality will increase and reaction will not be inherently safe because this scenario can cause an increase in temperature and can be a reason for runaway. Furthermore, the substances in the reactor are toxic (Acute Toxicity (0.7) exceeds the safe limit; see Table 4.1.1.9 and Figure 4.1.1.1) so safety technologies for secondary hazards are necessary. The prediction of safety technologies for handling released substances (secondary runaway hazards) is set #S$_3$ (dump/catch tank with scrubber/flare and vent (-0.3)) or set #S$_4$ (quench tank with scrubber/flare and vent (-0.3)) in Table 2.5.6 in Chapter 2. Parington and Waldram (2002) recommended for this scenario (external variations in process conditions) a special reactor manufactured with two bottom outlets of sufficient capacity to permit rapid dumping of the contents into an appropriately sized quench tank. They also proposed a pressure relief vent sizing to cope with other specific, and less arduous, mal-operations. Their findings are supported by the results from SREST method. ***The Remaining Primary Runaway Hazard Index (RPRHI) is***

0.0 and Remaining Secondary Runaway Hazard Index is 0.4 as shown in Table 4.1.1.9 that are in acceptable region.

Safety

Acceptable limit

EHS Index (Before Using Safety Technologies)

Mobility　　　　　　Fire/Explosion　　　　　Acute Toxicity

EHS Effect Categories (Safety)

⊠ aromatic-amine　　　□ nitrosyl-sulfuric-acid　　　⊠ sulfuric-acid
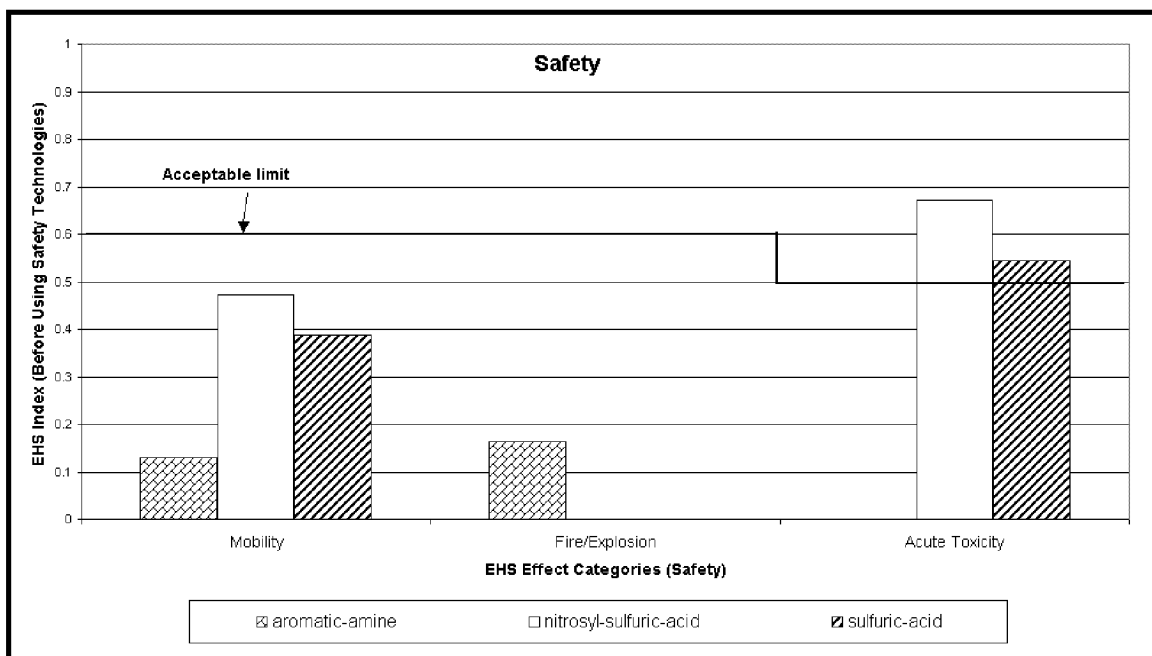
Figure 4.1.1.2a: Production of an azo dye intermediate: SAL results in the form of Effective Dangerous Property index (as defined in EHS method) before using safety technologies. Decomposition of diazonium-salts is handled in EAL.

Reduction factors have been applied only to the substances whose safety hazard indexes were above the acceptable limit.

Safety

Safety Technologies (Acute-Toxicity):
a) Leak detection, Interlocks and Emergency-shutdown system (Total reduction factor = -0.3).
Or
b) Single containment (-0.3).
(See Table 2.5.3)

Acceptable limit

EHS Index (After Using Safety Technologies)

Mobility　　　　　　Fire/Explosion　　　　　Acute Toxicity

EHS Effect Categories (Safety)

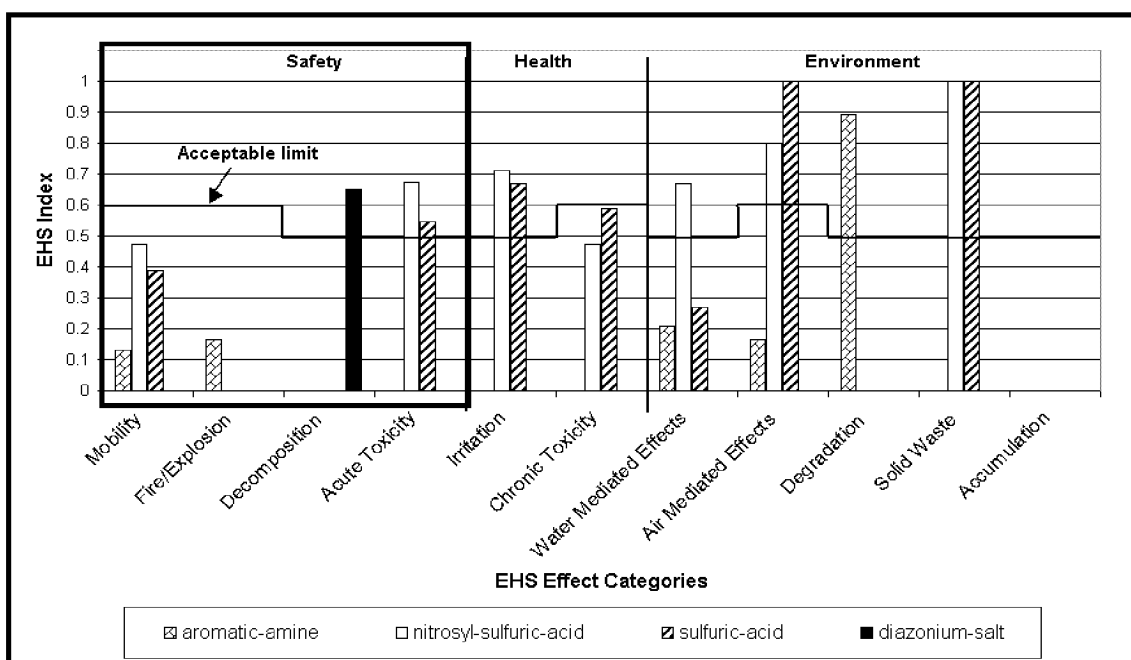⊠ aromatic-amine　　　□ nitrosyl-sulfuric-acid　　　⊠ sulfuric-acid
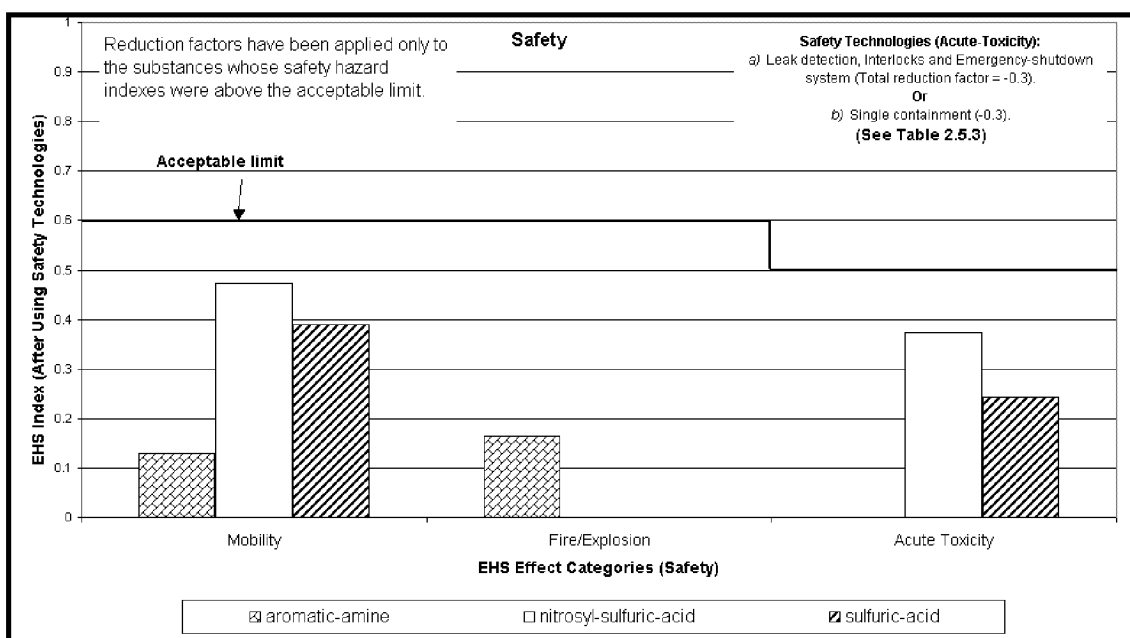
Figure 4.1.1.2b: Production of an azo dye intermediate: Safety-Technology Assessment Layer (STAL) results in the form of Effective Dangerous Property index (as defined in EHS method) after using safety technologies. Decomposition of diazonium-salts is handled in EAL.

Case study 2: Sulfonation of a nitro-aromatic compound

Substances present: Raw materials used in this case study are nitro-aromatic compound (31.5 wt%), oleum 65% (37.8 wt%) and sulfuric-acid (30.7 wt%).

Reaction recipe (Keller, 1998): A given quantity of the nitro-aromatic compound is dissolved in anhydrous sulfuric-acid. Then oleum 65% is added within 10 hours at a constant rate while the mixture is kept at 90 °C.
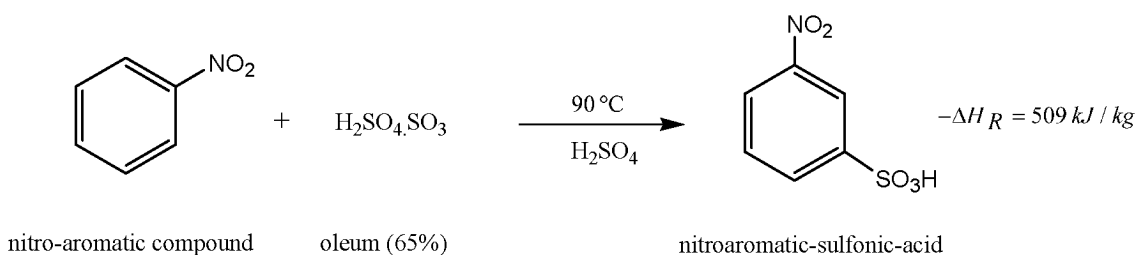
nitro-aromatic compound   oleum (65%)   nitroaromatic-sulfonic-acid

Substance Assessment Layer: **Results from SAL with acceptable limit line are presented in Figure 4.1.1.3.** The data for Effective Dangerous Property Index (with the priority data) and fate indices are given in the Table A2 in Appendix A. The problems of sulfuric-acid were already discussed in the first case study (production of an azo dye intermediate). **Oleum poses higher toxic and environmental problems than sulfuric-acid because of its high volatility.** A major disadvantage of oleum sulfonation is that oleum is an extremely oxidizing agent; the resulting by-products are often gummy tars that must be disposed of. The mother liquor after product separation is also an environmental problem (Sikdar and Howell, 1998). **To handle these substances in the vessel, different safety technologies are proposed and used (see STAL in this case study).**
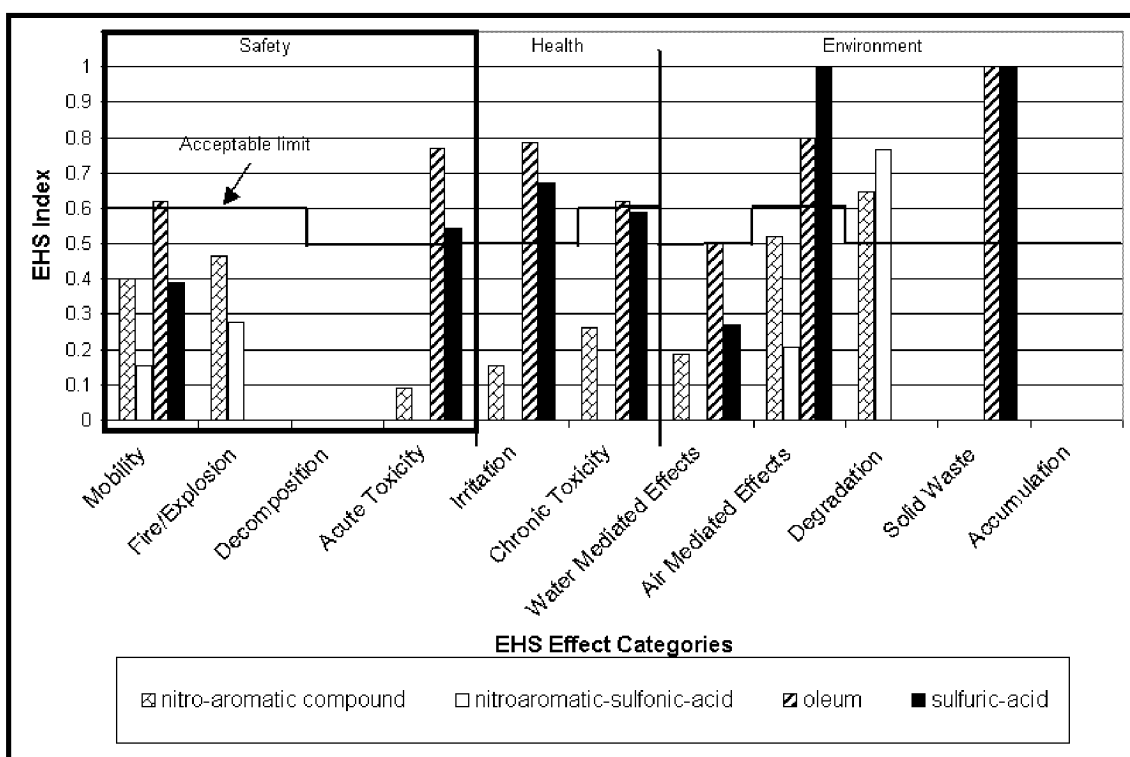
Figure 4.1.1.3: Sulfonation of a nitro-aromatic compound: Substance Assessment Layer (SAL) results in the form of Effective Dangerous Property index (as defined in EHS method).

Reactivity Assessment Layer: The reactivity matrix and reactivity indices (Intended and Incompatible Reaction Indices) are given in Table 4.1.1.3 and Table 4.1.1.4. It shows high reactivity problems of substances present in the sulfonation process. *In particular, oleum and sulfuric-acid pose reactivity problems with water and stainless-steel. The information on intended exothermic reaction between sulfuric-acid, oleum and the nitro-aromatic compound is also available. The high heat release in sulfonation reaction makes Intended Reaction Index high.* All these indicators propose to perform detail assessment for runaway scenario. The detail assessment of runaway scenario due to intended reaction and decomposition of reaction mixture is performed in EAL.

Table 4.1.1.3: Results from RAL obtained for sulfonation case study. An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	nitroaromatic-sulfonic-acid	nitro-aromatic	sulfuric-acid	oleum	air	water	stainless-steel
nitroaromatic-sulfonic-acid	SI						
nitro-aromatic		SI	X	X			
sulfuric-acid			SI			X	X
oleum						X	X

Table 4.1.1.4: Results from RAL obtained for sulfonation case study. The reactivity indices are defined for intended and incompatible reactions.

Reactivity Indices (acceptable limit ≤ 0.5)	Index values
Intended reaction (nitro-aromatic compound sulfonation)	1.0 (sulfonation reaction)
Incompatible reaction (sulphuric-acid/water)	0.8 (NFPA = 2, heat release)
Incompatible reaction (oleum/water)	1.0 (violent reaction, explosive)
Incompatible reaction (sulphuric-acid/steel)	0.6
Incompatible reaction (oleum/steel)	0.6

Equipment Assessment Layer: The results from SAL (Figure 4.1.1.3) present that there can be **toxic vapour cloud** scenario, for example, in the case of release from the vessel. This scenario is considered as a primary hazard and safety technologies are recommended for this scenario in STAL in this case study.

Results of the sulfonation reaction can be seen in Table 4.1.1.9. The criticality class, probability and severity factors show that there is high probability of a severe accident in the case of cooling failure if this reaction is performed in a batch reactor. In the case of a semi-batch reactor, the accumulation of reactants will be less compared to the batch reaction and at the same time increasing process temperature from 90 to 120 °C can make reaction faster. In the case of maximum 20% accumulation and increased process temperature to 120 °C, MTSR is decreased to 174 °C as compared to 362 °C in batch reactor with process temperature 90 °C. The TMR_{ad} at MTSR is increased from 0 hours to 1.3 hours as shown in Table 4.1.1.9. Increased TMR_{ad} will provide time to take counter-measures in case of a cooling failure but there is still large probability of severe accident in this case because ADT_{24} is still lower than MTSR. These results indicate

that the reaction in batch and semi-batch reactors is not inherently safe and detailed risk analysis should be done. *The Primary Runaway Hazard Index (PRHI) is 1.0 because criticality class is 5, probability and severity are high (see Table 2.4.1.1). The Secondary Runaway Hazard Index is 0.77 because of high Acute Toxicity index (see Figure 4.1.1.3).*

Safety-Technology Assessment Layer: The vapour and toxic cloud scenarios are considered here as primary hazards and safety technologies (see STAL in Chapter 2) are proposed to handle the substances and to prevent any accident occurring in the plant. For vapour cloud scenario, safety technologies are Set #P_1 (pressure measurement system with alarm (-0.2)) and Set #P_4 (sufficient cooling capacity (-0.2)) from Table 2.5.1 in Chapter 2. For toxic release scenario, safety technology is Set #P_8 (single containment (-0.3)) from Table 2.5.3. The safety technologies used and resulting indices are shown in Figure 4.1.1.4b and Table C2 in Appendix C. The resulting indices are below the acceptable limit as shown in Figure 4.1.1.4b.

The safety technologies for runaway scenario are presented here. If reaction is performed in a semi-batch reactor with process temperature 120 °C (to make reaction faster) instead of 90 °C, a far better policy should be devised and that is not to allow an exothermic decomposition runaway to occur by defining the safe limit of temperature and dumping the contents of the equipment in quench tank before any hazardous event. *In early development stage, this scenario should not be processed further and inherent-safety-principles (see Chapter 3) should be used to make reaction less hazardous, for example, by changing process conditions or by changing unit-operations.* In SREST method, the recommendation for performing this reaction or this type of scenario is to use inherent-safety-principles, for example, designing a special continuous reactor with high cooling capacity and control systems.

Figure 4.1.1.4a: Sulfonation of a nitro-aromatic compound: SAL results in the form of Effective Dangerous Property index (as defined in EHS method) before using safety technologies.
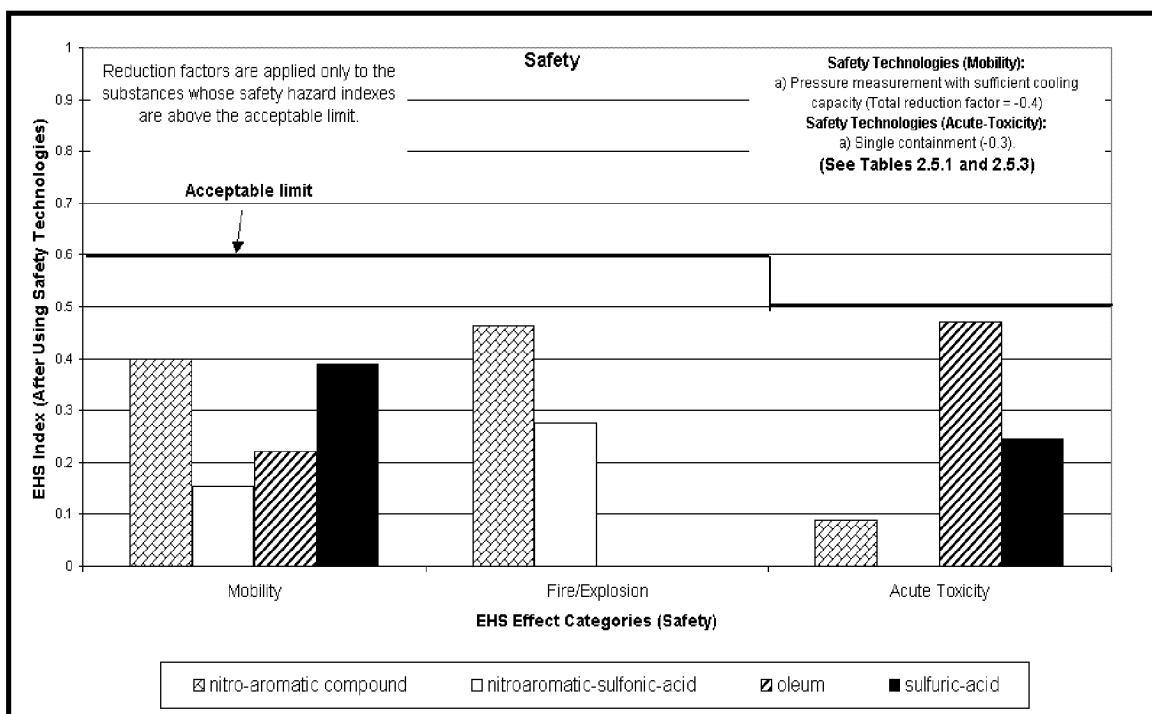
Figure 4.1.1.4b: Sulfonation of a nitro-aromatic compound: Safety-Technology Assessment Layer (STAL) results in the form of Effective Dangerous Property index (as defined in EHS method) after using safety technologies.

Case Study 3: Production of mono-nitro-toluene

Chen et al. (1998) and Chen and Wu (1996) studied worst-case scenarios for safety evaluation of an existing nitration process with the data obtained from calorimetric experiments. This scenario is reconsidered here to highlight the capabilities of the SREST methodology.

Substances present: Raw materials used in this case study are **toluene, mixed acid (nitric-acid (of 70-wt%), sulfuric-acid (of 99.8-wt%) and water with weight ratios of 30/56/14)** and the product is mono-nitro-toluene (MNT).
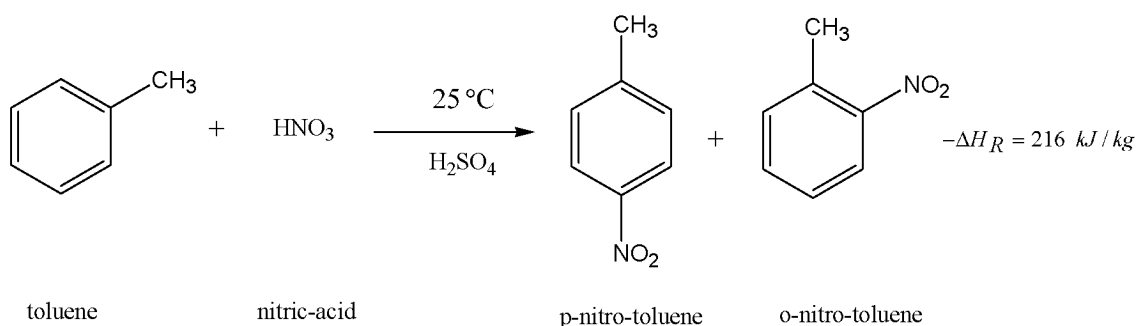
toluene   nitric-acid   p-nitro-toluene   o-nitro-toluene

Substance Assessment Layer: Results from SAL with acceptable limit line are shown in Figure 4.1.1.5 and in Table A2 in Appendix A. Both sulfuric-acid and nitric-acid show high health and environmental effects and therefore measures for handling these substances are required. **The major safety problem of the mono-nitro-toluene and nitric-acid is high Decomposition index. This indicates that the detail assessment should be done for runaway scenario in EAL. Toluene also shows high Mobility and Fire/Explosion index.** These substances should be handled carefully in the plant. The safety technologies are proposed to handle these substances in STAL in this case study.
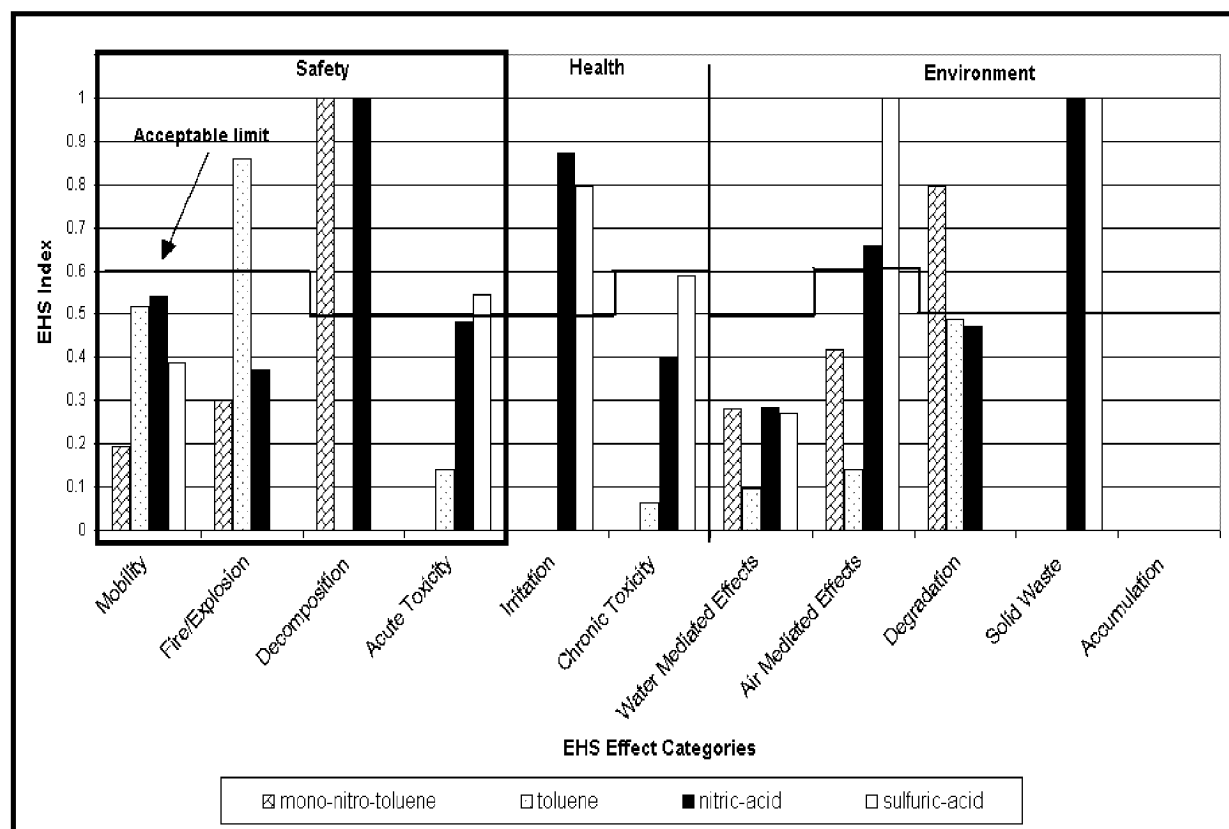
Figure 4.1.1.5: Production of mono-nitro-toluene: Substance Assessment Layer (SAL) results in the form of Effective Dangerous Property index (as defined in EHS method).

Reactivity Assessment Layer: The reactivity matrix based on information available in Bretherick's database (Urben, 1999) and Chemical Reactivity Worksheet (NOAA, 2000) is shown in Table 4.1.1.5. The reactivity indices for intended and incompatible reactions are defined in Table 4.1.1.6. **The high index for incompatibility of water and stainless-steel with sulfuric-acid and nitric-acid is helpful in taking measures to prevent contact with water and in selecting material of construction. This scenario has been discussed in the first case study (production of an azo dye intermediate).** The knowledge of exothermic reaction of mono-nitro-toluene with sulfuric-acid is available from database (Bretherick's database (Urben, 1999)) as shown in the Table 4.1.1.5. **The Intended Reaction Index (nitration of toluene) is high and therefore detail assessment should be performed for this reaction.**

Table 4.1.1.5: Results from RAL obtained for mono-nitration of toluene case study. An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	toluene	nitric-acid	sulfuric-acid	mono-nitro-toluene	water	air	stainless-steel
toluene	SI	X	X				
nitric-acid		SI			X		X
sulfuric-acid			SI	X	X		X
mono-nitro-toluene				SI			

Table 4.1.1.6: Results from RAL obtained for mono-nitration of toluene case study. The reactivity indices defined for intended and incompatible reactions.

Reactivity Indices (acceptable limit $\leq$ 0.5)	Index values
Intended reaction (toluene nitration)	1.0 (nitration reaction)
Incompatible reaction (sulfuric-acid/water)	0.8 (NFPA = 2 and heat evolution)
Incompatible reaction (nitric-acid/water)	0.75 (heat evolution)
Incompatible reaction (sulfuric-acid/steel)	0.6
Incompatible reaction (nitric-acid/steel)	0.6

Equipment Assessment Layer: **The results from SAL show the indication for fire/explosion and toxic release scenarios.** These scenarios are considered as primary hazards and safety technologies are predicted in STAL in this case study.

The scenarios in batch and semi-batch reactors are compared and runaway assessment is performed. In the case of cooling failure, the maximum temperature attained by the desired reaction (MTSR) in batch reactor where 100% reactants are charged at once, or maximum accumulation is more than 50% in semi-batch reactor, exceeds ADT_{24} (see Table 4.1.1.9). This shows that decomposition of nitric-acid (onset temperature 140 °C) can be triggered in the case of cooling failure. Accordingly the investigated scenario results in criticality class 5. If maximum accumulation of reaction mixture is 20% then MTSR will be lower than ADT_{24}. This decreases criticality class from 5 to 2 (see Table 4.1.1.9). The Time to Maximum Rate at adiabatic conditions (TMR_{ad}) will increase from 0.9 hours in the batch reactor (100% accumulation) to 25 hours in semi-batch reactor (20 % accumulation) and will provide enough time to take safety measures in the case of deviations in process conditions or cooling failure. In the case of 20% maximum accumulation, criticality class is 2, probability is low, and severity is high and therefore **Primary Runaway Hazard Index is 0.4** (see Table 2.4.1.1

in Chapter 2). *The Secondary Runaway Hazard Index is 0.86* (see Table 4.1.1.9). The substances present are highly flammable and toxic and can cause severe hazards after release from the reactor.

Safety-Technology Assessment Layer: **The primary hazards can be fire/explosion and toxic release from the vessel, for example, in the case of leakage therefore these substances should be handled with the help of proper safety measures.** The safety technologies to mitigate fire/explosion scenario are set #P_{12} (explosion zones (-0.2)) and set #P_{13} (inertization (-0.3)) and for toxic release are set #P_4 (no manual handling (-0.1)) from the Tables 2.5.2 and 2.5.3 in Chapter 2, and presented in Figure 4.1.1.6b and in Table C3 in Appendix C. The safety indices are reduced to the acceptable limit as shown in Figure 4.1.1.6b.

The safety technologies for primary and secondary runaway scenarios are presented here in detail. Since the criticality class is 5 in the case of batch reactor and probability and severity are high; reaction should not be performed in a batch mode. The criticality class 2 in the case of semi-batch reactor (maximum 20% accumulation) shows that the reaction can be carried out in the semi-batch mode but precaution should be taken in the case of cooling failure not to keep reacted material uncontrolled for a long time in the reactor. The sets of safety technologies recommended are set #P_1 (back up cooling system (-0.1)) and set #P_3 (pressure relief device (-0.3)) (see Table 2.5.5, Chapter 2).

In the case of a variation in process conditions or cooling failure due to any error, the degree of non-ideality will increase and reaction will not be inherently safe because this scenario can cause an increase in temperature and can be a reason for runaway.

Furthermore, the substances in the reactor are toxic and flammable (see Figure 4.1.1.5); so safety technologies for secondary hazards are necessary. The set of safety technologies recommended for handling substance release is set #S_1 (explosion zone 2 (-0.2)) and set #S_2 (Catch tank (-0.3)) (Table 2.5.6 in Chapter 2). *The final potential of danger (20% maximum accumulation in the reactor) after applying safety technologies, is 0.0 (using combined set of set #P_1 and set #P_3) for Remaining*

Primary Runaway Hazard Index (RPRHI) and is 0.36 for Remaining Secondary Runaway Hazard Index (RSRHI) as shown in Table 4.1.1.9, which is in the acceptable region.
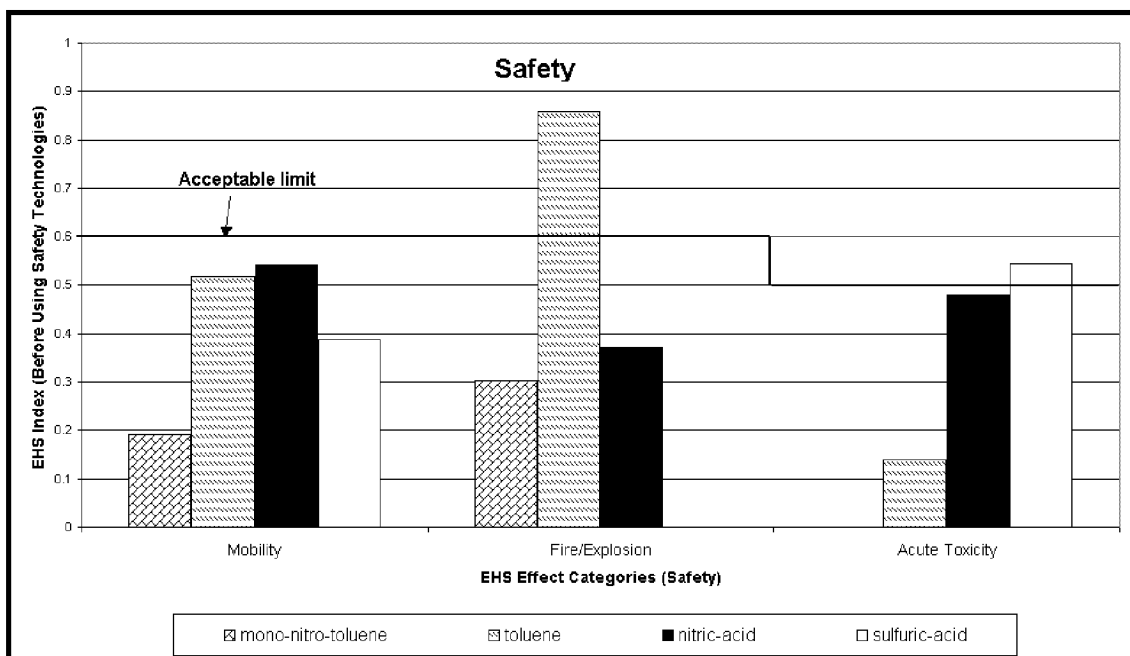
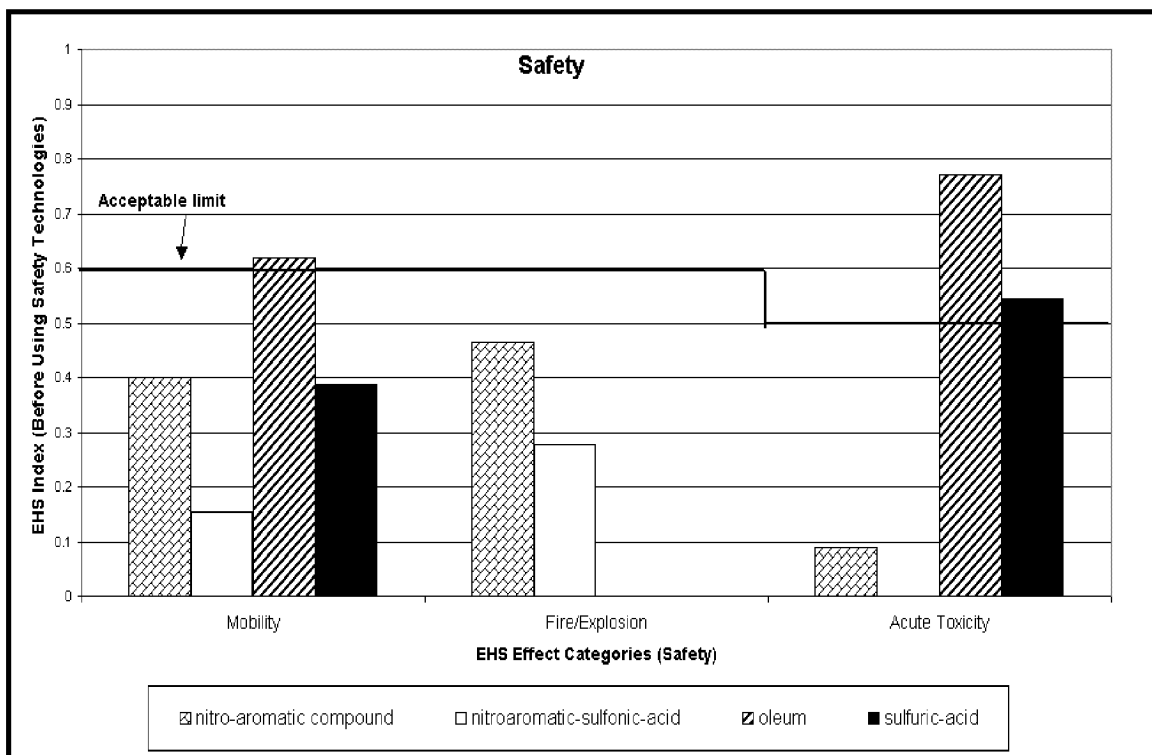**Figure 4.1.1.6a:** Production of mono-nitro-toluene: SAL results in the form of Effective Dangerous Property index (as defined in EHS Method) before using safety technologies.

Figure 4.1.1.6b: Production of mono-nitro-toluene: Safety-Technology Assessment Layer (STAL) results in the form of Effective Dangerous Property index (as defined in EHS method) after using safety technologies.

## *Case Study 4: Production of poly-acrylonitrile*

Substances present: Initially, a mixture of acrylonitrile (AN, 7 wt%) and water (90 wt%) is charged into the batch reactor. Potassium-persulfate is employed as the initiator. The polymerization is conducted in nitrogen atmosphere at a temperature not exceeding 50-60°C and atmospheric pressure (Surinarayanan, 1998).
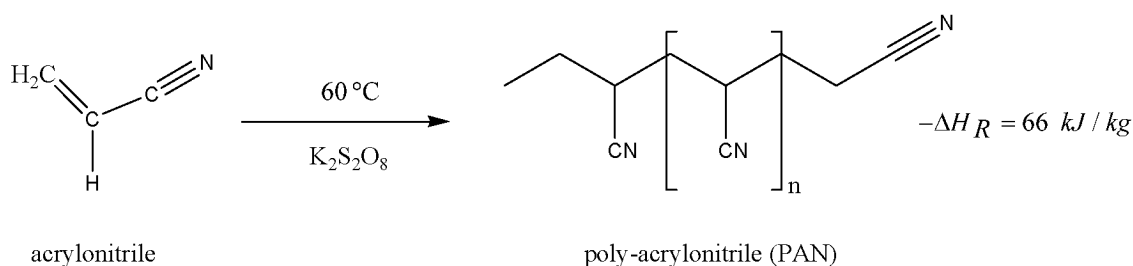
acrylonitrile   poly-acrylonitrile (PAN)

Substance Assessment Layer: Results from SAL with acceptable limit line are presented in Figure 4.1.1.7 and in Table A2 in Appendix A. **Acrylonitrile is flammable, toxic and non-degradable with high mobility,** which can cause severe problems after release from the equipment. Poly-acrylonitrile (PAN) is stable and pure polymer (without any traces of acrylonitrile) is non-toxic. **Potassium-persulfate is used in less quantity as an initiator but due to its high Decomposition index it can cause decomposition problems.** The safety technologies to handle acrylonitrile in the vessel are proposed in STAL in this case study.
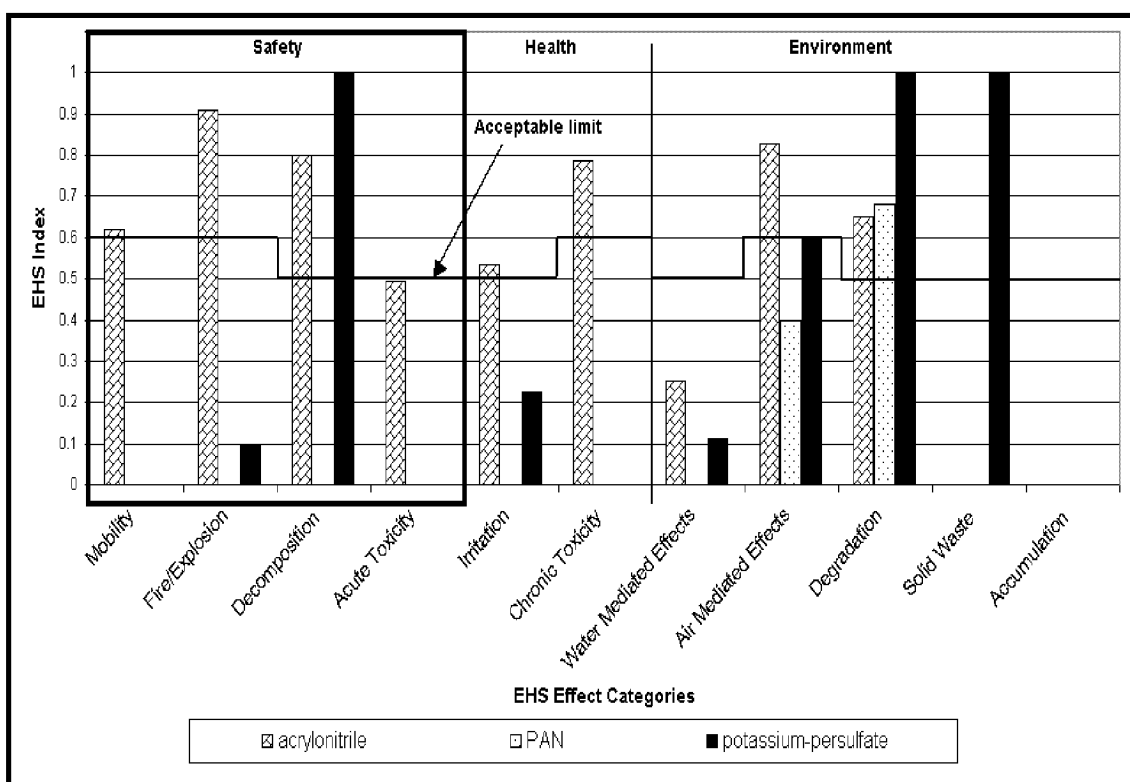
Figure 4.1.1.7: Production of poly-acrylonitrile (PAN) from acrylonitrile (AN): Substance Assessment Layer (SAL) results in the form of Effective Dangerous Property index (as defined in EHS method).

Reactivity Assessment Layer: The reactivity matrix and reaction indices are given in Tables 4.1.1.7 and 4.1.1.8. *It shows incompatibility problems of potassium-persulfate with water. The salt rapidly liberates oxygen above 100°C when dry, but at only 50°C when wet (Bretherick's database, (Urben, 2000)).* Substance information in Bretherick's database (Urben, 1999) is available for all the substances present in this process. *The acrylonitrile monomer is sensitive to light, and even when inhibited (with aqueous ammonia) it will polymerise exothermally at above 200°C.* The design strategy should be defined to avoid the contact of potassium-persulfate with water. The detail runaway assessment should be performed for intended acrylonitrile polymerization reaction.

Table 4.1.1.7: Results from RAL obtained for acrylonitrile polymerization case study. An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	acrylonitrile	potassium -persulfate	poly-acrylonitrile	water	air	stainless-steel
acrylonitrile	SI					
potassium-persulfate		SI		X		
poly-acrylonitrile			SI			

Table 4.1.1.8: Results from RAL obtained for acrylonitrile polymerization case study. The reactivity indices are defined for intended and incompatible reactions.

Reactivity Indices (acceptable limit ≤ 0.5)	Index values
Intended reaction (acrylonitrile polymerization)	1.0 (polymerization reaction)
Incompatible reaction (potassium-persulfate/water)	0.75 (gas (oxygen) release)

Equipment Assessment Layer: The Results from SAL show that **acrylonitrile is a flammable and toxic chemical and therefore there can be primary hazard scenario (flammable and toxic vapour cloud)** due to leakage or release of this substance from vessel. The safety technologies for handling this scenario are given in STAL in this case study.

Results of acrylonitrile polymerization can be seen in Table 4.1.1.9. For 100% accumulation, the criticality class is 5, severity is high but probability (23 hours) is medium. In the case of cooling failure, there is enough time to take the actions for preventing any accident. However, ADT_{24} is lower than MTSR and there is no boiling barrier, it is not recommended to proceed with 100% accumulation. In the case of lower than 90% accumulation of reactants, the criticality class is 2, severity is still high but probability is low. This process layout can be performed in the chemical plant with recommended safety technologies. **The Primary Runaway Hazard Index is 0.4** (in the case of less than 90% accumulation) but **the Secondary Runaway Hazard Index is 0.9** because of high flammability and toxicity of acrylonitrile (AN).

Safety-Technology Assessment Layer: **The safety technologies for handling substances in vessel are taken from Tables 2.5.1, 2.5.2 and 2.5.3 in STAL in Chapter 2.** The use of some selected safety technologies and resulting substance indices are shown in

Figure 4.1.1.8b and in Table C4 in Appendix C. These safety technologies for Mobility are set #P_4 (sufficient cooling capacity to avoid undesired volatility (-0.2)). The safety technologies for fire/explosion are set #P_{12} (explosion zones (-0.2)) and set # P_{13} (inertization (-0.3)). The safety technologies for toxic release are set #P_4 (no manual handling of toxic substances (-0.1)). The resulting indices are below the acceptable limit as shown in Figure 4.1.1.8b.

The safety technologies for runaway scenario are presented here in detail. The criticality class 2 in the case of accumulation lower than 90% shows that the reaction can be carried out in the semi-batch mode. Precaution should be taken in the case of cooling failure not to keep reacted material uncontrolled for a long time in the reactor. The sets of safety technologies recommended are set #P_1 (back up cooling system (-0.1)) and set #P_3 (pressure relief device (-0.3))(see Table 2.5.5 in Chapter 2). Furthermore, acrylonitrile is toxic and highly flammable (see Figure 4.1.1.7); so safety technologies for secondary hazards are necessary. The set of safety technologies recommended for handling substance release is set #S_1 (explosion zone 2 (-0.2)) and set #S_4 (quench tank with scrubber/flare and vent (-0.3)) (Table 2.5.6, Chapter 2).

The remaining potential of danger (for less than 90% maximum accumulation in the reactor) after applying safety technologies, is *0.0* (using combined set of set# P_1 and set# P_3) *for Remaining Primary Runaway Hazard Index (RPRHI)* and is *0.4 for Remaining Secondary Runaway Hazard Index (RSRHI),* which is in the acceptable range.
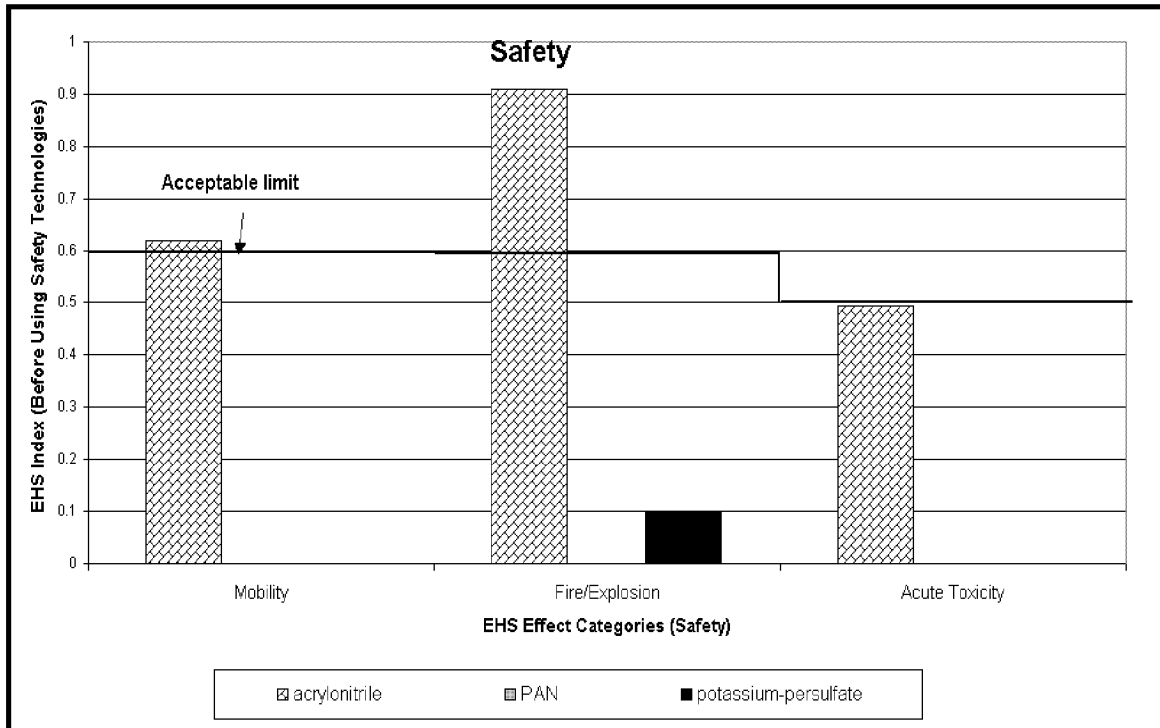
Figure 4.1.1.8a: Production of poly-acrylonitrile (PAN) from acrylonitrile (AN): SAL results in the form of Effective Dangerous Property index (as defined in EHS method) before using safety technologies.

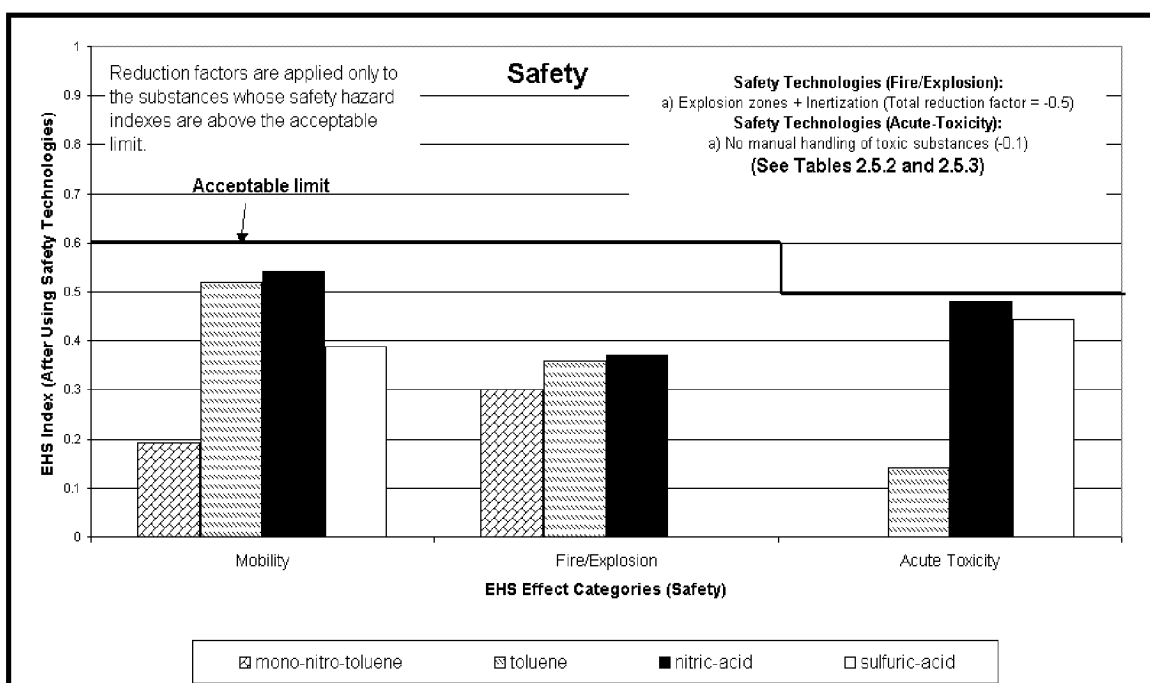**Figure 4.1.1.8b:** Production of poly-acrylonitrile (PAN) from acrylonitrile (AN): Safety-Technology Assessment Layer (STAL) results in the form of Effective Dangerous Property index (as defined in EHS method) after using safety technologies.

Table 4.1.1.9: EAL results obtained for four case studies and the investigated runaway scenarios.

Type of parameters	#	Parameter [Unit]	Case study 1 (production of an azo dye intermediate)	Case study 2 (sulfonation of a nitro-aromatic compound)	Case study 3 (production of mono-nitro-toluene)	Case study 4 (production of poly-acrylonitrile)
Recipe, physical and chemical properties and laboratory data	1	Process temperature [°C]	40	90 or 120	25	60
	2	Average boiling point of mixture (initial) [°C]	194	234	110	98
	3	T_{onset} [°C]	110	180	140	205
	4	q_{onset} [W/kg]	20 (assumption, Keller et al., 1997)	23	20 (assumption, Keller et al., 1997)	20 (assumption, Keller et al., 1997)
	5	Activation energy E_a (kJ/mol)	114	98	50 (assumption, Keller et al., 1997)	50 (assumption, Keller et al., 1997)
Assessment results (e.g. criticality class, probability and severity)	6	Primary adiabatic temperature rise (100% Acc.) [°C]	58	272	108	33
	7	Accumulation: Maximum Temperature of Synthesis Reaction (MTSR) [°C]				
		a) 100%	98	362 (Process Temp. = 90 °C)	133	93 (89 for 90% acc)
		b) 50%	69	226 (Proc. Temp. = 90 °C)	79	77
		c) 20%	52	174 (Proc. Temp. = 120 °C)	46	67
	8	ADT_{24} or $T_{0,24}$ (100% Acc.) [°C]	62 (equation 2.4.1.2)	112 (equation 2.4.1.2)	47 (equation 2.4.1.2)	90 (equation 2.4.1.2)
	9	Accumulation: Criticality Class				
		a) 100%	5	5	5	5
		b) 50%	5	5	5	2
		c) 20%	2	5	2	2
	10	Accumulation: TMR_{ad} [hours] at [Maximum Temperature of Synthesis Reaction (MTSR)] (probability)				
		a) 100%	0.6 (High)	0 (High)	0.9 (High)	23 (Medium)
		b) 50%	6.3 (High)	0 (High)	7 (High)	53 (Low)
		c) 20%	64 (25% acc.) (Low)	1.3 (High)	25 (Low)	81 (Low)
	11	Severity	High	High	High	High
Secondary hazards (EHS index values)	12	Maximum EHS substance index for Mobility/Fire /Toxicity	0.47/0.50/0.70	0.63/0.50/0.77	0.55/0.86/0.55	0.61/0.90/0.50
Primary Runaway Hazard Index (PRHI)	13	Accumulation: Primary Runaway Hazard Index (PRHI)				
		100%	1.0	1.0	1.0	1.0
		50%	1.0	1.0	1.0	0.4
		20%	0.4	1.0	0.4	0.4

Secondary Runaway Hazard Index (SRHI)	14	Maximum EHS Substance Index	0.70	0.77	0.86	0.90
Recommended safety technologies (reduction factors (STRF) are given in brackets)	15	Accumulation:	Mitigation of Primary Runaway Hazards (see Tables 2.5.5 and 2.5.6)			
		100%	Recommendation is to use inherent-safety-principles.	Recommendation is to use inherent-safety-principles.	Recommendation is to use inherent-safety-principles.	Recommendation is to use inherent-safety-principles.
		50%	Recommendation is to use inherent-safety-principles.	Recommendation is to use inherent-safety-principles.	Recommendation is to use inherent-safety-principles.	a) Set #P_1 and set #P_3 (Table 2.5.5)
		20%	a) Set #P_1 and set #P_3 (Table 2.5.5)	Recommendation is to use inherent-safety-principles.	a) Set #P_1 and set #P_3 (Table 2.5.5)	a) Set #P_1 and set #P_3 (Table 2.5.5)
		Mitigation of Secondary Runaway Hazards				
			a) Set #S_3 (-0.3) b) Set #S_4 (-0.3) (Table 2.5.6)		a) Set #S_1 (-0.2) and set #S_2 (-0.3) (Table 2.5.6)	a) Set #S_1 (-0.2) and set #S_4 (-0.3) (Table 2.5.6)
Remaining potential of danger	16	RPRHI	a) 0.0		a) 0.0	a) 0.0
		RSRHI	a) 0.4 b) 0.4		a) 0.36	a) 0.4

4.1.2 Storage tank

Methyl-ethyl-ketone-peroxide (MEKPO) is widely used as a curing agent of unsaturated polymer resin to mold products. Many thermal explosions caused by MEKPO subjected to external fires and other heat sources are reported (Yeh et al., 2003). MEKPO is normally produced in the phlegmatizer (dimethyl phthalate) with acid as a catalyst. In the addition, the product with a concentration up to 10% active oxygen is neutralized, and then is brought to the desired concentration by further dilution with phthalate. Subsequently, a drying procedure is executed in one of the production steps. Finally, before packaging, the product is stored in temporary storage vessels, which are made of stainless-steel or polyethylene. Yeh et al. (2003) and Li et al. (2004) have presented a thermal hazard analysis and decomposition scenario of monomer and dimer MEKPO. The case study of MEKPO dimer (32-wt%) has been used here to show applicability of SREST method for temporary storage tank.
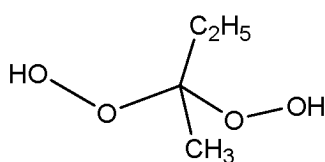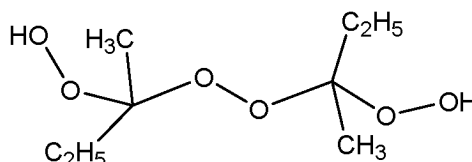
monomer MEKPO   dimer MEKPO

Substance Assessment Layer: The results for MEKPO from Substance Assessment Layer (SAL) with acceptable limit line are presented in Figure 4.1.2.1. *The chart shows that MEKPO is moderately flammable and toxic (the indices are above the acceptable limit as shown in Figure 4.1.2.1) and the effect category Decomposition is high which indicates that substance can decompose with high heat evolution.* There are also environmental problems related with this substance as shown in Figure 4.1.2.1. There can be different possible worst-case scenarios in temporary storage of MEKPO, i.e., *flammable and toxic release (primary hazard) or decomposition of MEKPO (primary hazard) with toxic-flammable-vapor cloud (secondary hazard).* These scenarios are assessed carefully in EAL and safety technologies are recommended in STAL in this case study.
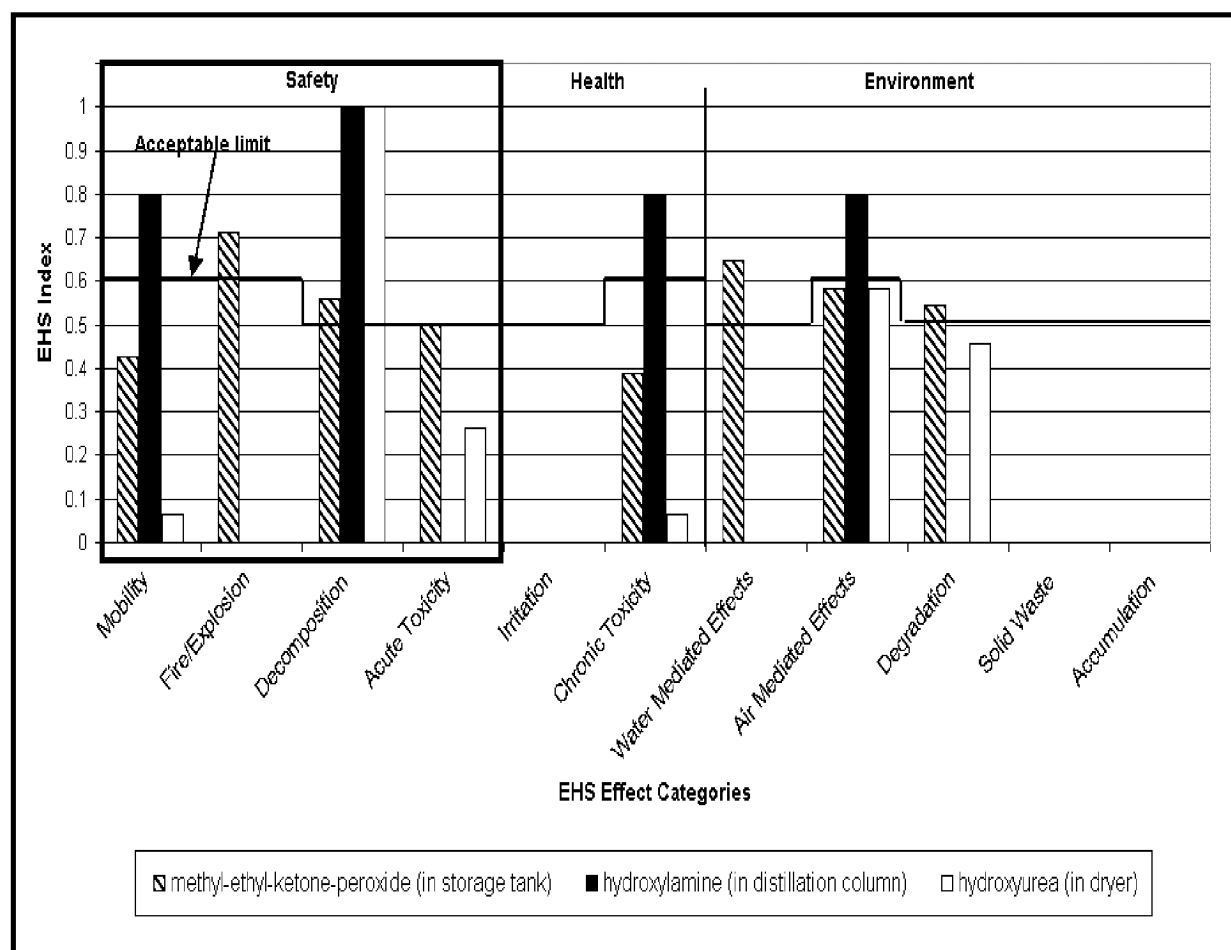
Figure 4.1.2.1: Substances present in storage tank, distillation column and dryer case studies: Substance Assessment Layer (SAL) results in the form of Effective Dangerous Property index (as defined in EHS method).

Reactivity Assessment Layer: The result for MEKPO reactivity is presented in Table 4.1.2.1. The information about MEKPO is available in Bretherick's database (Urben, 1999) in "Ketone-Peroxide" group of chemicals. *There is no intended reaction in storage tank and no interaction of MEKPO with water, air or material of construction present.* Therefore Intended and Incompatible Reaction Indices are negligible. *The information about decomposition of MEKPO is already obtained from SAL.*

Table 4.1.2.1: Results from RAL obtained for MEKPO storage tank case study. An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	methyl-ethyl-ketone-peroxide	air	water	stainless-steel
methyl-ethyl-ketone-peroxide	SI			

Equipment Assessment Layer: **Since MEKPO is flammable and toxic, safety technologies are recommended in STAL to handle flammable-toxic-vapors release scenario in this case study.**

The onset temperature of decomposition decreases considerably if sulfuric-acid, which is also used in manufacturing MEKPO, is present with MEKPO (Li et al., 2004). There has been an accident at a factory in Korea where MEKPO is produced. The final product, i.e. MEKPO, was left for more than 60 hours in temporary storage vessels before packaging. An explosion occurred and destroyed the entire factory (Li et al., 2004). If the substance, i.e., MEKPO is temporarily stored at atmospheric temperature (25 °C), it cannot be kept longer than one and half day because TMR_{ad} at storage temperature is 37 hours (see Table 4.1.4.2). Since substance can be temporary stored for more than 24 hours if there is no external heating to the temporary storage tank or no impurities present with the substance, probability of decomposition is medium. The substance decomposes with high heat evolution, i.e. decomposition enthalpy is 1650 kJ/kg, and therefore severity is high. *The Primary Decomposition Hazard Index is 0.9 (see Table 2.4.2.1) because probability is medium and severity is high. Substance is moderately flammable and toxic (see Figure 4.1.2.1) therefore the Secondary Decomposition Hazard Index is 0.71.*

Safety-Technology Assessment Layer: The safety technologies for handling MEKPO in temporary storage tank (to prevent release of flammable and toxic MEKPO by leakage or spillage (primary hazards)) are given in Tables 2.5.1, 2.5.2 and 2.5.3 in Chapter 2. The safety technologies for preventing fire/explosion in MEKPO (temporary) storage vessel are set #P_{12} (explosion zones (-0.2)) and set #P_5 (fire water and foam monitors (-0.1)) in Table 2.5.2 in Chapter 2. The safety technology for handling toxic MEKPO is set #P_4 (no manual handling of toxic substances e.g., use of gloves, masks (-0.1)). The reduction factors are used to reduce the safety category indices of MEKPO to show the realistic hazards and are presented in Figure 4.1.2.2b and in Table C5 in Appendix C.

The safety technologies for handling decomposition scenario of MEKPO in temporary storage tank can be selected from Tables 2.5.5 and 2.5.6 in Chapter 2. The substance should be stored in refrigerated conditions with enough cooling capacity. Special storage tank should be designed with bottom outlet to dump the chemical in bigger quench tank. The substance should be stored separately with thick containment walls so that storage tank is not heated externally by any means and in the case of decomposition, released heat and material both can be contained in the defined area. The predicted sets of safety technologies for primary decomposition hazards are set #P_1 (-0.1) and #P_5 (-0.8) (see Table 2.5.5). *The Remaining Primary Decomposition Hazard Index is 0.0* (see Table 4.1.4.2). The recommended set of safety technology for secondary decomposition hazard is set #S_1 (explosion zone 2 (-0.2)) and set #S_4 (quench tank with scrubber and flare (-0.3)) (see Table 2.5.6). *The Remaining Secondary Decomposition Hazard Index is 0.21* (see Table 4.1.4.2).
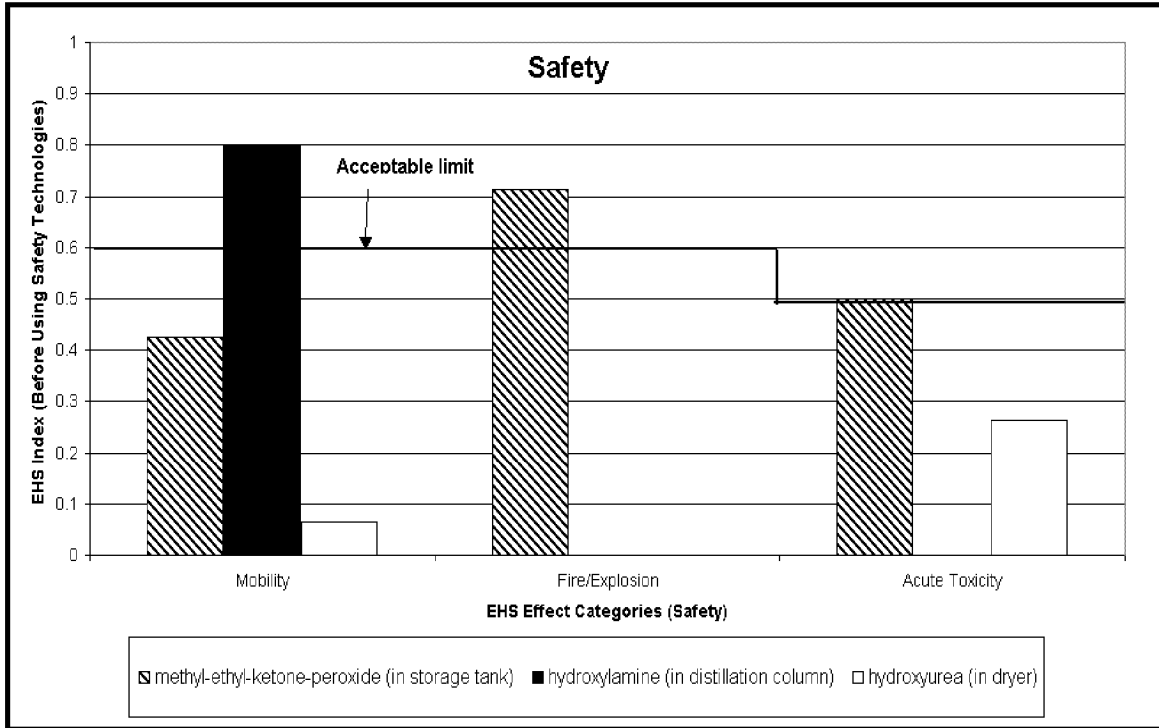
Figure 4.1.2.2a: Substances present in storage tank, distillation column and dryer case studies: SAL results in the form of Effective Dangerous Property index (as defined in EHS method) before using technologies.
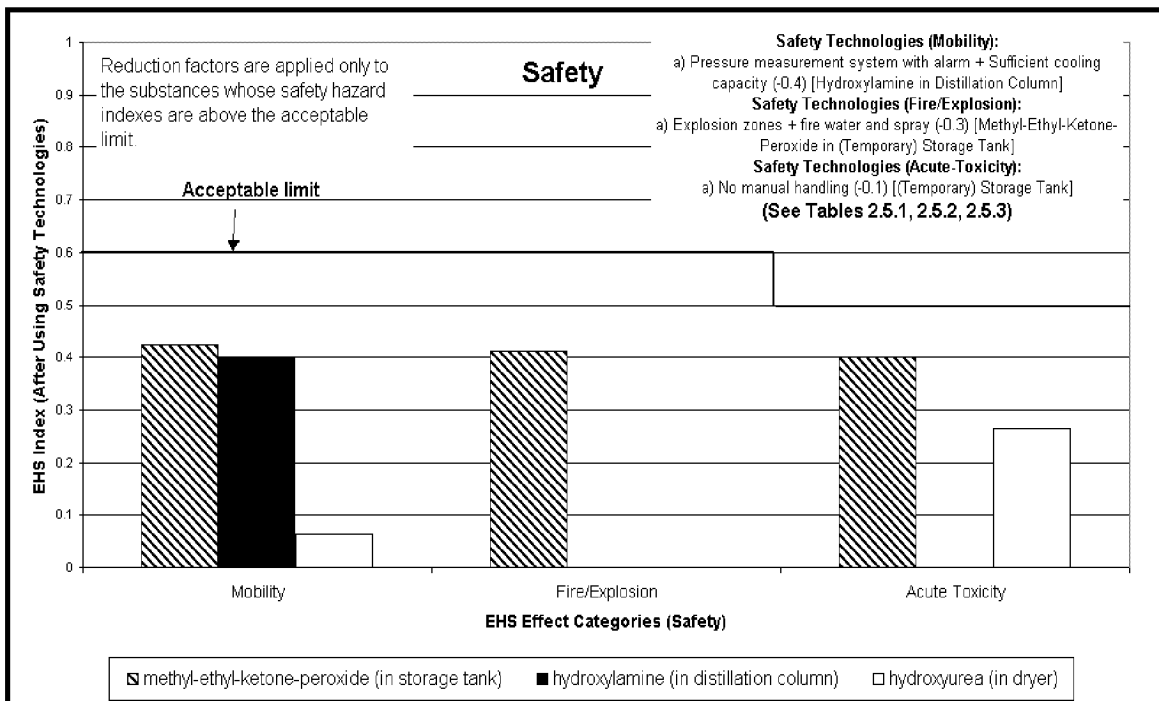
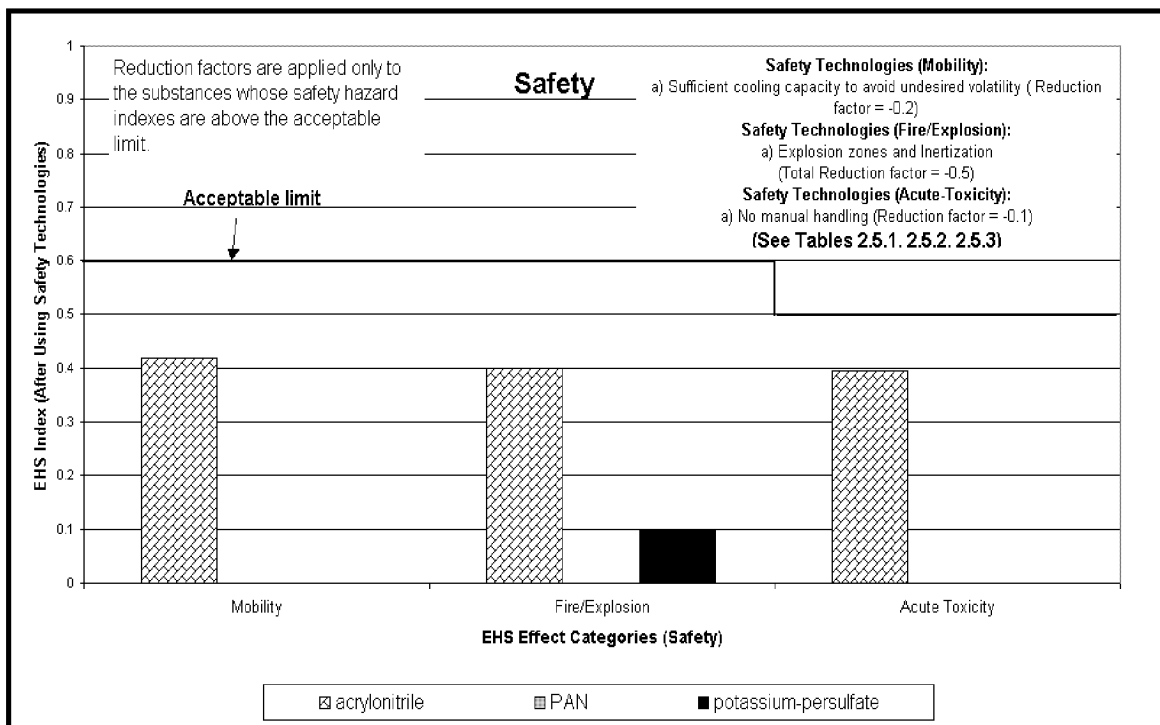**Figure 4.1.2.2b:** Substances present in storage tank, distillation column and dryer case studies: Safety-Technology Assessment Layer (STAL) results in the form of Effective Dangerous Property index (as defined in EHS method) after using safety technologies.

4.1.3 Distillation column

US Chemical Safety Board (CSB) (2002) published a report concerning its findings on the Concept Sciences Inc. (CSI) incident involving hydroxylamine (HA). HA solution (50-wt%) is used in semi-conductor manufacturing industry in cleaning formulations to strip process residues from integrated circuit devices. HA and its derivatives are also used in the manufacture of nylon, inks, paints, pharmaceuticals, agrochemicals and photographic developers. The process, involved in the incident, has the four basic steps to manufacture HA. Reaction of HA-sulfate and potassium-hydroxide to produce a 30 wt% HA and potassium-sulfate aqueous slurry; filtration of the slurry to remove precipitated potassium-sulfate solids; vacuum distillation of HA from the 30-wt% solution to separate it from the dissolved potassium-sulfate and produce a 50-wt% HA distillate; and purification of the distillate through ion exchange cylinders. The objective of the production unit is to manufacture 50-wt% HA aqueous solution, which is the maximum possible HA concentration permissible to be transported in the US. In the incident, an explosion occurred in the distillation system where HA 30-wt% solution is distilled to obtain 50-wt% HA product. The distillation step has been taken here as a case study to show the hazards related with distillation process and usefulness of SREST concepts in highlighting the problems.
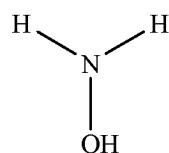
hydroxylamine

Substance Assessment Layer: The results for HA from Substance Assessment Layer (SAL) with acceptable limit line are presented in Figure 4.1.2.1. ***The substance presents high decomposition problem because of high Decomposition category. HA is also volatile and in the case of decomposition, accident can be severe.*** There are also some environmental problems related with substance because Degradation and Water Mediated Effects categories are high.

Reactivity Assessment Layer: The result for reactivity of HA from RAL is presented in Table 4.1.3.1. **There is no intended reaction in distillation column and no interaction of HA with water, air or material of construction present.** Therefore Intended and Incompatible Reaction Indices are negligible. **The information about decomposition of HA is already obtained from SAL.**

Table 4.1.3.1: Results from RAL obtained for hydroxylamine distillation column case study: An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	hydroxylamine	air	water	stainless-steel
hydroxylamine	SI			

Equipment Assessment Layer: Since HA is volatile, safety technologies are recommended in STAL to handle **vapor release scenario** in this case study.

The decomposition scenario is assessed here in detail. If HA is distilled at 50 °C and at atmospheric pressure in distillation column, there can be decomposition hazards of HA in the case of external heating or cooling failure in condenser. The TMR_{ad} for HA (50-wt%) at distillation temperature, i.e. 50 °C, is 14 hours (see Table 4.1.4.2) that makes probability of decomposition high. Since decomposition energy of HA is high, adiabatic temperature rise will be high and that will result in high severity. To achieve TMR_{ad} of at least 24 hours, distillation should be done below 36 °C. This could indicate that the distillation should be done in vacuum conditions at lower temperatures (however, there are different hazards involved in vacuum conditions). **The Primary Decomposition Hazard Index (in the case of 50 °C distillation column temperature) is 1.0** because of high probability and high severity (see Tables 2.4.2.1 and 4.1.4.2). Since substance is volatile but not toxic, there will be less secondary hazards to humans and **the Secondary Decomposition Hazard Index is 0.8** (see Table 4.1.4.2).

Safety-Technology Assessment Layer: To handle **mobile substances** in the vessel, safety technologies are proposed in Table 2.5.1 (see STAL in Chapter 2). The safety technologies are set #P_1 (pressure measurement system with alarm (-0.2)) and set #P_4

(sufficient cooling capacity (-0.2)). These safety technologies with reduction factors are used to reduce the Mobility index of HA below the acceptable limit. The result is shown in Figure 4.1.2.2b and in Table C6 in Appendix C.

Since Primary Decomposition Hazard Index is 1.0 (high), the recommendation is not to proceed with these process conditions but to search other process conditions, for example, vacuum distillation, by use of inherent-safety-principles. The substance should be distilled in vacuum and at lower temperature conditions with enough cooling capacity (precautions should be taken in case vacuum conditions are used).

4.1.4 Dryer

Lunghi et al. (2002) presented a thermo-analytical and calorimetric study of an accident in which a vessel exploded during the concentration step of hydroxyurea (HU) production. Hydroxyurea is used as an antineoplastic and in the treatment of Aquired Immune Deficiency Syndrome (AIDS) but few data are available about it in the literature (Lunghi et al., 2002). The industrial production process of hydroxyurea is carried out in different stages; synthesis reaction; concentration of the aqueous solution obtained from 5% to 30% and first crystallization from water; second crystallization of the product in ethanol; and final drying. Here drying step of the process has been taken as a case study to show the hazards related with drying and the concepts of SREST method have been used to evaluate the hazards.

Substance Assessment Layer: The results for HU from Substance Assessment Layer (SAL) with acceptable limit line are presented in Figure 4.1.2.1. The substance shows high index for Decomposition category and low Fire/Explosion and Acute Toxicity categories. *The major safety problem is decomposition of HU at higher temperature.*
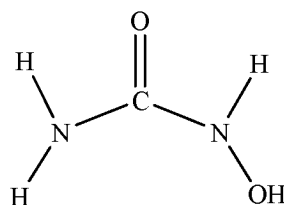
hydroxyurea

Reactivity Assessment Layer: The result from RAL is presented in Table 4.1.4.1. **There is no intended reaction in dryer and no interaction of HU with water, air or material of construction present.** Therefore Intended and Incompatible Reaction Indices are negligible. The information about decomposition of HU is already obtained from SAL.

Table 4.1.4.1: Results from RAL obtained for hydroxyurea dryer case study: An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	hydroxyurea	air	water	stainless-steel
hydroxyurea	SI			

Equipment Assessment Layer: If HU is dried at 40 °C, the probability of decomposition of HU is moderate (TMR_{ad} at drying temperature (40 °C) is 60 hours) (see Table 4.1.4.2). **The Primary Decomposition Hazard Index is 0.9** (see Table 2.4.2.1) and **the Secondary Decomposition Hazard Index is 0.26** (which is below the acceptable limit).

Safety-Technology Assessment Layer: Since Fire/Explosion and Acute Toxicity indices from SAL show very low values, there are no safety technologies recommended to handle HU in dryer. Since Primary Hazard Index is high, one should avoid these drying conditions and devise new drying conditions (drying temperature should not, at least, be in the range of TMR_{ad} = 64 hours) with the help of inherent-safety-principles.

Table 4.1.4.2: EAL results obtained for the three case studies and the investigated storage tank, distillation column and dryer equipment units.

Type of parameters	Parameter [Unit]	Storage tank (MEKPO)	Distillation column (hydroxylamine (HA) and water)	Dryer (hydroxyurea (HU))
Recipe and physical and chemical properties	Process Temperature (°C)	25	50	40
	Heat capacity [kJ/kg K]	2	2	2
Laboratory data (e.g., DSC)	T_{onset} (°C)	110	120	150
	q_{onset} (W/kg) [assumption (Keller et al., 1997)]	20	20	20
	Activation energy [kJ/mol] [assumption (Keller et al., 1997)]	50	50	50
	Decomposition enthalpy (kJ/kg)	1650	1000	2200
Assessment results (e.g. probability and severity)	Adiabatic temperature rise (ΔT_{ad}) (°C)	825	500	1100
	ADT_{24} or $T_{0,24}$ (°C)	29 [Equation 2.4.1.2]	36 [Equation 2.4.1.2]	52 [Equation 2.4.1.2]
	ADT_{64} or $T_{0,64}$ (°C)	6 [Equation 2.4.1.2 by taking TMR_{ad} = 64 hours]	11 [Equation 2.4.1.2 by taking TMR_{ad} = 64 hours]	28 [Equation 2.4.1.2 by taking TMR_{ad} = 64 hours]
	TMR_{ad} in hours (at process temperature)	37	14	60
	Probability	Moderate	High	Moderate
	Severity	High	High	High
Secondary hazards (EHS index values)	Maximum EHS substance index for Mobility/Fire/Toxicity	0.42/0.7/0.5	0.8/0.0/0.0	0.06/0.0/0.27
Primary Decomposition Hazard Index (PDHI)		0.90	1.0	0.90
Secondary Decomposition Hazard Index (SDHI)		0.71	0.80	0.26
Recommended safety technologies (reduction factors (STRF) are given in brackets)		Set #P_1 (-0.1) and Set #P_5 (-0.8) [Table 2.5.5] and Set #S_1 (-0.2) and set #S_4 (-0.3)[Table 2.5.6]	Recommendation is to use inherent-safety-principles. [For example, distilling at lower temperature, designing column for maximum pressure]	Recommendation is to use inherent-safety-principles. [For example, drying at lower temperature]
Remaining potential of danger	RPDHI	0.0		
	RSDHI	0.21		

4.2 A process case study: Polymerization of acrylic monomers

Acrylic monomers react to form high molecular weight resins via free radical polymerization. Acrylic monomers are highly reactive and are capable of undergoing rapid polymerization that can generate substantial heat and pressure if not controlled properly. There are many runaway accidents noted in the past due to acrylic polymerization (Kao and Hu, 2002). Here some major equipment units are assessed to define hazards in the process and to show the applicability of SREST method. The major unit-operations with possible worst-case scenarios are:

a. Runaway scenario in polymerization reactor,

b. Decomposition and fire/explosion scenario in temporary storage tank,

c. Decomposition and fire/explosion scenario in distillation column.

Substances present: Raw materials used in this case study are methyl-acrylate (MA, 52.5 wt%), acrylonitrile (AN, 4.2 wt%), methacrylic-acid (MAA, 0.75 wt%), acrylic-acid (AA, 0.75 wt%), benzyl-peroxide (BPO, 1.8 wt%), methyl-alcohol (20 wt%) and isopropyl-alcohol (IPA, 20 wt%).

Reaction recipe (Kao and Hu, 2002): To start the batch reaction, the desired amount of solvent and monomers comprising methyl-alcohol, IPA, MAA, AA, AN and MA are sequentially pumped into the reactor and mixed well. In a second step, the initiator BPO is added as powder into the reactor and blended. The reactor is heated to 60-65 °C.
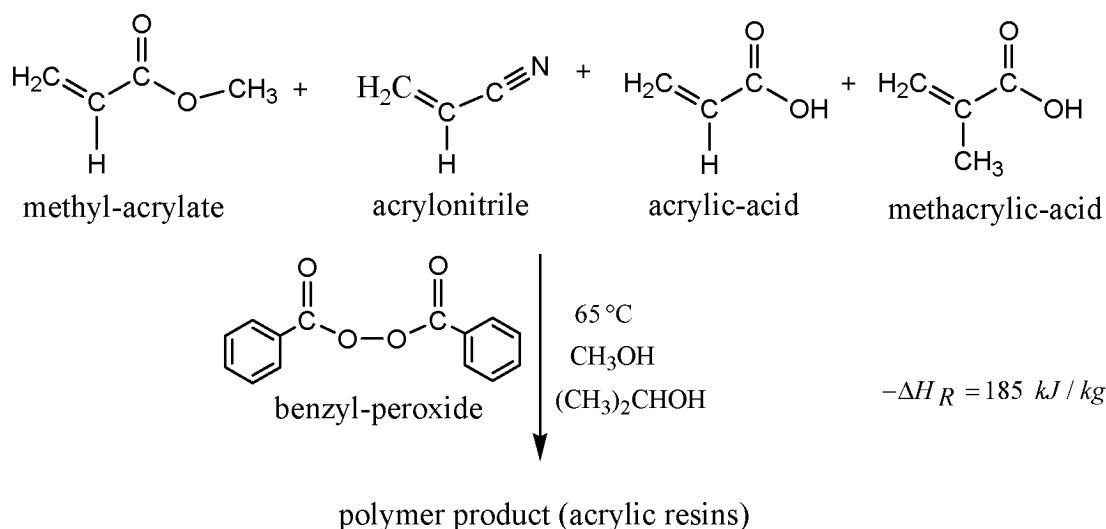
methyl-acrylate   acrylonitrile   acrylic-acid   methacrylic-acid

benzyl-peroxide

65 °C
CH_3OH
$(CH_3)_2CHOH$

$-\Delta H_R = 185 \ kJ / kg$

polymer product (acrylic resins)

Substance Assessment Layer: Results from SAL with acceptable limit line are shown in Figures 4.2.1. **Most of the substances present in the polymerization process are highly flammable, toxic and not rapidly degradable.** High Fire/Explosion and Mobility indices indicate the **fire/explosion scenario (primary hazard)** in equipment units and the possibility of **vapour cloud scenario (primary hazard)** if released from any equipment unit or release from the reactor in runaway scenario as secondary hazards. Inherent safety can be achieved by substituting flammable solvents with non-flammable ones.
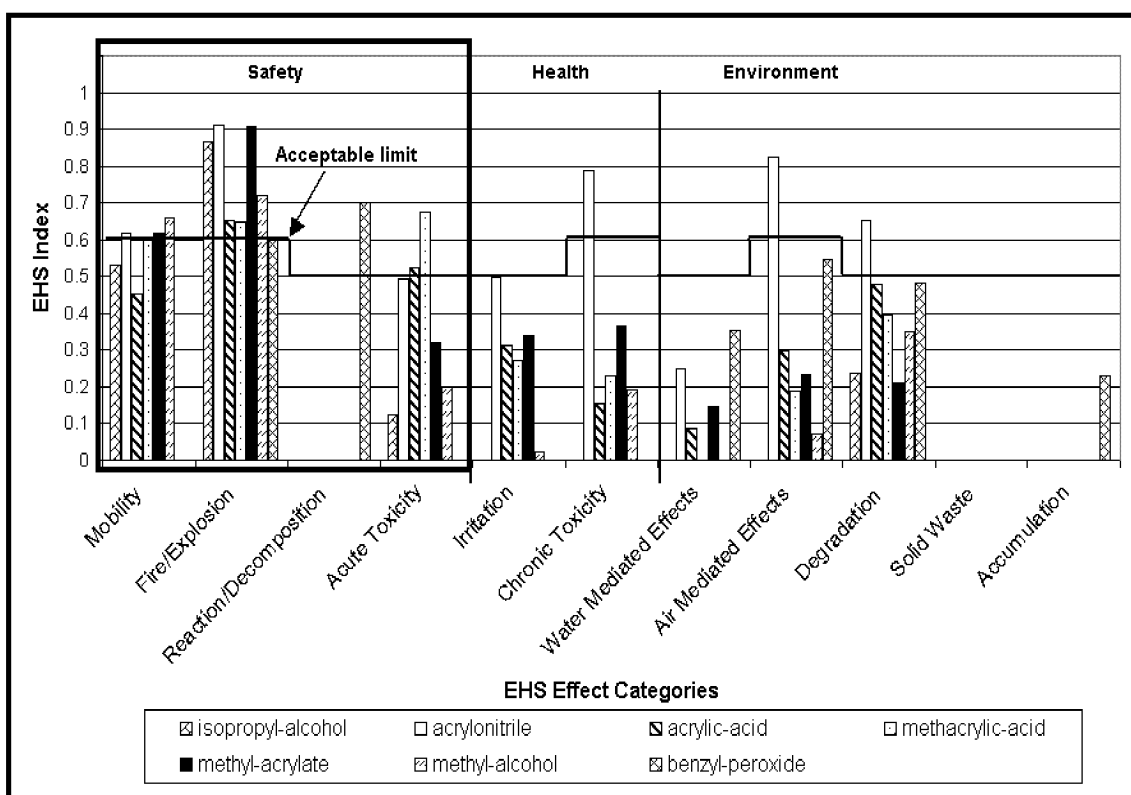
Figure 4.2.1: Production of acrylic resins by polymerization: Substance Assessment Layer (SAL) results in the form of Effective Dangerous Property index (as defined in EHS method).

Reactivity Assessment Layer: The reactivity matrix and reaction indices are shown in Table 4.2.1 and Table 4.2.2. The information available helps in making decisions about performing detail assessment and in designing reacting vessel with safety technologies. **The reactants involved in this reaction polymerize themselves and pose problems by releasing heat in exothermic polymerization.** The undesired polymerization should be handled and the detail assessment should be made.

Table 4.2.1: Results from RAL obtained for acrylic polymerization case study. An 'X' signifies interaction between two substances and SI represents information about one substance (Information is collected from Bretherick's database or Chemical Reactivity Worksheet).

Substance-name	methyl-alcohol	methyl-acrylate	methacrylic-acid	isopropyl-alcohol	acrylonitrile	acrylic-acid	benzyl-peroxide	air	water	stainless-steel
methyl-alcohol										
methyl-acrylate	SI						X			
methacrylic-acid		SI					X			
isopropyl-alcohol										
acrylonitrile				SI			X			
acrylic-acid						SI	X			
benzyl-peroxide							SI			

Table 4.2.2: Results from RAL obtained for acrylic polymerization case study. The reactivity indices are defined for intended and incompatible reactions.

Reactivity Indices (acceptable limit ≤ 0.5)	Index values
Intended reaction (acrylic-acid polymerization)	1.0 (polymerization)
Incompatible reaction (methacrylic-acid polymerization)	1.0 (polymerization)
Incompatible reaction (methyl-acrylate polymerization)	1.0 (polymerization)
Incompatible reaction (acrylonitrile polymerization)	1.0 (polymerization)

Equipment Assessment Layer:

a) **Substance handling in any vessel:** The substances present in this process are highly *flammable, volatile and toxic*. These substances should be handled very carefully in any vessel. The safety technologies to prevent any primary hazard scenario, for example, release of this substance by leakage, are recommended in STAL in this case study.

b) **Runaway scenario in polymerization reactor:** Kao and Hu (2002) carried out DSC (Differential Scanning Calorimeter) and VSP (Vent Sizing Package) runs for various compounds, a basic recipe mixture; the basic recipe mixture with 50% undercharged solvent i.e., methyl-alcohol; and the basic recipe mixture with double charge of initiator BPO. They found that in the case of undercharged solvents or double charge of initiator, onset temperature decreases (from 120 °C to 110 °C in the case of undercharged solvents and from 120 °C to 100 °C in the case of double charge of initiator) and exothermic heat increases (from 185 J/g to 339 J/g in the case of undercharged solvents and from 185 J/g to 436 J/g in the case of double charge initiator). Here, one scenario considering the basic recipe is taken and assessment is performed with the help of DSC data

available from Kao and Hu (2002). The results in Table 4.2.3 show high probability and severity of runaway polymerization. *The Primary Runaway Hazard Index (PRHI) is 1.0* because criticality class is 5 and probability and severity are high (see Table 2.4.1.1). Criticality class 5 with boiling point below MTSR indicates that the scenario is highly dependent on heat release of synthesis and decomposition reaction at the boiling point of the reaction mixture. Evaporation heat of solvents could be used here to create a boiling barrier against runaway. In this scenario, the amount of solvents and the cooling capacity of condenser used for evaporative cooling are vital factors to mitigate the runaway. In the case of less solvent, the boiling point of the reaction mixture can increase and this could pose a hazard since the condenser capability might not achieve the complete condensation of all solvent vapors at higher temperature (Kao and Hu, 2002). Secondary containment systems are necessary in the case of runaway scenario due to high Fire/Explosion and Acute Toxicity indices. *The Secondary Runaway Hazard Index (SRHI) is 0.9* (see Table 4.2.3).

c) **Decomposition and fire/explosion scenario in storage tank:** Caution must be undertaken during storing, shipping and manufacturing as acrylic monomers are reactive, toxic and flammable, as shown in SAL and can undergo *rapid polymerization*. Here, the problems regarding temporary storage of acrylic-acid and acrylonitrile have been evaluated.

The results from SAL show that both the chemicals are flammable and toxic (Fire/Explosion and Acute Toxicity indices are shown in Figure 4.2.2a) so safety technologies to handle these substances in temporary storage tank should be considered deliberately. Acrylonitrile has a flash point of −1.1 °C therefore *Fire/Explosion* category is high and precautions should be taken to handle this substance in the storage tank.

The onset temperatures for decomposition of acrylic-acid and acrylonitrile are 145 and 245 °C respectively (see Table 4.2.3). Substances should be stored at such conditions that temperature does not reach the onset temperature for

avoiding decomposition. The maximum allowable storage temperature, in the case of acrylic acid, for TMR_{ad} equal to 24 hours is 49 °C and for TMR_{ad} equal to 64 hours is 35 °C. TMR_{ad} at storage temperature (25 °C) is 120 hours therefore probability is low of reaching onset temperature if substance is stored temporarily not more than 120 hours at 25 °C with cooling device but in the case of decomposition, severity is high because of high decomposition energy (see Table 4.2.3). *The Primary Decomposition Hazard Index is 0.7* (see Table 2.4.2.1). Since acrylic-acid is flammable and toxic, *the Secondary Decomposition Hazard Index is 0.65.* The maximum allowable storage temperature, in the case of acrylonitrile, for TMR_{ad} equal to 24 hours is 120 °C and for TMR_{ad} equal to 64 hours is 80 °C. The probability of reaching onset temperature is low at storage conditions (storage temperature (25 °C)) and substance can be stored for longer period (2200 hours) with safety technologies to handle flammable substance. Since decomposition energy is high, severity is high. *The Primary Decomposition Hazard Index is 0.7 and the Secondary Decomposition Hazard Index is 0.9.*

d) **Decomposition and fire/explosion scenario in distillation column:** The separation of acrylic-acid monomer from solvents, i.e. methyl-alcohol and isopropyl-alcohol via distillation should be handled carefully because of presence of flammable solvents and monomer.

The Fire/Explosion and Acute Toxicity indices are shown in Figures 4.2.1. The release of solvents or monomer from distillation column by any means can cause severe fire and explosion in the plant.

There can also be decomposition of acrylic-acid if it reaches the onset temperature (145 °C, see Table 4.2.3). The maximum column temperature should be 49 °C (from equation 2.4.1.3, (Keller et al., 1997)) to have TMR_{ad} equal to 24 hours, i.e., time to take safety measures after loosing temperature control. This indicates that distillation should be done in other separation conditions e.g., lower temperature conditions, to avoid the decomposition of acrylic-acid in the case of cooling failure. If distillation is performed at 80 °C,

TMR$_{ad}$ is 8 hours, which renders the probability of decomposition of acrylic-acid high. *Since severity and probability are high, the Primary Decomposition Hazard Index is 1.0. The Secondary Decomposition Hazard Index is 0.65.*

Safety-Technology Assessment Layer: The results for this process case study are presented in Table 4.2.3 and Figure 4.2.2b. The lists of safety technologies to handle flammable, volatile and toxic substances in equipment unit are given in Tables 2.5.1, 2.5.2 and 2.5.3 in Chapter 2 and are used to reduce the safety category indices of the substances. The safety technology for preventing fire/explosion scenario or toxic-release scenario or vapour-cloud scenario is set #P$_6$ (single containment (-0.3)) in Table 2.5.1, set #P$_{12}$ (explosion zones (-0.2)) and set #P$_{15}$ (single containment (-0.3)) in Table 2.5.2 and set #P$_8$ (single containment (-0.3)) in Table 2.5.3 in Chapter 2. This is shown in Figure 4.2.2b and in Table C7 in Appendix C. The resulting indices are below the acceptable limit. The inherent-safety-principle, i.e., replace flammable solvents with non-flammable ones, can be used to make process more inherent safe.

The list of safety technologies to mitigate runaway, decomposition or incompatibility scenarios is given in Tables 2.5.4, 2.5.5 and 2.5.6 in Chapter 2. *In early development stage, the runaway scenario in batch/semi-batch reactor should not be processed further and inherent-safety-principles (see Chapter 3) should be used to make reaction less hazardous, for example, by changing process conditions or by changing unit-operations.* Some inherent-safety-principles are, for example: replace batch operations with semi-batch or continuous operations; use low boiling point solvents to lower the reaction temperature such that runaway will less likely to be initiated; design equipment to take maximum possible pressure; can be used to operate this process in the plant.

In the case of acrylic-acid and acrylonitrile (temporary) storage tank, a better back up cooling system should be designed. For long time storage, substance should be stored in refrigerated conditions with inhibitor to polymerization. The safety technologies are set #P$_1$ (-0.1) and set #P$_4$ (-0.5). *The Remaining Primary Decomposition Hazard Index is 0.1* for acrylic-acid and acrylonitrile (temporary) storage. The safety technology to

handle the release of the substance is set #S_1 (explosion zone 2 (-0.2)) and set #S3 (dump/catch tank with scrubber/flare and vent (-0.3)). *The Remaining Secondary Decomposition Hazard Index is 0.15 for acrylic-acid (temporary) storage and 0.4 for acrylonitrile (temporary) storage.*

Since Primary Decomposition Hazard Index is 1.0 (high) in the case of distillation column, the recommendation is not to proceed with these process conditions but to search other process conditions, for example, lower temperature separation, by use of inherent-safety-principles. The substance should be distilled at lower temperature conditions with enough cooling capacity.
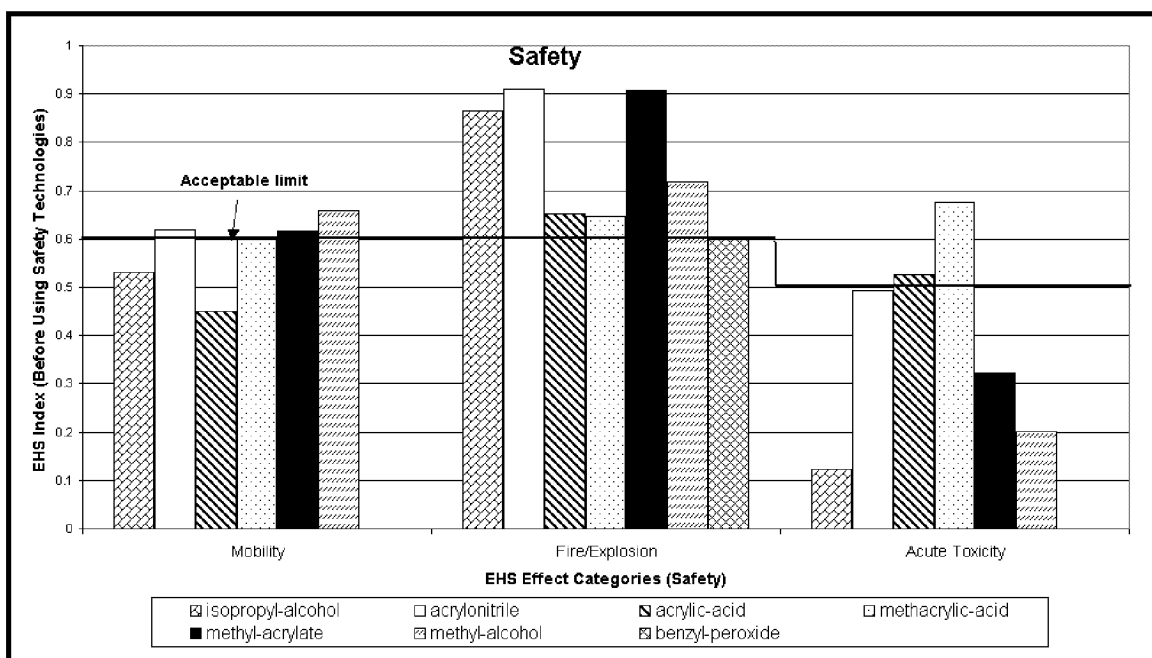
Figure 4.2.2a: Production of acrylic resins by polymerization: SAL results in the form of Effective Dangerous Property index (as defined in EHS method) before using safety technologies.
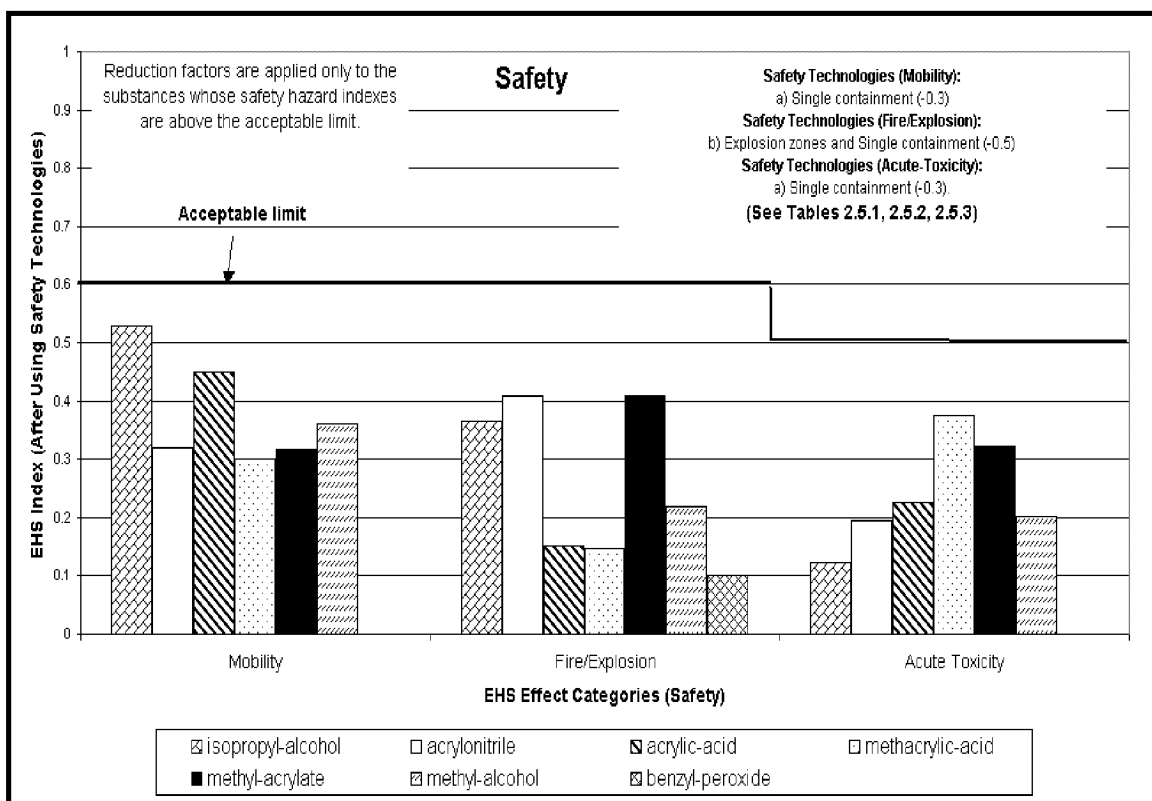
Figure 4.2.2b: Production of acrylic resins by polymerization: Safety-Technology Assessment Layer (STAL) results in the form of Effective Dangerous Property index (as defined in EHS method) after using safety technologies.

Table 4.2.3: EAL results obtained for the process case study (polymerization of acrylic monomers).

Type of parameters	#	Parameter [Unit]	Process (acrylic polymerization, basic recipe (40% solvents) in batch/semi-batch reactor)	Process (acrylic-acid (AA) and acrylonitrile (AN) in (temporary) storage tank)	Process (acrylic-acid and solvents separation in distillation column)
Recipe, physical and chemical properties and laboratory data	1	Process temperature [°C]	65	25	80
	2	Average boiling point of mixture (initial) [°C]	80		65 (methyl alcohol) 80 (isopropyl alcohol)
	3	T_{onset} [°C]	120 (reaction mixture)	145 (AA) and 245 (AN)	145 (AA)
	4	q_{onset} [W/kg]	20 (assumption, Keller et al., 1997)	20 (assumption, Keller et al., 1997)	20 (assumption, Keller et al., 1997)
	5	Activation energy E_a (kJ/mol)	50 (assumption, Keller et al., 1997)	50 (assumption, Keller et al., 1997)	50 (assumption, Keller et al., 1997)
Assessment results (e.g. criticality class, probability and severity)	6	Primary adiabatic temperature rise (100% Acc.) [°C]	84		
	7	Maximum temperature of reaction (MTSR) [°C]	149 (100% accumulation)		
	8	ADT_{24} or $T_{0,24}$ (100% Acc.) [°C]	33 (equation 2.4.1.3)	49 (AA) and 120 (AN) (equation 2.4.1.3)	49 (AA) (equation 2.4.1.3)
	9	ADT_{64} or $T_{0,64}$ (100% Acc.) [°C]		35 (AA) and 80 (AN) (equation 2.4.1.2 by taking TMR_{ad} = 64 hours)	35 (AA) (equation 2.4.1.2 by taking TMR_{ad} = 64 hours)
	10	Criticality Class	5 (100% accumulation)		
	11	TMR_{ad} [hours] at MTSR or at storage or distillation temperature (probability class)	0.2 (High)	120 (AA) [Low] and 2200 (AN) [Low]	8 (High)
	12	Severity	High	High	High
Secondary hazards (EHS index values)	13	Maximum EHS substance index for Mobility/Fire /Toxicity	0.63/0.9/0.68	0.45/0.65/0.53 (AA) 0.61/0.9/0.49 (AN)	0.45/0.65/0.53 (AA)
Primary Hazard Index (PHI)	14		1.0	0.7 (AA) and 0.7 (AN)	1.0

Secondary Hazard Index (SHI)	15	Maximum EHS Substance Index	0.9	0.65 (AA) 0.9 (AN)	0.65
Recommended safety technologies (reduction factors (STRF) are given in brackets)	16	Mitigation of Primary Hazards	Recommendation is to use inherent-safety-principles.	a) Set #P_1 (-0.1) and #P_4 (-0.5) [Table 2.5.5]	Recommendation is to use inherent-safety-principles.
		Mitigation of Secondary Hazards	Recommendation is to use inherent-safety-principles.	a) Set #S_1 (-0.2) and set #S_3 (-0.3) [Table 2.5.6]	Recommendation is to use inherent-safety-principles.
Remaining potential of danger	17	RPHI		a) 0.1 (AA) a) 0.1 (AN)	
		RSHI		a) 0.15 (AA) a) 0.4 (AN)	

5. Conclusions and outlook

5.1 Conclusions

The SREST-Layer-Assessment method and an automated EHS tool have been developed for the assessment of environmental, health and safety aspects and for revealing the degree of nonideality in an early stage of chemical process design in the following way: for substance assessment, EHS method (which is slightly modified in SREST method) by Koller et al. (2000) has been used because of its flexibility to include all available information with the help of using different priority levels; for getting information about reactivity between substances, the connection has been made between EHS tool (Koller et al., 1999) and reactivity databases; for the assessment of possible worst-case scenarios in major equipment units, more specific screening methods have been used; and recommendation or prediction of safety technologies have been defined with reduction factors to show realistic hazards.

The degree of non-ideality of a chemical process is expressed by the magnitude of the indices in SAL, by reactivity indices and the number of interactions between chemicals as identified in RAL, by the magnitude of hazards identified in EAL and by the number, type and reduction factors of safety technologies recommended in STAL. Different case studies have been chosen to illustrate the complete methodology. The results of these case studies reveal the degree of inherent safety in these processes and provide information on how the degree of inherent safety can be increased by using inherent-safety-principles. The method is useful in screening possible synthesis routes, in obtaining commonly available knowledge quickly via interfaces with databases, in assessing worst-case scenarios and in predicting different safety technologies to mitigate the possible worst-case scenarios. SREST-Layer-Assessment method can be used efficiently and quickly in laboratory where substance data and reaction recipe is defined and in conceptual flow-sheet stage where a rough sketch of flow-sheet is prepared with the list of major unit-operations involved. Use of this automated tool can help to conduct a systematic safety evaluation under high time pressure in early stages of process development but it has to be emphasized that it is not meant to replace rather support a detailed risk analysis conducted by a panel of experts.

5.2 Outlook

Here various topics are presented in which future work can be done. SREST method can be augmented with systematic procedures for major worst-case scenarios in other major unit operations.

Autocatalytic reactions in runaway assessment: An important point for the assessment of thermal risk is the identification of autocatalytic reactions because they require a special attention to control. Bou-Diab and Fierz (2002) have developed a new screening method based on dynamic DSC measurements for the identification of autocatalytic decompositions. The method consists of fitting a first order kinetic model to the measured heat release rate curve (from dynamic DSC measurement) and determining the apparent activation energy. They concluded that if the apparent activation energy is higher than 220 kJ/mol, the decomposition is autocatalytic and by taking into account the cases with the boundary value of the apparent activation energy (180 – 220 kJ/mol), the new screening method should be applicable to about 80% of the cases. This screening method can be used to recognize autocatalytic reactions if DSC measurements are available. The runaway model in batch/semi-batch reactor can be augmented with the assessment method of autocatalytic reactions

Gas evolution in runaway assessment: To be on the conservative side, gas or vapour evolution should be considered in all the cases and detailed assessment should be done in the case of high-pressure rate data (obtained from the laboratory). Hentschel and Schliephake (1993) have presented a survey of the experimental methods to detect gas evolution and pressure increase during undesirable chemical reactions. Bretherick (2003) has also presented different scenarios regarding unexpected gas evolution that may cause or aggravate hazardous situations. The runaway model should consider gas or vapor evolution in detail for complete risk assessment.

Other major equipment units and worst-case scenarios: Inclusion of the assessment of other major worst-case scenarios, for example, dust-air explosion, filling and emptying tanks, in major equipment units can extend the method for complete process assessment. There have been a number of dust explosion accidents reported in solid

storage tank or in dryer because of ignition of fire due to electrostatic discharges. The knowledge of the ignition behaviour of dust-air mixtures is important for risk assessments in chemical production plants. Jaeger (2001) described in his paper the strategy of performing a "Risk Analysis" for a systematic hazard search and evaluation of dust-air explosion based on a practical example. Kao and Duh (2002) investigated a severe dust explosion that occurred in the silos area of an acrylonitrile-butadiene-styrene (ABS) plant and presented a systematic investigation procedure. Hoppe et al. (2000) presented the hazards related with handling of combustible powders during transportation, charging, discharging and storage. They described the use of the minimum ignition energy and minimum ignition temperature as very important safety indices to assess dust-air explosion. A systematic procedure can be developed by taking minimum ignition energy and minimum ignition temperature values in account to analyse dust explosion. Preventive measures against the occurrence of electrostatic discharges and mechanically generated sparks during powder handling operations should also be considered in detail.

A systematic procedure can be developed to assess filling/emptying of tanks. Planas-Cuchi et al. (1999) surveyed 738 accidents of loading and unloading operations in the transportation of hazardous material and identified the accident type distribution and their causes. They discussed briefly the flammable mixtures and the procedures to avoid these mixtures occurring when filling or emptying a tank.

Defining reduction factors for safety technologies: Detailed lists of safety technologies for other major worst-case scenarios in different equipment units can be prepared with reduction factors, in a similar way, as it is done for runaway or decomposition or incompatibility scenarios. These reduction factors are helpful in showing the realistic hazards present in a chemical process.

Learning from past accidents: 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. There are a number of databases specifically dealing with case histories. They include the following:

1. 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).

2. The Major Accident Reporting System (MARS), described by Drogaris (1991, 1993) etc.

The assessment software tool can have an interface with accidental database available from different organizations to highlight the similar past accidents occurred due to similar hazardous chemicals used or happened in a similar equipment unit to control the reoccurrence of similar type of accidents.

Nomenclature

ADT_{24}	adiabatic decomposition temperature for 24 hours, [K] [= $T_{0,24}$]
C_p	specific heat capacity, [J kg^{-1} K^{-1}]
E_a	activation energy, [J mol^{-1}]
$-\Delta H_R$	enthalpy of the reaction, [J kg^{-1}]
q_{onset}	heat release rate at the onset temperature in a DSC run, [W kg^{-1}]
q	heat release rate, [W]
R	general gas constant, [J mol^{-1} K^{-1}]
T_0	temperature at which TMR_{ad} is calculated, [K]
$T_{0,24}$	initial temperature at which TMR_{ad} = 24 hours, [K] [= ADT_{24}]
T_{onset}	onset temperature in a DSC run, [K]
TMR_{ad}	time to maximum rate at adiabatic conditions, [S]
ΔT_{ad}	adiabatic temperature rise, [K]
X_{acc}	the degree of accumulation

Abbreviations

AIT	auto ignition temperature
ARC	accelerating rate calorimetry
BP	boiling point
CEI	chemical exposure index
DP	dangerous property
DSC	differential screening calorimetry
EAL	equipment assessment layer
EDP	effective dangerous property
EHS	environment, health and safety assessment
$ESCIS$	expert commission for safety in the swiss chemical society
$F\&EI$	fire and explosion index
FF	fate factor
FP	flash point

GK	giftklasse (Swiss poison class)
HA	hydroxylamine
HU	hydroxyurea
IDLH	immediately dangerous to life and health
ISP	inherent-safety-principles
MEKPO	methyl-ethyl-ketone-peroxide
MIC	methyl-isocyanates
MTIR	maximum temperature of incompatible reaction (in adiabatic runaway scenario)
MTSR	maximum temperature of synthesis reaction (in adiabatic runaway scenario)
MP	melting point
NFPA	national fire protection association
PDHI	primary decomposition hazard index
PHI	primary hazard index
PID	pipe and instrumentation diagram
PRHI	primary runaway hazard index
QSAR	quantitative structure activity relationship
RAL	reactivity assessment layer
RPDHI	remaining primary decomposition hazard index
RPHI	remaining primary hazard index
RPRHI	remaining primary runaway hazard index
RSDHI	remaining secondary decomposition hazard index
RSHI	remaining secondary hazard index
RSRHI	remaining secondary runaway hazard index
SAL	substance assessment layer
SDHI	secondary decomposition hazard index
SHI	secondary hazard index
STAL	safety-technology assessment layer
STRF	safety technology reduction factor
SREST	substance, reactivity, equipment, safety-technology layer assessment method
SRHI	secondary runaway hazard index
VP	vapour pressure

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Appendix A – Modified EHS method

The Figures for 11 effect categories in modified EHS method (Koller, 2000) are presented here.

a) Mobility

relative amount of substance releasable into air

Index value	0	0.4	0.8	1	
Physical value	0.0001	0.01	1	10	(kg/kg)

Priority					chemical class
A1.	solid,gas dissolved suspended	gas dissolved but releasable	dust gas	pressurized gas	chemical class
A2.	0.0001	0.01	1	10	pi° (bar)
A3.	200	100	0		Δbp (°C)
A4.	200	0			Δmp (°C)
A5.	solid	liquid	gas		chemical class
B1.	-20<x<20 -5<x<5				Δmp or Δbp (°C)
	?				no data

pi°   partial pressure of pure comp. at process temperature (measured or estimated)
mp or bp   melting point or boiling point (danger of undesired condensation, crystallisation)
Δbp   temp. difference between stand. boiling point and process temperature
Δmp   temperature difference between melting point and process temperature
gas dissolved   aqu. HCl,...
gas dissolved but releasable   aqu. NH3, CO2,... depending on pH at process conditions

b) Fire/Explosion

probable energy potential for reaction with oxygen

Index value	0	0.5	1	

Priority				
A1.	200	100	0	Δfp (°C)
A2.			F F+	EC classification
A2.	other R-codes	10	11 12,15, 30 17,18	R-codes (EC)
A2.	0	1 2	3 4	NFPA-flamm
B1.	8	-10	-12	log (λ) (s/m)
B1.	200	100	0	Δait (°C)
B2.	O,N,S,Br,I in compound	n-alkane, toluene benzene, CCl4, Et2O		substance
B2.			0	EC classification
B2.	other R-codes		7,8,9,17	R-codes (EC)
C1.	other R-codes		7,8,9	EC classification
C1.			0	EC classification
	?			no data

Physical value = -ΔH$_{combust}$ x 10 ^ (4 x Index value - 4)   (kJ/kg)

Δfp   temperature difference between flash point and process temperature
NFPA-flamm   flammability hazard class of US National Fire Protection Agency
log(λ)   logarithm of electric conductivity
ΔH combust   combustion enthalpy
Δait   difference between auto ignition temperature and process temperature

c) Acute Toxicity

amount of air polluted to immediately dangerous concentration

Index value	0	0.5	1	
Physical value	0 0.0001	0.001	0.1	(m3/mg)

Priority				
1.	100000	1000	10	ERPG3 (mg/m3)
2.	100000	1000	10	IDLH (mg/m3)
3.		X$_n$ T T+		EC classification
3.	no 5	4 3	2 1	GK
3.	other	20,21,22 23,24,25 31	26,27,28 29,32	R-codes (EC)
4.	20	2	0.5	LC50 inhal. (mg/m3)
4.	2000	200	25	LD50 oral (mg/kg)
4.	4000	400	50	LD50 dermal (mg/kg)
	?			no data

ERPG   Emergency Response Planning Guideline (American Industrial Hygiene Association)
IDLH   Immediately Dangerous to Life and Health (National Institute for Occupational Safety and Health
GK   Giftklasse (swiss poison class)

d) Decomposition

Index value	0	0.5	1	

Priority				
A1.	0	100	400	-ΔH decomp, meas. (kJ/kg)
A1.	0	100	400	-ΔH decomp, est. (kJ/kg)
A2.	200	100	0	ΔT decomp. (°C)
A3.	-240 +160	-180 +120	-120 +80	Oxygen balance (%)
A4.			5,19, 44 1,2,3, 6,17	R-codes (EC)
A5.	no instable group found	azo, cyanat	nitro,ether peroxo, dinitro	Substance types
A6.		gaseous	toxic flammable	Decomp. products

ΔH decomp, meas.   Decomposition enthalpy (measured)
ΔH decomp, est.   Decomposition enthalpy (estimated)
Oxygen balance   % (wt/wt) external oxygen required for complete combustion (not bound within molecule)
Decomp. products   Decomposition products produced
ΔT decomp. (°C)   Difference between decomposition (e.g., T$_{onset}$ from DSC) and process temperature

Figure A1: Effect categories for assessing safety aspects in modified EHS method.

a) Irritation

substances where direct contact should be avoided

Index value	0	0.5	1
Physical value	0 0.001 0.01		1 (m3/mg)

considered aspects	Priority				
	1.		Xi	C	EC classification
dermal irritation	1.	other	36,37,38	34 35	R-codes (EC)
eye irritation	2.	5 4 3 2 1 8.5 9.5 10.5 11.5 12.5			pH
	2.	4000 400 50		5	LD50 dermal (mg/kg)
to humans and animals	3.	no corrosive group	weak acids, alkalines	strong acids, alkalines	substance
	4.	no	estimat.	light	known	irritation eye,skin
					? no data

pH   pH-value at process conditions or 1 molar concentration

b) Chronic Toxicity

amount of air polluted to a MAK/TRK value

Index value	0	0.6	1
Physical value	0 0.001	0.1	10 (m3/mg)

considered aspects	Priority				
	A1.	1E-9	1E-6	1E-4	unit risk
	ABC2.	10000	10	0.1	TRK (mg/m3)
A:carcinogenicity	ABC3.		3	2	EC classification
B:mutagenicity	ABC3.		3 2B	2A 1	IARC classification
C:reproductive toxicity	ABC4.	other R-codes	40,62,63,64	45,46,47 49,60,61	R-codes (EC)
D:sensitization immunotoxicity	A5.	no	poss	probable yes	qualitative information
E:other specific (liver, lung,neural) toxicity	B5.	no	est.	probable yes	mutagenicity
F: odour	C5.	no	est.	probable yes	reproductive toxicity
	ABC6.		N-nitroso, epoxid, aromat. amin,...		chemical class
	D1.	other R-codes	42,43		R-codes (EC)
	D2.	no,?	est.	known	sensitization, immunotox.
to humans and animals	E1.	10000	100	1	MAK (mg/m3)
	E2.		Xn T	T+	EC classification
	E2.	no 5	4 3	2 1	GK
	E2.		31,33	29,32,48	R-codes (EC)
	E3.	2	0,2 0.05		NOEL inhal (mg/m3)
	E3.	200	20 2,5		NOEL oral (mg/kg)
	E4.	0	0,5	1	Index acute toxicity
	F1.	1000	10 1		odour threshold (mg/m3)
	F2.	other substance	volatile amins thiols, pyridin volatile phosphits		substance
			?		no data

unit risk	cancer risk when exposed to an air concentration of 1µg/m3 during life (US-EPA)
TRK	Technische Richtkonzentration (defined by Deutsche Forschungsgemeinschaft)
poss	possible est. estimated
MAK	workplace threshold value (Maximale Arbeitsplatz Konzentration)
GK	swiss poison class (Giftklasse)
NOEL	No Observed Effect Level

Figure A2: Effect categories for assessing health aspects in modified EHS method.

a) Water mediated effects

amount of water polluted to emission limit (critical water volume)

	Index value	0		0.5		1	
	Physical value	0	0.1	1		100	(m3/g)

considered aspects	Priority						
	1.	1000		10		0.1	LC50/EC50 acute (mg/l)
considered aspects	2.	100		1		0.01	other toxdata (mg/l)
toxicity to aquatic environment	3.		52	51	50		R-codes (EC)
	3.	1		2		3	WGK
	4.	100		1		0.01	emission limit (mg/l)
	4.	10		0.1		0.001	imission limit (mg/l)
	4.	sulfat,nitrat chlorid,alkali, erdalkali	Al F	Fe,Ni,Zn,Sn phosphat nitrit,sulfit	metal sulfid, amin	Hg	substance
	5.	0		0.5		1	Index acute toxicity
						?	no data

WGK   german water hazard class (Wassergefährdungsklasse)

b) Degradation

relative factor for the mass of organic substances at steady state conditions

	Index value	0		0.5		1	
	Physical value	0.01	0.032	0.1	0.32	1	(kg / kg)

considered aspects	Priority						
	1.	1	3.2	10	32	100	persistency (days)
considered aspects	2.	1	3.2	10	32	100	halflife (days)
aquatic: biodegradation hydrolysis	3.	1	3.2	10	32	100	halflife reviewed (days)
air: photolysis	4.	1	99.8	85	54	20	OECD 28d (%)
soil: biodegradation	5.		readily	inherent		no	EU-classification
	5.	1	3.2	10	32	100	halflife QSAR (days)
	6.	0.97	0.7	0.3	0.1	0.05	BOD5 / COD
	6.	1	3.2	10	32	100	halflife unknown (days)
	7.	hydrolysable, inorganics			tert.amin,ether subst.aromat		substance
						?	no data

persistency   halflife measured in environment or calculated with environ. model (Mackay III,...)
halflife   overall halflife in relevant compartment (=air or water or soil, default: water)
halflife reviewed   halflife data from handbooks (Howard, Mackay)
OECD   biodegradability after 28 days or other results from other standardized tests
halflife QSAR   halflife estimated with quant. struct. activity relat. (Syracuse Biodeg Program,...)
BOD/COD   ratio of Biological Oxygen Demand to Chemical Oxygen Demand
halflife unknown   halflife measured at unknown conditions

c) Air mediated effects

amount of air polluted to emission limit (critical air volume)

	Index value	0		0.6		1	
	Physical value	0	0.001	0.1		10	(m3/mg)

considered aspects	Priority						
	A1.	0		0.6		1	Index chronic toxicity
carcinogenicity mutagenicity	A2.	1000	100	10	1		emission limit (mg/m3)
reproductive tox sensitization	A3.		3 2	1			LRV class organic
other specific tox odour	A3.		4	3	2 1		LRV class inorganic gas
	A3.				3 2 1		LRV class inorganic particle
to humans and environment		LRV	swiss air pollution class (Luftreinhalte Verordnung)				

d) Solid waste

total amount of inorganic solid waste (dry)

	Index value	0	1	
	Physical value	0	1	(kg / kg)

considered aspects			
solid waste for disposal via landfill or waste water	H2O, organics, gases	other substances	substance

e) Accumulation

relative factor for potential to accumulate in the food chain

	Index value	0	0.5	1	
	Physical value	1	10	100	(kg / kg)

considered aspects	Priority				
	1.	2	3	4	log BCF
accumulation in food chain	2.	3	4	5	log (Kow)
	3.	other R-codes	33	48,53,58	R-codes (EC)
accumulation in soil and organic matter	4.	no low	possible	probable high	qualitative info
				?	no data

BCF   bioconcentration factor
KOW   octanol / water partitioning coefficient

Figure A3: Effect categories for assessing environmental aspects in modified EHS method.

Effective Dangerous Property (EDP) index calculation in EHS method (Koller, 2000): In EHS method, depending on the substance information available, different measures or properties can be used to calculate an index value (see Figures A1, A2 and A3 in Appendix A for details of indices for 11 effect categories). The index for Mobility for instance can be calculated using the VP (vapour pressure data) or BP (boiling point) or MP (melting point) etc. This index representing a Dangerous Property (DP) of a substance can vary between 0 and 1 depending on the size of the EHS-effect. In the next step, this index is modified by the fate factors, i.e., mobility, degradability or accumulation potential of the substance. These fate factors are calculated as shown in Table A1. Toxic substances that are solid or degradable are considered less dangerous in safety respectively environmental assessment. This modified value indicates the Effective Dangerous Property (EDP) of a substance.

Table A1: Calculation of fate factors (FF) in EHS method (Koller, 2000). $PhysVal_{Mobility}$ represents the physical value of Mobility effect category.

Safety effect categories [Effective Dangerous Property (EDP) = Dangerous Property + Fate factors]	Fate factors (FF)
Mobility, Decomposition	0
Fire/Explosion	$0.1 * \log (PhysVal_{Mobility})$
Acute Toxicity	$0.2 * \log (PhysVal_{Mobility})$

Table A2: Effective Dangerous Property indices for all substances presented in the case studies. The range of indices is between 0 and 1.

EHS Effect Categories (Index values) [Safety]				
Substances	**Effective Dangerous Property Index (EDP) [After considering fate factors, i.e., Mobility, Degradation and Accumulation]**			
	Mobility	Fire/Explosion	Decomposition	Acute Toxicity
aromatic-amine	0.13 (MP = 155.5 °C)	0.17 (Flash point = 120 °C). [Fate factor = -0.33 (from Mobility)]. Index without FF = 0.5	0.0 (AIT = 440 °C)	0.0 (acute,oral: LD50:LC50! letal#acute). [Fate factor = -0.67 (from Mobility)]. Index without FF = 0.26
nitrosyl-sulfuric-acid	0.47 (BP = 120 °C)	0.0 (R-Codes = 35) [Fate factor = -0.16 (from Mobility)]. Index without FF = 0.0	0.0 (R-Codes = 35)	0.68 (gift klasse = 1) [Fate factor = -0.32 (from Mobility)]. Index without FF = 1.0
sulfuric-acid	0.39 (VP = 0.0087 bar)	0.0 (R-Codes = 35) [Fate factor = -0.2 (from Mobility)] Index without FF = 0.0	0.0 (R-Codes = 35)	0.54 (IDLH = 15 mg/m3) [Fate factor = -0.41 (from Mobility)] Index without FF = 0.96
diazonium-salt	0.0 (VP = 0.0001 bar)	0.0 (NFPA-Flamm = 1) [Fate factor = -0.4 (from Mobility] Index without FF = 0.25	0.66 (substance class – diazo)	0.0 (NFPA = 1) [Fate factor = -0.8 (from Mobility)] Index without FF = 0.25
nitro-aromatic-compound	0.4 (VP = 0.01 bar)	0.46 (Flash point = 87.2 °C) [Fate factor = -0.2 (from Mobility)] Index without FF = 0.66	0.0 (AIT = 485 °C)	0.09 (IDLH = 1098.5 mg/m3) [Fate factor = -0.4 (from Mobility)] Index without FF = 0.49
nitroaromatic-sulfonic-acid	0.15 (BP = 217.5 °C)	0.27 (Flash point = 100 °C) [Fate factor = -0.33 (from Mobility)] Index without FF = 0.6	0.0 (AIT = 355 °C)	0.0 (gift klasse = 4) [Fate factor = -0.66 (from Mobility)] Index without FF = 0.38
oleum	0.62 (VP = 0.126 bar)	0.0 (NFPA flamm = 0) [Fate factor = -0.08 (from mobility)] Index without FF = 0.0	0.0 (No instable group found)	0.77 (IDLH = 15.59 mg/m3) [Fate factor = -0.17 (from Mobility)] Index without FF =

				0.95
sulfur-trioxide	0.8 (VP = 1.013 bar)	0.0 (NFPA flamm = 0) [Fate factor = 0.0005 (from mobility)] Index without FF = 0.0	1.0 (Oxygen balance = 19.98)	0.79 (IDLH = 71.43 mg/m3) [Fate factor = .001 (from Mobility)] Index without FF = 0.786
nitro-toluene	0.19 (VP = 0.0009 bar)	0.3 (Flash point = 98.8 °C) [Fate factor = -0.3 (from Mobility)] Index without FF = 0.6	1.0 (NFPA = 4)	0.0 (IDLH = 1223.4 mg/m3) [Fate factor = -0.6 (from Mobility)] Index without FF = 0.48
toluene	0.51 (VP = 0.039 bar)	0.86 (Flash Point = 5 °C) [Fate factor = -0.l4 (from Mobility)] Index without FF = 1.0	0 [AIT = 515]	0.14 (IDLH = 2055.4 mg/m3) [Fate factor = -0.28 (from Mobility)] Index without FF = 0.42
nitric-acid	0.54 (VP = 0.051 bar)	0.37 (EU-Class = "O" and R-codes = 8-22-36/37/38-42/43) [Fate factor = -0.13 (from Mobility)] Index without FF = 0.5	1 (Oxygen balance = 76.79)	0.48 (IDLH = 111.6 mg/m3) [Fate factor = -0.25 (from Mobility)] Index without FF = 0.73
acrylonitrile (AN)	0.61 (Vapor Pressure = 0.125 bar)	0.90 (Flash point = -2.75 °C) [Fate factor = -0.1 (from Mobility)] Index without FF = 1.0	0.8 (NFPA = 2)	0.49 (IDLH = 201.2 mg/m3) [Fate factor = -0.18 (from Mobility)] Index without FF = 0.67
potassium-persulfate	0.0 (MP = 164.4 °C & BP = 892 °C)	0.1 (EU Class = "O" and R-codes = 8-22-36/37/38-42/43) [Fate factor = -0.4 (from Mobility)] Index without FF = 0.5)	1.0 (oxygen balance = 23.67)	0.0 (EU Classification = Xn) [Fate factor = -0.8 (from Mobility)] Index without FF = 0.38)
methyl-ethyl-ketone-peroxide	0.42 (BP = 134.7 °C)	0.52 (Flash point = 77.4 °C) [Fate factor = -0.19 (from Mobility)] Index without FF = 0.705	0.55 (oxygen balance = 173)	0.49 (GK = 2) [Fate factor = -0.37 (from Mobility)] Index without FF = 0.88
hydroxyl amine (HA)	0.0 (MP = 171.2 °C)	0.0 (EU-Class: other) [Fate factor = -0.4 (from Mobility)] Index without FF = 0.0	1.0 (NFPA = 4)	0.0 (GK = 3) [Fate factor = -0.8 (from Mobility)] Index without FF =

				0.63
hydroxyurea	0.06 (MP = 141 °C & BP = 244.7 °C)	0.0 (NFPA flamm = 0) [Fate factor = -0.37 (from mobility)] Index without FF = 0.0	1.0 (oxygen balance = 42.07)	0.27 (GK = 1) [Fate factor = -0.73 (from Mobility)] Index without FF = 1.0
isopropyl-alcohol	0.52 (VP = 0.044 bar)	0.865 (Flash point = 13.14 °C) [Fate factor = -0.14 (from Mobility)] Index without FF = 1.0	0.0 (AIT = 418 °C)	0.12 (IDLH = 2684 mg/m3) [Fate factor = -0.27 (from Mobility)] Index without FF = 0.39
methyl-acrylate	0.616 (VP = 0.121 bar)	0.9 (Flash point = -2.8 °C) [Fate factor = -0.09 (from Mobility)] Index without FF = 1.0	0.0 (AIT = 420 °C)	0.32 (IDLH = 960.22 mg/m3) [Fate factor = -0.18 (from Mobility)] Index without FF = 0.5
acrylic-acid	0.45 (VP = 0.017 bar)	0.65 (Flash point = 54.9 °C) [Fate factor = -0.18 (from Mobility)] Index without FF = 0.82	0.0 (AIT = 400 °C)	0.52 (GK = 2) [Fate factor = -0.35 (from Mobility)] Index without FF = 0.88
methacrylic-acid	0.6 (VP = 0.1 bar)	0.64 (Flash point = 70.69 °C) [Fate factor = -0.1 (from Mobility)] Index without FF = 0.74	0.0 (AIT = 420 °C)	0.675 (GK = 2) [Fate factor = -0.2 (from Mobility)] Index without FF = 0.88
methanol	0.65 (VP = 0.198 bar)	0.71 (Flash point = 62.35 °C) [Fate factor = -0.07 (from Mobility)] Index without FF = 0.78	0.0 (AIT = 427 °C)	0.2 (IDLH = 4292.6 mg/m3) [Fate factor = -0.14 (from Mobility)] Index without FF = 0.34
benzyl-peroxide	0.0 (VP = 0.0001 bar)	0.6 (Flash point = 0 °C) [Fate factor = -0.4 (from Mobility)] Index without FF = 1.0	0.7 (AIT = 80 °C)	0.0 (IDLH = 750.7 mg/m3) [Fate factor = -0.8 (from Mobility)] Index without FF = 0.53

Appendix B – Reactivity prediction

The lists of "reactions having high and moderate hazard potential" and "atom groupings enhancing molecular instability" are taken from the paper presented by Leggett (2003). These lists are used in Reactivity Assessment Layer (RAL, see Chapter 2 for detail) to predict hazards related with desired and undesired reactions. The incompatibility chart (Figure B1) is also used in RAL to show incompatibilities among different chemical groups.

Table B1: Reactions having high hazard potential.

Reaction (high hazard potential)	Example of concern
Curtius rearrangements	Use of acyl azides, nitrous acid or hydrazine.
Decarboxylation	Removal –COOH with CO_2 evolution – possible pressure hazard.
Diazotizations	Especially if followed by reduction to the hydrazine ($SnCl_2$ reaction); replacement with a –OH or to replace the –NH_2 with –H.
Displacements	Uses oxalyl chloride to displace –OH. (CO_2, CO, HCl generated)
Epoxidations	Epoxides are high-energy strained rings.
Esterification	When using oxalyl chloride.
Friedel crafts ($AlCl_3$)	Friedel crafts reactions and their quenches due to use of $AlCl_3$, BCl_3, H_2SO_4, HF.
Grignard reactions	Reactions require an activation period and are highly exothermic.
Hydrolysis	Hydrolysis of a cyano to an amide oxidatively using H_2O_2.
Metallations	Uses n-BuLi, t-BuLi, LDA, NaHMDS
Nitrations	Uses Nitric-Acid and strong acids like sulphuric or triflic acid (trifluoromethane-sulfonic acid). Nitrations are very exothermic. The potential for thermal runaway, initiating violent decompositions and explosions exists.
Oxidations	Uses of Jones reagent [K2Cr2O7/H2SO4], O3, H2O2 (with large exotherms), peroxo acids, cleavage-using sodium periodate.
Peptide formations	Use of HOBT (1-hydroxybenzotriazole hydrate).
Quenches	When PCl_5 or $POCl_3$ have been used in a previous step and water is the quench.
Reductions	Any nitro compound or high-energy functional group reduction. Reductions using $LiAlH_4$, Fe or Zn powder with HCl or acetic acid, hydrazine in caustic; hydrogenations by generating H_2 in-situ using hydrazine, $NaBH_4$ in CH_3OH or C_6H_{12}.
Sulfonation	Sulfonation of an amine to form sulphonamide.

Table B2: Reactions having moderate hazard potential.

Reaction (moderate hazard potential)	Example of concern
Acylations	Use of acetic anhydride or acid chloride acylations of amines.
Additions	Additions of alkyl metals to ketones or aldehydes, cyano groups, carboxylic acids or esters or any other functionality.
Alkylations	Alkyl halide or amine (aromatic or aliphatic) used with a phenol.
BOC protections-deprotections	BOC (t-butoxycarbonyl) used to protect/deprotect amines. Unreacted BOC anhydride in waste streams can liberate CO_2 and isobutylene.
Condensations	C-C bond or C-N bond formation with elimination of small molecules.
Cross coupling reactions	These reactions involve the use of a metal to mediate a C-C bond formation, usually a Pd(0) species (Pd(triphenyl-phosphene)$_4$; Suzuki coupling; zincate coupling by transmetalating a Grignard or a lithium species with zinc chloride.
Dealkylation	Demethylation of methoxy group using HBr or HCl to generate methyl bromide or methyl chloride. BBr_3 and BCl_3 used at low temperatures.
Displacement	Displacement of –OH with –Cl using PCl_5.; reactions are heated, the distilled PCl_5 is difficult to quench due to the delayed water reaction. Use of LiCl in NMP to displace a triflate ($CF_3SO_3^-$).
Esterification	Using oxalyl chloride and acid followed by alcohol addition. Reaction liberates CO and HCl – pressure hazard. Also by using acid and $SOCl_2$ and then adding the alcohol.
Ether formations	Ethers formed via Williamson synthesis by alkylating with alkylhalide.
Halogenations	Reactions of alkyl or aryl groups with halogens such as Br_2, Cl_2 or I_2.
Hydrolysis	Of a cyano with Lewis acid (e.g. BF_3). See other categories for hydrolysis/quench reactions.
Peptide formations	Coupling of an amine with an acid using EDC, EEDQ (N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline), or alkyl-chloroformate mediated peptide coupling, or N-hydroxy succinamide.

Table B3: Examples of functional groups that indicate or enhance molecular instability.

Atom Grouping with Molecule	Example of Functional Group	
	Structure	**Name**
C-C double bonds	-C=C-; -C=C-C=C-	alkenes, dienes
C-C and C-N triple bonds & their metal salts	-C≡C-; -C≡N	acetylenic; cyano
adjacent N-O atoms – many combinations	$C-NO_2$; C-O-N=O	aryl, alkyl nitro; alkyl nitrite
adjacent and consecutive N atom pairs, triplets and higher	-C-N=N-C; $-C-N_2^+$	azo compounds, diazonium-salts
adjacent and consecutive N atom pairs, triplets and higher	-C-N≡N; -N-N≡N	diazo; azide
adjacent O-O pairs	-C-O-O-H; C-O-O-C	peroxyacids; esters; peroxides
O-X atomic pairs	-O-X; $-ClO_3$	hyprhalites; chlorates
many N-Metal atomic pairs	=N-M	N – metal salts

Notes:

H	Represents heat generation.
F	Represents fire.
G	Represents innocuous and non-flammable gas generation.
GT	Represents toxic gas generation.
GF	Represents flammable gas generation.
E	Represents explosion.
P	Represents violent polymerization.
S	Represents solubilization of toxic substances.
U	Means may be hazardous but unknown.
Example: H,F,GT	Represents heat generation, fire, and toxic gas generation.

Chemical groups:

1. Acids, Mineral, Nonoxidising
2. Acids, Mineral, Oxidising
3. Acids, Organic
4. Alcohols and Glycols
5. Aldehydes
6. Amides
7. Amines, Aliphatic and Aromatic
8. Azo and Diazo Compounds, and Hydrazines
10. Caustics
11. Cyanides
13. Esters
14. Ethers
15. Fluorides, Inorganic
16. Hydrocarbons, Aromatic
17. Halogenated Organics
18. Isocyanates
19. Ketones
20. Mercaptanes and Other Organic Sulphides
26. Nitriles
27. Nitro Compounds, Organic
29. Hydrocarbons, Aliphatic, Saturated
30. Peroxides and Hydroperoxides, Organic
31. Phenols and Cresols
33. Sulphides, Inorganic
34. Oxidising Agents, Strong

Incompatibility matrix (reactions with groups 1, 2, 3, …):

Group	1	2	3	4	5	6	7	8	10	11	13	14	15	16	17	18	19	20	26	27	29	30	31	33
3	G,H																							
4	H	H,F	H,P																					
5	H,P	H,F	H,P																					
6	H,	H,GT																						
7	H	H,GT	H	H	H																			
8	H,G	H,GT	H,G	H,G	H		G																	
10	H	H	H	H	H			H																
11	GT,GF	GT,GF	GT,GF				G																	
13	H,	H,F							H															
14	H	H,F																						
15	GT	GT	GT																					
16		H,F																						
17	H,GT	H,F,GT	H,G				H,GT	H,G			H,GT			H										
18	H,G	H,F,GT	H,G		H,P		H,P	H,G			H,P				H,G									
19	H	H,F					H,G	H							H,G	H								
20	GT,GF	H,F,GT	H,F					H,G							H,G									
26	H,GT,GF	H,F,GT	H													U								
27		H,F	H														H,E							
29		H,F	H,F																					
30	H,G	H,E					H,F,E	H,F		H,E,GT					H,F		H,E	H		E				
31	H	H,F						H,G							H,P							H,P		
33	GT,GF	H,F,GT	GT					E							H								H	
34	H,GT	H,F,GT	GT	H,F	H,F	H,F,GT	H,F,GT	H,F,GT	H,E,GT	H,F	H,F	H,F		H,F	H,F,GT	H,E,F	H,F,GT	H,E,GT	H,F			H,F,GT	H,E,GT	H,F,GT

Figure B1: Incompatibility chart (Winder and Zarei, 2000) for predicting reactivity of different functional groups of chemicals.

Appendix C – Results from Safety-Technology Assessment Layer (STAL)

The results from Safety-Technology Assessment Layer (STAL) to prevent primary toxic, flammable vapour releases from any vessel are presented here.

Table C1: Production of an azo dye intermediate: Safety technologies selected in STAL to prevent primary toxic, flammable vapour releases.

Case Study 1: Production of an azo dye intermediate (safety technologies used to mitigate possible worst-case scenarios)			
Scenarios	**Hazard Index**	**Safety Technology Reduction Factors**	**Remaining Hazard Index**
Primary toxic release scenario	0.68	a) Single containment (-0.3) **Or** b) Leak detection (-0.1) + interlocks, remote control valves (-0.1) + emergency shutdown system (-0.1) *Total Reduction Factor = (-0.3)* **[Table 2.5.3]**	a) 0.38 b) 0.38

Table C2: Sulfonation of a nitro-aromatic compound: Safety technologies selected in STAL to prevent primary toxic, flammable vapour releases.

Case Study 2: Sulfonation of a nitro-aromatic compound (safety technologies used to mitigate possible worst-case scenarios)			
Scenarios	**Hazard Index**	**Safety Technology Reduction Factors**	**Remaining Hazard Index**
Primary vapour cloud scenario	0.62	a) Sufficient cooling capacity (-0.2) **[Table 2.5.1]**	a) 0.42
Primary toxic release scenario	0.77	a) Single containment (-0.3) **[Table 2.5.3]**	a) 0.47

Table C3: Production of mono-nitro-toluene: Safety technologies selected in STAL to prevent primary toxic, flammable vapour releases.

Case Study 3: Production of mono-nitro-toluene (safety technologies used to mitigate possible worst-case scenarios)			
Scenarios	**Hazard Index**	**Safety Technology Reduction Factors**	**Remaining Hazard Index**
Primary fire/explosion scenario	0.86	a) Explosion zones (-0.2) + inertization (-0.3) *Total Reduction Factor = (-0.5)* **[Table 2.5.2]**	a) 0.36
Primary toxic release scenario	0.54	a) No manual handling of toxic substances (-0.1) **[Table 2.5.3]**	a) 0.44

Table C4: Production of poly-acrylonitrile: Safety technologies selected in STAL to prevent primary toxic, flammable vapour releases.

Case Study 4: Production of poly-acrylonitrile (safety technologies used to mitigate possible worst-case scenarios)			
Scenarios	**Hazard Index**	**Safety Technology Reduction Factors**	**Remaining Hazard Index**
Primary vapour cloud scenario	0.61	a) Sufficient cooling capacity to avoid undesired volatility (-0.2) **[Table 2.5.1]**	a) 0.41
Primary fire/explosion scenario	0.9	a) Explosion zones (-0.2) + inertization (-0.3) *Total Reduction Factor = (-0.5)* **[Table 2.5.2]**	a) 0.4
Primary toxic release scenario	0.5	a) No manual handling (-0.1) **[Table 2.5.3]**	a) 0.4

Table C5:   Methyl-ethyl-ketone-peroxide in storage tank: Safety technologies selected in STAL to prevent primary toxic, flammable vapour releases.

Methyl-ethyl-ketone-peroxide in storage tank (safety technologies used to mitigate possible worst-case scenarios)			
Scenarios	**Hazard Index**	**Safety Technology Reduction Factors**	**Remaining Hazard Index**
Primary fire/explosion scenario	0.71	a) Explosion zones (-0.2) + fire water and foam monitors (-0.1) *Total Reduction Factor = (-0.3)* **[Table 2.5.2]**	a) 0.41
Primary toxic release scenario	0.5	a) No manual handling (-0.1) **[Table 2.5.3]**	a) 0.4

Table C6:   Hydroxylamine (HA) in distillation column: Safety technologies selected in STAL to prevent primary toxic, flammable vapour releases.

Hydroxylamine (HA) in distillation column (safety technologies used to mitigate possible worst-case scenarios)			
Scenarios	**Hazard Index**	**Safety Technology Reduction Factors**	**Remaining Hazard Index**
Primary vapour release scenario	0.8	a) Pressure measurement system with alarm (-0.2) + sufficient cooling capacity (-0.2) *Total Reduction Factor = (-0.4)* **[Table 2.5.1]**	a) 0.4

Table C7: Production of acrylic resins: Safety technologies selected in STAL to prevent primary toxic, flammable vapour releases.

Process case study: Production of acrylic resins (safety technologies used to mitigate possible worst-case scenarios)			
Scenarios	Hazard Index	Safety Technology Reduction Factors	Remaining Hazard Index
Primary vapour cloud scenario	0.65	a) Single containment (-0.3) **[Table 2.5.1]**	a) 0.35
Primary fire/explosion scenario	0.91	a) Explosion zones + single containment (-0.5) **[Table 2.5.2]**	a) 0.41
Primary toxic release scenario	0.68	a) Single containment (-0.3) **[Table 2.5.3]**	a) 0.38

Appendix D - EHS tool

The goal of chemical industry to bring the product speedily onto the market generates a big time pressure on chemists and chemical engineers in the laboratory and R&D in the process development stage. This pressure can cause minor or major flaws, shallow assessment of the EHS aspects and process conditions, which can lead to accidents in the plant or high toxic level in the product or in chemical plant and even sometimes the refusal in acquiring license from government agencies to perform the process or to bring the product onto the market. This all can lead to property and environmental damages and fatalities. This necessitates the use of automated tool that can assess EHS aspects and can evaluate the degree of inherent safety in the plant under the expert's supervision. This tool has been created after extending assessment tool developed by Koller et. al (1999) for EHS assessment. The EHS manual (Fischer et al., 2003) is also prepared for explanation of the working of the tool. The tool is explained here in detail for each layer of SREST method:
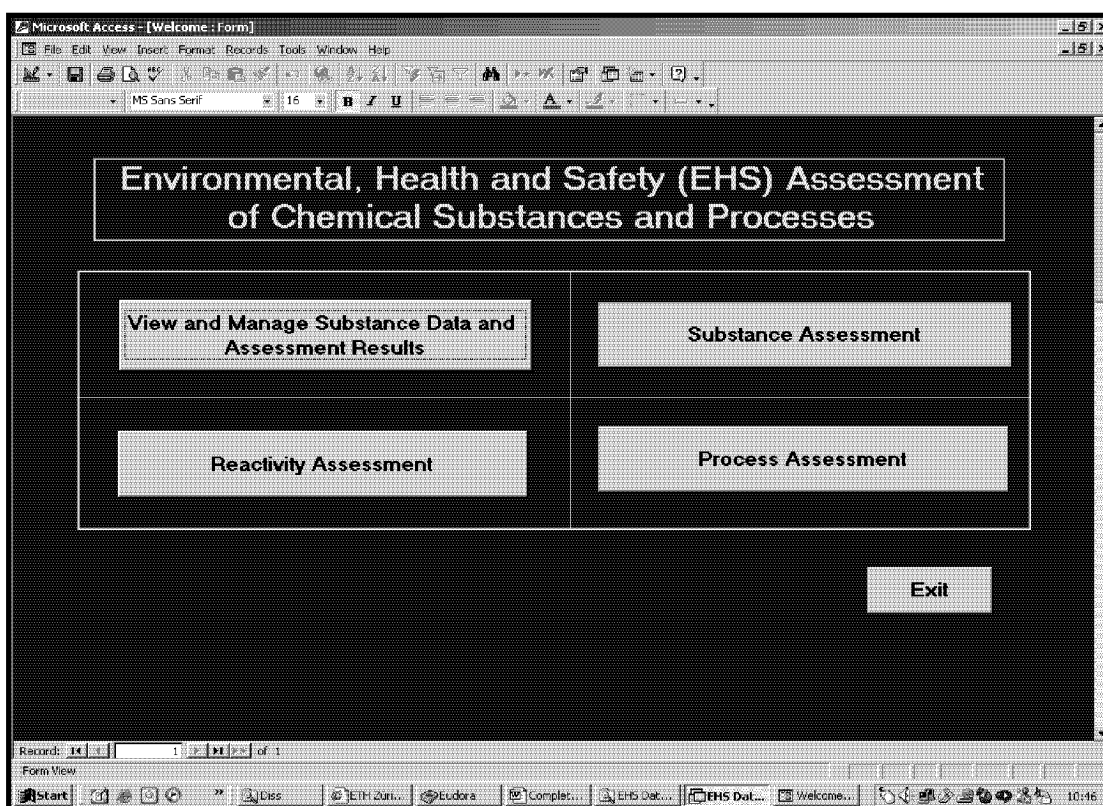
Figure D1: User interface for major steps in EHS tool.

Substance Assessment Layer: The different tasks of the tool in this layer are data acquisition via interfaces to various databases and MS-Excel sheet; data combination and analysis; missing property data calculation; substance assessment by EHS method (Koller, 2000); user interface to simplify the use of the tool; and result presentation in MS-Excel as shown in Figure 3.1.1 in Chapter 3.

It is well known that in early stages of design, there is a big gap in information and property data of chemicals (intermediate, by-products and products) available. Industries and scientists perform experimental work to collect the data (physical and chemical properties, toxicity and environmental data etc.) of various chemicals. Different organizations and government agencies are working to collect these data with the help of industries and are preparing user-friendly databases (IUCLID, IGS, CHRIS etc.). Chemical industries are providing Material Safety Data Sheets (MSDS) with their products according to the safety rules. These efforts are worth enough to provide possible exchange of information among industries and academia; to provide chemical data to assess different aspects (for example, environment, safety, health and economic etc.), especially, in early design stage when there is lack of data; help chemists and chemical engineers in the laboratory to get data easily from user-friendly databases.

The efforts are undertaken by Koller et. al (1999) to develop an MS-Access tool which collects data from different databases, combines these data with the help of statistical methods, calculates missing properties and assesses the substances with the help of EHS method. This tool has been augmented with the new user-interface and the possibilities of:

1. Collecting data via interfaces to some new databases,
2. Importing user's data with the help of MS-Excel connection,
3. Combine data from user's choice of databases or to use the user's data for assessment,
4. Tracking data from different databases with the help of new IDs given to each database and each combined and calculated data,
5. Calculation of minimum and maximum values of substance properties available from different databases, etc.

There have been accidents reported due to wrong data or information coming from different databases or MSDSs (Material Safety Data Sheet). One should analyze and compare these data or information before using them in detailed process design. In this tool, comparison of the data quality from different sources could be done with the help of results in the form of standard deviation, minimum and maximum values of properties etc. Unreliable sources could be recognized and possible errors could be avoided. In the case of missing property data, connection with QSAR and simulation code for some environmental models is made to fill the gap.

Figure D2: User interface for viewing results of substance assessment in EHS tool.

Reactivity Assessment Layer: In this tool, reactivity information is collected from Bretherick's reactivity database (Urben, 1999), Chemical reactivity worksheet (NOAA, 2000) and user's experimental results about reactivity via MS-Excel sheet as shown in Figure 3.2.1 in Chapter 3. Reactivity is predicted from the list of hazardous reactions and group incompatibility chart. After collecting all the data, automatic crosscheck is made for all the substances present in the plant with Air, Water, cooling/heating media

and other substances and result is produced in the form of matrix in MS-EXCEL with the detail information in text file.
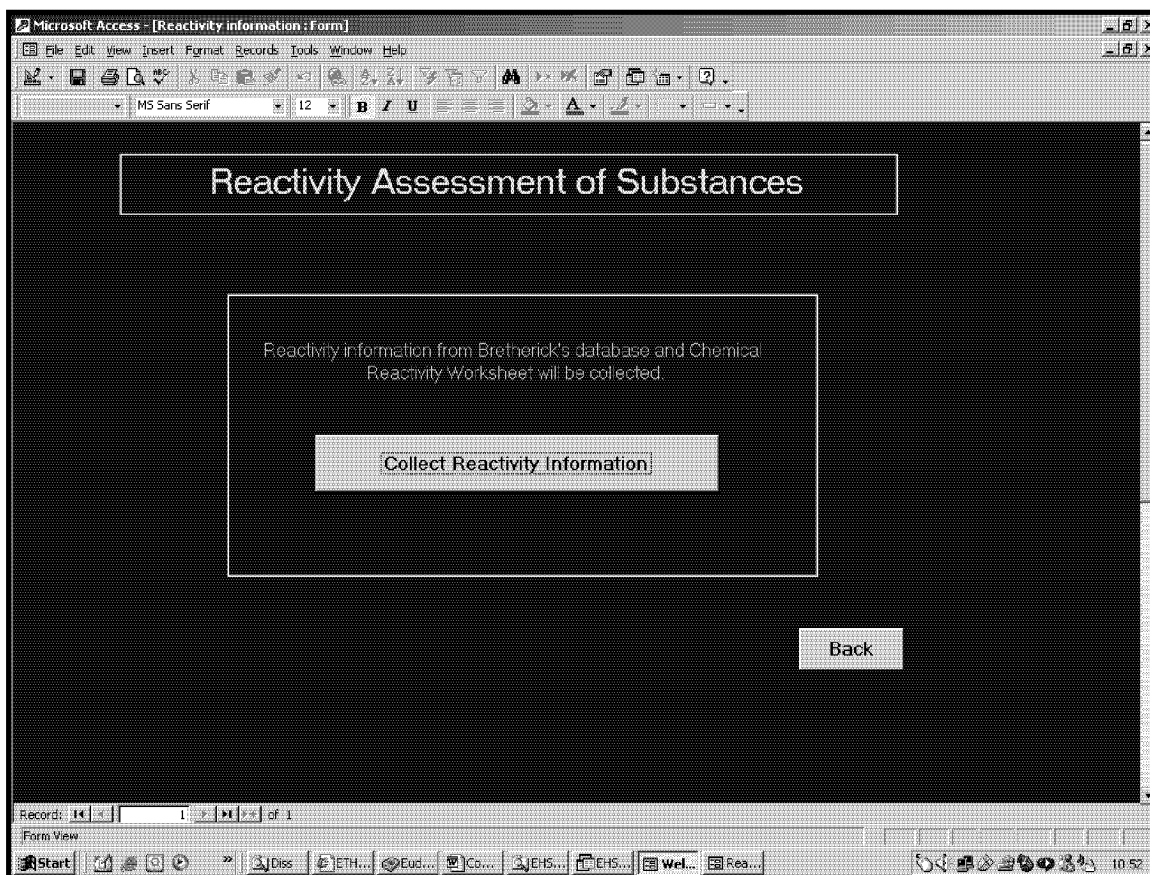

Figure D3: User interface for collecting and displaying reactivity information from different databases in EHS tool.

Equipment Assessment Layer: In the tool, substance properties are collected from various databases; laboratory data (for example, DSC data), process conditions in equipment unit and mass of the substances are acquired via user interface or Batch Plus^{TM} as shown in the Figure 3.3.1 in Chapter 3. Possible worst-case scenarios could be identified with the help of substance hazards from SAL (for example, Fire/Explosion, Acute Toxicity, Reaction/Decomposition etc.) and reactivity hazards from RAL (for example, incompatibility with Water, Air or other substances) etc. After identifying different worst-cases, these scenarios could be assessed by simulation code in this code and results can be obtained in the form of hazard indices for each unit operation and for each worst-case as shown in Figure 3.3.1 in Chapter 3.

Safety Technology Assessment Layer: In this tool, different lists of safety technologies for different possible worst-case scenarios and for handling toxic or flammable substances in unit operations are presented with reduction factors to select and assess the safety level related with a specific scenario and equipment.

Appendix E - Safety-technology design and costing for thermal runaway scenario in batch/semi-batch reactor

Exothermic reactions are employed in numerous chemical processes in industry. A major hazard is the development of thermal runaway, which could lead to reactor explosion and release of contaminants. If inherent design is not possible, the risk of such negative consequences can be significantly minimized by introducing an emergency relief system. The aim is to outline the methodology in designing and sizing emergency relief systems. The effectiveness and suitability of each design are compared using pioneering hazard reduction analysis and preliminary costing. A software program has been produced incorporating all of these objectives, and can be implemented in Safety-Technology Assessment Layer (STAL) in the SREST method. Different case studies have been performed to show the applicability of this design methodology.

a) Reaction system types

Complete relief system design and sizing can only be achieved by initially determining whether the pressure generated by the specified reaction, is that due to a vapour, gassy or hybrid system. The characteristics of each reaction type are:

a) *Vapour systems*: The pressure increase generated by a runaway reaction is solely that of the vapour pressure of the reacting mixture alone. This characteristically rises as the temperature of the mixture increases during runaway.

b) *Gassy systems:* The generated pressure resulting in a runaway reaction is entirely due to a permanent gas that is evolved by the chemical reaction.

c) *Hybrid systems:* The pressure produced is contributed from the evolution of a permanent gas and the increasing vapour pressure with increasing temperature.

Each reaction type can be determined from caliometric experiments, and are classified as either 'tempered' or 'untempered'. A taxonomy ordering each reaction type is provided in Figure E1.
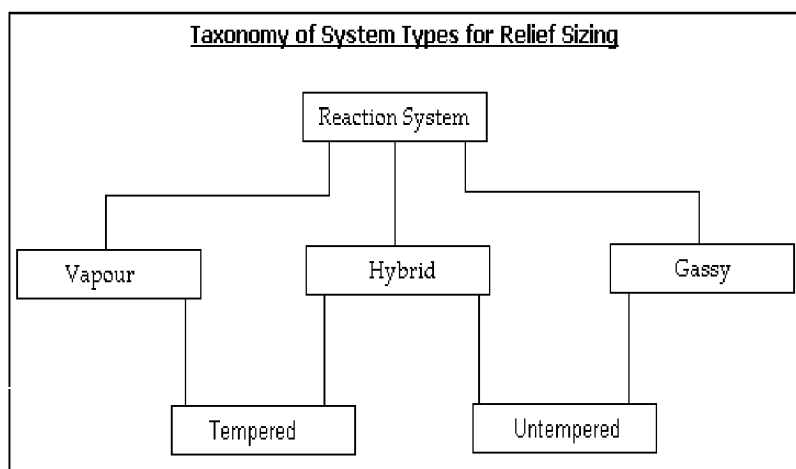
Figure E1: Taxonomy of reaction system types for relief sizing.

From Figure E1, it is noticeable that vapour reaction system types can be classified as tempered. Conversely gassy systems are treated as untempered. Hybrid systems are only classified as tempered if the contributing vapour pressure is greater than 10% of the total pressure.

Tempered systems are often defined as those in which the temperature and the pressure of a reaction can be significantly controlled by the removal of vapour (and therefore latent heat). However for untempered systems, the removal of gas from the reactor will not prevent the temperature and the corresponding rate of volumetric gas generation from increasing. Venting of untempered systems will only serve to remove material from the reactor. This difference in behaviour between tempered and untempered systems will ultimately determine which methodologies and formulae should be used to design a pressure relief system.

b) System arrangement

Industrial design for relief system indicates that a relief system should generally consist of three separate stages – a pressure relief device, a containment stage and a treatment system, which are all connected via intermediatory piping (see Figure E2).

A. Pressure Relief Device
B. Containment Stage
C. Treatment Stage
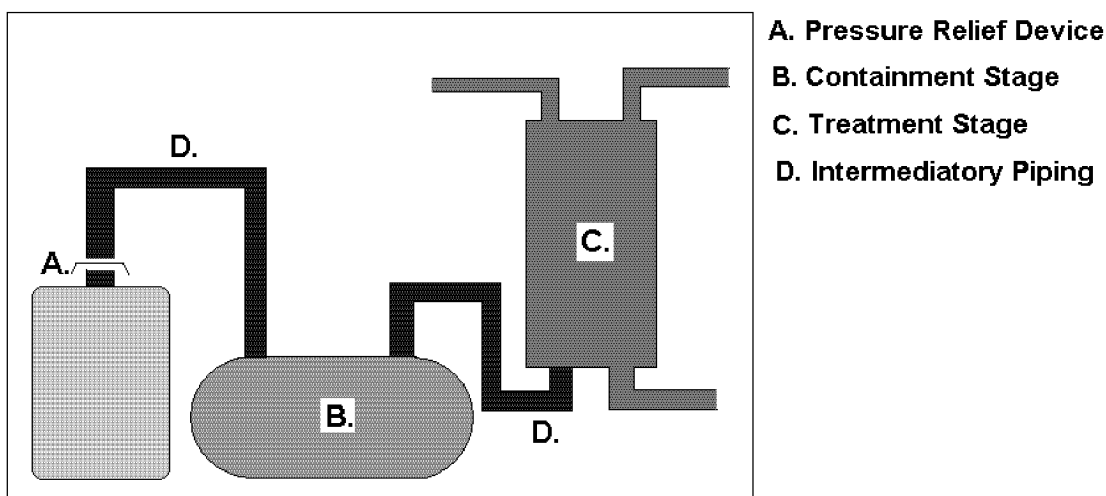D. Intermediatory Piping

Figure E2: General arrangement of a pressure relief device system.

Each system stage has various objectives that are to be met. The pressure relief device (A) is implemented to protect the reactor from overpressurisation, and can also be used to prevent an exotherm reaction system from fully developing into a thermal runaway. The containment stage (B) is considered since it is able to contain material removed from the reactor, and prevent potentially hazardous chemicals from being released into the environment. The treatment stage (C) is implemented to treat dangerous vapours that have a high potential of mobility, and also prevent overpressurisation of the complete system.

This general system arrangement is the basis for complete relief system design and sizing. A table with the most commonly used component types for each stage is provided in Table E1.

Table E1: Available component types for each stage in pressure relief design.

Relief system stage	Available component types
A. Pressure relief device	Bursting disc
	Safety relief valve
B. Containment stage	Cyclone separator
	Dump tank
	Quench tank
C. Treatment stage	Gas absorber
	Flare

c) Design methodology

To design a complete relief system, one suitable component must be selected for each stage. This can be achieved by comparing the characteristics of each component and the corresponding advantages and disadvantages. The key characteristics, advantages and disadvantages for the components are presented in detail in Tripuraneni (2002).

Pressure relief system sizing: To decide upon which sizing method to apply for the selected bursting disc or safety valve, the reaction system type (vapor, gassy or hybrid) must first be defined from caliometric experiments. A suitable decision tree can be used as the first step to obtain a suitable sizing method for each reaction system type. These decision trees or flowcharts (see Figures E3, E4 and E5) are provided by DIERS (**D**esign **I**nstitute of **E**mergency **R**elief **S**ystems), who are the internationally recognized as the world leaders in the research of emergency relief systems. These decision trees and design of bursting disc or safety valve for each reaction system type are given in detail in Tripuraneni (2002) in the following sections; Section 4.1.1 for a vapour system; Section 4.1.2 for a gassy system and Section 4.1.3 for a hybrid system. All sizing methods/assumptions/flowcharts/ advantages and disadvantages of pressure relief system sizing in Tripuraneni (2002) are taken from "Workbook for Chemical Reactor Relief System Sizing (Etchells and Wilday, 1998)".
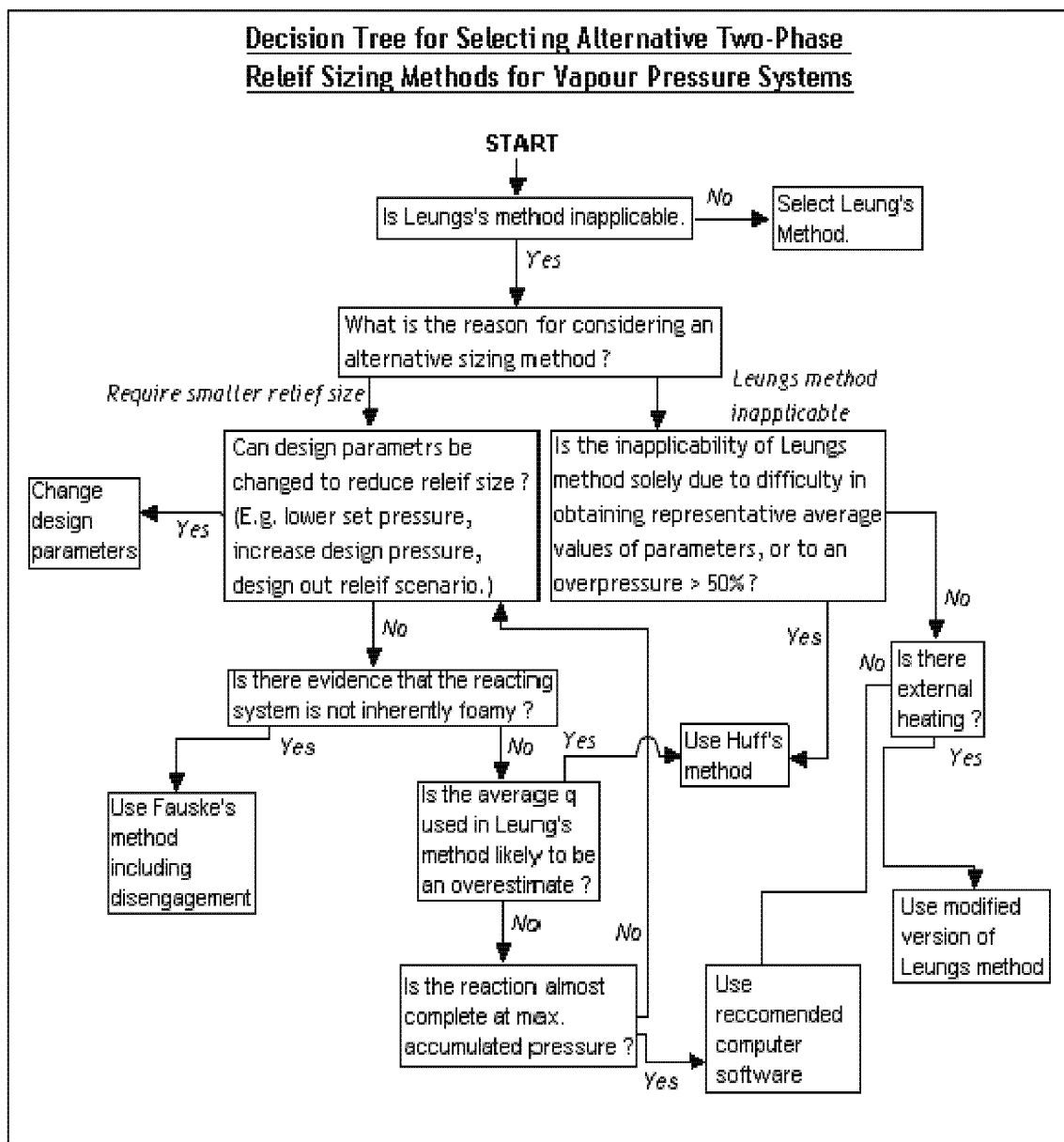
**Decision Tree for Selecting Alternative Two-Phase
Releif Sizing Methods for Vapour Pressure Systems**

Figure E3: Decision tree for the selection of a vapour system sizing method (Etchells
and Wilday, 1998). All the methods mentioned in this figure are explained
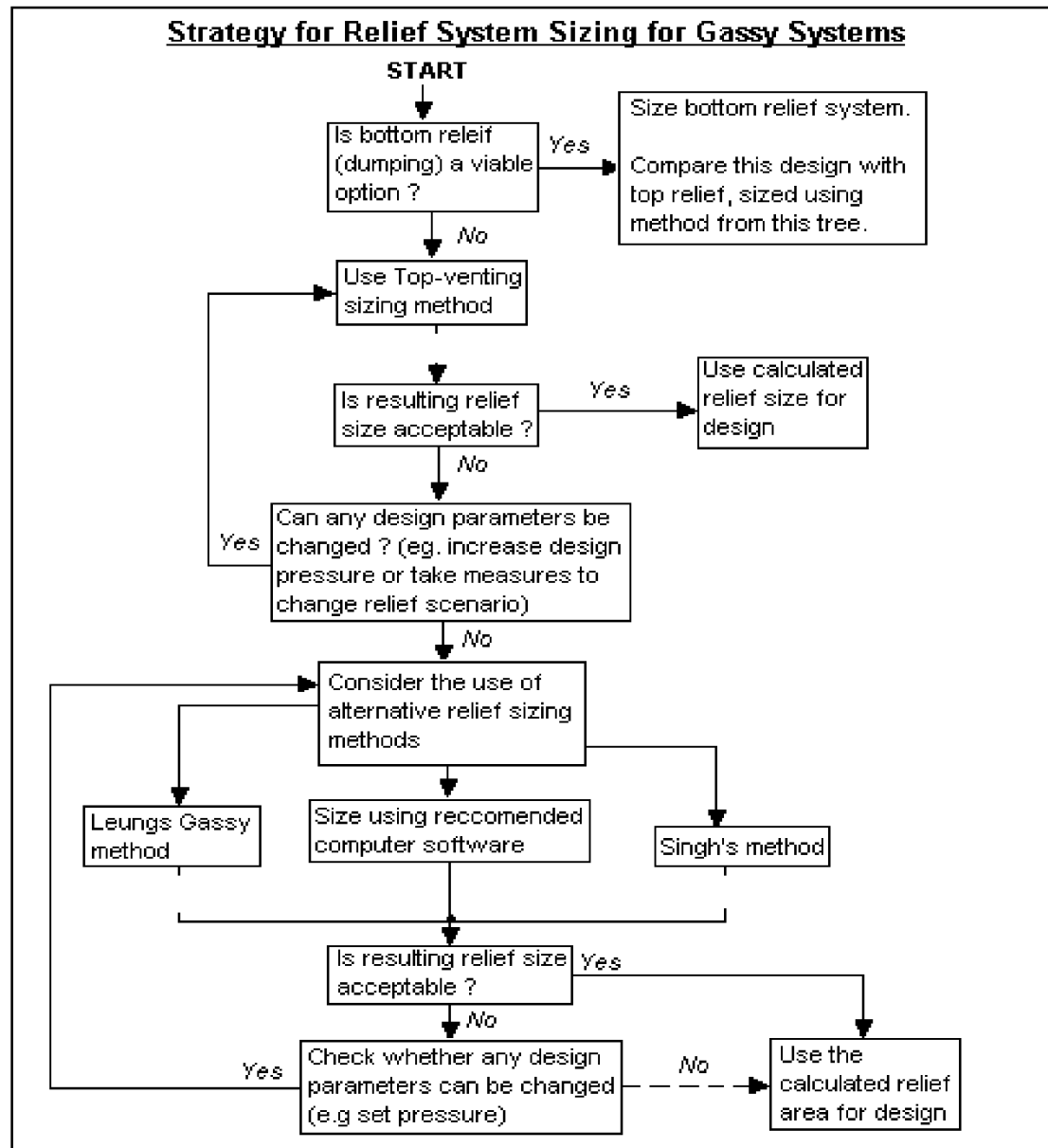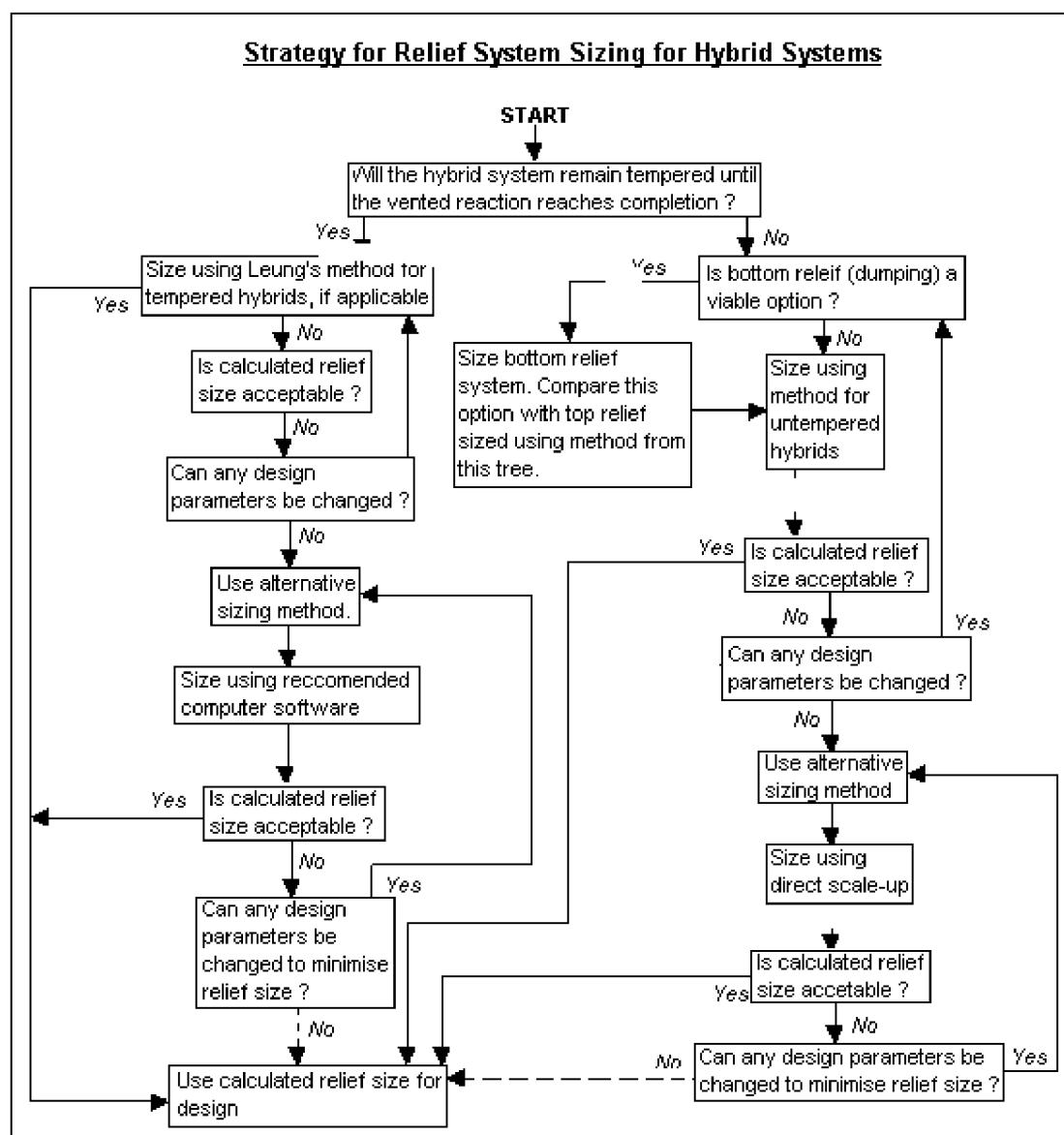in detail in Etchells and Wilday (1998) and in Tripuraneni (2002).

Figure E4: Decision tree for the selection of a gassy system sizing method (Etchells and Wilday, 1998). All the methods mentioned in this figure are explained in detail in Etchells and Wilday (1998) and in Tripuraneni (2002).

Figure E5: Decision tree for the selection of a hybrid system sizing method (Etchells and Wilday, 1998). All the methods mentioned in this figure are explained in detail in Etchells and Wilday (1998) and in Tripuraneni (2002).

Containment system selection and sizing: Once the safety valve or bursting disc has been sized and the piping section calculated to be suitable, a component for system containment must be chosen. This can be done with the help of decision tree available (see Figure E6). A final check is required to ensure that a particular containment system is a feasible component for the containment stage. This can be achieved by viewing the assumptions and conditions of applicability of the component and the sizing method given in Tripuraneni (2002). All sizing methods/assumptions/flowcharts/ advantages and disadvantages of containment system sizing (dump tank, cyclone separator and quench tank) in Tripuraneni (2002) are taken from McIntosh et al. (1995a, 1995b) and McIntosh and Nolan (2000).
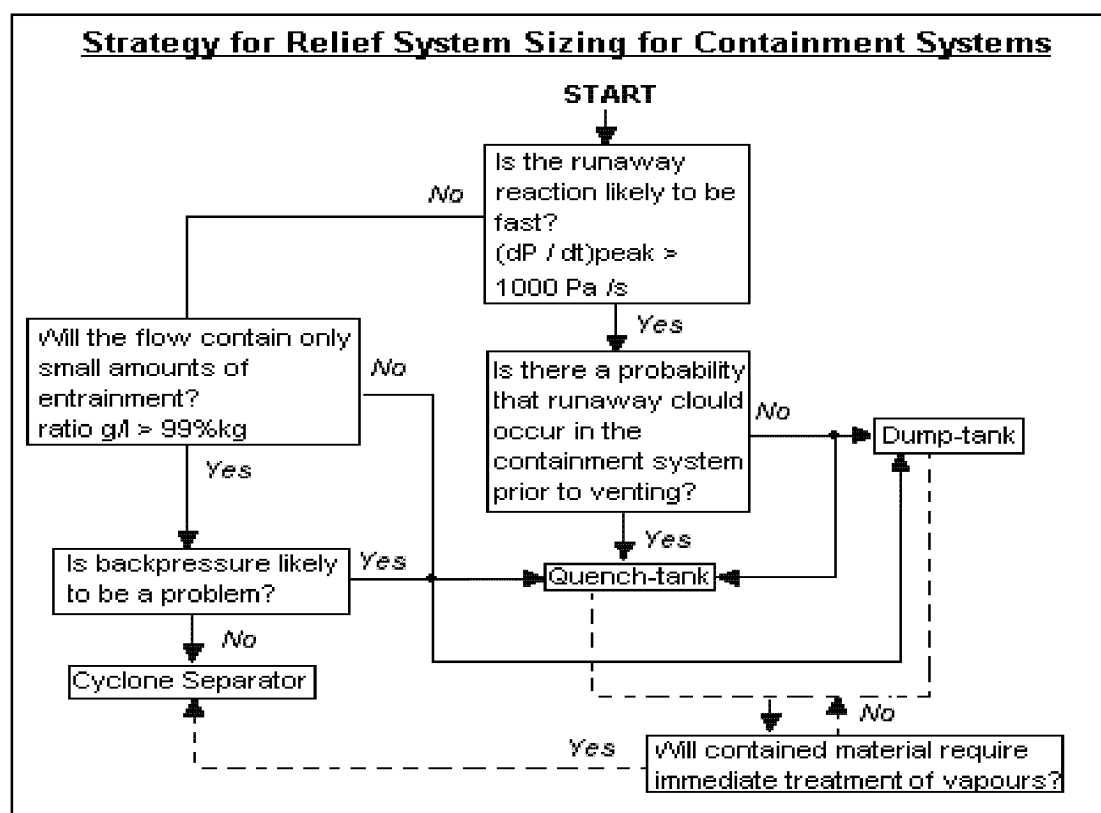

Figure E6: Decision chart for containment component selection.

Treatment system sizing: Once the containment system section has been determined to be suitable, only the treatment stage must be selected, designed and sized to complete the relief system. This can be done with the help of a decision tree (see Figure E7). The treatment system sizing methods are given in detail in Tripuraneni (2002). All sizing methods, assumptions, flowcharts, advantages and disadvantages of treatment system sizing (gas absorbers or flare) in Tripuraneni (2002) are taken from McIntosh and Nolan (2000), http://www.uop.com/gasprocessing/TechSheets/UPak.pdf, http://www.efunda.com/formulae/fluids/calc_pipe_friction.cfm, http://www.epa.gov/ttn/catc/dir1/cs5-2ch1.pdf and "Environmental engineering lecture notes, professor Livingston, imperial college London".

If flaring, venting or gas absorption is not an option, the vapours should not be treated and left in the containment vessel. If containment of vapours is not possible (i.e., in a cyclone separator), a containment tank must be added to the relief system for containment of gases. This step must also be applied if a runaway scenario is possible in the containment stage and immediate treatment of vapour is not possible.

Direct venting of vapours or gases into the atmosphere should only be considered if the substances will have no diverse environmental, health or safety effects. Notification to the national regulatory body of the substances involved is required prior to a venting scenario.
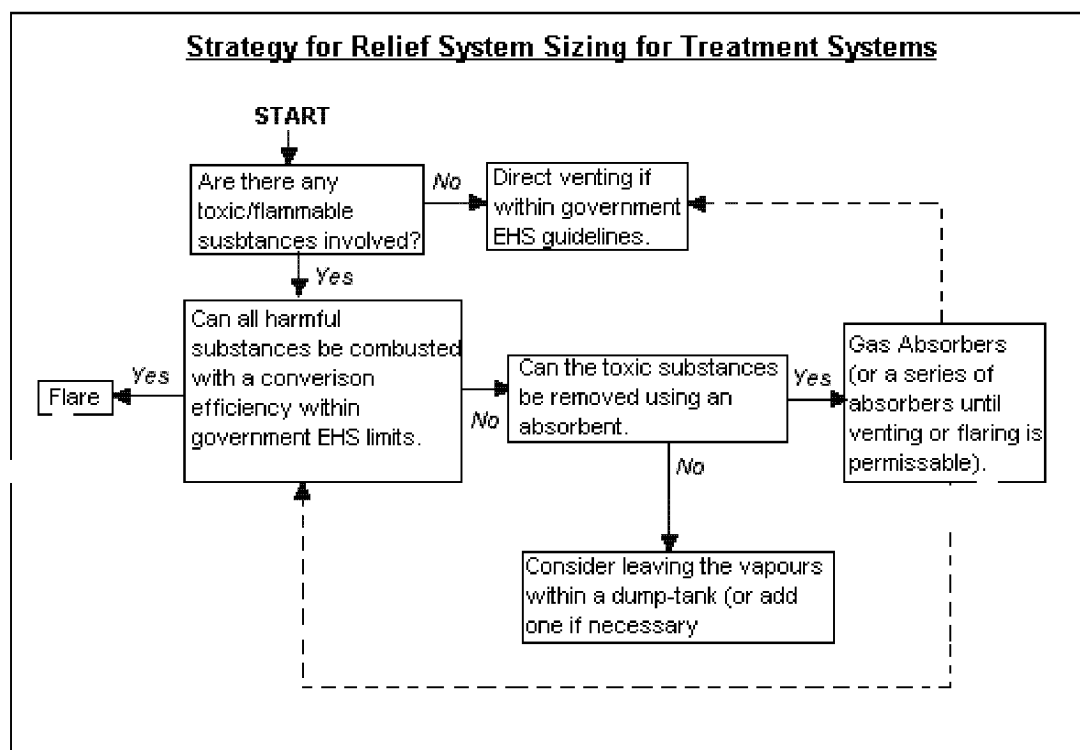
Figure E7: Decision tree to determine most suitable method of treatment.

d) Costing of system components

The cost correlations given in Tripuraneni (2002) have been determined from readily available industrial data, reliable costing programs and verified literature. Marshall and Swift indices have been used to make the results applicable to 2002. These correlations have been aimed to be accurate to an order of magnitude (40-60%), and for preliminary plant equipment purchase analysis. The assumptions and process applied to formulate these equations are provided in Appendix F1 in Tripuraneni (2002).

e) Software tool

A program incorporating the selection, design and sizing of a complete safety relief system for thermal runaway has been produced incorporating all the methods, formulae, and conditions of applicability. A cost assessment for different safety technologies has also been implemented. The detail of the tool is given in Tripuraneni (2002).

Curriculum Vitae

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Qualifications

Ph.D. in Chemical Engineering, [August 2000 - February 2004]
Swiss Federal Institute of Technology Zürich (ETHZ), Switzerland.
Title: *A Hierarchical Approach for Assessment of Principal Hazards in Early Stages of Chemical Process Design.*
    Examiner: Prof. Konrad Hungerbühler (ETHZ).
    Co-examiners: Prof. Francis Stoessel (EPFL and Sicherheitsinstitut) & Dr. Ulrich Fischer (ETHZ).

Master's degree [M.S. (Research)] in Chemical Engineering, [July 1998-June 2000]
Indian Institute of Technology Delhi (IITD), New Delhi, India.
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Bachelor's degree [B.E.] in Chemical Engineering (Honours, 79%), [July 1994-June 1998],
Government Engineering College, Ujjain, M.P., India.
Title: *Some Studies in Fluidization and Determination of Minimum Fluidization Velocity and Suitable Particle Size.*

Languages

Gujarati (Mother tongue), Hindi, English, German

Computer Knowledge

Visual Basic, Fortran, C++, Java, MS-Access database, SQL, Aspen Plus®, Batch Plus^{TM}, g-PROMS, etc.

Industrial Training

1. Viscos Staple Fiber Plant, Grasim Industries Ltd., Karnataka, India (June 97- July 97).
2. BASF, Ludwigshafen, Germany (1st Jan. 2000 to 29th Feb. 2000).

Software Experience

1. Experience in improving super database (developed in MS-Access and connected with different databases, e.g., Oracle), called, EHS (Environment, Health and Safety) assessment tool.
2. Experience in developing reactivity database (MS-Access) [generation of reactivity matrix automatically with the help of interface with Bretherick's chemical reactivity database.
3. Experience in developing SREST (Substance-Reactivity-Equipment-Safety-Technology layer assessment method) tool (MS-Access).

Extra and Co-Curricular Activities

1. Student member of "Indian Institute of Chemical Engineers".
2. Executive member of Chemical Engineering Society, Ujjain.
3. Service in National Cadet Corps (NCC) (1990 to 1991) and in National Service Scheme (NSS) (1998).
4. Interested in singing (Hindi songs), playing cricket, ice-skating, snowboarding, swimming etc.