The *INSET* Toolkit

INherent **S**HE **E**valuation **T**ool

Combined Version in Single Document

Volumes 1 and 2 - The Full Toolkit

The *INSIDE* Project Team Partners:

AEA Technology

Eutech Engineering Solutions

INBUREX

Kemira Agro

TNO

VTT Manufacturing Technology

Integrated Version, November 2001

The *INSIDE* Project

Important Information!

About this Version

This version of the *INSET* Toolkit was collated in 2001 from the original toolkit Wordperfect files. Limited format changes have been applied to the document to aid navigation and clarity, including the regeneration of certain figures in a compatible electronic format, addition of a hyperlink contents list, and changes to the page numbering, headers and footers. There are some format, layout and page break discrepancies between this version and the original version, since the original toolkit was made up of many different individual files; however the technical content remains the same.

Disclaimer

The *INSET* Toolkit presented in this document was developed as part of a research project to promote the use of inherent safety, health and environmental (SHE) approaches to process plant development and design. The material contained within the *INSET* Toolkit is designed to act as a catalyst for improved inherent SHE management. It contains a number of ideas for tools and methods that may assist chemists, engineers and project managers address inherent safety, health and environmental aspects. However, it should be recognised that the Toolkit does not represent a comprehensive or proven approach to SHE management and has not been extensively trialed or tested; the material it contains should therefore be treated with caution.

The material in this document version of the *INSET* Toolkit has been made available to obtain comments from industry and the scientific community. Organisations may wish to use its contents to help promote inherent SHE, but this is on the strict understanding that this is entirely at the users own risk. The *INSIDE* Project Team Partners DO NOT WARRANT or make any representation that this document is suitable for any purpose. The information in the Toolkit is given in good faith and belief in its accuracy, but does not imply the acceptance of any legal liability or responsibility whatsoever, by the authors or the *INSIDE* Project Team Partners, for the consequences of its use or misuse in any particular circumstances.

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The *INSET* Toolkit

INherent **S**HE **E**valuation **T**ool

Volume 1

The *INSIDE* Project Team Partners:

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The *INSET* Toolkit

INherent **S**HE **E**valuation **T**ool

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Foreword

This *INSET* Toolkit is one of the outputs of a three-year European Union co-funded research project to encourage the systematic application of inherently safer principles to process development and plant design. It consists of a framework and a number of tools to help chemists, engineers and others consider inherent safety, health and environmental (SHE) aspects of performance in the early stages of a project. The toolkit also includes a brief introduction to inherent SHE, providing a means to raise awareness of inherent SHE and its benefits. Its application should lead the user towards an inherently safer, environmentally friendlier, and better optimized design.

We are satisfied with what we have achieved. Nevertheless, as with many research projects, there has not been sufficient time to do everything we would have liked, and this is reflected in the scope and status of some of the tools. The toolkit includes many tools that we think merit further development or validation, and some important areas remain poorly covered – we ask users to bear these shortcomings in mind when applying the tools and interpreting any results. We hope that users will take these initial ideas and tools, and develop them further to meet their particular needs and ways of working so that inherent SHE becomes an accepted part of any project. If you have any queries or suggestions please contact one of the *INSIDE* Project main partners. We would be happy to advise on the application and further development of the toolkit and inherent SHE in general.

Finally, please note that the *INSET* tools are, by their nature, focused on inherent safety, health and environmental (SHE) aspects of performance. They should provide a useful complement to other hazard and SHE studies, but are *not* a substitute for these. Users will still need to ensure that any process or plant they intend to operate will be safe and meet all relevant regulatory and company requirements.

We hope you find the *INSET* Toolkit as useful and stimulating to apply as we did in its development.

The *INSIDE* team

Acknowledgement

This toolkit is the main result of the *INSIDE* Project, a European-wide research project to progress the adoption of inherently safer approaches to chemical process development and plant design. The research was carried out by a joint industry and research organization team drawn from AEA Technology, TNO, VTT Manufacturing Technology, Eutech Engineering Solutions, INBUREX, Kemira Agro and ICI Polyurethanes under the Major Hazards research programme of the European Commission, DG XII (Contract No. EV5V-CT94-0416).

The project team wishes to acknowledge the support from the European Commission and the organizations involved. We also wish to thank the UK Health and Safety Executive and the Dutch Ministry of Social Affairs and Employment for their additional financial support.

Finally we would like to offer our thanks to all those individuals that have been involved in the surveys during the *INSIDE* Project or in the trials of the *INSET* Toolkit. The following companies and organizations were represented:

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Executive Summary

"A clever man is one who finds ways out of an unpleasant situation into which a wise man would never have got himself" (D.A. Segre)

Inherent SHE

The expansion of the chemical industry in the 1960s and 70s, both in the size of plants and the complexity of processes, resulted in the development of techniques such as HAZOP, risk assessment and inherent safety as means to manage these risks more effectively. HAZOP and quantified risk assessment (QRA) are methods that are in common use today. However, the ideas of inherent safety have not been as successfully adopted. This may be due to many reasons, but one of the main factors has been the lack of recognized methods or tools to address inherent SHE at the early stages of process development and design. This toolkit provides the first major attempt to turn this concept into a set of practical tools so that inherent safety can enjoy the same level of application as other methods.

Principles such as *substitution, intensification, moderation* and *simplification* are often used to capture the essence of the "inherently safer" approach. It is widely recognized that the timely and effective use of these principles can make a process and plant cheaper to build and operate as well as improve safety, health and environmental performance. Why?

- Conventional plant design often relies on extensive "add-on" engineered safety systems and waste treatment facilities to achieve an appropriate level of safety, health and environmental (SHE) performance. These systems can be expensive to provide and maintain, and do little, if anything, to improve the performance or operation of the plant.
- If the basic process or plant design can be developed such that any hazards and wastes are avoided, eliminated or minimized at source, the need for, or reliance on, these "add-on" systems and facilities may be removed or reduced. The process and plant may also become simpler to design, build and operate. Such a process or plant may be termed "inherently safer". It may offer the prospect of a plant that has improved SHE performance and lower capital or operating costs.

We believe inherent SHE (safety, health and environment) offers more cost-effective SHE performance, and can add real commercial value to the process and design unlike HAZOP and risk assessment which usually simply provide some cross-check that the design is "safe enough".

An "inherent SHE" approach would benefit industry, the workforce, the public at large, and the environment, and could help provide the competitive edge needed for continued successful business performance in the increasingly competitive world market. It encompasses the key elements of waste minimization, clean technology, energy efficiency and sustainable development – key factors for future investments. An inherently SHE plant would require less costly safety systems, less waste treatment facilities, less management attention, fewer operational procedures, and less effort to run it, and would impose less risk to those who operate it or live or work near it and to the environment around it.

The *INSIDE* Project

The *INSIDE* Project was set up in August 1994 to bring together industry and researchers in this field to develop practical ways to encourage the use of inherent SHE in process development and plant design. As a starting point for our work, a survey was carried out across the European process and chemical sector. This found a lack of awareness of the inherently safer concepts and benefits outside the established safety specialists field. As a result, few organizations actually recognize, promote and use the concept in development and design. Where good examples of inherently safer processes and plant were found, these had generally arisen from economic pressures or as a result of accidents or near-misses in the past, rather than a systematic application of the inherent safety principles. A few leading companies are starting to implement inherent SHE into their projects in a more systematic way, and most of the managers we spoke to recognized the potential commercial and economic benefits of an inherently safer process and plant.

Several suggestions for improving the use of inherent SHE in industry were proposed:
- the attitude of the regulators to inherent SHE,
- the need for good case studies and evidence of the benefits of inherent SHE,
- the need to convince some senior managers and project leaders of the benefits of inherent SHE, so it can be championed throughout the design and development departments,
- the need to include inherent safety as an integral part of education and training, and
- the need for tools and methods for addressing inherent SHE through the life-cycle of a project.

The result of our work on the *INSIDE* Project has been a collection of tools and methods, the *INSET* Toolkit, that is specifically designed to meet the needs of this latter point.

The *INSET* Toolkit

This *INSET* Toolkit serves two functions:
- it is a means to raise the awareness of persons directly or indirectly involved either in the selection of the process by which a desired chemical product is produced or in the design of the corresponding chemical plant, and
- it is a practical toolkit to be used by these persons as an integral part of the development, design and decision-making processes.

Many of the decisions determining the basic process and unit operations are taken early in a project, sometimes before formal safety studies are initiated. It is therefore important that inherent SHE issues are considered at these early stages where the basic safety and environmental characteristics of the process are determined.

The *INSET* Toolkit provides chemists, engineers and managers with the framework and tools to systematically identify, evaluate, optimize and select inherently SHE processes and designs. It can be applied to projects for a completely new process or plant, an existing process in a new plant, or modifications to an existing plant and process. The *INSET* Toolkit treats safety, health and environmental hazards in an integrated way to ensure the conflicts and synergies between these aspects are recognized and effectively managed. The versatile and flexible toolkit concentrates on the key early stages of a project where almost all the main decisions which determine the SHE performance of the plant are taken:
- Stage I: Chemistry route selection
- Stage II: Chemistry route detailed evaluation
- Stage III: Process design optimization
- Stage IV: Process plant design.

It is recognized that process selection and plant optimization are constrained and guided by many factors other than merely safety considerations. Feasibility and economic factors are also vital aspects, and this has been addressed in the development of the toolkit. The optimizing methods it offers can be used to optimize against many criteria, and not just those for SHE, and the decision support elements provided allow for these other factors to be included. It is hoped that the *INSET* Toolkit will find use as a more general means of encouraging the search for better alternatives, not just those for inherent SHE.

The *INSET* Toolkit can also play an important role in raising the awareness of an inherent SHE approach, some of the main principles behind this, and the advantages such an approach can bring to the industry and society as a whole. It includes a general introduction to inherent SHE and, via the tools and supporting information, it gives suggestions and lessons from past experience on how to implement inherent SHE in practice and on some of the main issues that need to be considered.

INSET Contents

The *INSET* Toolkit is divided into four parts which are presented in two volumes. Part 1 is concerned with a general introduction to inherent SHE and the toolkit. Chapter 1 is well worth reading if you are interested in introducing the concept and principles of inherent SHE into your work practices. It provides ideas which will help you to understand, establish and develop inherent SHE in your company and assist you when you wish to implement it into projects and day-to-day working. Chapter 2 introduces the *INSET* Toolkit, describing its philosophy and overall use. It includes flowcharts to help users navigate around the toolkit. Chapters 3 to 6 describe some of the key SHE aspects of the Stages I to IV, and provide detailed advice on what tools to use at each of these stages and how to optimize this to suit the needs of your project and process characteristics.

Part 2 is concerned with the actual tools themselves. Each of these tools comes with its own user guide and forms.

Part 3 contains general supporting material, such as a summary of a number of industrial trials, a list of inherent SHE examples, and a glossary of terms. It also includes a presentation package to help you communicate the inherent SHE principles and benefits and explain the use of the *INSET* Toolkit to others in your organization – and their managers.

Examples of tool applications and any useful supplementary information are given in Part 4.

The rest is up to you

We hope you will find the *INSET* Toolkit of value to your work and business. Remember it is not intended as some rigid procedure, but as a flexible toolkit that you can adapt to suit your own requirements. We wish you good luck in your endeavours.

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Part 1 - Inherent SHE and the *INSE*T Toolkit

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1. INTRODUCTION TO INHERENT SHE AND THE *INSET* TOOLKIT

While most may be familiar and quickly identify with the term "safety", the same can not be said for "inherent safety", and in the same vein "inherent SHE" conjures up similar unfamiliarity. In an attempt to amend this situation, this chapter introduces the underlying concepts of inherent SHE and points out the various possible advantages of adopting such an approach to process development and design.

The major aspects arising from the results of the literature review and the interviews conducted in the *INSIDE* Project are here presented briefly, as is a contrast of regulations with regards to inherent SHE principles. By gaining an understanding of the differences between inherent SHE and passive safety aspects, and acknowledging and considering classic ISHE conflicts, a framework for hazard management in design can be developed. The *INSET* Toolkit is introduced as a collection of tools that aim to ensure that inherent SHE principles are considered and implemented from the earliest stages of process development and design.

1.1 Inherent SHE

The concept of the "inherently safer" plant has been with us now for many years [1], but despite its clear potential safety, health, environmental (SHE) and cost benefits, there have been few deliberate or recognized examples of its application in chemical plant design.

If the hazard potential of the plant can be reduced or even eliminated by careful selection of the process, together with good design of the plant, then the need for "add-on" safety systems and detailed management controls is reduced. The plant can be said to be "inherently safer" because its safety performance is less reliant on "add-on" engineered systems and management controls which can and do fail.

In practice, of course, many of the processes we operate do require hazardous materials to be held sometimes in considerable quantities, or pose the threat of runaway reactions. The question to be asked therefore is: "Can we change the process or the equipment to make it inherently safer?" Kletz [2] sets out the routes by which we can achieve an inherently safer plant:

- *intensification:* reducing the hazardous inventories;
- *substitution:* substituting hazardous materials with less hazardous ones (but recognizing that there could be some trade-offs here between plant safety and the wider product and life-cycle issues);
- *attenuation:* using the hazardous materials or processes in a way that limits their hazard potential, e.g. dissolved in a safe solvent, stored at low pressure or temperature; and
- *simplification:* making the plant and process simpler to design, build and operate, hence making it less prone to equipment, control and human failings.

Adopting an "inherent safety" approach such as that described above offers several advantages. Minimizing the inherent hazard of the plant offers savings by reducing the need for expensive safety systems and instrumentation, easing the burden on personnel and procedures, and simplifying on-site and off-site emergency plans. In the extreme, the hazards and risks may be so low that many of these controls may not be required at all.

Reducing complexity reduces the need for instrumentation and operator supervision, and cuts the maintenance bills. Smaller inventories may mean smaller plant and storage facilities, possibly lowering equipment costs together with costs related to the site size. Substitution for less harmful chemicals or processes could reduce the environmental impact of any wastes produced.

With all these potential benefits, it is considered surprising that inherent safety has such a low profile.

1.1.1 Current process development and plant design practices

A review of current process development and plant design practices has been carried out by interviewing over 20 companies across Europe. The companies were selected to represent a broad spectrum of the process and chemical industry. A number of design and engineering contractors and also a process licensor were included. The interviews provide a key insight into the way SHE issues are addressed in process development and design, and into the status of inherent approaches in these. They also reveal industries' views on the role of regulations and standards and inherent approaches.

Although no clear divisions emerged in the type of approach to process development and plant design, some typical characteristics indicated were:

- an informal team approach, with chemists and engineers working together and most of the SHE expertise residing in the group. This was typical of the smaller companies or divisions, or those developing many products utilizing existing or modular plants.
- a clear distinction between the development and design activities with less communication between these and possible conflicts of objectives. This was typical of most medium-sized and larger-sized companies who had separate engineering and R&D functions or used contractors for the design and engineering. SHE expertise could reside within the group or be sought from a separate department.
- projects where both the process development and design are carried out by the process design function. This was typical of engineering contractors or engineering departments in the heavy chemical and petrochemical sectors. The projects tend to be large and complex, and involve many design disciplines working in a very formal and structured way. Most use separate SHE functions to liaise with the design and development teams.

Although there were a few differences in the status and views of inherent SHE between the different types of organizations, the main findings were common to all sectors of industry and types of organization.

Few organizations had any formal SHE specialist involvement at the process development stage, relying on the skills of the development team themselves to be aware of SHE issues. SHE techniques used in the development stages included life-cycle analysis (LCA), process hazards analysis/review and calorimetric studies, but few organizations did more than one of these. By the design stage, around a third of the companies had brought in a SHE specialist, but for many the HAZOP of the detailed design schemes was the first structured safety review and by that time it is too late to make significant changes.

Most companies have some form of development and design procedures, and these usually covered most or all SHE aspects. However, only around a quarter of these procedures mentioned inherent SHE or any of its underlying principles. Inventory reduction and substitution were the two most commonly mentioned. A few of the procedures asked for alternative options to be considered at the development stage, though few criteria or objectives were offered to help selection.

Awareness of the inherent SHE principles was mainly confined to SHE specialists, with only around one-fifth of companies indicating any significant awareness in their development or design departments. This perhaps reflects the level and type of training, with only a small proportion of organizations including inherent SHE in their training programmes.

Despite the apparent lack of awareness, many of those interviewed thought that inherent SHE approaches would offer a competitive advantage and be worthwhile following. It was recognized that the benefits would best be achieved by considering inherent SHE at the earliest stages of any project. Still, several of those interviewed expressed reservations about the cost-effectiveness of inherent SHE, and suggested that some good case studies would be needed to persuade them of the benefits of introducing inherent SHE into their organization.

The most influential factor on the way the companies approach the development and design activities, and the way SHE is addressed within this, was the need to drive down costs of the development, design and plant installation. Plant life-cycle costs are also becoming a factor, and these can take account of the trade-offs between higher capital costs and lower running costs that some inherent safer designs may offer. Companies are also coming under increasing pressure to get products to the market place ahead of the competition, and this is reducing the programmes for development and design, increasing the need for parallel working and giving less time to think about alternatives or make late changes. The case for inherent SHE, therefore, needs to be able to demonstrate that time and effort spent at the early stages of the project can produce greater savings later on by reducing the need for costly changes or remedial action late in design.

The need for flexibility in manufacturing and products to react to market demands was also mentioned as a key pressure in some sectors.

The main hurdles to adopting inherent SHE were considered to be the lack of awareness, and conservatism in the design and general management. Prescriptive regulatory requirements and cost and time pressures were also cited as problems. The different approaches of the various agencies responsible for safety, health and the environment in EU member states may also hinder an integrated approach by industry to these aspects.

One of the key aspects relating to awareness was that of the education of chemists and engineers, and this point was made specifically by some of the people interviewed. They considered that SHE management principles are not given sufficient attention during degree or equivalent courses, and that even when SHE topics are taught, they are treated as a separate subject, and not as an integral part of plant development and design.

The nature of the relationship between client and contractor was also noted as a key influence on SHE. More open relationships may be needed to encourage the dialogue between the contract engineers and client chemists, and to ensure the contractor takes steps to evaluate design options and optimize accordingly.

Many companies noted that a lot of effort was currently going into modifying and extending existing plants, rather than building new ones. These situations place constraints on the design which can inhibit the adoption of inherent SHE. However, there should still be many opportunities to use inherent SHE principles for modifications, and revamps often provide the opportunity to upgrade the process and its ancillaries to take account of the latest advances in production and SHE performance.

Of course some speciality chemical manufacturers use the same plant to make a wide variety of products, and in these cases the chemistry and process need to be evaluated to check that the manufacture can be carried out safely in the plant. Attention needs to be focused on the generic inherent SHE design of the equipment, as well as on the inherent SHE chemistry and processing measures that can be taken for that specific batch.

Many recognized that in practice some form of systematic method would be needed to integrate inherent SHE into the development and design activities, and that these would have to start at a very early stage in a project to be worthwhile.

1.1.2 Inherent SHE in the literature

Searches of open literature and other available sources unearthed a large number of papers and publications on inherent SHE. In all, over 100 references were reviewed. These covered the principles of inherent SHE, example applications, discussions of the main hurdles and drivers affecting the way SHE issues are addressed, and possible methods and tools to address inherent SHE. Authors such as Kletz, Gygax, Englund and Hendershot were responsible for many of the papers.

The review found that many of the references repeated the same points and examples, often adding little to the early publications by Kletz, although Kletz's main principles of inherent SHE have been extended by some authors [3-6] to include segregation and leak path minimization.

Although the references often listed some of the hurdles to adopting inherent SHE approaches, few related any practical experience of how best to overcome these. The overall impression was that inherent SHE approaches are still in the early stages of development, supported by a small number of safety specialists but not generally recognized or accepted by the industry at large. As a result, few of the papers could offer any practical, tried and tested advice on how to promote the use of inherent SHE.

Several authors put forward ideas for methods and tools to address inherent safety (and some health and environment aspects), but again these do not appear to have been applied in practice. The tools range from systematic open methods such as "What-If" analysis [7] and "critical examination" [8], through to detailed check-lists [7,9-13]. Several authors have suggested the use of indices to measure the degree of inherent SHE of a process, either using existing methods such as the DOW/MOND indices [14,15] or specific indices for inherent SHE [16].

More recently, Hendershot [17] has proposed the use of decision analysis techniques to help address the economic, engineering and SHE factors that need to be addressed when optimizing route selection and plant design. Similar approaches are being considered or used by other leading companies.

Overall, the literature review gave the impression that there has been little substantial progress on inherent SHE theory or practice over the last 18 years.

Accident investigations have been rarely found to go into the detail required to find how inherently safer approaches could have helped prevent or mitigate the accident. Most concentrate on the immediate failures of the containment and control or safety systems concerned. Key lessons from some of the major disasters often point to a lack of appreciation of the hazards and their causes at the design stage. Inherent safety cannot help here, you need to know the hazards first. The same design shortcomings often appear time after time, e.g. poor plant segregation and siting, inadequate containment, and failures in protective systems. However, the main factors in the accidents are inevitably the large inventories of hazardous materials, or the presence of very reactive materials in an unstable state, often due to some process deviation or human intervention.

The main lesson from accidents seems to be the need to learn from past experience. That said, inherently safer approaches provide a good way of minimizing the hazard potential of a plant, but cannot make up for a lack of detailed understanding of the hazards.

1.1.3 Regulations and inherent SHE

Some of the more influential regulations, codes and standards affecting process development and design were reviewed to see to what extent they encourage an inherent SHE approach. Regulations and codes are seen by industry as by far the main influence on how they manage SHE. If inherent SHE principles are not embodied in regulations, then it is unlikely that they will ever come into widespread use. Equally, emphasizing the role of inherent approaches in regulations would probably be the best way to ensure such approaches come into common use.

OSHA 1910 in the United States [18] and the Seveso Directive in Europe [19] are two of the main major-hazard safety requirements. Both these use inventory-based threshold quantities. This can drive a company to reduce inventories from just above the threshold level to below it, but it has little impact in the majority of cases. In some cases inventories have been reduced at receipt or dispatch facilities, leading to an increased risk from transport and transfer operations. These regulations are generally goal-setting in approach and would permit inherently safer approaches. However, they do not mention the concept of inherent safety or its principles, and do not encourage an inherently safer approach. These regulations also focus on the plant as operated rather than on its design, and so may fail to influence the early part of design so crucial to inherent SHE.

In contrast, the recent UK regulations for offshore installations [20], brought in following the "Piper Alpha" disaster, specifically ask for a design safety case to be drawn up. This case must state how the principles of inherent safety have been implemented in the concept and detailed design. This has increased awareness of inherent safety design issues in an industry that has traditionally tried to use segregation and simplification as a key part of its hazard management strategy. Further, the principles of inventory reduction and simplification can bring major capital and operating cost savings by reducing topside weight, equipment costs, and maintenance and operating requirements. The regulations show that inherent SHE principles can form a key part of a successful goal-setting regulatory regime which benefits both safety and the industry as a whole.

In the UK, the COSHH regulations [21] provide the main framework for occupational health and safety. These do not mention "inherent safety" specifically, but do place a real emphasis on its principles of substitution, inventory reduction and attenuation. As a result, they probably provide the best example of regulations aimed at persuading industry to deal with the hazards at source rather than to rely on add-on safety.

There has also been a trend in recent years throughout the EU to regulate activities which have the potential to pollute the environment. In particular, there have been a number of initiatives to ensure that the control of polluting activities is undertaken in an integrated way. Some EU members have already established integrated pollution laws. The EU has also recognized the need to adapt existing environmental pollution controls to incorporate the strategies of integrated pollution control; the Commission's thoughts on the subject have been published as a proposal for a directive on integrated prevention pollution control (IPPC) [22].

The philosophy of IPPC is goal-setting; it encourages industry to prevent pollution and, if that cannot be achieved, to minimize it. Emission limits are likely to be set for many substances, and industry will be encouraged to better these by the use of "best available technology". Whilst the IPPC Directive may not specifically mention "inherent SHE" and its principles, its approach is compatible, and may encourage the use of inherent SHE methods through its emphasis on prevention.

In contrast to more recent goal-setting regulations, many older safety and environmental regulations, engineering standards and codes of practice are very prescriptive in nature, and can prevent the use of inherently safer approaches. Some pressure-protection regulations are a good example, where relief valves are required even if the vessel can be designed to take the maximum foreseeable pressure. The relief valve not only provides a source of leaks and unreliability, but also presents a vent management problem.

In some cases there can be real conflicts between safety and environmental requirements, especially in the areas of relief venting and leak/spill management. For example, it may be safer to dilute and wash away some plant spillages, but concerns over environmental effects may mean that the material needs to be contained and kept in high concentrations for recycle or separation. Also, fitting vent-capture systems can lead to overpressurization problems. These conflicts place increasing pressures on designers and operators, and prescription may mean that novel or alternative solutions are not implemented.

To conclude, older regulations and standards tend to be prescriptive in nature and prevent or hinder the application of inherent SHE approaches. More recent goal-setting regulations often permit inherent SHE, but do not actively encourage its application. Some of the latest regulations and some future legislation are recognizing the role inherent SHE principles can play and are encouraging its use.

1.2 Overall framework for hazard management in design, including ISHE management strategy

An effective framework to hazard management can be built upon the "defence-in-depth" approach. Examples of how an inherently SHE approach to design fits into the "defence-in-depth" approach to hazard management – using elimination, prevention, control and mitigation – is shown in Table 1.1. This may help in understanding what is and what is not inherently SHE, and how passive or active add-on measures can be used to augment or replace inherent SHE aspects.

Table 1.1 A framework for hazard management in design

Inherent design measures	**Add-on passive measures**	**Add-on active measures**
Elimination		
Design to remove need for hazardous material, condition, equipment or activity (e.g. remove need for second separation train or avoid need for offshore separation by use of multi-phase pump). Design the basic process so hazard cannot arise (e.g. design process so thermal runaway cannot occur, or design heater so it cannot overheat the process fluids).		
Prevention		
Design features to make hazard less likely to occur/to be realized (e.g. simpler plant, fewer leak points, good ergonomics).	Measures to prevent or reduce likelihood of hazard being realized which do not require initiation or are self-initiating (e.g. use of intrinsically safe electrical equipment to prevent ignition).	Measures to prevent or reduce likelihood of the hazard being realized which require initiation (e.g. process pressure, speed and temperature control systems).
Control		
Design to fully contain hazard within design envelope (e.g. design for maximum pressure). Design process to be self-limiting (e.g. heat transfer capacity or limit temperature of heating medium to slow down thermal runaway). Design process so deviations/errors are obvious/easy to detect and remedy. Design the process so any hazards/effluents are of a type that is well known and easily handled by established and effective passive/add-on means or effluent treatment technology.	Measures to control the hazard and stop it being realized (i.e. stop it becoming an accident) which do not require initiation or are self-initiating.	Measures to control the hazard and stop it being realized (i.e. stop it becoming an accident) which require initiation (e.g. feed isolation systems; high-pressure, high-temperature and high-level trips).
Mitigation		
Design to limit or reduce magnitude of hazard if realized (e.g. reduce inventory, reduce pressure, use a less hazardous material). Design to limit/reduce effects of hazard if realized (e.g. good layout, natural ventilation, segregation).	Measures to limit the magnitude or effects of a hazard if realized (i.e. as an accident) which do not require initiation or are self-initiating (e.g. fire and blast walls, structural fire-protective coatings).	Measures to limit the magnitude or effects of a hazard if realized (i.e. as an accident) which require initiation (e.g. fire water deluge, water mists for explosion suppression, HALON extinguishing systems).

1.3 Classic ISHE conflicts

A list of some common inherent SHE conflicts that arise during process selection and design, and ideas on how to deal with these, is shown in Table 1.2. For example, the increasing pressures to produce "friendly" *products* may mean that some of the manufacturing *processes* were becoming more hazardous due to the need to use more active reagents. In many ways, this may still be "inherently safer" overall, since it ensures the more serious hazards are on the plant where they can be dealt with effectively, and not at large in society.

Table 1.2 Some common inherent SHE conflicts

Issues	**Comments**
Storage vs transportation risks	
Transport risks (road, rail, pipeline) and loading/unloading risks can exceed those of on-site storage for hazardous materials. A larger on-site storage inventory may be justified if it reduces the number of transfer operations.	Select the storage volume and load size to match each other. One full load every few weeks is likely to be safer than several part loads every week. In general, pipelines are the safest means of transfer. Rail and road are similar, but this depends on the route taken. It is worth looking at route options. Some may be much safer than others by avoiding accident black spots and areas of population or environmental sensitivity.
Process vs product SHE	
Some friendly products may require more hazardous processes and feeds.	In general, product SHE should come before process SHE, since hazards outside the factory gate are far more difficult to control than those within the factory.
Your process hazards vs those at others, e.g. suppliers	
Using a different feedstock or producing a different product may help reduce the risks of your operation, but could mean that those who have to produce your feedstock or use your product now carry a higher risk.	An overview of the total materials, processing, transport and energy life-cycle (e.g. by LCA) may help show if SHE gains on your plant are being achieved at the expense of increased risks elsewhere.
Containment vs render harmless	
Leaks of hazardous materials can be made safe by either allowing them to rapidly disperse to "safe" levels, or by capturing them in some controlled manner. These two approaches are normally in opposition. Several methods of vent-stream capture are available, as are drains and bund systems for liquids, but fugitive emissions are more problematic.	Increasing concerns over the environmental effects of emissions mean that containment is increasingly preferred to dispersion. Containment of toxics can be achieved by the use of double containment, with the plant sited within enclosures or indoors. This places the need for tighter control on fugitive emissions and personnel protection. Explosive materials may be difficult to contain safely, since the containment may allow explosive concentrations to form. Containment to withstand any overpressures developed may only be practical on small plants.
Reduced pipework inventories vs segregation	
The physical segregation of plant units is often used to prevent escalation and to help access in emergencies. This results in longer pipe runs and a higher materials inventory.	Compare the escalation risks with those from the extra inventory in the pipework. Well-built welded connection pipework is generally very reliable.

Capital costs vs running costs	
It could be worth spending more on the plant equipment, since this could reduce operating costs, and lead to an overall lower plant life-cycle cost. Inherent SHE aspects include thicker vessels... more resistant to corrosion, which may mean: - less inspection, or fewer pressure relief systems; - longer-lasting seals and gaskets, which reduce maintenance and the chance of leaks arising from maintenance; - higher-quality valves and fitting which also reduce maintenance/chance of leaks.	Consider using life-cycle costing to strike a better balance between capital and operating costs. ***Note*** High discount rates will favour low capital costs, so try to be realistic: could the plant operate longer than expected, how are economics likely to change in future (may need to have lower operating cost in future to stay competitive). Review proposed maintenance requirements to see where better design/equipment could significantly reduce hazards or chance of leaks, etc.

1.4 The *INSET* Toolkit

Although inherent SHE conflicts exist, the importance of inherent SHE concepts to industry (as has been outlined earlier in this chapter) is self-evident. The potential benefits to industry make the concept of the "inherently safer" plant a reality.

The concepts of inherent SHE, although being quite sound, have not been as successfully adopted as other methods. This may be due to many reasons, but one of the main factors has been the lack of recognized methods or tools to address inherent SHE at the early stages of process development and design.

The *INSIDE* Project was set up in August 1994 to bring together industry and researchers in this field to develop practical ways to encourage the use of inherent SHE in process development and plant design. The result of this work has been a collection of tools and methods, the *INSET* Toolkit, that is specifically designed for this purpose.

The *INSET* Toolkit provides chemists and engineers with the tools and methods to systematically identify, evaluate, optimize and select inherently SHE processes and designs. Whether the project is completely new, an existing process in a new plant, or whether considering modifications to an existing plant and process, safety, health and environmental hazards are treated in an integrated way to ensure the conflicts and synergies between these aspects are recognized and effectively managed. The versatile toolkit especially deals with the key early stages of a project where almost all the main decisions which determine the SHE performance of the plant are taken. It should be noted that the tools focus on inherent SHE aspects in the decision-making, not on the total SHE picture. Finally, it is emphasized that the tools do not replace the need to apply conventional safety studies and risk assessment to confirm overall SHE performance is acceptable.

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2. HOW TO USE THE *INSET* TOOLS

This chapter provides an overview of the *INSET* Toolkit structure and its contents, giving details on how to use the toolkit and navigate between the many toolkit elements. Details of how to use the individual toolkit elements are contained within the elements themselves.

The toolkit has been designed as a simple, paper-based system to help chemists, engineers and project teams consider inherent safety, health and environmental aspects relating to the process and plant during the critical development stages of the project. The framework allows safety, health and environmental performance to be explicitly included in the selection and decision-making processes in a way that allows these aspects to be considered alongside the more usual commercial aspects such as technical feasibility and costs.

The toolkit covers four main stages:

Stage I: Chemistry route selection
This stage is where potential chemistry routes to manufacture the product are sought; for some products there could be hundreds of routes available. Some simple screening is carried out on these to see which (say five) should be evaluated further.
Stage II: Chemistry route detailed evaluation
This stage involves taking a few potential chemistry routes, gathering the relevant chemical data, and assessing the routes in detail. A final selection of the best route, or perhaps two routes, to be further optimized/developed or to be used directly as the basis of the plant process should result. It is particularly applicable where the available options have many conflicting aspects and there is no immediately obvious route alternative.
Stage III: Process design optimization
The selected route(s) from *INSET* Stage II are assessed to optimize the conditions and take account of the practicalities of industrial scale processing and the implications of using particular processing equipment.
Stage IV: Process plant design
The initial process design is developed and "challenged" to identify further changes in sequencing, feed profiles, conditions, unit operations and equipment selection in order to improve the performance. The detailed aspects of equipment sizing and pipework fittings are subsequently evaluated to try to identify means of reducing the process inventories and eliminating complexity and hence the possible leak points.

The toolkit provides means to identify and assess inherently SHE options relevant to the issues and decisions at each stage. Typically, these may include assistance with:

- *identifying the objectives and constraints at that stage:* Guidelines to assist in the identification of the objectives and constraints of the project stage, aiding the assessment of which of these are "musts" and which are "wants". These can then be used as criteria for ranking, screening and decision-making at later stages. Assistance is given in setting safety, health and environmental criteria, but the methods can also be used to take account of other business aspects.
- *identifying synthesis methods:* An overview of the methods for identifying the synthesis routes is given, and references to the most relevant sources are made.

- *documenting findings:* Forms are suggested which allow the toolkit user to easily document the relevant data. The results sheets provide a permanent record and justification of the decisions made in choosing a particular alternative, and generate an indispensable audit trail.
- *identifying hazards and gathering other relevant data:* Methods and sources of data to help identify the key issues, hazards, problems and performance of the proposed scheme and any alternatives identified. This information provides the basis for screening and decision-making. Techniques for prioritizing the hazards and problems are also provided so that the search for inherently SHE alternatives can be targeted against the areas most in need of improvement.
- *identifying options/alternatives:* Techniques and sources of ideas are provided to help the developer and designer seek alternatives to the proposed scheme. These include conventional searching methods and "brainstorm" methods.
- *evaluating, ranking and screening these alternatives:* Tools and formats are suggested which could be used to help screen and rank alternatives to see which offer the best overall performance. These include SHE aspects and some simplistic feasibility and economic worth aspects. Qualitative and semi-quantitative measurement systems and criteria are suggested.
- *aids to decision-making:* A general overview and references to the sources of some decision aids are offered to handle more complex choices, or where "trade-offs" are involved.
- *other supporting information:* Guidance and background information is provided in the form of text discussing the issues that are likely to be relevant and the relative merits of various options at that stage. In some instances, the user is referred to other structured tools, methods or data, for the systematic identification and evaluation of alternatives.

In some cases, different tools or approaches are offered so that the user can pick the one most suited to their situation or way of working. The toolkit is intended to allow a "pick-and-mix" approach to addressing inherent SHE, matching the tools to the problem at hand and the systems used by the company. The toolkit is *not* intended to be a rigid procedure which has to be followed from start to finish. However, some projects may find it useful to use most or even all the toolkit elements at the relevant project stages.

2.1 Who should use the tools?

The tools are for use by the chemists and design engineers working on the project. They can be used by individuals, but some which involve brainstorming for ideas may benefit from a study-team approach. The chemist or designer may also need to consult specialists in some areas for relevant data and knowledge of hazards and problems, e.g. a toxicologist, an environmental or major-hazard risk assessor, an occupational hygienist, a reaction hazard specialist.

The tools could also be used informally as part of the chemist's or designer's ongoing job, or could be incorporated into existing hazard management systems and procedures.

2.2 Where should you start in the *INSET* Toolkit?

Where you should start in the toolkit will depend on the stage of the project you are in, and the nature of that particular project:

- For a new project that has had little if any work done on it so far, and where many chemistry routes may be available, it would be beneficial to start using the toolkit at Stage I, Chemistry route selection.
- However, if only a few routes are available and a more detailed evaluation is required, the investigation should be started at Stage II, Chemistry route detailed evaluation, although some aspects of Stage I may need to be reviewed for the sake of completeness.
- If the basic chemistry or process has already been decided, or is mainly fixed, but you still have some flexibility to optimize this (by laboratory trials, pilot-plant work or process flowsheet development), you should start at Stage III, Process design optimization.
- If the basic process is fixed (e.g. basic flowsheet and unit operations have already been decided), but you still have some flexibility to choose the types of equipment that will be used, and how to configure the plant, then Stage IV, Process plant design, may still provide insight to making the plant more inherently SHE. Also, if the only flexibility is in the area of the sizing of the main equipment (i.e. columns, reactors, heat exchangers, etc.), or sizing of pipework and selection of the minor plant items (i.e. pumps, valves, etc.), then you should also proceed from Stage IV.

No matter which stage of the project you are at, or how restrained you seem to be within the project, it may be worthwhile to take a quick look at some of the tools used in the previous stage to that suggested above if you have the time and resources to do this, especially if there is still a chance to change the route or the design and you feel that the current proposals could be significantly improved upon. In some cases, a tool may use information from an earlier-stage tool and this will allow you to reference these.

The transport tool, which is integrated into the siting and plant layout tool, can be used at any stage once an initial idea of the types and quantities of imports and exports have been identified. It may also be useful at the route selection stages to identify whether on-site generation may be better than transport for some of the more hazardous materials, or whether the plant could be located near to a supply of raw material or the product user(s).

Likewise, the plant layout tool can be used at any stage of the project once an initial layout has been developed. For many projects, this will be during the concept process design stage.

2.3 When should you use the tools?

The tools provide an ongoing support to the users, and the relevant tools should be applied at the beginning, during, or towards the end of each stage, depending on the purpose of the tool and its information requirements.

Tools that assist in the identification of objectives and constraints need to be applied early on in any project. Objectives and constraints help determine the direction and topics of investigation, as well as the "success" criteria for the stage.

In order to "challenge" the process routes and seek alternatives, option generation tools could be used once a preliminary scheme or schemes have been drawn up. These would need to go hand-in-hand with hazard identification and data-gathering in order to direct the search for options towards those areas that are most in need of improvement. An iterative process is envisaged of:

- set out proposal(s),
- identify hazards and performance data,
- look for suitable alternatives,
- select those worth pursuing,
- develop into new proposal(s),

and so on.

It must be noted that quite a broad overview of the process is required when "challenging" a stage of a process, as a positive change in one part of the process may cause a negative consequence somewhere else. Therefore, the iterative process should cover not only the unit operation which is being studied, but all others that may be affected as well, and all the trade-offs need to be considered.

Option ranking and screening tools should be used to select those options worth adopting or considering further. These could form part of an iterative development route such as that described above, or be applied at the end of a stage when a number of discrete options have emerged and need to be evaluated side by side.

The decision-making aids should only be required if the simple screening/ranking methods do not show any clear choice. These could then be used to make a more rigorous comparison of alternative options, especially where complex trade-offs are involved.

2.4 How to find your way around the *INSET* Toolkit?

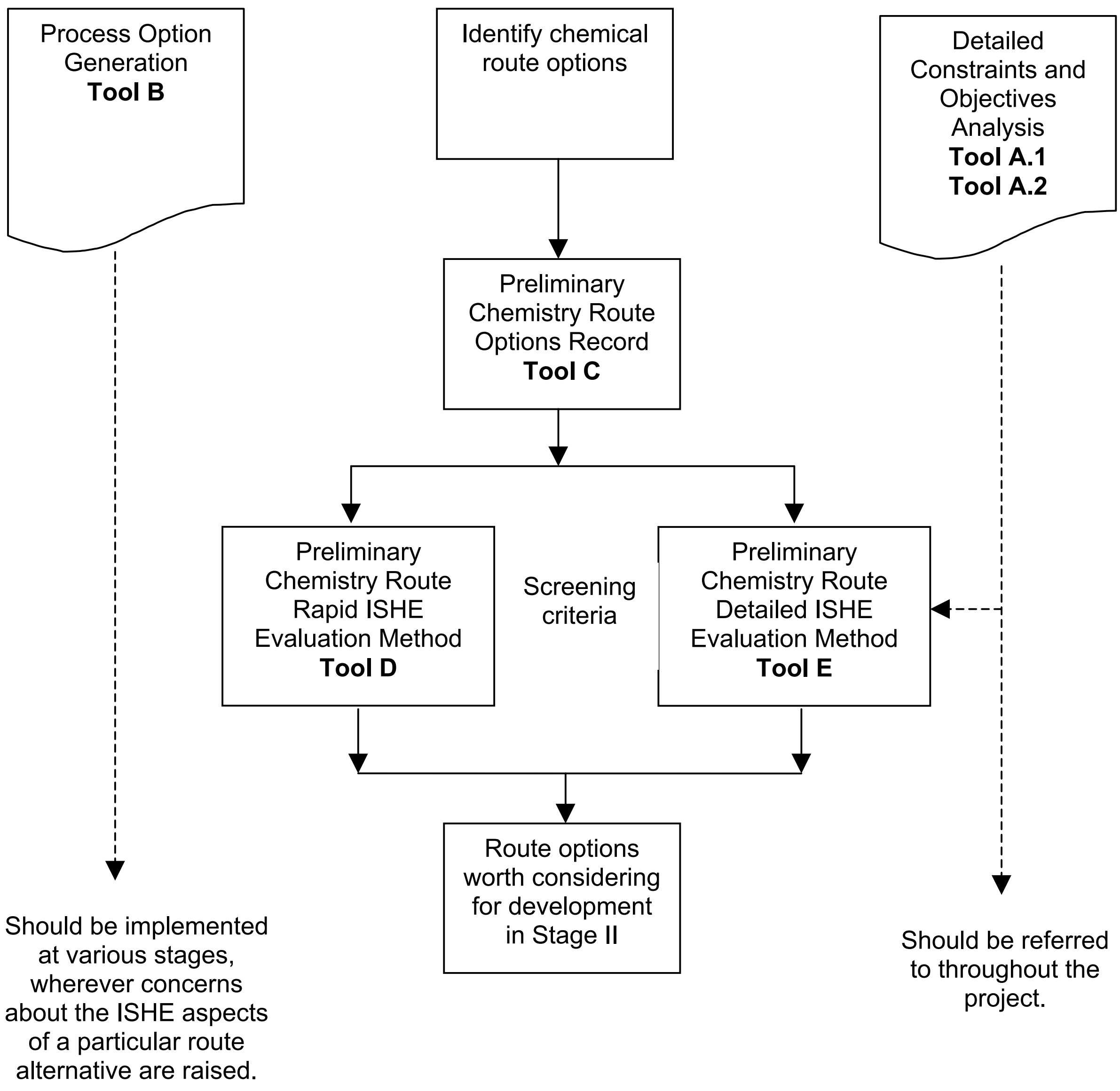
The overall structure of the *INSET* Toolkit follows the four basic sections, Stages I–IV, as stated at the outset of this chapter. These stages then call on the individual tool elements which are presented sequentially. Although many of the tool elements are specific to a particular stage, some others are generic in nature and can be used at a number of stages. The detail needed for various stages of the investigation may, however, vary. Some of the tools can be considered to be data collection or recording tools, while others are for analysis, or of the option generation and challenging type.

The ensuing application flowsheet gives a suggested approach to the process development procedure as defined by the *INSET* Toolkit. Navigation through the four stages of the *INSET* Toolkit is then just a matter of following this flowsheet. Subsequently, Table 2.1 presents a concise overview of the various tools and their aims.

It is important to note that Tool B, Process Option Generation, and Tool A, Detailed Constraints and Objectives Analysis, are *not* Stage I tools. Tool B and the results of Tool A should both be referred to throughout the entire project.

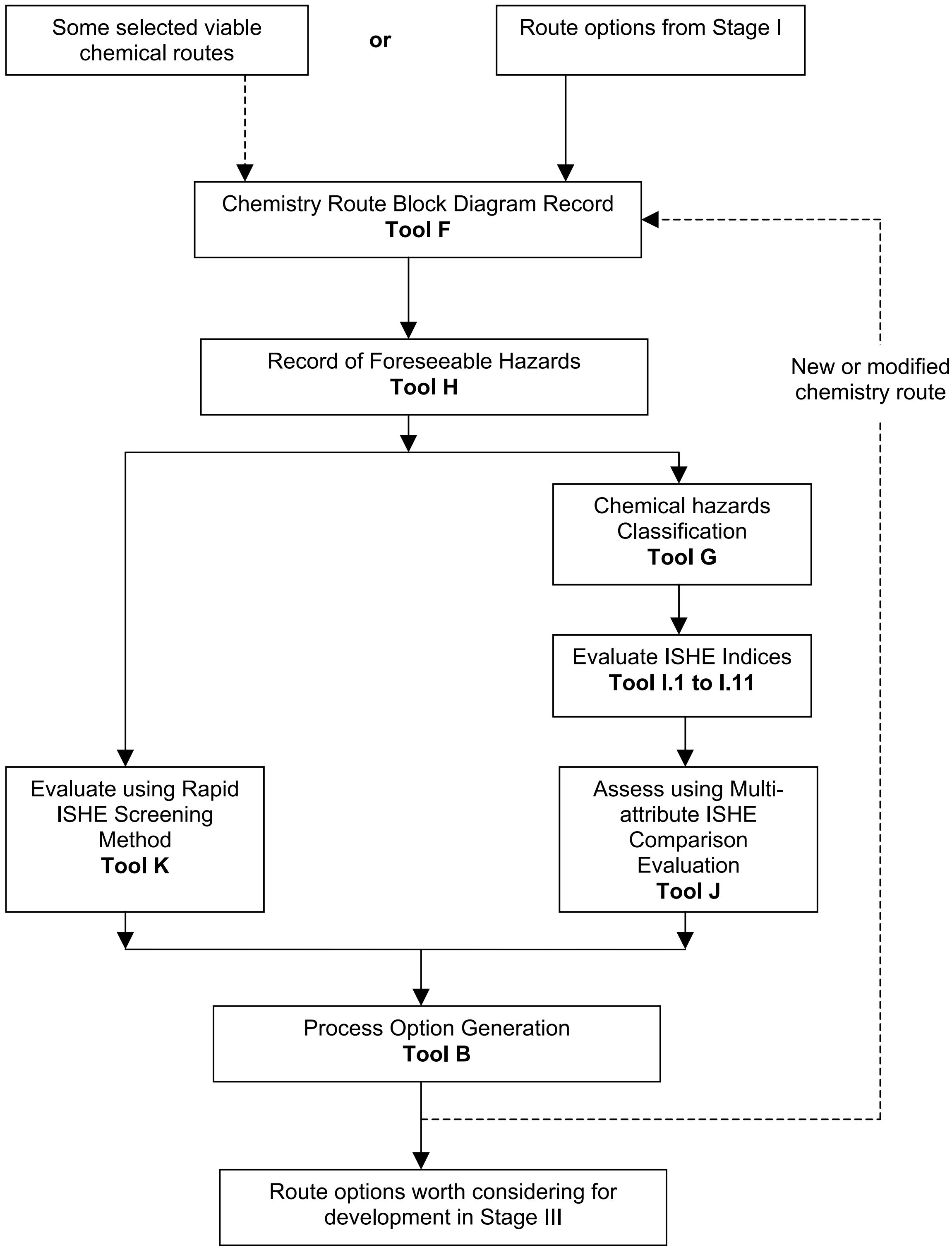
INSET Toolkit - Application Flowsheet

Stage I - *Chemistry route selection*



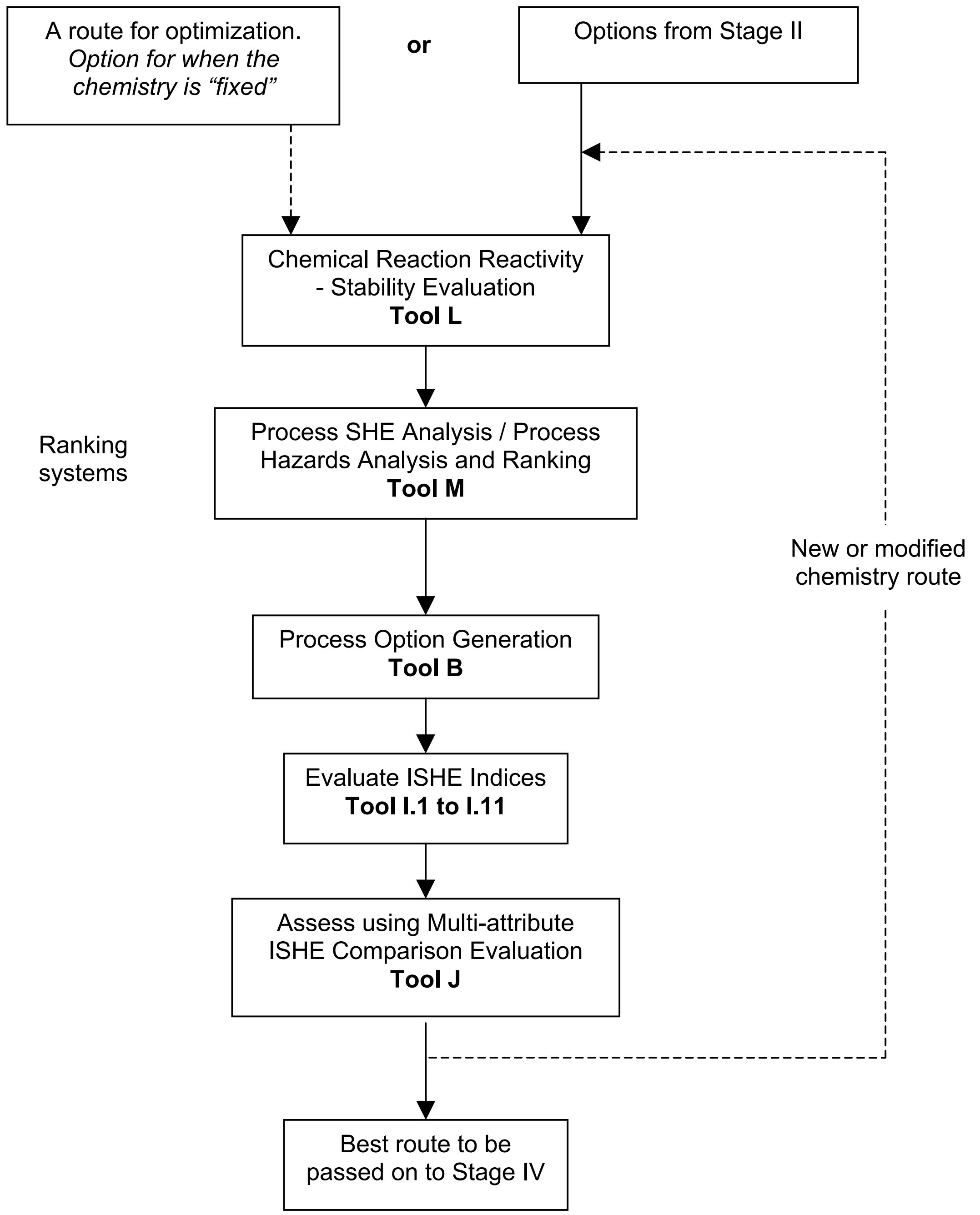
INSET Toolkit - Application Flowsheet

Stage II - *Chemistry route detailed evaluation*



INSET Toolkit - Application Flowsheet

Stage III - *Process design optimization*



INSET Toolkit - Application Flowsheet

Stage IV - *Process plant design*

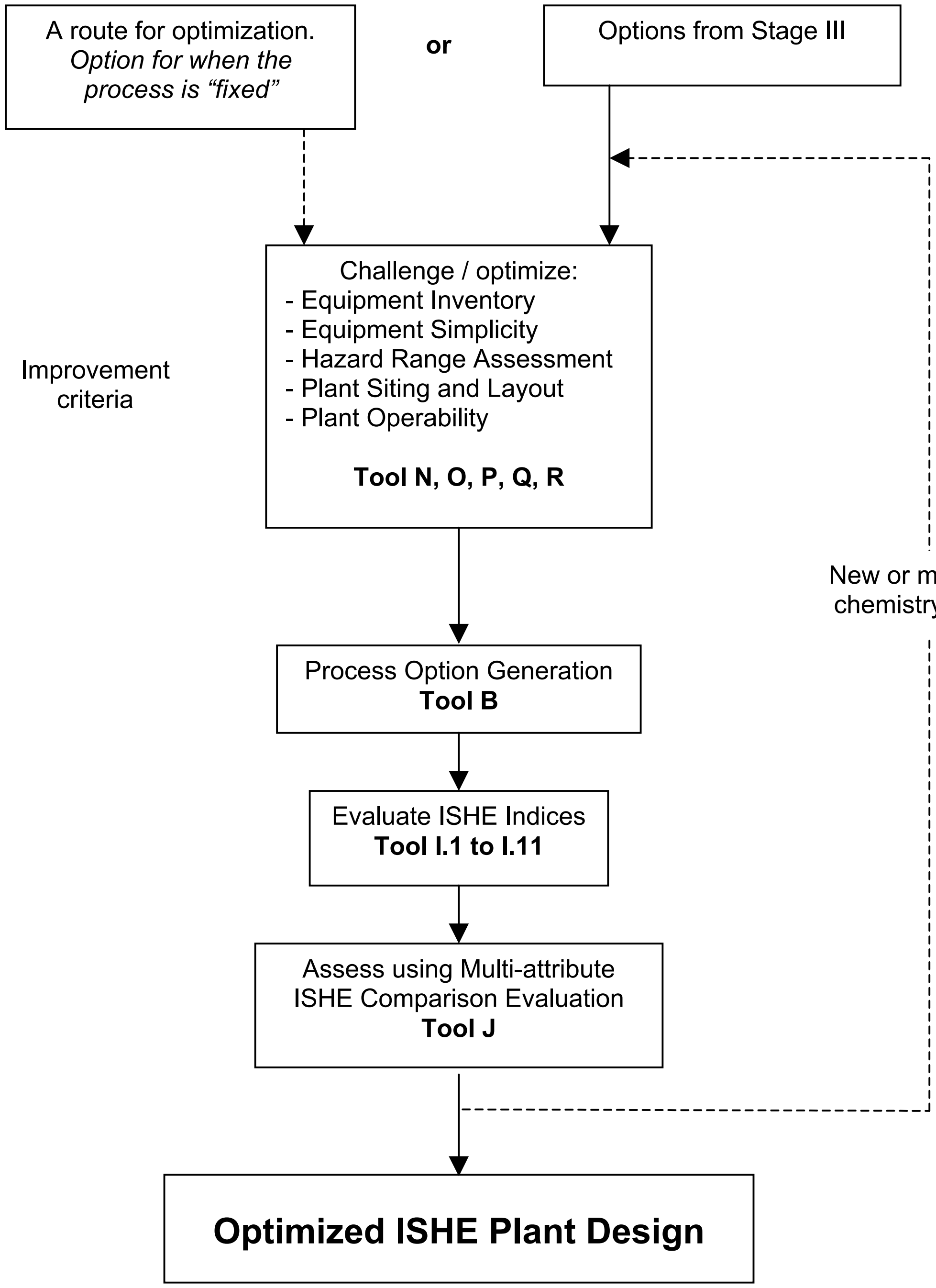


Table 2.1 Overview of the tools and their aims

Tool	Name and aim
A.1	*Detailed constraints analysis* – to define the limitations and boundaries of the project.
A.2	*Detailed objectives analysis* – to define the aims and goals of the project.
B	*Process option generation (incl. Process waste minimization guide)* – to rigorously challenge route and process alternatives in order to obtain a more ISHE process.
C	*Preliminary chemistry route options record* – to consistently present all the proposed chemical route alternatives.
D	*Preliminary chemistry route rapid ISHE evaluation method* – to provide a rapid assessment procedure to determine the most viable chemical route alternatives.
E	*Preliminary chemistry route detailed ISHE evaluation method* – to evaluate the chemical route alternatives with respect to the constraints and objectives which define the process.
F	*Chemistry route block diagram record* – to give an overview of the process involved for each alternative.
G	*Chemical hazards classification method* – to provide a simple and easy-to-apply means of classifying materials in terms of their hazardous properties.
H	*Record of foreseeable hazards* – to identify possible hazards caused by the desired or an undesired reaction, and record these.
I.1	*Fire and explosion hazards index* – to provide a means of comparing route alternatives on the basis of the potential for fire or explosion.
I.2	*Acute toxic hazards index* – to provide a means of comparing route alternatives on the basis of the acute toxic hazards.
I.3	*Health hazards index* – to provide a means of comparing route alternatives on the basis of their health hazard performance.
I.4	*Acute environmental incident index* – to provide a means of comparing route alternatives on the basis of the potential to cause acute environmental incidents.
I.5	*Transport hazards index* – to provide a means of comparing process route alternatives on the basis of their transport hazards (accidental releases of material during transport off-site).
I.6	*Gaseous emissions index* – to provide a means of comparing process condition and plant alternatives on the basis of the potential to cause routine/daily impact on the environment.
I.7	*Aqueous emissions index* – to provide a means of comparing process condition and plant alternatives on the basis of the potential to cause routine/daily impact on the environment.
I.8	*Solid wastes index* – to provide a means of comparing process condition and plant alternatives on the basis of the potential to cause routine/daily impact on the environment.
I.9	*Energy consumption index* – to provide a means of comparing process condition and plant alternatives on the basis of the potential energy usage and the resultant effect on the global environment.
I.10	*Reaction hazards index* – to provide a means of comparing process condition and plant alternatives on the basis of the potential for runaway reactions.
I.11	*Process complexity index* – to provide a means of comparing process options on the basis of their likely complexity, hence difficulty to control and prevent errors.

Tool	Name and aim
J	*Multi-attribute ISHE comparative evaluation* – to provide a means of evaluating and comparing the ISHE performance of various aspects of the route alternatives as a means to eliminate the more unfavourable process options.
K	*Rapid ISHE screening method* – to rapidly assess each route alternative with respect to its ISHE performance, as a fast-track alternative approach to Stage II.
L	*Chemical reaction reactivity – stability evaluation* – to identify any chemical process that may have runaway potential or in which other hazardous situations may occur due to chemical reactions.
M	*Process SHE analysis/process hazards analysis and ranking* – to provide a simple method to identify and rank any hazards in the proposed process.
N	*Equipment inventory functional analysis method* – to provide an understanding of why inventory is required on a plant, leading to the generation of ideas on how it might be minimized.
O	*Equipment simplification guide* – to challenge the need for valves, instruments, flanges and other pipework or equipment fittings that can increase the complexity of the plant and maintenance requirements.
P	*Hazards range assessment for gaseous releases* – to provide engineers with an easy-to-look-up indication of the magnitude of major accident hazards based on either the process inventory or the size of typical leak sites.
Q	*Siting & plant layout assessment* – to challenge the basis of the plant layout at the early stages of its development, in order to see how changes to the layout could improve segregation and make the layout more inherently SHE.
R	*Designing for operation* – to provide a simple aide-mémoir or check-list for those involved in the detailed design of plant to prompt them to consider ways in which to make the plant easier to operate and maintain.

3. *INSET* STAGE I: CHEMISTRY ROUTE SELECTION

INSET Stage I is intended to be a fast and a flexible toolkit that can be used where alternative synthesis routes to a desired product are documented and preliminarily assessed in order to end up with, say, five potential routes.

Project stage	**Key issues**	***Information used***
I – Chemistry route selection	Constraints and objectives of the project Routes to make the product Raw materials and wastes involved	*Legislation and company policies* *Known synthesis routes and techniques* *R&D chemists research*
II – Chemistry route detailed evaluation	Basic unit operation selection with flow rates, conversion factors, temperatures, pressures, solvents and catalyst selection Batch vs continuous operation Control/operation philosophy Waste management options/selection	*Knowledge of existing processes* *Knowledge of existing chemicals* *Initial process engineering design principles and experience* *Feasibility and cost information*
III – Process design optimization	Unit operation selection Optimization of the process Equipment selection and sizing Hazard evaluation Inventory of process Single vs multiple trains Utility requirements Overdesign/flexibility Recycles and buffer capacities	*Lab-scale and pilot-scale trials* *As above, plus equipment suppliers data, raw materials data, company design procedures and requirements*
IV – Process plant design	Instrumentation and control Location/siting of plant Preliminary plant layout Materials of construction Detailed specification based on concept design Minimize number of possible leak paths Make plant "friendly" to control, operate and maintain Avoid/simplify hazardous activities such as sampling, loading/unloading	*Process conceptual design and codes/standards and procedures* *Experience on past projects/designs*

Aim: To identify all possible chemical routes, no matter how difficult, unusual or esoteric some may at first seem, and then to evaluate these with regards to SHE, ISHE and other criteria so that the most "promising" routes (about five) are selected for further evaluation and optimization. Also: to promote the consideration of ISHE aspects and raise ISHE questions during the preliminary search for viable chemical routes.

Inputs: Various published information, computer-assisted synthesis and experience (e.g. in-house experience and expertise) are used to identify potential chemical routes. Identification of the most important SHE issues (toxicity, explosiveness, effluents, etc.), together with the identification of the most important non-SHE issues (e.g. costs, feasibility, plant constraints), is crucial.

Outputs: A comprehensive list of possible chemistry routes and the corresponding list of constraints and objectives for the particular project. A part-completed decision and information dossier for the top, say five, routes with the justification of the choice of the most favoured routes is important, together with a file of relevant background information/data and previous accounts and experiences.

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At the start of a new project, all chemical routes to the desired product should be sought. Some chemists can be conservative and may stick to methods they have used before, and so the decisions are often based on the experience of the chemists involved. On the other hand, some chemists are highly innovative, but in the desire to do new chemistry may forget old, well-tried methods. Two chemists may, therefore, come out with different solutions to the same problem.

In some cases, hundreds of ideas will easily be generated in a short time. Figure 3.1 shows an example indicating some routes to specific product. Unfortunately, it is inevitable that only a few routes can actually be tried out in the laboratory. Evaluation of the ideas is often the hardest part, and this is where the experience and literature knowledge of the chemist comes into play. It is also where the *INSET* Toolkit can provide useful tools and guidance.

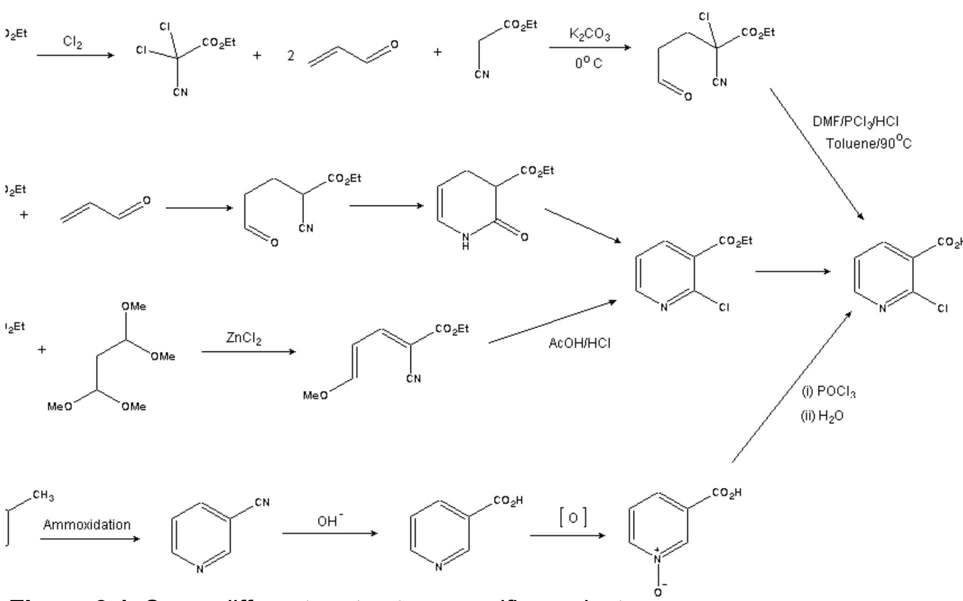

Figure 3.1 Some different routes to a specific product

In the *INSET* Toolkit, only the part of a product life-cycle is considered that is connected to the plant where the product is to be produced: the core manufacturing process. Environmental and social impacts over the whole life-cycle of a product are covered by life-cycle assessment (LCA) methods and related tools, and are not duplicated here. A simple matrix covering the SHE effects of the whole life-cycle, like the EC Eco-labelling Assessment Matrix published in Council Regulation (EEC) No. 880/92 of March 1992, can easily be used in parallel with the *INSET* Toolkit. Table 3.1 gives an overview of the differences between the *INSET* Toolkit and an LCA.

However, problematic stages of a synthesis are, in practice, sometimes "exported" to toll manufacturers or to another location within the company. As we are here looking only at inherently SHE alternatives for the production steps that are performed at the production site in question, the *INSET* Toolkit may not give a true indication of the entire process. These kinds of ways to make a process alternative look better than it is cannot be covered directly by this toolkit, and the assumption made is that the production of each starting material is equal from a SHE point of view (which, of course, is not necessarily the case in reality).

Consideration of the ISHE aspects of any associated activities such as the extraction of minerals and other natural resources, processing of raw materials, etc. may also be beneficial. If concerns about placing the "risk" of a particular process on another plant/manufacturer are raised, the *INSET* Toolkit could be applied to the activities on the other plants/sites in order to get an overview of the total "process". Most European chemical manufacturers subscribe to Responsible Care, where the implications of toll manufacture and transport also need to be considered.

Table 3.1 Comparison of the *INSET* Toolkit with the Product/Life-cycle analysis

Product/Life-cycle analysis		
	LCA	***INSET***
Research	–	–
Design	–	–
Construction (use of land, materials, transport, etc.)	Yes	Possible
Extraction of minerals and other natural resources	Yes	Some
Pre-processing of raw materials	Yes	Some
Use of energy	Yes	Yes
Transport of raw materials	Yes	Yes
Production process (including contract manufacture)	Yes	Yes
Processing of by-products	Yes	Yes
Wastes/effluents: gaseous, aqueous, solid/liquid	Yes	Yes
Transport of product	Yes	Optional
Use of product	Yes	No
Disposal of product	Yes	No
Decommissioning of the plant	Possible	Possible
Restitution of the land	Possible	Possible

Effluent and by-product considerations need to be discussed at an early stage, and may, in extreme cases, affect the choice of production route. The use of highly toxic raw materials or reagents, or the likelihood of explosion hazards, may also make a particular route unattractive. Although these and other factors may be taken into account in a paper study, it is difficult to quantify the relative importance of each.

The suggested initial screening procedure involves the elimination of any production routes that fail the constraints defined by the legislation, etc.: general and project-specific constraints (see Section 3.1). This procedure can be developed further by subsequently considering any objectives of the project. However, a route should not be simply discarded without implementation of a challenging procedure that may generate a viable alternative. Section 3.3 gives an overview of the screening and option generation facets of this stage.

A good approach would be to select not only options that appear to have a high chance of success for further investigation, but also some speculative routes which could be beneficial even if there is little literature precedent.

3.1 Criteria for the elimination of unfavourable routes

To achieve a basis for the integrated safe, environmentally responsible, economical and quality-oriented manufacturing of the desired product at the plant in question, all the criteria (i.e. constraints and objectives) relating to the manufacturing process and the product must be established. Often, the product constraints are defined by the customer, and this, in turn, affects the inherent properties of the product. Besides the requirements set by the customers, many other criteria exist for every process development project. For example, if the process is to be carried out in an existing plant, the plant itself will place certain constraints on the process alternatives chosen.

As it may not always be clear to the chemist what the criteria are, a systematic way of collecting information on these should be established for each process, and the elimination of unfavourable process routes needs to be based upon these predefined criteria. A framework for gathering this information has been suggested in Tool A.1, Detailed Constraints Analysis.

This phase of the *INSET* Toolkit should be done with care, since the subsequent decision-making will be based on a bounded decision context implied by the constraints stated. The lists of constraints determined in Tool A.1 indicate the minimum requirements for this stage.

When considering the criteria with which the alternatives will be evaluated, it is very important to distinguish between constraints and objectives. The constraints need to be considered and accounted for under all circumstances, that is, all the constraints must be fulfilled in order to make the process acceptable, while the objectives will be open for further negotiations and possible value trade-offs.

Decision criteria manifested as constraints usually have pre-defined target levels. The constraints can be either qualitative (e.g. the product must be manufactured in a particular plant) or quantitative (e.g. the chloride concentration in the effluents must be below "y" ppm).

The chemicals involved in each process alternative need to be screened against the appropriate regulatory lists. In the EU, the so-called "Black list" (Framework Directive 76/464/EEC, which concerns the discharge of dangerous chemicals to water – List I) covers the substances considered to be so toxic, persistent or bio-accumulative in the environment that priority should be given to eliminating any possible pollution by them. In the UK, the so-called "Red list" dictates a similar notion and is a subset of the "Black list". The "Grey list" (Framework Directive 76/464/EEC – List II) covers those substances which are considered to be less harmful when discharged to water, but also includes those substances which are awaiting formal List I categorization (see Tool A.1 Supporting Information).

In addition to the requirements set by the regulations, and together with other constraints from Tool A.1, various objectives exist for every process development project. Objectives can be recorded using the form in Tool A.2, Detailed Objectives Analysis.

A concern when considering new processes with new chemical substances is that the materials may not have been thoroughly investigated with regard to their properties. In order to avoid expensive testing as dictated by legislation, it is often important that the substances are listed in the EINECS (European INventory of Existing Commercial Chemical Substances) or ELINCS (European LIst of Notified Chemical Substances) databases.

Issues that will be mentioned on the final check-lists are partly due to national legislation, company policy, existing facilities, etc., while other factors are typical for the process in question only.

3.2 Identification and recording of possible chemical routes

The identification of possible chemical routes to the desired product is outside the scope of the *INSET* Toolkit and is covered only briefly. There are no obvious and completely guaranteed concepts for planning a chemical synthesis, organic or inorganic. Solution of a synthetic problem can be achieved, in principle, via a number of approaches. The goal is to find the starting materials and reactions with which the former can be converted to the desired product. There can be a large number of possible chemical reactions and consequently a large number of potential starting materials. In this step, the creativity of the chemist should be unbounded and we must consider all possible chemical routes, no matter how difficult or esoteric they at first seem. The information gathered here is mainly drawn from existing information and should, therefore, be a relatively fast search process without the consideration of SHE, or ISHE, aspects in any more detail. No laboratory experimentation is required at this stage. However, the identified routes should be documented in such a way that, if need be, the step can be revisited without the need for the possibly laborious search to be redone. Tool C, Preliminary Chemistry Route Options Record, gives an overview of how this can be carried out.

3.2.1 Published information based on experimental data

Information on possible synthesis routes can be found in different sources. The open literature (i.e. journals, patents, textbooks, and reference books such as Beilstein, Chemical Abstracts and GMELIN) is still useful and covers methods that are not included in modern databases. Databases normally cover only methods published during the last two or three decades. The various databases can be searched via international information services (e.g. **STN®** International). The services provide access to several useful databases such as CASREACT, CHEMREACT and CHEMINFORMRX. Chemical Abstracts, GMELIN, and Beilstein are also searchable via electronic methods.

Patents and patent applications are naturally important sources of information. No database covers all existing chemical patents and it can, in many cases, be a laborious task to get a complete overview of all patents and patent applications. For example, European patents can be found in databases such as INPADOC, PATOSEP and WORLD PATENT INDEX, while the JAPIO database provides the most comprehensive English-language access to unexamined Japanese patent applications. American patents can be found in, for example, the CLAIMS database. There are several other important databases, one of which is MARPAT. This database covers only chemical patents with so called Markush structures, i.e classes of compounds based on a particular parent structure.

Currently, even PC-based software is available, like SciFinder (from **CAS®**), KR ScienceBase (Helix Systems/Knight-Ridder Information Inc.), and CS ChemOffice (CambridgeSoft Corporation), which all allow desktop searching/browsing of the various important commercial and in-house databases, together with many other citation-search software packages.

See Appendix 5, in Part 3, for more information.

3.2.2 Computer-assisted synthesis

Computer programmes developed during the last two decades can be classified as chemical compound and reagent databases, reaction databases, programmes handling multi-step synthesis planning, and reaction simulating programmes.

Retrosynthetic analysis, designed originally by E.J. Corey, is philosophically and intellectually perhaps the most stimulating approach among those developed. Programmes for retrosynthetic analysis accept problems on an advanced level. The user tells a programme what structure they are interested in and the programme will usually come up with tens, or sometimes even hundreds, of potential solutions and synthesis suggestions. Retrosynthetic planning is performed "backwards", and starting materials (precursors) are derived from the target structure by transforms.

Another main category consists of programmes which try to predict the products of an organic reaction when the starting materials and reaction conditions are given. Examples of this reaction simulation approach are the CAMEO and EROS programmes.

See Appendix 6, in Part 3, for more information.

3.2.3 Use of in-house experience and external experts

It is important not to be inhibited by what has been carried out previously. A published route to a specific compound, for example, can have been chosen just because it has been possible to synthesize a lot of analogues using this method. There could, however, be more efficient routes to the specific compound we are interested in. Innovation cannot be taught, and brainstorming with colleagues can be very fruitful. In-house experts are, therefore, valuable sources of information – as are experts in other organizations such as universities and research institutes. It is important to create a network of experts with which can be easily consulted when the requirement for specific advice arises. A tool which allows this is the Internet, via e-mail and WWW (World Wide Web) connections.

See Appendix 7, in Part 3, for more information.

3.2.4 Documenting the identified alternative chemical routes

The need, in an increasing number of countries, to satisfy the authorities that the selected process represents the "best available technique not entailing excessive cost" makes it essential that the decisions taken during the research are well recorded. The records may then be used at a later stage during any discussions with the authorities.

The information gathered from the previously mentioned sources may be quite varied with respect to both details and relevance for the particular project. Ideally, *all* identified reaction schemes should be documented in case alternatives that at first seem to have the most potential, fail to meet initially the constraints of the project and secondly the project's objectives (Section 3.1). In reality, however, chemists tend to leave the most unattractive routes undocumented.

In order to be comprehensive and effective, the *INSET* approach requires that all alternatives are presented in a uniform, easy-to-read format. The suggested way of documenting the alternatives is presented in Tool C. All the alternatives must be presented in a similar way to ensure that the decisions taken are not in any way biased due to inconsistent presentation of the data, and there may be times when simplifications are needed in order to obtain comparable presentations. In many cases, alternatives can initially be grouped together, thus reducing the amount of resources needed for the documentation.

During the iterative decision-making process presented in Section 3.3, the previously rejected alternatives are reassessed and there may be a need for more detailed investigations/presentations for some of the alternatives at that stage. Tool B, Process Option Generation, would be used to challenge the alternatives that have been identified.

3.3 Screening and ranking of routes, and decision-making

It is not an easy task to assess the various alternative routes based solely on the information at hand at this stage, especially as the level of detail varies from one route to another. Since the criteria are mainly non-SHE issues at this stage, the *INSET* Toolkit does not cover this decision-making process in any detail.

As the decision-making and data-gathering for *INSET* Stage I may require extensive knowledge of company policy, legislation, previous experiences, etc., specific experts may need to be consulted. A chemical information management (CIM) system, as described in the introduction to *INSET* Stage II, may also be useful in this situation.

The screening and ranking of alternatives should be a fast and non-resource intensive method in an attempt to reduce the basic set of alternatives to a feasible set of alternatives which will later be subjected to more formal scrutiny.

A rapid assessment procedure (Tool D, Preliminary Chemistry Route Rapid ISHE Evaluation Method) could be used to screen the alternatives. The Tool D list would consist of the standard set of questions and would obviously include any that are deemed relevant to the specific project. It alone is not as rigorous as the Tool A/Tool E combination, but this method could be very effective in that it could also prompt for responses to questions that may usually be only considered at later stages in the toolkit. A review using

Tool D incorporated with the other tools in *INSET* Stage I may give the best representative overview of the chemical route alternative.

A more rigorous assessment method (Tool E, Preliminary Chemistry Route Detailed ISHE Evaluation Method) would also include a challenging procedure which will help identify more ISHE route alternatives. The recommended way to proceed through Tool E is to initially use only the constraints criteria from Tool A.1, followed by a screening using the objectives criteria from Tool A.2. Merely using the list of constraints from Tool A.1 may not be limiting enough for Tool E elimination, and more comprehensive lists of objectives are usually required to make well-informed judgements and satisfactory conclusions in obtaining a set of realistic alternatives.

The shortcomings of every alternative need to be assessed and solutions to improve the suggested process must be sought. For example, a route alternative should not be discarded if it merely involves a "Black list" material, as this material may actually perhaps be substituted for a safer chemical or solvent, which makes this route then be more inherently safe than other alternative routes.

The challenging type of approach using Tool B must be an iterative process: any unfavourably-screened alternatives should be reassessed in order to find possible modifications that would make them more attractive, and only when this iterative process shows that an alternative remains more unattractive than the others should it be discarded.

The alternatives that have not been eliminated are subsequently ranked to yield a candidate set of, say five, alternatives.

To rank the alternatives belonging to the candidate set, conjunctive ranking or weighted scoring methods could be used. At this early stage, however, it is normally possible to find the best alternatives without any formal decision aids. Should this not be the case, then methods such as those described in Appendix 8, in Part 3, could be used.

The results of the decision-making could be summarized on the Tool D/Tool E form (Dominant Alternatives Record) which would be transferred to Stage II of the *INSET* Toolkit. The reasoning behind the screening and ranking should be documented well in each case. Ideally, the reason for the rejection should also be documented.

The criteria bounding the project may change during its course. If this occurs, and the procedure has been documented well by using the *INSET* tools, the appropriate stages can be revisited and the alternatives re-evaluated.

3.4 Outputs of *INSET* Stage I

At the conclusion to *INSET* Stage I, in a project where all the aspects of *INSET* Stage I have been used, the following documents should have been prepared:

- *from Tool A.1:* lists of the initial constraints of the project (General Constraints of the Project Sheet, and Project-Specific Constraints Sheet).
- *from Tool A.2:* lists of the initial objectives of the project (General Objectives of the Project Sheet, and Project-Specific Objectives Sheet).
- *from Tool B:* list of guideword-modified alternative routes for the project (Project Option Generation Record Sheet).
- *from Tool C:* a set of alternative synthesis routes and suggested improved versions of these (Preliminary Chemistry Route Options Record), or similar documents.
- *from Tool D:* a result sheet for the general set of question prompts (General Screening Questions Results Sheet).
- *from Tool E:* an analysis matrix of the alternative routes with regard to the constraints and objectives of the project (Criteria Screening Matrix).
- *from Tool D or E:* documented grounds for the decisions taken in selecting the candidate set (Dominant Alternatives Record).

At this natural break point in the decision-making process, an initial review can be conducted whereby the decisions taken are approved by management or further discussed with the relevant groups. Based on these documents, a decision either to go ahead to the next stage of the project or to cease activities is taken. A recommendation of how to search for more attractive alternatives may also be considered.

The documents must be filed in a dossier of the project in case further assessment and investigation proves to be necessary at a later stage.

4. *INSET* STAGE II: CHEMISTRY ROUTE DETAILED EVALUATION

In *INSET* Stage II, although some preliminary experiments may be required to confirm the feasibility of the remaining routes, the emphasis will remain with collecting information from the literature as in *INSET* Stage I. This would normally be supplemented with some scoping calculations of hazardous properties (i.e. using computer-based aids, etc.). Based on decisions taken during this stage, only one or two main routes should remain. These routes are taken to the synthesis laboratory for further refinement (*INSET* Stage III is designed to give support then).

Project stage	**Key issues**	***Information used***
I – Chemistry route selection	Constraints and objectives of the project Routes to make the product Raw materials and wastes involved	*Legislation and company policies* *Known synthesis routes and techniques* *R&D chemists research*
II – Chemistry route detailed evaluation	Basic unit operation selection with flow rates, conversion factors, temperatures, pressures, solvents and catalyst selection Batch vs continuous operation Control/operation philosophy Waste management options/selection	*Knowledge of existing processes* *Knowledge of existing chemicals* *Initial process engineering design principles and experience* *Feasibility and cost information*
III – Process design optimization	Unit operation selection Optimization of the process Equipment selection and sizing Hazard evaluation Inventory of process Single vs multiple trains Utility requirements Overdesign/flexibility Recycles and buffer capacities	*Lab-scale and pilot-scale trials* *As above, plus equipment suppliers* *data, raw materials data, company design procedures and requirements*
IV – Process plant design	Instrumentation and control Location/siting of plant Preliminary plant layout Materials of construction Detailed specification based on concept design Minimize number of possible leak paths Make plant "friendly" to control, operate and maintain Avoid/simplify hazardous activities such as sampling, loading/unloading	*Process conceptual design and codes/standards and procedures* *Experience on past projects/designs*

Aim: To assemble and evaluate all relevant information in order to select the most favourable route for detailed examination and design.

Timing: The tools are best applied from the very start of the project after the decision to produce a particular product has been made. Market research on the product should have been carried out to determine the scale of production and which factors of the production will have an effect on the company image.

Input: Part-completed dossiers for the top, say five, route alternatives. Preliminary experiments and initial assessments of hazards associated with each route may be required. More extensive information searches to complete the dossiers may be required before, for example, feasibility is checked with the process engineer and project management.

Output: Nearly completed decision and information dossiers for the top routes, with a justification of the choice of the most favoured route.

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Considering the importance of the decision-making at this stage of the project, the necessity of having all the relevant information at hand becomes apparent. Not only do we need to gather and record the diverse data needed for *INSET* Stage II, it is also vital that the data is readily accessible for inspection and update purposes. Comprehensive computer-based chemical information management (CIM) systems have recently been proposed as a must for modern chemical companies as they play key roles in the:

- maintenance of SHE information (e.g. foreseeable reactions/incidents/...),
- maintenance of MSDSs,
- maintenance of chemical composition information,
- tracking of chemical inventory,
- tracking of regulations,
- tracking of wastes,
- authorization and approval of chemical requests, orders and usage,
- etc.

On the whole, a system that allows these fundamentals to be easily accessed is very important when ensuring chemical regulatory compliance and reporting. It is also, therefore, a valuable source of information concerning previous company policies, analysing trends, and when evaluating the chemical processes. The data from such a system would be used in conjunction with the *INSET* Toolkit in order to determine that the "best" process route is selected using informed decision-making and taking into consideration the major SHE aspects.

Obviously, a more detailed analysis needs to be carried out when considering a multi-product plant compared to a stand-alone single-product plant. The fact that the plant in question may already, or is planned to have, other syntheses running concurrently is another reason to have a CIM system implemented. A CIM system would allow a more thorough inherent SHE analysis of the process with regard to any other chemical processes that are or will be present.

4.1 The preliminary process block diagram

Operation and design of the production plant contributes to the overall SHE performance of a process, and should, therefore, not be overlooked even at this early stage. Some of the most important aspects connected to operation are elaborated in *INSET* Stages III and IV.

The complexity of a process alternative is usually determined by the operation steps, for example phase separations, recyclings with distillations, filtrations, washings and dryings. These require time and equipment, and so have a considerable influence on the production costs and the SHE aspects of a process. A quick and simple tool to analyse and compare process alternatives is a preliminary process block diagram which includes the reaction and operation steps. This kind of block diagram/flowsheet can be drawn at a very early stage of the evaluation, and additional information can be added when it becomes available.

It is suggested that the first version of the diagram should not differ too much from the procedure described in the source. There are, however, many operations that are not easily performed at the industrial scale (or not possible at all) even though they can be done in the laboratory. For example, very fast additions of reactants are not possible, and filtrations are normally very time-consuming. It is, therefore, not feasible to include in the diagram procedures that are typical for laboratory work but not realistic on a plant scale.

The constraints and objectives identified for the project may restrict the development of the candidate routes. This is particularly true when the proposed process must fit into an existing plant without too many alterations to the equipment layout. These boundaries may even lead to a situation where one of the alternative routes needs to be changed in a unfavourable direction, e.g. the best-suited separation technique is not available. In drawing up the diagram, knowledge is therefore needed on how the different phases of the process route can be carried out on a plant scale.

An experienced chemist is normally able to draw the first version of the preliminary block diagram, but even then it is recommended that engineers are given an opportunity to make their comments on the diagram as early as possible.

The diagram, as described in Tool F, Chemistry Route Block Diagram Record, should show the supply, reaction equipment, etc. and the interconnectedness of the respective vessels (which could represent piping or other transference means). This gives a very quick (and rough) indication of how many storage sites are required (either for reagents, products or wastes), the quantity and general type of equipment, and how many times the substances must be transferred around the plant. These indicators could be construed as being indicative of the cost, risk hazards (e.g. a process with many transfer points is considered to be potentially more hazardous as there are more possible leak paths) and overall simplicity of a process route.

In the case of an existing plant, the block diagram/flowsheet allows the rapid determination of the amount of different process steps, and one can easily ascertain whether new equipment or connections are needed. Bottle-necks in the production become evident, and obvious SHE problems are also easily located using this type of method.

4.2 Checking chemicals involved

It is crucial from a safety, health and environmental point of view to know enough about the properties of the chemicals involved in a process. Not only starting materials and main products need to be investigated, but also intermediates, by-products and any substances possibly formed if the process goes wrong.

Hazards can be generally said to arise from two types of event, acute/catastrophic and chronic. Major-hazard safety relates to acute events usually involving the release of energy or chemicals from a process. The effects are, therefore, generally related to the inventory and hazardous properties of the materials in the process. Chronic events can take two forms, those from authorized or flowsheet discharges (effluent streams) and those from fugitive emissions arising from non-designed weeps and minor leaks and from activities which breach the process containment (e.g. sampling, charging of raw materials, maintenance). The latter two aspects can generally be regarded as environmental and health issues respectively.

A systematic approach that deals with the main hazards, mainly by making sure that the aspects are considered, and analyses the process routes for likely ISHE problem stages, is presented in Tool K, Rapid ISHE Screening Method. Although the process is a rather "fast-track" approach to *INSET* Stage II, depending on the objectives of the project, this tool could raise sufficient overall awareness of the routes for a decision to be made as to which ones proceed to *INSET* Stage III.

A general classification of chemical hazards from a SHE point of view is needed to provide the basis for the assessment. Tool G, Chemical Hazards Classification Method, the proposed classification system for the hazardous properties of the chemicals, is based on the "Risk phrases" from EC Directive 84/449/EEC, together with the UN's "Recommendations on the transport of dangerous goods".

In *INSET* Stage II, preliminary information on chemicals and their hazardous reactions is collected for each of the remaining alternative synthetic routes. The same is done for the corresponding engineering-modified alternatives that also fulfil the criteria defined in *INSET* Stage I. In *INSET* Stage III, supplemental information will be added for the selected alternative(s).

4.2.1 Data on chemicals involved

The properties of the chemicals present greatly affect the inherent SHE performance of each synthetic route. It is, therefore, important to identify all the relevant properties of the substances proposed to be used. The amount and quality of information available for different chemicals varies and, especially for new chemicals, it may be difficult to find any data at all. Estimations and calculations using computer-based aids may supplement this lack of data.

Useful monographs have been published for the most common industrial chemicals. Information on various other chemicals can also be found in several databases available either on diskette, cd-rom or even on-line, e.g. via the Internet. Databases and tables that allow a chemist to search for a more inherently SHE alternative for a process that uses a hazardous substance have been previously published. For example, the US EPA's Pollution Prevention Information Exchange System (PIES) is aimed at developing and integrating "substitution" databases that allow a chemist to propose a more inherently SHE alternative synthetic route in which, for example, a complex multiple-solvent process could to be "simplified" by substitution, in multiple stages, to the same single solvent.

Solvents have traditionally been chosen merely on the basis of economics and effectiveness. Other factors that now need to be considered very early on in the process identification and selection stage include the regulations relating to exposure to solvent vapours as well as ozone effects and recovery aspects.

Operating and reaction conditions have a strong influence on the side-products formed. There may also be substances that are non-hazardous as such, but may cause problems that increase, for example, the level of occupational health hazards in a plant. These must be considered at this stage. Typical examples are solids or semi-solids that clog filters and other equipment, salts that cake the bottom of a vessel, strongly-coloured substances which must be removed by extensive washing, or substances that cause foaming or foam themselves. More examples where the consideration of ISHE aspects has been beneficial can be found in Appendix 4, in Part 3.

These properties can cause major additions to the block diagram of the process. Therefore, they need to be addressed as early as possible. The identified hazards could be included in the "comments" field of the chemicals' functions matrix in Tool G.

For the purpose of *INSET* Stage II, the properties of the chemicals can be estimated if they are not otherwise available. An experienced chemist can tell much about, for example, the chemical reactivity of a molecule just by looking at its structure. Properties that are easily estimated based on the structure are, for instance, freezing point, boiling point, flash point, and auto-ignition temperature. However, computer-aided estimations of some chemicals' properties may need to be substantiated experimentally. Although this situation is not particularly welcomed at this stage of development, any substances, or the reaction itself, that are hinted to have suspect hazardous properties may need to be checked in the laboratory even at this stage.

Tool H of the *INSET* Toolkit, Record of Foreseeable Hazards, provides a guideline for analysing the hazards that evolve from the reactivity and stability of the chemicals involved in the remaining route alternatives.

The documentation of the properties should be done carefully in order to avoid repetition of the work later on. A complete list of chemicals involved in the route together with the role of the chemicals in the process should be included (Tool G).

Much of the information for this stage will be gleaned from the MSDSs of the chemicals involved. Although these will often be found in electronic form, they should be filed in the dossiers of the route alternatives. See Tool G Supporting Information for more information.

4.2.2 Known incidents and foreseeable reactions

In addition to data on the properties of isolated substances, information is also needed on the behaviour of the chemicals in various environments. A complete survey of all the chemicals present in the different process routes assessed is not needed at this stage, but reactions of the most hazardous substances must be known when selecting the chemical route for further optimization in the laboratory. It is important to incorporate a study of chemical analogues as well, especially if the chemical itself has been seldom used in industry.

Information on previous incidents and foreseeable reactions is compiled in various books. Examples mentioned here include: Bretherick's Handbook of Reactive Chemical Hazards (two volumes; cd-rom version also available), NFPA's Manual of Hazardous Chemical Reactions, and US EPA's "A method for determining the compatibility of hazardous waste".

Databases containing information on industrial incidents are also available on diskette, cd-rom, or on-line. Several initiatives have been taken to provide high-quality information on industrial accidents (see Tool H Supporting Information).

The information on the incidents and possible hazardous situations can be recorded in a table (Tool H), together with a reference to the source of the information. Reactions such as decompositions, involving only one substance in the presence of heat, should also be documented.

Many chemical reactions that are operated on the industrial scale involve the release of heat, that is, they are exothermic. In addition, even greater amounts of heat can be released when decomposition reactions are initiated through unsuitable operating conditions. The consequences of a violent exothermic runaway reaction can be as severe as those from the ignition and explosion of a fuel/air mixture. It is important, therefore, that any exothermic reactions which could arise are identified and that possible chemical reaction hazards are considered.

In some cases, calculations can provide information on the reactivity of the chemical – such as the heats of reaction (see Tools H and L Supporting Information), and this data can also be included in the table.

The effect of scale-up is particularly important. A reaction which is apparently innocuous on the laboratory scale or even the semi-technical scale, can be disastrous on the manufacturing scale. Thus, the heat release from a highly exothermic process, for example the reduction of an aromatic nitro compound, can be controlled easily in laboratory glassware. If the same reaction is carried out in a large plant vessel with a much smaller surface area/vessel volume ratio, efficient cooling must be provided, or a runaway reaction and violent decomposition may occur.

Similarly, a large quantity of gas produced by, for example, the sudden decomposition of a diazonium compound, can be vented easily on the laboratory scale, but the same decomposition on the large scale could pressurize and rupture a plant vessel.

In addition to the above, the consequences of possible process maloperation must be considered, for example overcharging or omission of one of the reactants, agitation failure, or poor temperature control.

Chemical reaction hazards principally arise from:
- rapid exothermic reactions which can raise the temperature to the decomposition temperature or cause violent boiling of the reactants,
- thermal instability of reactant mixtures and products,
- rapid gas evolution which can pressurize and possibly rupture the plant.

Thus, a knowledge of the heat associated with the desired reaction, ΔH_r , and information on the thermal stability, i.e. the temperature at which any decomposition reaction may occur on the plant scale and its magnitude, are essential to evaluate the hazards.

Screening of the chemicals for reactivity and stability, and the subsequent comparison of the route alternatives, can be done using Tool L, Chemical Reaction Reactivity – Stability Evaluation.

Issues arising from problems with transportation are covered by various sections, including Tool Q in Stage IV.

4.3 Evaluation of the alternatives

The cost factor is usually the main driving force behind choosing a particular route over another, but, for instance, the scale of production may also affect the selection process. Various other aspects also influence the evaluation and decision-making, and these must be considered as well. Ideally, when comparing routes, all of the alternatives should be at the same stage of development. This is seldom the case, and estimations of yields, costs, etc. may therefore need to be based on different kinds of projections.

The maturity of the processes greatly influences the outcome of the first evaluation of different alternatives, and, based on the information available, an assessment of the stage of development of the process should be made. This is especially true if, for example, alternative 1 is a university synthesis, alternative 2 a well-known industrial process, and alternative 3 a novel idea presented by a colleague.

The "robustness" of the process should also be evaluated in order to estimate the inherent SHE performance of the foreseeable industrial process, but this is not so easily defined.

It is, however, outside the scope of this document to suggest evaluation tools for aspects other than safety, health and environment. If possible, the evaluation process should be carried out in a uniform way and by considering all aspects of all the alternatives. How rigorous the evaluation will be, is based on how much information is available and how detailed the evaluation has to be in order to achieve the aims of the study, i.e. forming the basis for the ranking of the different alternatives.

Three tools with different level of detail are suggested. Should a rapid screening tool be sufficient at this stage, the very simplistic index proposed in Tool K could be used, but normally the decisions made must be based on a more detailed analysis of the operations involved in the different chemical routes as described in Tool G.

As it is, in practice, very difficult to introduce only one index that covers all aspects considered at this stage, separate indices for health, safety and environment are suggested in Tool I, in order to provide a measure of the inherent hazard involved with process or plant. The scores determined using the indices should obviously be used with care as, only then, can they help the decision makers determine which alternative should be passed to INSET Stage III.

Various environmental indices have been introduced, for instance by ICI and HMIP in the United Kingdom, and by Dr Rossi in Finland. ICI's "environmental load factor" (ELF) is simple, but does not take any account of the degree of harm presented by any stream. The other two are very detailed and generally too rigorous for basic process screening.

Many of the *INSET* indices are based on the "Risk phrases" (EC Directive 84/449/EEC). Used at this stage, the advantage of this method is that it only requires some basic stream data and the R-phrase categories of the materials involved. It must be noted that only continuous and other scheduled releases are taken into account, leaving accidental releases to be evaluated separately.

The Tool I indices cover the following aspects: fire & explosion hazards, acute toxic hazards, health hazards, acute environmental incidents, transport hazards, gaseous emissions, aqueous emissions, solid wastes, energy consumption, reaction hazards, and process complexity.

The multi-attribute ISHE comparative evaluation tool is presented in Tool J. This tool is designed to pool the calculated indices in a way which will allow a direct comparison of the alternatives to be made. The core of the tool is the presentation of the indices in such a way that allows the better alternatives to be chosen, and the worse ones to be challenged further. The challenging procedure outlined in Tool B could be effectively used here.

4.4 Ranking and decision-making

Ranking of the remaining alternatives is usually an even more demanding procedure at this stage than in *INSET* Stage I, as much more information about the routes and their respective drawbacks should have been uncovered. It is not an easy task to assess the different alternative routes based on the information at hand, especially as the level of detail varies from one route to another.

The search for possible reactions giving the desired product often results in the discovery of interesting alternative reactions which are obviously not fully optimized. This may be due to the fact that the route was incorrectly or incompletely published, never experimentally tested (in the case of the computer-simulated or purely theoretical in-house routes), or never optimized. When challenging an alternative, one must realize that the potential for improvement during optimization of the process is greater if a route with initially lower yields is chosen for further investigation. With optimization, conversion, selectivity and isolated yields can normally be increased. On the other hand, large-scale production may decrease the isolated yield from that obtained in the laboratory. *INSET* Stage III addresses the optimization of a process in more detail.

Obviously, an alternative should not be unfavourably ranked solely on the basis of yield alone. A synthetic route that produces a large quantity of by-product may still be considered viable if that by-product is seen to be useful in another capacity. The alternative may then still warrant further investigation.

The two possible extremes arising from the alternative synthetic approaches are: a simple process with expensive raw materials, or a complicated process with cheap raw materials. The complicated process will, however, usually require a more expensive plant. The less complex process (and correspondingly simpler plant) is generally associated with smaller warehousing requirements and lower materials inventory. These "simple" plants usually require less instrumentation and add-on safety equipment, and, together with the lower costs for their corresponding maintenance and testing, certainly seem to be the more appealing from an inherent SHE perspective and so should be ranked favourably.

More formal ranking techniques are appropriate when alternative routes cannot be ranked with ease. Formal ranking techniques aim to identify the "best", or at most the "two best", inherent SHE alternatives by structuring the decision, for example by forcing detailed value assessments of key alternatives of each candidate.

Appendix 8, in Part 3, is devoted to a discussion of decision aids. Following a CCPS book on decision-making techniques, five categories are briefly introduced. Two of these are considered to be of most interest within the context of the *INSET* Toolkit:

- decision techniques which do not treat uncertainty and value separately,
- decision techniques that treat uncertainty and value separately.

Techniques belonging to the first category do not distinguish between the inputs (or values) and the uncertainties (or risks) associated with them. This category includes weighted scoring methods, one of which is the analytic hierarchy process (AHP). Whilst AHP is favoured because of its speed of operation and demands for explicit comparisons, it has the disadvantage that it cannot take account of risk or uncertainty.

In circumstances where uncertainty should be considered explicitly, then pay-off matrices or methods based on utility theory (decision analysis, multi-attribute utility analysis) should be used. When the uncertainty of the outcome is generally not dependent on the decision alternative or strategy, the pay-off matrix approach can be utilized. If this is not a reasonable assumption, the two latter methods should be considered. Decision analysis is appropriate when the objectives can be measured on a single attribute, whereas multi-attribute utility analysis should be adopted in the multiple attribute case.

Subsequent to the general introduction of decision-making techniques, two tables are included in Appendix 8 to summarize characteristics and applicability of various decision aids. Finally, application within *INSET* is also illustrated, with an example utilizing the AHP.

It should be remembered that selecting the best inherent SHE option is an iterative procedure. All the remaining set of alternatives (in addition to the top alternative) should therefore be ranked using the most appropriate ranking aid. This will allow the challenging and option generation procedure (Section 4.5) to be implemented in such a way that all the alternatives will iteratively be challenged and compared to the top alternative. This would continue until the user is satisfied that all proposed improvements have been investigated so that the best route will be eventually chosen. Only after extensive challenging should the final decision on which is the best route alternative be made. Ideally, the reason for the others' rejection should be recorded on the form in Tool C.

4.5 Challenging and option generation

The most attractive synthetic route will be contained in the candidate set of route alternatives, and the engineering-modified versions of these. While we could decide which route is the one chosen to proceed to the next stage of the *INSET* Toolkit merely by ranking (using the data gathered and the calculated indices), it is crucial for the whole project that no alternative is rejected without being "challenged". The challenging type of approach must be an iterative process where any unfavourably-screened alternatives should be reassessed in order to find possible modifications that would make them more attractive. By this we mean that improvements to the original process are suggested in order to arrive at a more ISHE alternative. Tool B has been proposed to challenge the alternatives and bring ISHE considerations into the selection process.

In practice, most process alternatives will not fulfil all the requirements set. Therefore, the shortcomings of every alternative need to be challenged, and solutions to improve the suggested process must be sought. The modified alternative should then again be compared with the previously best-ranked alternative.

The objectives should also be reassessed to determine whether the "cognitive coverage" is still adequate. What would happen if additional objectives were included or some of the original ones were relaxed? How would the modifications affect the candidate set of alternatives? Only when this iterative process shows that an alternative remains more unattractive than the best one should it be discarded.

One of the basic inherent SHE principles is the concept of simplification: the design of processes and facilities so that any operating errors, etc. are made less likely. Consideration of whether is it possible to make the overall process simpler, for instance simply by challenging the order of the different synthesis steps, should also take place at this stage. Tool B shows how to consider changes in the block diagram/flowsheet. The tool also shows alternative ways of carrying out a certain operation.

Due to the large amount of different types of chemical processes, not even general solutions can be given here. Some aspects that could be considered at the various points are highlighted in the appropriate tools and the corresponding examples.

Minor modifications to a route, as a result of challenging, may be included in the forms of Tools C, E, F, G, I, J (or K), but most other changes will require that the necessary information is documented as a new alternative route, or simply on a new form.

4.6 Outputs of *INSET* Stage II

At the conclusion to *INSET* Stage II, in a project where all the aspects of *INSET* Stage II have been used, the following documents should have been prepared:

- *from Tool B:* list of guideword-modified alternative routes for the project (Project Option Generation Record Sheet).
- *from Tool F:* a preliminary process block diagram for each alternative (Chemistry Route Block Diagram Records).
- *from Tool G:* chemical list that includes its function and comments (follows from Tool C), and the S, H, and E hazard classification (Chemical Function & Hazards Classification).
- *from Tool H:* forms that cover past incidents and foreseeable reaction hazards for the chemicals involved in the route (Record of Foreseeable Hazards).
- *from Tool L:* a Chemical Reaction Reactivity – Stability Evaluation Record.
- *from Tool K:* a "fast-track" Chemistry Materials Hazards Classification and a Process Hazard Index Classification.
- *from Tool I:* inherent safety, health, and environmental performance indices evaluation results sheets.
- *from Tool J:* multi-attribute ISHE comparative evaluation results sheets.
- *from Tool B applied to the process route alternatives:* modified or newly-generated route options derived from application of the "challenging" tool.

At this stage, we encounter a natural break point in the decision-making process where we must decide on the ≈1 or 2 most "practical" routes. An initial review can be conducted whereby the decisions taken are approved by management or further discussed with the relevant groups. Process engineers, safety experts, project management, production personnel, etc. would perhaps need to be consulted or discussions held in order to decide which process goes on to the next stage. A suggestion is to hold an ISO-steering group type of meeting with design and operation personnel.

Based on these discussions and the documents, a decision either to go ahead to the next stage of the project or to cease activities is taken. A recommendation of how to search for more ISHE alternatives should also be considered.

The documents must be filed in a dossier of the project in case further assessment and investigation proves to be necessary at a later stage.

5. *INSET* STAGE III: PROCESS DESIGN OPTIMIZATION

The intention of *INSET* Stage III is not only to collect sufficient information to pass over to the design engineers doing the detailed design, but also to flag up any key issues which should be made known to senior management. The tools are best applied once the outline of the chemical process, along with the main reactions, has been identified – including projects for which no alternative reactions have been available. This stage is likely to involve extensive efforts to accumulate and evaluate all relevant SHE information.

Project stage	**Key issues**	***Information used***
I – Chemistry route selection	Constraints and objectives of the project Routes to make the product Raw materials and wastes involved	*Legislation and company policies* *Known synthesis routes and techniques* *R&D chemists research*
II – Chemistry route detailed evaluation	Basic unit operation selection with flow rates, conversion factors, temperatures, pressures, solvents and catalyst selection Batch vs continuous operation Control/operation philosophy Waste management options/selection	*Knowledge of existing processes* *Knowledge of existing chemicals* *Initial process engineering design principles and experience* *Feasibility and cost information*
III – Process design optimization	Unit operation selection Optimization of the process Equipment selection and sizing Hazard evaluation Inventory of process Single vs multiple trains Utility requirements Overdesign/flexibility Recycles and buffer capacities	*Lab-scale and pilot-scale trials* *As above, plus equipment suppliers data, raw materials data, company design procedures and requirements*
IV – Process plant design	Instrumentation and control Location/siting of plant Preliminary plant layout Materials of construction Detailed specification based on concept design Minimize number of possible leak paths Make plant "friendly" to control, operate and maintain Avoid/simplify hazardous activities such as sampling, loading/unloading	*Process conceptual design and codes/standards and procedures* *Experience on past projects/designs*

During *INSET* Stage III in the project, the basic chemistry and manufacturing route will be determined. Opportunities to substitute hazardous materials or eliminate them will then have essentially passed. Many of the process conditions such as concentrations, temperatures and pressures will be set by the chemistry, so the opportunities for attenuation/moderation will also be limited.

Now is the time to select the appropriate process unit operations and equipment and determine how the plant will be operated. There will, therefore, be many opportunities to eliminate or reduce the need for process equipment and instrumentation, making the plant simpler, more user-friendly, and cheaper, and the selection of equipment and the operational regime can have a major impact in reducing the inventory of hazardous materials.

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Aim: The aim of the tools at this stage is to help the development chemist and the designer systematically challenge the basis of the chemical/process flowsheet to identify and assess any alternatives that may offer improved inherent SHE performance. It includes the basic elements of hazard identification, option generation, screening and decision support.

An "option generation" and "change" tool is provided to be applied to the flowsheet to challenge the sequencing and conditions of the proposed chemical/process flowsheet. Next, the "challenging" tool can be applied to help the designer break down the process into its key unit operations and functions, and identify and assess alternatives that may be more ISHE.

Where the chemistry route has not been finalized, it may sometimes be advantageous to scale up more than one route on the basis of SHE, ISHE and non-SHE performance and then optimize these before deciding on which one to use.

Timing: The tools are best applied as early as possible and as soon as the outline chemical process has been identified, along with the main reactions, conditions and unit operations. This would normally coincide with the laboratory scale optimization trials or during pilot-plant trials.

Input: A description of the basic chemical/process stages and conditions is required, preferably in the form of a block diagram, flowsheet or process flow diagram showing the sequence of the stages and any links between these. Information on the process materials and hazards is also required, for example in the form of a hazard file or data sheets. More detailed experimentation/laboratory optimization may be involved to identify hazards and operability aspects. Extensive information searches may be required to complete the information matrices.

Output: Identification of the key information (e.g. hazards, operability, safe operating limits, sensitivity to contaminants, sensitivity to off-spec conditions, the robustness of the chemistry) and justification of choice, with emphasis on ISHE, for senior management and design engineers should complete the dossiers with the completed modified flowsheet/flow diagrams showing the accepted changes. The record sheets should document the inherent SHE studies undertaken and the outcome of these.

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By working through *INSET* Stage III, a justification of the best route can be shown. The decision to proceed, stop, or re-visit other routes can be based on the information collected.

Study record sheets are included in the *INSET* Toolkit for this purpose. The overall outcome of the application of these tools should be a more inherently SHE process and unit operation selection, with the corresponding documentation to demonstrate and support this.

It is important that all relevant topics in *INSET* Stage III are considered several times during the progress of the project in order to check that a solution to one problem does not create a new one.

The minimum factors follow that any process development and plant design project should take into account. Consideration of all these factors is necessary at or before this stage.

- *Safety*
  - the possibility of deviations from design values,
  - the material inventory available to be released,
  - the hazardous properties of that material relating to major hazards, and perhaps
  - the likely discharge rate/amount in the event of a leak, and some indication of the frequency/likelihood of a leak (perhaps based on the size of the plant and its complexity).
- *Health*
  - the hazardous properties of the material in the process relating to health effects,
  - the likely fugitive emission rate of that material – since in small weeps/concentrations all material is likely to end up in the air in one form or another (volatility not that important), and perhaps
  - the chance that people are exposed to this.
- *Environment*
  - the mass of materials (per year) discharged into the environment,
  - the hazardous properties of those materials relevant to the local environment/medium they are introduced into (air, water, land),
  - the fate of the materials.

If more detailed approaches than those presented in *INSET* Stage III appear worthwhile, then, for example, the DOW Chemical Exposure Index Guide (2nd edition, Sept. 1993) and Fire and Explosion Index Hazard Classification Guide (6th edition, May 1987) (both available from the American Institute of Chemical Engineers) or the MOND Index (2nd edition, March 1985) can be used for fire and explosion and toxic release acute events. For environmental impact of discharges to air, water or land, the Consultation Document on Environmental, Economic and BPEO Assessment Principles for Integrated Pollution Control (HMSO, April 1994; compiled by the HMIP in the United Kingdom) provides a detailed methodology, albeit with many shortcomings and simplifications.

It should also be noted that any inventories or discharges of hazardous materials from services and utilities should also be included (e.g. refrigerants, heat transfer media, solvent recovery, waste treatment), in order to gain an appreciation of the overall impact of the process on SHE performance.

The tools mentioned in *INSET* Stage III of the toolkit can be used by individuals or by a study team. The tools developed are designed to be used from the phase when the chemical route has been decided and the laboratory work starts, and they also are useful up until the detailed design of the plant commences and established risk analysis methods, such as HAZOP studies, are used.

INSET Stage III is also the first part of projects where the chemical route has already been set and the design of the plant, including modifications of existing facilities, is the topic of interest. The overall sequence suggested for processes where the chemistry is fixed, and information from Stages I and II of the *INSET* Toolkit is therefore not available or is in a different format, is:

1. *Determine the constraints and objectives of the project*
   Many of the decisions taken should be based on the constraints and the objectives of the project, which can be documented on the Tool A.1 and A.2 forms.
2. *Draw up the process flowsheet/flow diagram*
   If not already done, draw up the chemistry and process stages in diagrammatic form (e.g. by using Tools C and F), showing each stage in turn, with its inputs, outputs and conditions.
3. *Information on chemicals*
   A substantial amount of information about the materials used is needed at this stage. This data should include past incidents and other foreseeable undesired reactions. Tools G, H, and I can be used for documenting these important aspects.

5.1 Data on chemicals involved

It is crucial from a safety, health and environmental point of view to know enough about the properties of the chemicals involved in a process. Not only starting materials and main products need to be investigated, but also intermediates, by-products and substances formed when the process goes wrong.

Ongoing European and world-wide research helps companies get the required information on the most common chemicals used in industry, thus minimizing the costs of testing and analysis work. Several European and American databases contain information on the properties of commonly used chemicals, and legislation requires the access and distribution of material safety data sheets (MSDSs) for every chemical that is present in the workplace.

It is self-evident, however, that the information from the available databases may not be comprehensive enough for many substances, and companies may need to investigate some properties of the chemicals themselves. This is generally a sizeable task. Many test procedures have been standardized in order to obtain comparable toxicity and other data for different chemical substances.

A section in Appendix 5, in Part 3, lists the above-mentioned and other on-line Internet databases together with many that are available on cd-rom or other formats. It is not the aim of *INSET* Stage III to describe in any more detail how to find data on chemicals in databanks or how to carry out the different tests needed to obtain the information. Neither is it suggested here how to store the collected data. Many companies have their own computerized systems which are designed solely for this purpose.

5.2 Hazard identification and evaluation

In *INSET* Stage I, constraints and objectives were set for the project. In *INSET* Stage II, the operability aspects of the most interesting routes were assessed based on information available at that stage and using expert judgement. In *INSET* Stage III, a deeper understanding of the influence of different operation alternatives on the plant is needed.

The first formal safety and environmental study is carried out at this stage. It is not the intention of the *INSET* Toolkit to give advice on how general safety and environmental studies should be conducted, but for companies having no hazard analysis method at all in place, Tool M, Process SHE Analysis/Process Hazards Analysis and Ranking, is presented. However, many companies have their own instructions for these studies (There are several published check-lists and formal hazard analysis methods which can be adopted if the company wants to improve its hazard study practices). It is important that these procedures are amended in such a way that the awareness of the potential of inherent SHE solutions is appreciated.

It may be useful to rank the listed hazards to see which ones deserve most attention. To do this, review the hazards identified, at the end of or during the hazard identification study, to assess their relative importance. Some suggested ranking categories are presented in Tool M. The highest ranking from the various categories should be used and can be noted on the Process Hazard Identification Record Sheet in Tool M. Alternatively, company or other ranking categories may be used.

When identifying the hazards based on a revised flowchart, it is especially important to assess that an inherent SHE solution at one point does not result in worsening of the situation in other parts of the plant. In other words, in evaluating the benefits of a process change it is necessary to also consider the hazards of the total process.

Towards the end of *INSET* Stage III, it may be worth revisiting the original list of hazards identified to see which of these have been addressed by the changes. Noting which hazards have been avoided, eliminated or reduced in seriousness, together with a new hazard ranking, should give a reasonable indication of the overall effectiveness of any changes made. A column on the Process Hazard Identification Record Sheet in Tool M is provided for this assessment. Note that the hazard ranking system in Tool M must be applied in full to the changed situation to ensure that an increase in inherent safety, for example, is not offset by a decrease in inherent environmental performance.

Important considerations of a safety and environmental study during the development stage include a variety of topics related to the materials and equipment used. For example, some safety factors to consider when assessing a reactor include the following:
- incorrect charging sequence,
- agitation failure leading to layering,
- contamination of reactants (e.g. exposed to metal),
- addition of reactants too quickly,
- temperature too low, leading to accumulation,
- temperature too high, caused by cooling failure,
- incorrect reactant concentration,
- removal of volatile diluents, leading to increased rates of reaction,
- etc.

In order to assess the hazardous consequences which may arise from individual substances in a plant, it is necessary to have information on, for instance, the flammability and toxicity characteristics of any gases, liquids and powders used.

The flammability characteristics include:
- *flammability* – does the material support combustion and under what conditions?
- *ignition sensitivity* – temperature/energy required for ignition.
- *ignition consequences* – rate and type of combustion/flame spread, pressure development during an explosion.

Data on the flammability characteristics of common liquids and gases in air are readily available in the literature. Inherently safer alternative substances should be sought for whenever feasible. However, information for powders is rarer, partly due to the fact that particle size and the moisture content of the solids markedly affect their flammability characteristics. Testing is, therefore, suggested if powders are really needed. Powders should, however, be avoided whenever possible.

Toxicity and eco-toxicity of chemicals need to be known for all main chemicals. The consequence of oral intake of a substance is, in this context, not as important as the effects of inhalation and skin contact. The relative importance of different eco-toxicology data for each substance is much dependent on the environment surrounding the site where the chemical is used. Eco-toxicology data is mainly based on tests carried out with standard species and, therefore, does not necessarily cover those species which are of importance in the vicinity of the plant.

Among the more critical uncertainties associated with extrapolation of toxicological and eco-toxicological data from experimental to actual conditions are assumptions about:
- *route-to-route extrapolation,* i.e. comparability of exposure by different routes of administration.

- *chronic-to-acute extrapolation,* i.e. comparability of different regimes of exposure.
- *high-to-low-dose extrapolation,* i.e. proportionality between external exposure, level and the resulting delivered dose for high-exposure studies, compared to lower levels typical of environmental exposure.
- *species-to-species extrapolation,* i.e. scaling or translation of dose to determine exposures yielding equivalent doses in different species (if the extrapolation is possible at all due to qualitative differences in species and strains).

Generally, relatively little is known of the consequences to nature caused by accidental releases of chemicals, and therefore Tool P, Hazards Range Assessment for Gaseous Releases, in *INSET* Stage IV concentrates on the hazardous consequences of gaseous substances to man only. Modelling of releases to water and soil is more complicated, and many of the models used are still under development. Therefore, no attempt is made to introduce a tool to assess these aspects but the reader should consult an expert or use methods published by, for example, the US EPA amongst others.

5.3 Option generation

Even when the main reaction sequence for a chemical process has been fixed, there are still many other changes that can be made. A review of the proposed flowsheet is needed to identify possible options/alternatives which may be inherently safer (or offer other advantages). The aim is to identify possible changes to the sequence of operation, ways in which steps can be combined or carried out simultaneously, or changes to materials or conditions that could make the process inherently safer. Most of the process optimization stage in the laboratory is part of this option generation phase, and a lot of time and effort is often spent trying to obtain a robust and competitive process. Consideration of inherent SHE aspects should be ongoing throughout the laboratory work, and the hazard evaluation should be repeated whenever changes to the process are made.

Following the principles outlined here in *INSET* Stage III means, for example, that the Process Change Guideword Prompt List (Tool B) should be applied in turn to each stage, input and output, of the flowsheet to help identify the alternatives. The Process Functionality Prompt List (Tool B) may also be applied to each function on the flowsheet to help identify alternative means of achieving the desired function. The newly generated alternatives can be recorded on the Process Hazard Identification Record Sheet (Tool M).

Both during and at the end of the study, the identified alternative options should be evaluated to see which merit further investigation. The conclusions of this review can be recorded in the "comments" column on the Process Hazard Identification Record Sheet in Tool M. It may be helpful to this assessment if the SHE benefits and technical and economic implications are considered. A simple ranking method is presented within Tool M for this purpose, giving scores for safety, health, environment and business performance. Alternatively, the qualitative indices presented in Tool J (Qualitative Scoring Method) could be used to explicitly address a more detailed number of factors.

In the sections below, some basic ISHE aspects are discussed.

5.3.1 Chemicals

The main chemicals, including reactants, solvents and products, should at this point have been checked against lists, regulations, MSDSs, etc., and the most important information received should have been gathered, for example in the matrix shown in Tool G or by using a computerized tool. In addition to this, hazards can be significantly reduced (or increased) depending on the grade of materials used. Some examples are given below.

For instance, in addition to the information on the pure substances, sufficient information on the anticipated technical grade of the different chemicals should be assessed as well. This is important since new SHE-related problems can occur with an impure substance. The level and identity of impurities in the starting materials can be crucial for the safety, health and environmental properties of that substance. If the impurities substantially affect the outcome of the process, the substance is not acceptable from an inherently SHE perspective. The impurities can affect the process, for instance, by slowing down or accelerating the reaction, by increasing the formation of side-products (e.g. decomposition), by making the work-up more difficult, or by causing material problems (e.g. corrosion).

In many cases, material specifications based on a certain percentage, say 98% purity, are not enough. The composition of the remaining 2% can make the difference. The situation is less critical if several impurities are present compared with the situation where the whole 2% consists of only one reactive impurity. Relatively benign impurities can also cause safety problems, e.g. due to accumulation or by poisoning catalysts.

Redistillation of solvents or regeneration of other chemicals are sources of impurities (e.g. water) and should be further evaluated. Other substances may be relatively sensitive to impurities, and this sensitivity obviously presents a potential problem, for instance if the chemical is contaminated while handled.

Technical-grade materials should be used during the process optimization stage in order to assure that the effect of impurities is recognized. If the starting material is a mixture of compounds, which is the case when biomass, oil or minerals are used, the whole optimization process must be designed in such a way that the differences between batches are taken into consideration.

The purity requirements of the final or intermediate product affects the inherent SHE properties of the process as a whole. In some cases the purification of the feedstock or the reaction mixture at an early stage can be beneficial, in other cases an impure intermediate product or a mixture can be accepted if a natural purification step can be identified downstream.

The purity requirements of the final product should be specified together with the buyer of the substance. Unnecessary purification, drying or concentration steps should be avoided as they add to the complexity of the process, and thereby increase the possibility for SHE problems. In addition, there is a need for careful testing of the shelf-life of all products that are stored. This includes substances that under normal circumstances are stored only for short periods of time, but which sometimes might be held in storage for an extended period of time, e.g. due to the summer shut-down or problems with transport.

Some chemicals can be purchased as different grades, e.g. as powders, granules, pellets, etc. Appropriate care must be taken in order to select the most inherently safe alternative. For instance, acids and bases are commonly used for pH regulation. A typical feature of many of these is their availability in many different forms (concentrated solution, oversaturated solutions, diluted solutions). Appropriate care must be taken when selecting the most suitable alternative as other grades are usually readily available (and often at the same site). There is often, then, the risk that material of a wrong grade is used. The effects of this happening must be considered.

The physical state of substances present in the production process should be chosen based on inherent SHE principles. For example, the formation of flammable/explosive dusts need to be considered. Such seemingly harmless and diverse materials as aluminium, coal, cork, corn, milk, sugar, zinc and many others are actually flammable as dusts.

Solidification of chemicals can cause SHE problems and should be avoided if possible. The most common example is the formation of ice, but chemicals can also solidify in pipelines preventing further transfer.

It is also well-known that liquid chemicals stabilized by the presence of suitable substances can cause a hazard if allowed to crystallize since the stabilizer will be unevenly distributed in the chemical (mainly in the liquid phase) and an auto-catalysed reaction may occur when the chemical has melted, due to poor mixing.

The problem with pressurized gases is commonly recognized and should be taken seriously when assessing the acceptability of the process from an inherent SHE perspective.

Although the synthetic route may remain substantially the same, it is sometimes possible to significantly improve the process by introduction of a minor change in the intermediate, that is by varying one of the following:

- change of a protecting group;
- change in, for example, the ester used in order to increase/decrease rate of reaction, to improve selectivity or to change the physical properties, e.g. the solubility;
- change in the derivative, e.g. the salt form, chain length or ester group of an intermediate, possibly to improve ease of isolation;
- change of the leaving group to increase rate of reaction or to circumvent a possible effluent problem.

The formation of small amounts of hazardous by-products is in many cases not critical as they can be disposed of in a controlled manner using end-of-pipe solutions, e.g. incineration, biological waste water treatment. There are, however, classes of substances that can accumulate or become concentrated in the system after work-up of the main product. Typical examples are the by-products formed during nitrations. The amount of these over-nitrated substances can be substantial, for example in residues from solvent redistillation, and can be the cause of explosions.

The aim of initiators and catalysts is to facilitate chemical reactions. With the help of a catalyst, the reaction finds a new way to progress, the activation energy of which is lower than that for the homogeneous reaction. Due to this, reactions can be carried out under milder conditions which, therefore, improves the inherent SHE performance of the process. A major concern is that catalysts may speed up not only the desired reaction, but also any side-reactions, or even generate other side-reactions. This lack of selectivity may cause unsafe situations.

Catalysts can either be classified as homogenous or heterogenous. In addition, enzymatic and photocatalysts also exist. The major advantage of homogenous catalysts is that the reaction mechanisms can be better controlled than with heterogenous catalysts, and so reaction conditions are typically milder. In general, the greatest problem is to separate the homogenous catalyst from the reaction mixture. However, in industry the largest group of processes are those where gaseous or liquid starting materials are converted using solid catalysts, that is using heterogeneous catalysts.

The stability of the catalyst is also important from an inherent SHE point of view since the change and regeneration of spent catalyst can include hazardous stages, for example a spent catalyst may catch fire if handled carelessly. Neither are extremely reactive catalysts good, for example due to heat transfer problems leading to an increased reaction rate at the higher temperature causing a runaway situation (though the reaction rate mostly can be adjusted by controlling the addition rate of a reactant). It is important that the activity and selectivity of the catalyst remains stable as long as possible, and that the difference between batches of catalysts is small as this can greatly affect the performance of the process.

For example, in the manufacture of Merck's cefoxitin a change from a complex catalyst (N-silyl-trifluoro-acetamide) to a cheaper and simpler material (powdered molecular sieves) allowed not only the required acid protection group to be removed, but also meant that a simpler amine protecting group could be used in the sequence. However, further scale-up indicated that batch-to-batch differences in the molecular sieves exert an unacceptable variation in the process, and the ultimate reagent chosen was the soluble catalyst trimethyl-silyl methyl carbamate.

Finally, in general, there is very little information available in the open literature on mixtures of chemicals and on the properties influencing the ISHE performance of the process. Still, it is a well-known fact that mixtures of chemicals can cause substantial SHE problems, for example thermal explosions, inseparable mixtures of chemicals ending up as waste, or the need for complicated separations.

The examples given above do not cover all aspects of ISHE that need to be considered during *INSET* Stage III. It will always be up to the project team to address problems relevant to the process in question.

5.3.2 Reaction optimization

Chemical development involves not only synthetic route selection (*INSET* Stage I and II) but also optimization, scale-up and further improvement of the synthetic method until a routine and efficient process is obtained, suitable for manufacture by operators who are skilled but have little chemical knowledge. Speedy plant throughput, safety of operations and cost of production are all considerations which must be borne in mind during the development phase. From the inherent SHE point of view, a robust and safe process should be discovered. Attention to detail at this stage is crucial for SHE, including a good understanding of the chemistry (mechanism, by-products and competing reactions).

In the process industry, there is a need to find the optimum for certain processes in relation to some standard factors. In fact, a major part of the resources in R&D are spent on solving optimization problems, sometimes unnoticed. Optimization of the synthetic route used to make a new substance involves not only maximizing the yield (and quality) at each synthetic step, but also involves obtaining a product of acceptable quantity at the minimum cost as measured at the manufacturing site.

Yield improvement is, however, in many instances the key to an inherently environmentally friendly process. Yields can be improved using either an investigative approach or empirical methods, such as factorial design and Simplex, which are based on achieving the optimal conditions in the minimum number of experiments. These processes can diagnose if a system can be adequately analysed by linear statistical procedures. If non-linearity and dynamics are a problem, one can shift to non-linear statistical procedures based on neural nets (paralleling the processes of conventional statistical experimental design). This approach is beginning to generate significant impact in practice.

It is, however, still common to search for the optimum point of a reaction by changing one factor at the time until the result is no longer improving. But, for instance, the standard practice often mentioned in the literature of carrying out a set of experiments under the same conditions for different substrates is in most cases meaningless, since the optimum for one substrate will be different from another. Therefore, it is very important to be sceptical of literature yields – it may be that the optimum has not been found or was not even sought. The development chemist's experience is that most reactions can be optimized to over 90% yield.

Experimental work is expensive and time-consuming, and it is therefore necessary to minimize the amount of experimentation needed for the optimization of a particular route. The investigative method mentioned above is very inefficient as it does not take into account the interactions between the different factors. In cases where the different factors have simultaneous influence on the measured quantity, the "optimum" found by this method may be a pseudo-optimum which could be quite far from the real one. The real optimum conditions will rarely be reached by one-step-at-the-time variations. It is obvious that processes "optimized" in this way can drastically affect the inherent SHE performance and the chemist needs to be aware of the shortcomings of this method.

It is also of importance, from the point of view of efficiency and productivity, that the correct decisions can be drawn from the experiments that have been carried out. A prerequisite for this is that the experiments have been designed in the proper way so that the results can be analysed using multivariate statistical methods and tools developed for this purpose. The skill involved in using these methods lies in the choice of parameters to optimize.

Methods for the statistical design of experiments have been developed since the 1920's. The original method developed by Fisher has been modified and refined by, for example, Box, Hunter, Cox, and Taguchi et al. Presently, these methods represent a versatile toolkit which can be used to solve almost every optimization problem.

The aim of the design of experiments is to plan a limited series of experiments in which all factors that influence the optimum are taken into consideration. Such a series should not contain more than 10–20 experiments, depending naturally on the amount of important variables.

By systematically altering one, two, three or even more variables from one experiment to the next, the experimental design method will give good estimates of the effects of variables from far fewer experiments than the classical investigative method. It will also give additional, important information which the method of altering only one variable at a time cannot. This additional information measures the magnitude of interactions which are common in chemistry. For example, a given change in reaction time would not be expected to give the same change in yield at different temperatures (there is a time-temperature interaction). Interactions are estimated automatically in appropriate experimental designs, with no extra effort, whereas they are virtually impossible to assess by the classical approach.

Statistically designed experiments not only identify significant factors and interactions, they also have considerable optimizing power. For example, a British company was contacted by a client with pilot-plant difficulties: long reaction times (about 20 hours), two filtration stages, failure to meet specification, and solvent recovery problems. They needed a rapid investigation, so a fractional factorial of only eight runs was chosen to study five variables, three of which were found to be significant. This high rate of return was dependent on shrewd selection of the factors and levels – good chemistry – as well as statistical design efficiency. The information gained, together with common sense and discussion with the client, gave a greatly improved process: reaction time of about five hours, milder conditions, no need for filtration, very high conversion of starting material and consistently in-spec product, i.e. a substantial improvement of the inherent SHE performance of the production process.

Another type of optimization procedure, evolutionary operations (EVOP), was devised by Box to be applied to full-scale manufacturing processes by process operators while still producing satisfactory product. It follows that changes of factor levels can only be small, so that the manufacturing process is not seriously affected. As a consequence, it may be necessary to repeat the experiments a number of times before systematic changes of the result become apparent. This method and others, e.g. those based on neural networks, are outside the scope of the *INSET* Toolkit and are therefore only mentioned briefly here.

The statistical approach to process optimization normally gives graphical presentations of how the response varies when different factors are changed. These graphs can be used to predict the robustness of reaction, i.e. the values of the different factors can be selected as far as possible from areas where steep changes in the response are expected. As a result, there is more room for errors at the plant without causing major changes to the inherent SHE performance of the process.

5.3.3 Engineering aspects

In spite of the fact that chemicals cause most of the hazardous consequences in a chemical process plant, this can be mitigated by looking at the equipment used. This does not only include those equipment that are in direct contact with the process media. Utilities and service systems, materials and conditions should also be looked at to see if changes, for example to the compressed-air delivery pressure, steam supply temperature and pressure, or the heat transfer fluid, could make the process safer by preventing certain accident conditions or easing process control problems. For example, an electric heater or steam heater can only supply heat to a system, whereas a high-pressure hot-water system can provide heat and a degree of cooling once the temperature exceeds the hot water temperature – this may be useful for preventing or slowing down some reactions prone to runaway. The "thermal inertia" in a hot-liquid system may also offer better (more robust) control where temperatures have to be kept within a close band.

There may also be opportunities to minimize the waste streams by efficient unit operation selection and design, and by careful tuning of the process and its control. Any waste streams should also be evaluated to see if joining or segregating these could help ease their management, and also to see if changes to the waste streams could be made to make "end-of-pipe" clean-up or recovery systems more effective.

Manual handling or "open process" operations should be identified and evaluated to see if these can be redesigned to eliminate or reduce personnel exposure to hazardous materials, and to cut down any fugitive emissions.

The layout of the plant can also be developed to make good use of segregation to minimize the effects of hazards and prevent escalation, as well as provide good access and conditions to reduce the chance of human error. A logical and consistent layout of equipment and facilities should also help reduce the chance of error during construction and operation since it should make equipment easier to find and identify and access/egress more straightforward.

If there is not time to generate options to all the process, then it may be worth using the list of hazards and rankings to focus attention on the areas of the process where the main hazards are, and to see how these could be "designed out" or reduced in scale or likelihood.

If problem areas or choices are identified and you do not feel you have sufficient information or ideas on how to deal with these, then these should be noted in the study/record sheet, and can be used to prompt further work later on. Some of the Tools N to R described in the chapter on *INSET* Stage IV may be able to help stimulate ideas or give comparative information on different unit operations to help with selection. In particular Tool N, Equipment Inventory Functional Analysis Method, should be used if the main hazards are arising from large process inventories as this tool will help the designer clarify the need for the inventory and identify changes which could reduce it.

If the inventories of concern are in the storage areas (feedstock or products storage), then use the inventory challenging tools (Tool N) together with the transportation aspect of Tool Q, Siting & Plant Layout Assessment, to see how transport and storage hazards can be balanced and optimized.

Tool B, Process Option Generation, can also be used to analyse the process and suggest ways in which its environmental impact can be reduced. Refer to this tool if waste discharges appear to be a major problem for the process, or if you run out of ideas when considering changes or alternatives that could improve the environmental performance of the process.

Similarly, the health-type indices of Tool I, and Tool R, Designing for Operation, may be useful for looking at occupational health aspects of the process.

The preliminary plant layout can be developed with help from Tool Q. This provides a structured prompt list to help the layout specialist to make best use of inherently safer layout features.

5.4 Decision-making

The aim of Sections 5.1 – 5.3 has been to show chemists and engineers that an inherent SHE approach can and should be applied throughout a project. Not only is it important that the selected basic chemical route is as safe and environmentally friendly as possible (*INSET* Stages I and II), but also that many opportunities exist to improve the process after the key starting material(s) and key chemistries have been decided (*INSET* Stage III). The proposed flowsheet or preliminary block diagram must be reviewed on a regular basis in order to identify possible options/alternatives which may be inherently safer (or offer other advantages).

Decision-making is an integral part of process development and conceptual plant design. Identified alternative process options must be evaluated. Their influence on other parts of the process and plant design must be an integral part of this study. Often an improvement in one part of the system creates a new problem somewhere else. Problems that arise can be solved either by the individual chemist or engineer, or by a team of experts. It is most important that the *INSET* Toolkit is used whenever any change to the process is made. This ensures that the information handed over to engineers in charge of detailed design or of plant operations is always up-to-date. The repeated use of the suggested forms in the various *INSET* tools guarantees an audit trail of the decisions taken.

Both during and at the end of the study, an evaluation of the alternative options identified must be carried out to see which may merit further investigation or adoption. It may be useful to rank the hazards listed to see which ones deserve most attention. Ranking is complicated by the many different and varied effects on safety, health and the environment, as well as by the way hazard is realized and by its effects (which can be acute, chronic or both). Several ranking systems to address the acute effects of accidental events have been published, often to assist with HAZOPs or other hazard studies. But these do not address the longer-term effects, or deal with occupational health effects or long-term releases into the environment.

The process hazards analysis and ranking method presented in Tool M is proposed as a means of bringing all the above-mentioned aspects together. The tool can be used to assess the change in hazard severity achieved by the proposed changes to the flowsheet. This provides a more direct and absolute comparison, but may be difficult to apply where proposed changes affect several hazards, or where one hazard is avoided/reduced by several proposed changes. The highest ranking from the various categories should be used and should be noted on the Process Hazard Identification Record Sheet in Tool M. Alternatively, company or other ranking methods as well as expert judgement could be used.

The ISHE performance indices (Tool I) can also be used to measure the change in performance between the original plant scheme and the version following the changes suggested above.

If the choice between two or three "leading options" is not straightforward, you could use Tool J, Multi-attribute ISHE Comparative Evaluation, to compare these options against a wide range of ISHE and business performance factors. This should help clarify the situation and aid the selection of the most favourable option.

After identification of new alternative options, it may be worth looking back at the list of hazards to ensure that attention has been paid to those areas where hazards still exist, and to see how these could be "designed out" or reduced in scale. Noting which hazards have been avoided, eliminated or reduced in seriousness, together with the new hazard ranking, should give a good indication of the overall effectiveness of any changes made. A column on the Process Hazard Identification Record Sheet in Tool M is provided for this assessment. Note that the hazard ranking method must be applied in full to the changed situation to ensure that an increase in inherent safety, for example, is not offset by a decrease in inherent environmental friendliness/performance.

Indices may help in the evaluation of process and design options. No attempt has been made to combine health, safety and environmental questions in order to obtain one single index. One index will be generated for each SHE aspect according to the approach as presented in Tool I.

5.5 Outputs of *INSET* Stage III

At the conclusion to *INSET* Stage III, in a project where all the aspects of *INSET* Stage III have been used, the following documents should have been prepared:

- *from Tool L:* a Chemical Reaction Reactivity – Stability Evaluation Record.
- *from Tool I:* inherent safety, health and environmental performance indices.
- *from Tool M:* a Process Hazard Identification Record Sheet.

At this stage, we encounter a natural break point in the decision-making process where we must decide on the most ISHE route alternative. An initial review can be conducted whereby the decisions taken are approved by management or further discussed with the relevant groups. Process engineers, safety experts, project management, production personnel, etc. may need to be consulted or discussions held in order to decide which process goes on to the next stage. A suggestion is to hold an ISO-steering-group type of meeting with design and operation personnel.

Based on these discussions and the documents, a decision either to go ahead to the next stage of the project or to cease activities is taken. A recommendation of how to search for more ISHE alternatives should also be considered.

The documents must be filed in a dossier of the project in case further assessment and investigation proves to be necessary at a later stage.

6. *INSET* STAGE IV: PROCESS PLANT DESIGN

At Stage IV in the *INSET* Toolkit, the basic process, the main unit operations, and its control regime will have been determined. Opportunities to substitute hazardous materials or eliminate them will generally have passed. Many of the process conditions such as concentrations, temperatures and pressures will have been set by the chemistry, early process design, and flowsheeting, so the opportunities for attenuation/moderation will also be limited. Many of the major equipment items may also have been selected, so the main inventories of materials may have been set. However, there are still many opportunities during the detailed design and engineering stages to trim back inventories and simplify the plant by challenging the need for equipment and fittings, and seeking instances where equipment could be combined or simplified (e.g. using an ejector to transfer material, rapidly and effectively mix two streams, and control the flow of one using the other at the same time).

Project stage	**Key issues**	***Information used***
I – Chemistry route selection	Constraints and objectives of the project Routes to make the product Raw materials and wastes involved	*Legislation and company policies* *Known synthesis routes and techniques* *R&D chemists research*
II – Chemistry route detailed evaluation	Basic unit operation selection with flow rates, conversion factors, temperatures, pressures, solvents and catalyst selection Batch vs continuous operation Control/operation philosophy Waste management options/selection	*Knowledge of existing processes* *Knowledge of existing chemicals* *Initial process engineering design principles and experience* *Feasibility and cost information*
III – Process design optimization	Unit operation selection Optimization of the process Equipment selection and sizing Hazard evaluation Inventory of process Single vs multiple trains Utility requirements Overdesign/flexibility Recycles and buffer capacities	*Lab-scale and pilot-scale trials* *As above, plus equipment suppliers data, raw materials data, company design procedures and requirements*
IV – Process plant design	Instrumentation and control Location/siting of plant Preliminary plant layout Materials of construction Detailed specification based on concept design Minimize number of possible leak paths Make plant "friendly" to control, operate and maintain Avoid/simplify hazardous activities such as sampling, loading/unloading	*Process conceptual design and codes/standards and procedures* *Experience on past projects/designs*

Aim: The aim of the tools at this stage is to challenge the equipment and pipework design with regard to inventory and complexity, in order to identify and assess any alternatives that may be more inherently SHE. The main inherent SHE principles covered are intensification (reducing inventory) and simplification.

Timing: The tools are best applied once the process front-end or conceptual design has been completed. This would normally coincide with the issue of the P&IDs and development of the ELDs and equipment datasheets.

Input: A description of, and functional specification for, the main plant items. Diagrams showing the main equipment and pipework fittings, instruments, etc.

Output: Modified equipment datasheets or drawings showing the changes agreed.

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During Stage IV, the main unit operations and proposed major equipment items can be reviewed to see how the risks arising from inventories of hazardous materials could be reduced by careful attention to design details. The overall objectives should be:

- to identify those plant areas with the most significant hazardous inventories or greatest potential for fugitive or accidental leaks,
- to minimize the hazardous inventory in those areas (reduce the consequences of any leak that may occur),
- to minimize the chance of a leak/unauthorized emission,
- to optimize the plant layout, in order to mitigate the effects of any leaks, prevent escalation, allow access for effective emergency response action, and minimize exposure of personnel or environmentally sensitive areas.

The overall sequence suggested involves the following steps:

1. Identify key areas.
2. Minimize inventory.
   2.1 Unit operation/equipment selection.
   2.2 Challenge the need for the inventory.
3. Minimize the chance of a leak.
4. Consider ancillary plant and services.
5. Optimize the layout.

(1) Identify key areas

The output from the Stage III tools should give an indication of where the main problem areas are in the process. These areas should be the target for the Stage IV tools. An alternative approach would be to simply list the inventories (in suitable units, e.g. tonnes, kg) together with their hazard classification (see Tool G, Chemical Hazards Classification Method). A simple weighted value of their potential for harm can then be obtained by multiplying the mass by the factor from the table below. This should allow the key problem areas to be identified (select, say, the top three to six for investigation).

Simple Weighting Factor for Inventory Analysis	
Materials classification from Tool G	**Weighting factor**
Very high	1000
High	100
Medium	10
Low	1

Example: 200 kg of high-hazard material gives: $200 \times 100 = 20000$
4500 kg of low-hazard material gives: $4500 \times 10 = 45000$

Alternatively, Tool P, Hazards Range Assessment for Gaseous Releases, could be used to assess the relative importance of each inventory. This could be decided on by the area affected by the relevant "worst case" hazard arising from the leak. Unfortunately, this method only applies to gaseous emissions, so it may not be suitable for looking at all the plant inventories.

(2.1) Minimize inventory: Unit operation/equipment selection

Make the inventory in the plant work harder, by getting it to fulfil more than one function at a time. For example, use an ejector to transfer and mix fluids at the same time, or use the heat exchanger as the reaction vessel, or use a in-line mixer to combine transfer and mixing operations. These ideas should have already been covered with the application of Tool B, Process Option Generation, at Stage III, but consider using them again here.

(2.2) Minimize inventory: Challenge the need for the inventory

Ask why the inventory is required. Could the underlying reasons be tackled so that the inventory can be reduced? By reducing inventory, the consequences of leaks and spills can be reduced, and this may lead to a more compact plant which may be cheaper to buy and site. An inventory-challenging tool is provided which can be used if the inventory of a particular section of the plant, or piece of equipment, is a particular problem. The tool proceeds by asking the designer why the inventory is there, and using this to see if this need can be changed or is valid.

Tool N, Equipment Inventory Functional Analysis Method, offers a systematic method for challenging inventory in this way, and also suggests a simpler check-list method for the more common aspects of equipment and pipework inventory minimization. The check-list is quicker to apply, can be used by an individual, and would be useful in many circumstances. The systematic method works best in a team study, and is intended for more problematic situations where some inventory is dominating the risk from the plant, and where there appear to be no obvious ways to reduce the inventory.

(3) Minimize the chance of a leak

The likelihood of leaks can be reduced by simplifying the plant so that there is less equipment that may leak, especially by reducing the number of small bore connections and fittings which can be particularly prone to leaks or damage. Also, if we make the process and plant more ergonomic (more people-friendly), then it should be easier to control, operate and maintain, so the chance of making errors which can result in leaks should be reduced.

Tool O, Equipment Simplification Guide, is provided to question the need for fittings to see if the "need" is justified or valid. This can be applied as a stage-by-stage and line-by-line review of fittings such as instrumentation, connections, drains and vent points, etc. to challenge the need for these, and see if the duty required could be met by a simpler or safer method, for example by using non-intrusive ultrasonic instrumentation, welded rather than flanged connections, etc.

Reducing the number of fittings needed within the proposed plant has many advantages:
- it can reduce the amount of fugitive emissions which typically affect occupational health and also impact on the environment,
- it can reduce the chance of a major accident since there are less places for leaks to occur and less fittings that may fail, and
- it also saves the cost of providing the fitting, and any operating and maintenance costs associated with them.

This tool would probably be used by an individual designer, or a small informal group of designers to try to simplify the areas of the plant which are likely to be prone to leaks and which contain the significant hazardous inventories.

Tool R, Designing for Operation, is provided to help the designer consider how people will interact with the plant during operation and maintenance, and to identify ways in which the plant can be made more "friendly" – reducing the likelihood and consequences of any errors.

The design should consider how people will interact with the plant, so it can be made more ergonomic, making the plant status more evident, and tasks easier to perform and less prone to human error. Some manual tasks may also be eliminated by careful design or by the use of automated or semi-automated systems. This can be important in reducing operator exposure to hazardous materials during operation and maintenance activities when the plant is essentially "open" to the workforce.

(4) Consider ancillary plant and services

It may also be worthwhile, using some of the above methods, to look at ancillary parts of the process and plant, such as reagent preparation/storage/feed systems and utilities (especially heat transfer and effluent systems as well as treatment processes). These often contain hazardous materials, or involve complex processes which can cause a hazard themselves or trigger hazards in the main process.

(5) Optimize the layout

Finally, the detailed plant layout should be reviewed to check that it makes best use of space and equipment to mitigate the effects of hazards and reduce the risk of escalation. Good access is also important: it can help make day-to-day activities easier and make egress easier in an emergency. Tool Q, Siting & Plant Layout Assessment, provides a prompt list to help the designer(s) systematically evaluate the layout from an inherent SHE point of view. Information from Tool P, Hazards Range Assessment for Gaseous Releases, may be useful when considering the distances between different parts of the plant and between the plant and other plants or public areas, environmentally sensitive areas, etc. Alternatively, the team could use the findings from preliminary quantified risk assessments or other hazard studies done to help gain an appreciation of the escalation and affected areas.

Method of application: The various tools can be used by individuals or by a study team.

Tool N, Equipment Inventory Functional Analysis Method, has two simple prompt lists, one for equipment, the other for pipework, which prompt the reviewer to question the need for the inventory and suggest ways in which these needs could be changed, or met in a different way. It can be used by an individual designer as a quick check on the basis of the inventory and to prompt any changes. The more systematic part of the tool is best used to guide a team brainstorm of a particular problem inventory.

Tool O, Equipment Simplification Guide, provides a simple list of suggestions and alternatives for some of the more common plant fittings. It could be used as a prompt for the review of the fittings on a P&ID or an ELD. Its aim is to challenge the need for each item, and to help the designer find better ways of meeting these requirements.

Tool P, Hazards Range Assessment for Gaseous Releases, should be applied in order to assess the extent of the hazard that will be present for the chosen configuration, once the equipment and unit operations have been decided upon, and the inventories are known. The information gleaned from this tool would assist the designer with their efforts to come up with the most inherently SHE plant layout with respect to hazardous gaseous releases.

Tool Q, Siting & Plant Layout Assessment, can be used to review the proposed plant layout (e.g. plot plans) to check/identify that this is making best use of the inherently SHE layout principle of segregation. The assessment from Tool P may yield valuable information for this tool.

Tool R, Designing for Operation, is a prompt list to help with the evaluation of manual operation on the plant, and to help improve plant ergonomics on the whole. It can be used as a simple reference/awareness guide by individual designers, or could be applied to a team study review of key operational and maintenance tasks.

Although it is possible, the above-mentioned tools should probably not just be applied singularly: an iterative application, keeping the other tools in mind or actually even applying them concurrently, could be advantageous.

Results: It is suggested that the findings of the studies are recorded to provide an audit trail for decision-making. Study record sheets are included in the toolkit for this purpose. The overall outcome of the application of these tools should be a more inherently SHE process and unit operation selection, with documentation to demonstrate and support this.

Outputs: At the conclusion of *INSET* Stage IV, in a project where all of the aspects of the toolkit have been used, the following documents should have been prepared:

- *from Tool N:* optimized inventories for key equipment.
- *from Tool O:* simplified instrumentation and fittings.
- *from Tool P:* hazard ranges for accidental emissions from key hazardous material inventories.
- *from Tool Q:* optimized plant layout.
- *from Tool R:* a more ergonomic design of plant, control interfaces, and maintenance and operation tasks.

Part 2 - The Tools

Part 2 – Table of contents

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Chemical hazardous properties classification table *(from Tool G)*

Blank tool forms

TOOL A – DETAILED CONSTRAINTS AND OBJECTIVES ANALYSIS

Aim: To define the limitations/boundaries and aims/goals of the project in terms of constraints and objectives.

Timing: To have an idea of the limitations/boundaries and aims/goals of the project at hand throughout the project, this tool should be completed before any investigations are initiated and must then be amended during the project in order to reflect possible changes in the criteria.

Input: The general constraints applying to all projects.
The project-specific constraints.
The general objectives applying to all projects.
The project-specific objectives.

Output: Tool A.1 results: lists of constraints.
Tool A.2 results: lists of objectives.

Background

Much of the decision-making in the *INSET* Toolkit is a reflection of the constraints and objectives set for the process development and the plant design project in question. This tool helps to identify the important criteria that the project team needs to consider from the earliest stages of chemical route selection.

When considering the criteria with which alternatives will be evaluated, it is very important to distinguish between constraints and objectives. *Constraints* need to be considered and accounted for under all circumstances (all constraints must be fulfilled in order to make a process acceptable), while *objectives* will be open for further negotiations and possible value trade-offs.

Instructions

For each project, your organization will need to compile their own lists of criteria, for instance in the following way:

- List 1: General constraints for all projects (Tool A.1).
- List 2: Project-specific constraints (Tool A.1).
- List 3: General objectives for all projects (Tool A.2).
- List 4: Project-specific objectives (Tool A.2).

If there are only a small number of criteria, one list for the constraints and another for the objectives may be sufficient.

Note An objective for one particular project may indeed be a constraint in another and vice versa. It is imperative that you construct these lists carefully in order to correctly define the "boundaries" of the respective project. Project criteria, other than ISHE aspects, include:

- *Scoping:* What is the need for support service areas, e.g. utilities and environmental facilities? etc.
- *Cost:* What is the required, competitive unit cost? In justifying change, what is the investment hurdle? etc.
- *Schedule:* What is the required mechanical completion date? Start-up date? etc.
- *Capacity:* What is the required yield? What is the necessary plant capacity? etc.
- *Technology utilization:* What specific technology is allowed to be employed (commercially proven, pilot plant, R&D)? etc.
- *Maintainability:* Are there peculiar maintenance requirements that must be taken into account? At what point does capital investment in maintenance give way for administrative procedures? etc.
- *Expandability:* Should the design provide for additional, future capacity? What level of investment is allowed for future growth? etc.
- *Ongoing operations:* What down-time, if any, can be scheduled in the operating facility? What are the safety issues facing construction? etc.
- *Operating philosophy:* What are the start-up and shut-down requirements, including clean-outs? Manual or automated handling? Continuous or batch processing? Staffing and its utilization?
- *Environmental management:* How will waste be disposed of? Limits for fugitive emissions? What about streams from emergency vents? etc.
- *Safety:* Are there existing corporate guidelines and standards? At what point does capital investment in safety give way to administrative procedures? etc.
- *Quality:* What are the product's quality specifications? Are they competitive in the world market? etc.

You may need to extend or update the criteria check-list parts of Tool A.1 and Tool A.2 during the different phases of the project. The lists should be amended if needed and previously made decisions reassessed in order to guarantee that they are in accordance with the new criteria. The "date" field is important here, as we require the most current criteria with which to define the boundaries of the project. The lists should be part of the project file and known by all involved parties.

Tool A.1 – Detailed constraints analysis

Aim: To define the limitations and boundaries of the project.

Timing: Should be completed upon initiation of the project, and then consulted, reviewed and amended throughout its duration.

Input: The general constraints applying to all projects.
The project-specific constraints.

Output: General Constraints of the Project Sheet.
Project-Specific Constraints Sheet.

Background

Much of the decision-making in the *INSET* Toolkit is a reflection of the criteria set for the process development and the plant design project in question. This tool helps to identify the constraints that the project team needs to consider from the earliest stages of chemical route selection. It also gives an example of forms that can be used to record the various constraints.

A constraints list is valuable as it is a means of recording information on current practices. A hypothetical list of a few constraints is shown in Tool A.1 Examples (see Part 4, Support for Tool A.1). The example check-list is not intended to be comprehensive, but it gives an indication of the various types of constraints that may influence the decision-making process of a project.

Instructions

The overall sequence suggested involves the following steps:

1. Identify general and project-specific constraints.
2. Defining the constraints.
    - 2.1 Document the general constraints.
    - 2.2 Document the project-specific constraints.
3. Checking and amending the check-lists.

(1) Identify general and project-specific constraints

Consider issues that are due to national legislation, company policy, existing facilities, etc. together with factors that are typical for the process in question only. This task should involve persons from different parts of the company, e.g. directors responsible for the general policy of the company, sales people who can estimate the price of the product, plant managers that know the limitations of the existing production facilities, SHE experts with knowledge about waste-water permits, transport restrictions, etc.

Note There is no need to sort the constraints into any "ranked" order as the generated option always must comply with these criteria, and therefore you really only need to see if the constraints are achieved by the alternatives.

(2) Defining the constraints

Use the appropriate forms from Tool A.1 to list the constraints relevant to the project. The General Constraints of the Project Sheet and the Project-Specific Constraints Sheet would together be used later, e.g. to assess the alternative routes (Tool E).

(2.1) Document the general constraints

Make this check-list as comprehensive as possible. The constraints listed here would usually be legislation-specific together with high-level company policies. This list would be project-independent and may be taken directly from a previous project. However, changes to the legislation may require that the list is reviewed before continuing.

On this type of form, the constraints of the particular project are unambiguously defined so that consistent and informed judgements can be made, for example in the Tool E elimination stage.

(2.2) Document the project-specific constraints

Start compiling this list when the project has been defined. This check-list would deal with the particular constraints of the project at hand and would include things like the available budget and location constraints, together with other company policies. For example, the particular fixed location may place further emission control constraints on the process which need to be considered. Other constraints could include minimum plant output capacity, investment criteria, and raw material cost/kg restrictions.

(3) Checking and amending the check-lists

Add any constraints identified during the project to the check-lists as soon as they have been identified. Check that all the process or design alternatives under development fulfil the new constraints.

Check the lists regularly during the project in order to ensure that all new constraints have been included.

Tool A.1 form (1)

Project title:		
Date: ___ / ___ / ______	General Constraints of the Project Sheet (Tool A.1)	Page: ___ / ___
Author: ________________	Proj. #: ________________	Ref. #: ________

ID	Constraint	Date
C_{G1}		
C_{G2}		
C_{G3}		
C_{G4}		
C_{G5}		
C_{G6}		
C_{G7}		
C_{G8}		
C_{G9}		
C_{G10}		
C_{G11}		
C_{G12}		
C_{G13}		
C_{G14}		
...		

Tool A.1 form (2)

Project title:

Date: ___ / ___ / ______ **Project-Specific Constraints Sheet (Tool A.1)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

ID	Constraint	Date
C_{P1}		
C_{P2}		
C_{P3}		
C_{P4}		
C_{P5}		
C_{P6}		
C_{P7}		
C_{P8}		
C_{P9}		
C_{P10}		
C_{P11}		
C_{P12}		
C_{P13}		
C_{P14}		
...		

Tool A.2 – Detailed objectives analysis

Aim:	To define the aims and goals of the project.
Timing:	Should be completed upon initiation of the project, and then consulted, reviewed and amended throughout its duration.
Input:	The general objectives applying to all projects. The project-specific objectives.
Output:	General Objectives of the Project Sheet. Project-Specific Objectives Sheet.

Background

Much of the decision-making in the *INSET* Toolkit is a reflection of the criteria set for the process development and the plant design project in question. This tool helps to identify the objectives that the project team should consider at the earliest stages of chemical route selection. It also gives an example of forms that can be used to record the various objectives.

A list of objectives is usually necessary already in the screening phase. An objectives list is valuable as it is a means of recording information on current practices. The General Objectives of the Project form and the Project-Specific Objectives Sheet would then be required.

Instructions

The overall sequence suggested involves the following steps:

1. Identify general and project-specific objectives.
2. Defining the objectives.
   - 2.1 Document the general objectives.
   - 2.2 Document the project-specific objectives.
3. Ranking the objectives.
4. Checking and amending the check-lists.

(1) Identify general and project-specific objectives

Consider issues that are due to national legislation, company policy, existing facilities, etc., together with factors that are typical for the process in question only. This task should involve persons from different parts of the company, e.g. directors responsible for the general policy of the company, sales people who can estimate the price of the product, plant managers that know the limitations of the existing production facilities, SHE experts with knowledge about waste-water permits, transport restrictions, etc. You should complete Tool A.2 concurrently with Tool A.1 (where the constraints of the project are defined).

(2) Defining the objectives

Use the appropriate forms from Tool A.2 to list the objectives relevant to the project. The General Objectives of the Project Sheet and the Project-Specific Objectives Sheet would together be used later, e.g. to assess the alternative routes (Tool E).

On the forms, the objectives of the particular project are unambiguously defined so that consistent and informed judgements can be made, for example in the Tool E elimination stage. Judicious judgement, so as not to include frivolous objectives, could be time-saving.

(2.1) Document the general objectives

This list would be project-independent and may be taken directly from a previous project. However, the list should be carefully reviewed before continuing. General objectives of the project could contain topics such as "We want processes to use chemistry we know well" or "We want you to use mainly existing equipment" or "We hope that no alterations of the existing waste-water treatment plant are needed". These objectives would be generally governed by the high-level company policies, standards, or marketing factors, and would probably not address the objectives of the chemist and engineers themselves. These objectives would generally be fixed but would normally need to be reviewed before continuing, and they should be considered.

Consider the entire lifetime of the process. An important general objective would, for example, be the consideration of changes in future legislation. These may affect some of the chemicals involved in a particular route alternative to the extent that a particular substance may be banned or restricted in the future. An example is the EU directive pertaining to the discharges to water. In this case, the possibility always exists that a substance initially listed in the EEC List II Chemicals, the "Grey list", could be moved into the EEC List I Chemicals, the "Black list". It may be worthwhile to avoid any processes involving such "high-risk" substances.

(2.2) Document the project-specific objectives

Start compiling this list when the project has been defined. Make sure that at least the most relevant project-specific objectives are covered. Items such as "We want to have 50% of current allowable emission levels" in order to allow for changes in prospective legislation, or "We don't want to store any

XYZ in our plant" are examples of the type of objectives listed here. It should become apparent that in attempting to cover all the inherent SHE aspects, this objective list could become quite extensive.

Add new objectives to the list whenever the decision-making process so requires. In practice, alternatives are often so closely related that several objectives are needed in order for the decision maker to be able to get a proper view of the options as a basis for the decision. It may in most cases be advantageous to include not only SHE aspects on the list but, for instance, also cost-related issues.

(3) Ranking the objectives

Some form of ranking of the objectives, at least in some simple way, could be beneficial (although not crucial) as more formal decision-making aids may need to be considered when completing Tool E and deciding on the candidate set of "dominant alternatives".

By filling in the "attribute" column of the following forms, a multi-attribute criteria decision-making aid (see Appendix 8 in Part 3) could be employed, for instance when assessing the route alternatives in Tool E. In the case of a tangible property, this attribute would be a scale of performance. More detailed knowledge of the decision-making aid, however, would be needed when evaluating intangibles.

(4) Checking and amending the check-lists

Add any objectives identified during the project to the check-lists as soon as they have been identified. Check that all the process or design alternatives under development fulfil the new objectives.

Check the lists regularly during the project in order to ensure that all new objectives have been included.

Tool A.2 form (1)

Project title:

Date: ___ / ___ / ______ **General Objectives of the Project Sheet (Tool A.2)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

ID	Objective	Attribute	Date
O_{G1}			
O_{G2}			
O_{G3}			
O_{G4}			
O_{G5}			
O_{G6}			
O_{G7}			
O_{G8}			
O_{G9}			
O_{G10}			
O_{G11}			
O_{G12}			
O_{G13}			
O_{G14}			
...			

Tool A.2 form (2)

Project title:

Date: ___ / ___ / ______ **Project-Specific Objectives Sheet (Tool A.2)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

ID	Objective	Attribute	Date
O_{P1}			
O_{P2}			
O_{P3}			
O_{P4}			
O_{P5}			
O_{P6}			
O_{P7}			
O_{P8}			
O_{P9}			
O_{P10}			
O_{P11}			
O_{P12}			
O_{P13}			
O_{P14}			
...			

TOOL B – PROCESS OPTION GENERATION

Aim:	To rigorously challenge route and process alternatives in order to obtain a more ISHE process.
Timing:	The tool is best applied once the outline of the chemical process has been identified, along with the main reactions, conditions and unit operations. This would normally coincide with the later stages of laboratory-scale optimization trials or during pilot plant trials. However, it should also be used to challenge the early stages of the chemical route and process development and give insight into the aspects that need to be considered later in the process design.
Input:	Dossiers from the previous *INSET* stages, e.g. dominant alternatives (and the engineering-modified versions). A description of the basic chemical/process stages and conditions is required, preferably in the form of a chemical route block diagram, flowsheet or process diagram showing the sequence of the stages and any links between these. Information on the process materials (including wastes) and hazards is also required, for example in the form of a hazard file or data sheets.
Output:	Dossier of the "challenged" remaining route(s) or design option(s) to be passed on to the next stage with a list of suggested changes to the process and equipment that may be inherently safer or environmentally friendlier.

Background

By challenging the basis of the chemical/process flowsheet, the user will identify and assess an alternative which may be inherently safer. The tool encourages all personnel involved with the design of chemical processes and plants to consider the effects that their decisions will have on the environment during subsequent stages of a design project.

It may be worthwhile using the tool to also look at ancillary parts of the process and plant, such as reagent preparation/storage/feed systems and utilities (especially heat transfer and effluent systems as well as treatment processes). These often contain hazardous materials, or involve complex processes which can cause a hazard themselves or trigger hazards in the main process.

Once the likely impacts and issues have been identified, designers are then encouraged to search for environmentally better alternatives. It has been recognized that conflicts are likely to exist between safety, health and environmental issues. It is for instance understood that the complete elimination of waste is unlikely to be a realistic goal.

This tool can be used by individuals or by a study team. At the heart of the tool are the option generation prompt lists. This tool is also designed to be of assistance for the process option generation at later stages in the project and therefore covers more advanced procedures as well. The challenging should not only cover the engineering and chemistry, but could also involve assessment of the ISHE benefits, the feasibility, and the economic aspects of the route alternative.

It is also suggested that the findings of the studies are recorded to provide an audit trail for decision-making. A study record sheet is included in the tool for this purpose.

Instructions

The overall sequence suggested involves the following steps:
1. Draw up process block diagram/flowsheet.
2. Focus on the main hazards or problem areas.
3. Identify alternative process options.
4. Identify alternative unit operations or functional options.
5. Identify alternative options for waste minimization.
6. Identify the alternative transport options.
7. Evaluate the options.

(1) Draw up process block diagram/flowsheet

Draw up the process/chemistry stages in diagrammatic form (the block diagram or flowsheet) showing each stage in turn, with its inputs, outputs and conditions. Tools for this are provided for by the *INSET* Toolkit. Each stage could, for instance, be shown as a box on the diagram, with arrows showing the transfer (and direction of flow) of material from one box to another. Key process conditions can be shown inside the box (temperature, pressure, pH, concentrations, etc.). There should also be a brief description of the process to accompany the flowsheet, stating the main process objectives, limiting conditions/constraints, the purpose of each stage, the feed/reagent and type of equipment or unit operation proposed, and how the process is expected to operate.

(2) Focus on the main hazards or problem areas

The tool can be usefully applied to all the processes including services and utilities. If there is no time to do this, then use the results of previous hazard assessments, if available, or your judgement to identify those areas of the process with the greatest hazard potential (i.e. most hazardous materials, reactions, conditions, processes, or most waste, emissions, etc.) – and apply the tool to these first.

(3) Identify alternative process options

Review the proposed diagram to identify possible options/alternatives which may be inherently safer (or offer other advantages). The aim is to identify possible changes to the sequence of operation, ways in which steps can be combined or carried out simultaneously, changes to the unit operations or equipment (see below) or changes to materials or conditions that could make the process inherently safer or environmentally more friendly. The Process Change Guideword Prompt List should be applied to each stage input/output of the block diagram/flowsheet in turn to help identify alternatives. The possible alternatives can be recorded on the Process Option Generation Record Sheet.

Process Change Guideword Prompt List	
Change applied to:	**Guideword**
chemical conditions	concentration composition catalyst solvent
materials	material form (particle size, pure or in carrier, or as compound)
physical conditions	temperature pressure state (solid, liquid, vapour) level mixing
process stage	eliminate/avoid elsewhere combine split segregate
timing	sequence duration timing feed profile batch/semi-batch/continuous
equipment	size geometry type location orientation see Process Functionality Prompt List for each function identified

Change is intended to encapsulate the concepts of "more of", "less of", "other than", "as well as" and "none of".

Alternatively, the Process ISHE Option Identification Guideword List could be applied as well as, or instead of, the Process Change Guideword Prompt List. This may be especially useful if the process is not suited to "flowsheet" representation, say for a mechanical plant or where a series of tasks are carried out or if the plant as a whole is being considered.

Process ISHE Option Identification Guideword List	
Guideword	**Aids**
Eliminate	Remove the hazard or the material, equipment item or task creating it.
Avoid	Avoid situation where hazard could arise, or "be realized", e.g. remove ignition sources, remove need to open up to inspect.
Reduce severity at source: **Intensify** **Attenuate** **Moderate**	Minimize consequences if hazard is realized, e.g. reduce inventory, maximize chance for safe dispersion, venting for explosions.
Reduce likelihood at source: **Simplify** Reduce frequency/number Operator-friendly	Minimize number of hazard/initiation sites or tasks, e.g. weaknesses in containment such as fittings, instruments, or number of maintenance operations. Minimize chance of an error occurring, e.g. make easy to control, easy to operate and maintain, easy to identify correctly. Maximize visibility of plant status – is it clearly on/off, open/shut, running/not running, pressurized/vented, full/empty. Maximize chance of timely recovery if things start to go wrong – by good feedback from task or control system.
Segregate from hazard: Distance Barriers Protect	Locate away from external hazard and effects of these. Use distance/plant/natural features as barriers to limit effects on people, plant and environment. Limit chance of escalation. Maximize chance of escape.
Others: Passive protection Active protection Operator/management controls	Not inherent safety, but passive may be better than active, which may be better than operator controls.

(4) Identify alternative unit operations or functional options

While the block diagram/flowsheet is being assessed, also look for alternative ways of achieving the main unit operations/functions required. The block diagram/flowsheet should be used as the basis for the study. At each stage of the flowsheet, identify the main functions to be performed (e.g. addition, reaction, separation, heat or mass transfer, mixing) and then try to think of alternative ways of achieving these functions, or try to combine the functions. The aim is to try to identify inherently safer ways (and equipment) for achieving the function of the unit operation. The Process Functionality Prompt List can be used to help identify the functionality and see what other options could be considered. The results of the study can be recorded as described in Step 3 above.

Process Functionality Prompt List		
Function	**Option**	
mix	dissolve agitate blend jet mix	inject fluidize in-line batch/continuous
separate	settle extract vaporize condensate precipitate enhanced g pressure swing	reverse osmosis filter adsorb ion-exchange membrane distil batch/continuous
size change	coalesce agglomerate stick crush	grind smash batch/continuous
store	reduce inventory (see detailed tools on inventory assessment)	
heat/cool	direct process stream utility stream regenerative	recovery limit heat flow/temperature heat transfer media batch/continuous
transfer (internal)	pump eject siphon gravity	container convey compression batch/continuous
transfer (external) – see also transport	pipeline road rail loading/unloading – see also transfer (internal)	watercourse process internally
dry	flash freeze direct heat	rotary vacuum fluidized bed squeeze
reaction	in-line pot batch/continuous/semi-continuous	tube in existing equipment

(5) Identify alternative options for waste minimization

The reaction itself dictates many of the other waste streams. Once the reaction route has been decided, much of the flexibility to make savings in the areas of separation, recycle, utilities, etc. are constrained. Therefore, review the proposed diagram to identify possible options/alternatives which may be less inherently wasteful. The desire to prevent the generation of waste at source closely matches the philosophy of inherent safety. It must be stressed that waste minimization is concerned with prevention, minimization and recycling of wastes. The European Community have established a hierarchy of waste management options:

Prevention		*Best option*
	⇑	
Minimization		
Recycling		
Disposal		*Worst option*

The list is presented in descending order of acceptability: prevention of waste generation at source is the preferred option, waste disposal is the least desirable, non-ISHE option. End-of-pipe techniques are undesirable since they do not prevent the unwanted generation of waste but instead offer management some method of control by altering the form of the waste and/or the final disposal route of the waste.

Use the tool to assess both main types of waste:

1. process waste	⇑	
a. reactor waste		*First efforts*
b. separation and recycle waste		
2. utility waste		
a. waste from heat exchanger network		
b. utilities waste		*Last efforts*

In the hierarchy of wastes, the arrow indicates the order of importance and where waste minimization efforts should be devoted to ensure the best "savings".

In an effort to help designers to seek and implement waste minimization approaches, some methods and lists are included in Tool B as aids to stimulate the search for alternatives and/or solutions to problems.

The High-Level Keyword Lists to Assist Waste Minimization may be used within a waste minimization brainstorming session.

The results of the study can be recorded as described in Step 3 above.

High-Level Keyword Lists to Assist Waste Minimization – Fugitive releases (non-routine releases of liquid, solid or gas)	
Keyword	**Action**
Avoid	"ad-hoc" releases positive pressures venting fittings maintenance cleaning sampling contact with stormwater
Minimize	positive pressures venting fittings maintenance cleaning sampling contact with stormwater
Mitigate	capture and render harmless use higher-integrity fittings double-skin containment recovery
Treatment	see Table 1 in Tool B Supporting Information (Part 4, Support for Tool B)

High-Level Keyword Lists to Assist Waste Minimization – Routine releases to air

Keyword	Option
Avoid	runaway positive pressures temperature fluctuations by recycling by regeneration by re-use venting fittings storage transfer operations transfer into other media cleaning sampling secondary releases particulates/dusts gases/vapours
Elsewhere/otherwise	re-order other part of process best environmental option
Minimize	runaway temperature positive pressures temperature fluctuations venting fittings storage transfer operations transfer into other media cleaning sampling secondary releases particulates/dusts gases/vapours
Mitigate	capture and render harmless use higher-integrity fittings double-skin containment recovery
Abatement	see Table 1 in Tool B Supporting Information (Part 4, Support for Tool B)

High-Level Keyword Lists to Assist Waste Minimization – Routine releases to water	
Keyword	**Option**
Avoid	stormwater contamination water treatment chemicals contamination (by segregation) direct contact (e.g. heat transfer media) by recycling by regeneration by re-use venting fittings transfer operations transfer into other media cleaning sampling secondary releases
Elsewhere/otherwise	re-order other part of process best environmental option
Minimize	stormwater contamination water treatment chemicals contamination (by segregation) direct contact (e.g. heat transfer media) by recycling by regeneration by re-use fittings transfer operations transfer into other media cleaning sampling secondary releases
Mitigate	capture and render harmless use higher-integrity fittings double-skin containment recovery
Abatement	see Table 1 in Tool B Supporting Information (Part 4, Support for Tool B)

High Level Keyword Lists to Assist Waste Minimization – Routine releases to land	
Keyword	**Option**
Avoid	stormwater contamination contamination (by segregation) by recycling by regeneration by re-use venting of dusts fittings transfer operations transfer into other media cleaning sampling secondary releases packaging
Elsewhere/otherwise	re-order other part of process best environmental option
Minimize	stormwater contamination water treatment chemicals contamination (by segregation) direct contact (e.g. heat transfer media) by recycling by regeneration by re-use sludges catalyst losses fittings transfer operations transfer into other media cleaning sampling secondary releases
Mitigate	capture and render harmless use higher-integrity fittings double-skin containment recovery
Abatement	see Table 1 in Tool B Supporting Information (Part 4, Support for Tool B)

(6) Identify the alternative transport options

A necessary part of industrial activity is that materials be moved between manufacturing facilities. Apply the table below to each process alternative in order to consider the ISHE aspects concerning the transport of chemicals. There may be occasions where the choice of process routes or choice of plant location can either incur or avoid the transport of hazardous materials. The guideword list is mainly intended for transport by road and rail. However, in some cases materials may be transported by pipeline, by ship or even by air.

Transport ISHE Option Identification Guideword List	
Keyword	**Option**
Avoid	Use of less hazardous materials. Safer location of plant – reduce distance, avoid routing near sensitive areas. Splitting the production so that a less hazardous material is transported (transport in a more benign form).
More of/less of	Evaluation of larger or smaller container sizes.
Protect	Different type of container/transporter (see Tool Q Supporting Information, in Part 4, Support for Tool Q).

Siting of the plant is an important aspect that has considerable implications, and especially on the transport aspects. For existing plants, the aspects may not be as flexible as those for a new plant whose location has not been specifically determined. Tool Q, Siting & Plant Layout Assessment, gives a more detailed overview of the implications of transport options with respect to location of the plant.

(7) Evaluate the options

Either during or at the end of the study, evaluate the alternative options identified to see which may merit further investigation or adoption. The conclusions of this review can be recorded in the "comments/recommendations" column on the Process Option Generation Record Sheet.

The newly generated process alternatives would then also be scrutinized as the original "dominant alternatives" were, with the routes being evaluated and then possibly even challenged further. It is of vital importance that the newly generated alternatives be reassessed against the constraints of the project, that is the lists obtained from Tool A.1, to determine whether the new alternative has remained within the boundaries originally defined for the particular project. It may also be useful to reassess whether the newly generated alternative is also still within the desired objectives boundaries determined by the lists from Tool A.2.

At the end of these studies, going back to the list of hazards identified may be worthwhile, in order to see which of these have been addressed by the changes. Noting which hazards have been avoided, eliminated or reduced in seriousness, together with the hazard ranking should give a good way of assessing the overall effectiveness of any changes made.

Tool B form

Project title:

Date: ___ / ___ / ______ **Process Option Generation Record Sheet (Tool B)** **Page: ___ / ___**
Stage/input/output: ______________________________
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Guideword	Effect of options in terms of SHE performance	Inherent SHE benefit (note as + , 0, or –)			Feasibility	Other benefits or disadvantages (e.g. cost)	Comments/ recommendations
		Safety	Health	Env.			

TOOL C – PRELIMINARY CHEMISTRY ROUTE OPTIONS RECORD

Aim: To consistently present all the proposed chemical route alternatives.

Timing: The recording of the chemical route alternative provides crucial information regarding the stage of development of the uncovered route and its complexity. In order to gain a comparative overview of the route alternatives, this needs to be done early on in the process.

Input: The chemical route that has been identified, together with the relevant information that defines the route.

Output: A "chemical route data sheet" that allows the user to quickly identify the chemistry involved and the relevant reaction information, together with any comments of improvements or possible problems that may be encountered with the chemical route alternative.
A list of all the chemicals involved (related to their function) to input to the form in Tool G.

Background

An important aspect of the *INSET* methodology is the systematic and rigorous way data is recorded. Once the potential chemical route alternatives have been identified, we must be able to present the gathered information quickly and easily in a standard way, in a format that will be just as easy to interpret and allows relatively efficient comparisons of the route alternatives at later stages.

The form presented here includes most of the vital information that can be obtained after a route has been identified using the various avenues suggested in the *INSET* Stage I overview. This data sheet should stimulate the chemist to consider immediate route "problems" and allow him to make any suggestions as to possible variations due to, for example, a hazardous substance, or just to note that one should seek an alternative for a certain step in the "comments" section.

Instructions

The overall sequence suggested involves the following steps:
1. Gather information about the chemical route.
2. Draw up the basic chemical routes.
3. Draw up prospective chemical route alternatives.
4. List the chemicals involved.

(1) Gather information about the chemical route

Information from literature and other sources on all chemical routes leading to the desired chemical should be gathered. To ensure that all alternatives can be easily identified at any time, the following aspects should at least be included:
- the project title and project number
- the route title and route reference number
- identification of the source(s) of this alternative
- the date that it was identified/documented and the identifier
- the basic reaction scheme.

The suggested form would, therefore, show the initial chemical scheme, found from the various sources mentioned previously (or from the other respective sources, in the case of a proposed scheme), and would outline the details of the route such as information about reaction conditions (like temperatures, pressures and phase of materials), solvents used, processing and residence times, and overall yield. That is, all relevant data should be transposed to the data sheet and the route alternative should be assigned a reference number.

As the first stage of documenting alternatives from a literature search is usually done "on-the-fly" as a route alternative is found, it should be simply a matter of filling in the form by hand.

The overall yield may need to be estimated for the particular process, if no values have been cited.

(2) Draw up the basic chemical routes

Using the form given, record the chemical routes as found in the literature and other sources. The form also includes a space for recording information on various initial comments, vital abnormal conditions, as well as any informative guesses at problem areas or just points that may need follow-up work. The form has been partitioned in order to include a field on the reason why this particular route eventually "fails" (and at what stage). Date and author information, as well as any new reference number leads should also be recorded on the form.

The chemist should also be able to jot down any ideas that come to mind (i.e. anything that he may consider warrants further investigation), including any comments regarding possible problems, types of solvents required, or phases of the substances involved. Notes on the ratio quantities of amounts of solvents required may be added if believed to be important, and the recipe itself should also be attached if thought appropriate.

If the route is multi-stepped, the chemist should not try to "cram" the scheme and data onto only the single sheet, but rather he should keep the record sheet clear and cross-reference it to any associated sheets.

It often may be the case that the scheme may not be fully outlined, that is the information may be sketchy or the reaction proposed may be for the production of an analogous compound. The chemist should not, in this case, try to incorporate guesstimates in the initial scheme (i.e. he should retain an initial scheme without any modifications) and make note of all the "other" details in a section which would then be followed up later.

(3) Draw up prospective chemical route alternatives

Once the basic chemical routes have been challenged and new options with the potential for improvement have been identified, you should also draw up a new diagram for these. At this stage, most of the new alternatives will just be borne from experience and of known hazardous steps/processes. However, further aspects may only be identified upon implementation of a challenging procedure like that described in Tool B. Reading the entire article which refers to a general procedure may uncover other hints, for example regarding specific group reactivity.

Notes should be made on any documented variations, as well as any variations (no matter how obscure) the chemist thinks may be possible and noteworthy of recording. In addition to the information given above, a comparison to another previously noted route could easily be made. If the change is only a minor modification (e.g. a change of solvent), the initial process forms may merely need to be updated. Note, however, that larger spinoffs from a minor change may also occur and that the subtle change may have not so subtle effects to subsequent stages in the process.

The route alternative can then be filed away so that it is readily available for further investigation in the following stages of the analysis using the *INSET* tools. The search for alternative routes continues until all the major data sources have been scoured, the time allocated to this stage has been exceeded, or it is deemed that a sufficient number of routes have been identified.

It may be necessary, at a later stage of the *INSET* process development procedure, to refer to the initial concepts in the routes that were identified. This may even mean that the sheet will be analysed by non-chemists. In any case, the general form must allow an investigator to easily back-track if a variation of an alternative needs to be investigated. The use of clear and concise documentation would also allow anyone to follow the process of investigation and elimination in order to justify the certain route that was selected.

(4) List the chemicals involved

A list of the chemicals involved in every route alternative may be useful and you could use the form proposed in Tool G. Although the analysis of the SHE properties of all the chemicals may be too time-consuming at this stage, the list itself, combined with a comment and the role of the chemical in the process, may provide useful information for the decision-making at the end of *INSET* Stage I, for example as some chemicals are restricted with respect to their usage as solvents. This information could also be used in preliminary waste stream and recycle analyses. The fields identifying the SHE aspects would only be filled in during *INSET* Stage II.

Tool C form

Project title:

Date: ___ / ___ / ______ **Preliminary Chemistry Route Options Record (Tool C)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________ **Route for:** ________________________________

Source: **Lead to new ref.:**

Reaction conditions		Overall yield	Possible variations	Other comments	Reason for failure
Step					
Temp.					
Pressure					
Time					
Yield					

TOOL D – PRELIMINARY CHEMISTRY ROUTE RAPID ISHE EVALUATION METHOD

Aim:	To provide a rapid assessment procedure to determine the most viable chemical route alternatives.
Timing:	The evaluation process naturally follows after all the route alternatives have been identified.
Input:	General Screening Questions List. Tool C *or* list of chemicals involved (with their functions) from Tool G.
Output:	The extended General Screening Questions List together with the General Screening Questions Results Sheet. Dominant Alternatives Record.

Background

In order to proceed to Stage II of the *INSET* Toolkit, we must screen all the alternative routes to allow only the most viable ones to be carried on to the next stage for further investigation. A rapid procedure involving a check-list type approach is one way to do this. The screening procedure proposed here is more "flexible", but much less rigorous, than the alternative combination of Tool A and Tool E.

Instructions

The overall sequence suggested involves the following steps:
1. Complete the list of questions.
2. Answer the questions and fill in the results sheet.
3. Investigate the unknowns.
4. Make a decision.
5. Challenge the route.
6. Record the dominant alternatives.

(1) Complete the list of questions

Add any specific company-related, site-related or project-related issues to the list of questions in the tool. These may include: consideration of the yield, an estimation of the cost and the comparison to the capital, the feasibility of the alternative, and an estimation of the time required and comparison to the time limit. When adding more questions you must note that the questions must be *correctly phrased* in order to get a systematic indication of the merits of the alternatives.

(2) Answer the questions and fill in the results sheet

Answer the basic set of compulsory questions supplied in the tool. It is recommended that these are applied to all process options as they outline the major SHE concerns of every route alternative.

Various priority list for chemicals exist and these will probably need to be consulted in order to answer the questions posed in this tool. The EU "Black list" and "Grey list", and others, are mentioned in Tool A.1 Supporting Information (Part 4, Support for Tool A.1).

It is regarded to be important that the project team also considers the additional question list that covers items from the greenhouse effect, the use of limited natural resources, etc. to issues of local importance only. The extended list would be initially reviewed to determine its relevance to the given project. Other factors which are considered, for example when doing LCAs, are acidification, eutrophication, smog production, pesticides, heavy metals, etc., and questions regarding these may be also be relevant.

Using a simple but consistent marking system, answer the questions and record the results on the General Screening Questions Results Sheet. The following may be appropriate:

Response	Inferred intention	Decision symbol
No	Good	+
Yes	Bad	–
Unknown	Unknown	?

(3) Investigate the unknowns

Investigate further any questions for which "unknown" applies, usually together with others who have expertise in that particular field.

(4) Make a decision

Complete the "decision" column shown in the General Screening Questions Results Sheet using a "yes/no/unknown" system where the verdict is against, for, or pending (depending on further analysis) with the reason behind the verdict explained in the subsequent column. The reason why an alternative is eliminated should also be documented on the corresponding sheet from Tool C as well.

If this screening does not produce the desired result, by either eliminating too few or all the alternatives, it is suggested that the more rigorous approach of Tool E be applied.

(5) Challenge the route

Challenging the route alternatives is regarded to be quite important, and if it is deemed necessary when using this screening method, you can consult Tool B.

(6) Record the dominant alternatives

You can use the optional Dominant Alternatives Record to either merely further justify the selection of the favoured alternatives in *INSET* Stage I, or simply use it for easy transference of the selected alternatives to *INSET* Stage II.

Tool D form (1)

Project title:			
Date: ___ / ___ / _____	**General Screening Questions List (Tool D)**		
Author: ________________	**Proj. #:** ________________	**Ref. #:** ________	
Compulsory questions		**Additional questions**	
Q1	Are any of the materials on the EU "Black list" (banned)?	**Q11**	Are "greenhouse effect" chemicals involved?
Q2	Are any of the materials on the EU "Grey list" (dangerous)?	**Q12**	Are persistent toxic chemicals or heavy metals involved?
Q3	Are carcinogenic/teratogenic materials involved?	**Q13**	Does the process use raw materials that are limited or under threat?
Q4	Are any ozone-depleting chemicals involved?	**Q14**	Does the process introduce hazards that are new to the company/site?
Q5	Are any highly toxic materials involved?	**Q15**	Are there likely to be problems during the site decommissioning?
Q6	Are unstable/explosive materials involved?	**Q16**	________________ ?
Q7	Do any of the materials react violently with air or water?	**Q17**	________________ ?
Q8	Will the wastes need further treatment?	**Q18**	________________ ?
Q9	Is the ultimate fate of any the materials unknown?	**Q19**	________________ ?
Q10	Will hazardous materials need to be imported/exported?	**Q20**	________________ ?

Tool D form (2)

Project title:

Date: ___ / ___ / ______ **General Screening Questions Results Sheet (Tool D)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Ref. #	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	...	Reason	Decision
A_1															
A_2															
A_3															
A_4															
A_5															
A_6															
A_7															
...															

Summary sheet for *INSET* stage I

Project title:

Date: ___ / ___ / _____ **Dominant Alternatives Record (Tool D/Tool E)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Alternative Ref. #	**Grounds for favourable assessment**

TOOL E – PRELIMINARY CHEMISTRY ROUTE DETAILED ISHE EVALUATION METHOD

Aim: To evaluate the chemical route alternatives with respect to the constraints and objectives which define the process.

Timing: The evaluation process naturally follows after all the route alternatives, and the constraints and objectives, have been identified.

Input: Tool A.1 and Tool A.2.
Tool C *and* list of chemicals involved (with their functions) from Tool G.

Output: Criteria Screening Matrix.
Dominant Alternatives Record.

Background

In order to proceed to Stage II of the *INSET* Toolkit, we must screen all the alternative routes to allow only the most viable ones to be carried on to the next stage for further investigation. A rigorous approach to the difficult decision-making process of elimination of unfavourable chemical route alternatives is described in this section.

Alternatively, Tool D can be used if a less rigorous method is deemed to be sufficient.

Instructions

The overall sequence suggested involves the following steps:
1. Complete Tools A.1 and A.2.
2. Rate the alternatives in relation to the constraints.
3. Investigate the unknowns.
4. Challenge any unfavourable alternatives.
5. Make the decision.
6. Rate the alternatives in relation to the objectives.

(1) Complete Tools A.1 and A.2

Check that Tool A.1 as well as Tool A.2 are up-to-date. The minimum requirement is that at least Tool A.1 has been completed. However, consideration of the results from Tool A.2 will usually be required in order to make satisfactory conclusions.

Extend the list of requirements developed in Tool A.1 and Tool A.2 to reflect the need for more specific grounds to base the decisions on. Complement and/or modify the list with specific criteria in a way that reflects the decision maker's multiple and often conflicting aspirations in a particular decision problem.

(2) Rate the alternatives in relation to the constraints

Rate the alternatives in relation to the constraints from Tool A.1. A simple classification system would probably suffice in this assessment and a 6-tiered rating scale as described below could be applied. Use the Criteria Screening Matrix to document whether the different alternatives fulfil (+ or ++) or fail to fulfil (–) the constraints as listed in the Tool A.1 forms. A "?" can be used if it is impossible to give an answer at this stage.

Rating	Definition
++	Easy to see that the criteria are fulfilled. Passes easily.
+	Criteria fulfilled. Passes.
+?	Criteria possibly fulfilled. May pass – further investigation needed.
?	Not at all sure. Follow up with other experts.
–?	Criteria possibly not fulfilled. May not pass – further investigation needed.
–	Criteria not fulfilled. Can an alternative be found? Obviously fails if no chemical change to the alternative is possible.

(3) Investigate the unknowns

Investigate further any rank that includes a "?", possibly with the aid of an expert in that particular field. It may be necessary to revisit and reassess the alternative at a later stage, for example if the required data needed to make a definite decision is not yet available.

(4) Challenge any unfavourable alternatives

Complete the form provided. When completing the screening of the alternatives with regard to the constraints, fill in the "meets constraints" column according to the worst rating of the individual constraints for that particular alternative.

Whether an alternative passes a certain constraint with a "++" or a "+" is not seen to be so important, as long as all the constraint criteria are fulfilled. If an alternative does not fulfil all the constraints, it should be "challenged" in regard to the failing-step. Should a new alternative be generated from the challenging procedure, it should then also be subjected to the same screening procedure. If a particular alternative is rated a "–" when screening against the constraints, it will be eliminated, unless a solution can be found to the suspect area of the route (see Figure 1).

The search for a change that will make the alternative again viable is an important aspect in the search for the top synthesis route. Without challenging a particularly unfavourable route, a new exceptional process may remain concealed. The importance of discovering this route is self-evident.

Use the relevant parts of the challenging procedure contained in Tool B of the *INSET* Toolkit. Although this, as a whole, may be too involved at this stage of proceedings, the Process Change Guideword Prompt List may be used to generate new alternatives.

Alternatively, a very basic set of sample questions that could be the basis of a simple challenging/option generation procedure follows:

- Are potentially hazardous raw materials, reagents and intermediates involved? Can they be substituted?
- Is the order of steps most appropriate for the synthetic route? Can some steps be eliminated?
- Do the intermediates need to be isolated? Can certain steps be easily combined?
- What needs to be changed to make the process safe to scale-up?
- Are the raw materials available on the scale required or do they need to be synthesized?
- Are the by-products likely to lead to effluent problems?
- etc.

This list could be further developed and could aid in the identification of relevant SHE-related questions to pose in the decision context at this stage.

Minor modifications uncovered by challenging would be recorded simply as an amendment to the form completed in Tool C. However, where a major modification is proposed, a new alternative reference number should be generated and the corresponding details entered onto the new form.

(5) Make the decision

Try to identify those, say five, alternative routes that should be investigated further in *INSET* Stage II. Any difficult decisions or comments regarding the follow-up of any of the alternatives should be noted with some explanatory note in the footnotes at the bottom of the form.

Use the Dominant Alternatives Record presented in Tool D (and included here as well) to either merely further justify the selection of the favoured alternatives in *INSET* Stage I, or simply to transfer the selected alternatives to *INSET* Stage II.

Time permitting, all the unfavourable alternatives should be challenged in order to generate better routes, as this is the stage where a potential top route could be overlooked. Finally, when the best alternatives have been identified, also make a note on the form in Tool C as to why a certain route has been rejected.

Tool E can be regarded to have been completed when, after challenging the deficient routes, only the five most favourable synthetic routes remain. In practice, it may be impossible to make a well-founded decision based on the information gained as too many of the alternatives pass the screening or all of them fail. A further rating based on the objectives is then required.

(6) Rate the alternatives in relation to the objectives

Once all the alternatives have been screened with respect to the constraints of the project, screening with regard to the objectives may be necessary.

When screening against the objectives, any unfavourably marked alternatives need to be challenged, possibly again by using Tool B. Any newly generated routes arising from the challenging procedure would again be subject to the entire screening process.

Rate the "meets constraints" alternatives in relation to the objectives from Tool A.2 using the same classification system as for the constraints (see Step 2). Use the Criteria Screening Matrix to document whether the different alternatives fulfil (+ or ++) or fail to fulfil (–) the objectives as listed in the Tool A.2 forms. A "?" can be used if it is impossible to give an answer at this stage.

Whether an alternative passes a certain objective with a "++" or a "+" is not seen to be so important. However, the use of educated judgement in "ranking" the strength of compliance to the particular objective may aid the selection of the preferred set (perhaps five) of alternative synthetic routes. Some decision aids are reviewed in Appendix 8, in Part 3.

The "passes initial screen" column is appropriately marked to indicate which alternatives have passed this stage of the assessment with regards to both the constraints and objectives. Once the best candidate set has been determined, the other favourably marked alternatives should obviously be further challenged, or at least remain "open" for future consideration in case the alternatives in the chosen set are all deemed to be unsatisfactory in the ensuing stages.

The dominant alternatives should be listed in the Dominant Alternatives Record together with a description of the grounds for the favourable assessment. The reason that a particular route alternative fails should, on the other hand, be noted on the form in Tool C.

The iterative nature of the procedure undertaken when initially evaluating the process route alternatives is outlined in the logic diagram described in Figure 1.

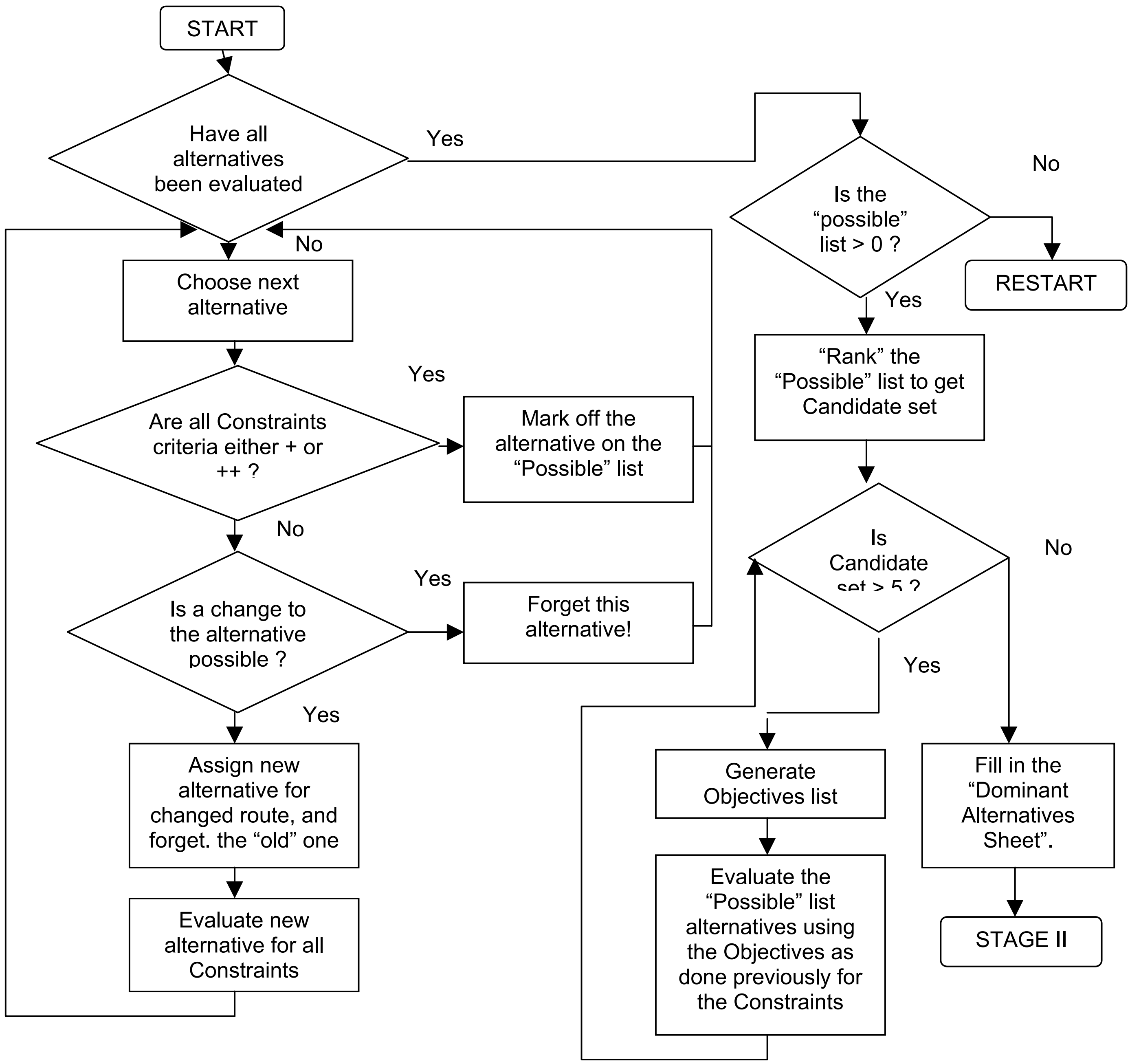

Figure 1 Simple decision flowchart: Route alternatives vs constraints

Tool E form

Project title:

Date: ___ / ___ / ______ **Criteria Screening Matrix (Tool E)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Alternative Ref. #	Constraints										Meets constraints	Objectives										Passes initial screen
	C_{G1}	C_{G2}	C_{G3}	...	C_{P1}	C_{P2}	C_{P3}	C_{P4}	C_{P5}	...		O_{G1}	O_{G2}	O_{G3}	O_{G4}	O_{G5}	...	O_{P1}	O_{P2}	O_{P3}	...	
A_1																						
A_2																						
A_3																						
A_4																						
A_5																						
A_6																						
A_7																						
A_8																						
A_9																						
A_{10}																						
...																						

Footnote 1	
Footnote 2	
Footnote 3	

Summary sheet for *INSET* stage I

Project title:

Date: ___ / ___ / ______ **Dominant Alternatives Record (Tool D/Tool E)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Alternative Ref. #	Grounds for favourable assessment

TOOL F – CHEMISTRY ROUTE BLOCK DIAGRAM RECORD

Aim:	To give an overview of the process involved for each alternative.
Timing:	To get an overview of the selected route alternatives with respect to their complexity and with regards to both equipment and possible waste streams and recycles, this tool should be completed before more data is collected for the process, and whenever a new engineering-modified alternative has been generated.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool A.
Output:	Chemistry Route Block Diagram Record forms for the dominant alternatives and any modified versions of these.

Background

It is important that, in order to gain an overview of the processes and process equipment involved in the selected chemical route alternatives, the recording of this information is done in a systematic way. The *INSET* Toolkit provides sample forms that enable the user to accomplish this.

In Tool F, the possible waste streams, the recycles, the plant equipment and the overall complexity, all factors that need to be considered as early as possible, are recorded to give an overview of the process alternative.

Transportation aspects, although not usually a priority in these early stages of route alternative analysis, should obviously be analysed as early as possible with the aim of covering that the inherently designed process also caters inherently for the transport of the raw materials to the site and the waste materials from the site.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the constraints and objectives.
2. Assess the route alternatives.
3. Draw the block diagram.
4. Generate new options.
5. Check the engineering-modified alternatives.

(1) Identify the constraints and objectives

Tool A should be completed before commencing Stage II of the *INSET* Toolkit. This is a necessity, as the limitations and boundaries of every project should be at hand throughout the duration of the entire project.

(2) Assess the route alternatives

The assessment of the chemistry route alternatives that have been presented here, using the constraints and objectives as the limiting factors, is then required. This is only necessary if Stage I of the *INSET* Toolkit has not been completed. The assessment with respect to the constraints and objectives is necessary even in those cases where the chemical process is "fixed". Tool E would be used to record this type of assessment.

(3) Draw the block diagram

Draw the block diagrams for the alternatives under consideration in a uniform way, since the diagrams form the basis for subsequent assessments. In some cases, where detailed information is available, this means simplification, and in other cases, such as for novel ideas, educated guesses based on experience from other processes must be applied.

The level of detail of the block diagram increases when more information becomes available, but you should, from the beginning, be able to include most of the following blocks in the diagram:
- storages,
- product streams,
- reaction units,
- cooling/heating systems,
- separation units,
- purification units,
- waste streams,
- transportation.

When drawing the process for the first time you should follow the published information as much as possible, changing only those parts of the process which are not possible to be carried out on a plant scale. The initial alternatives should be given their own identification codes. In some cases, it may be beneficial to divide the process into sections, for instance drawing up the reaction phase separate from the work-up phase. Consequently, you must redraw only the latter should the work-up procedure be changed at a later stage, but not the reaction procedure.

The aspects of transportation should also be incorporated into this block diagram, as analysis of the required transportation, as early as possible, is important to the ISHE performance of the plant. Procedures involving transportation of raw materials to the site and the waste materials from the site would be appropriately labelled on the block diagram.

Note It is strongly suggested that an A3 version of the supplied form be used.

(4) Generate new options

Use Tool B, Process Option Generation, in order to find better options (later to be referred to as "engineering-modified versions") for all but the best of the initial alternatives. The improved processes should retain the original identification code only if the change is a minor one. Normally a new identification number is given, and, as a consequence, earlier tools should be used to check that no new problems have been created by the proposed change.

Continue the iterative process of comparing all options and drawing new alternatives as long as significant progress is observed.

(5) Check the engineering-modified alternatives

It may be helpful to have the constraints and objectives lists from Tool A at hand to make sure the project is still within the boundaries set.

Tool F form

Project title:

Date: ___ / ___ / ______ **Chemistry Route Block Diagram Record (Tool F)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________ **Block diagram for:** __________________________

Source: **Lead to new ref.:**

Possible variations	Other comments	Reason for failure

TOOL G – CHEMICAL HAZARDS CLASSIFICATION METHOD

Aim:	To provide a simple and easy-to-apply means of classifying materials in terms of their hazardous properties. This includes providing a consistent basis for classifying and comparing safety, health and environmental hazardous properties. This classification provides a direct means of comparing material hazards but also provides a basis for various means of ranking and comparing chemistry and process routes and plant inherent SHE performance.
Timing:	The classification system can be applied at any time during or following chemistry route identification and screening. It is suggested that it is applied in full at *INSET* Stage II, Chemistry Route Detailed Evaluation – as a means of comparing the inherent hazards of various route options to screen out those that offer the best potential inherent SHE performance. The classification system is also used in a number of ranking systems and indices at later stages in the toolkit.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). A list of all materials in the process, including any utilities such as heat transfer fluids (Tool C). Material Safety Data Sheets for these materials, or labelling information where available for R-phrase information.
Output:	If completing *INSET* Stage I Tool C, the output will be a chemical list with function and comment information. *Otherwise:* Tool G – A list of all materials in the process classified in terms of their safety, health and environmental hazardous properties.

Background

Hazards can be generally said to arise from two types of events, acute/catastrophic and chronic. A general classification of material hazards from a SHE point of view is needed to provide the basis for any assessment. In the *INSET* Toolkit, various tools require a simple "standard" and consistent way for the chemicals to be classified.

Various methods of classifying hazardous chemicals have been proposed. The classification method in this tool outlines a proposed system for classifying the hazardous properties of each chemical based on the "risk phrases" from EC Directive 84/449/EEC. In many cases, the information needed to complete this tool will be derived from an MSDS of the particular chemical (see Tool G Supporting Information). A general "word picture" of each category is provided to assist in the classification of materials or mixtures for which R-phrase information is not readily available. It could be used to rank process hazards in order to identify the main areas where risks could be reduced, and be used to compare the relative chemicals-related hazards (S, H & E) of a number of process options.

Instructions

The overall sequence suggested involves the following steps:
1. List the chemicals involved.
2. Classify the chemicals.
3. Generate better options.
4. Keep the list current.

(1) List the chemicals involved

List all the identified chemicals for each route alternative using the record sheet included in this tool. If Tool C has been used, this list should already exist. The function of the chemical should also have been noted on the form at that stage. The proposed method for filling in the "function" field is as follows:

Description	Code
By-product	B
Catalyst	C
Decomposition product	D
Extinguishing agent	E
Heat transfer material	HTM
Inhibitor	Inh.
Initiator	Ini.
Intermediate	Int.
Product	P
Reactants	R
Solvent	S
Specific atmosphere	A
Waste product	W

Comments to highlight potential problems for each individual chemical substance should be included as well. Examples of these types of comments are:
- chemical is allowed to be used as a reactant but not as a solvent,
- foaming agent,
- potential to clog filters,
- forms dust/mist,
- potential to polymerize,
- pungent odour,
- non-biodegradable.

The "comments" field can also be used to make reference to sources, and to document other information, e.g. to record the quantity/concentration of material involved (e.g. 2 kg of 2M nitric acid, or 150 kg of 30% hydroxylamine in acetone). The "comments" field also provides space to enter the state of the chemical, e.g. gas, vapour, liquid, slurry, solid.

(2) Classify the chemicals

Using the classes (VH, H, M, L) given in the Chemical Hazardous Properties Classification table, fill in the hazardous properties of the chemicals in the Chemical Function & Hazards Classification form for each of the route alternatives. This table is also required when calculating the indices in Tool I.

Note The classifications are for the pure substances only and cannot easily be applied to mixtures of materials.

If the particular chemical substance has not previously been classified and estimates of its hazardous potential cannot easily be made, structure-activity estimates and various other modelling approaches could be used to classify the "unknown" chemicals. The functional groups of the chemical can be a quick means of indicating whether a substance is, for example, a possible "high-energy substance" (i.e. a substance that possesses a positive enthalpy of formation and, therefore, always releases energy on decomposition). It is advisable to consult a table of these substances when assessing new or novel substances.

A similar matrix, included in Tool K, enables more detailed and precise information (e.g. LC_{50} values) to be recorded for each chosen alternative and, in this way, may be most useful if accessed during *INSET* Stage III. Alternatively, the form in Tool K could be merely used as a prompt list guide that makes sure that all the major hazardous properties are considered.

(3) Generate better options

Substitution of the most hazardous chemicals in the matrix should be considered. Parts of Tool B can be used for this purpose. In some cases, however, there may be advantages to use a hazardous but reactive chemical (e.g. no accumulation of the reactant, see Tool I) and, therefore, the information in the matrix should be used with care and only as one aspect on which decisions will be based.

(4) Keep the list current

The list of chemicals should be kept up-to-date during the entire project. For instance, laboratory studies will inevitably reveal intermediates, by-products, etc. which were not initially identified. It should also be noted that when applying the tool at later stages of a project, any inventories or discharges of hazardous materials from services and utilities should also be included (e.g. refrigerants, heat transfer media, solvent recovery, waste treatment) in order to gain an appreciation of the overall impact of the process on SHE performance.

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Chemical Hazardous Properties Classification

Class	Safety	Health	Environment
Very high hazard **VH**	Materials which present hazards that endanger life at a large distance from the source of the material or in very small concentrations/amounts	Materials which present hazards that endanger life on contact with the source or following short-term exposure in the working environment	Materials which present hazards that could result in a significant loss of habitat or species
	Very toxic **R26/27/28** Category 1 carcino/muta/teratogenic Extreme risk of explosion **R3**	Very toxic **R26/27/28** Category 1 carcino/muta/teratogenic	Aquatic very toxic **R50** Very toxic **R26/27/28** Category 1 carcino/muta/teratogenic
High hazard **H**	Materials which present hazards that endanger life, or could result in serious injuries some distance from the source of the material or in small concentrations/ amounts	Materials which present hazards that could cause serious injury, or cause serious long-term adverse effects on contact with the source material or following short-term exposure in the working environment, or endanger life following prolonged exposure in the working environment	Materials which present hazards that could result in significant long-term damage to habitat or to certain vulnerable species
	Toxic **R23/24/25** Risk of explosion **R2** Extremely flammable **R12/13** Highly flammable **R11** Oxidizing **R9/11**	Toxic **R23/24/25** Category 2 carcino/muta/teratogenic Corrosive – severe burns **R35**	Aquatic toxic **R51** Non-aquatic toxic – various species Toxic **R23/24/25** Category 2 carcino/muta/teratogenic
Medium hazard **M**	Materials which present hazards that could result in injuries or long-term adverse effects close to the source of the material, or flammable materials of low flashpoint (21-55°C)	Materials which present hazards that could cause injury or long-term adverse effects on contact with the source or following prolonged exposure in the working environment	Materials which present hazards that could result in some slight loss of habitat or species or long-term adverse effects on habitat or species
	Harmful **R20/21/22** Flammable **R10** Oxidizing **R8**	Harmful **R20/21/22** Category 2 carcino/muta/teratogenic Corrosive – burns **R34** Irritant	Aquatic harmful **R52** Aquatic adverse effects **R53** Dangerous to ozone layer **R59** General adverse effects **R58** Harmful **R20/21/22** Category 2 carcino/muta/teratogenic
Low hazard **L**	Materials which present no hazard, or which present hazards that are unlikely to result in serious injury or long-term adverse effects	Materials which present no hazard, or which present hazards that are unlikely to result in serious injury or long-term adverse effects	Materials which present no hazards, or which present hazards that are unlikely to result in long-term adverse effects
	Not classified as "dangerous" under the 84/449/EEC Directive	Not classified as "dangerous" under the 84/449/EEC Directive	Not classified as "dangerous" under the 84/449/EEC Directive

Tool G form

Project title:

Date: ___ / ___ / ______ **Chemical Function & Hazards Classification (Tool C/Tool G)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Chemical	Function	Comments	Safety	Health	Environment

TOOL H – RECORD OF FORESEEABLE HAZARDS

Aim:	To identify possible hazards caused by the desired or an undesired reaction, and record these.
Timing:	These possible hazards are part of the vital information that needs to be considered before an alternative is accepted or rejected, and it may occur that the data is uncovered simultaneously when investigating the process.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions).
Output:	Record of Foreseeable Hazards form.

Background

It is crucial to get insight into safety problems inherent in a new route alternative or plant design at the earliest possible stage in order to prevent accidents at later stages of the process life-cycle. Information on the heat of reaction for the desired reaction – and foreseeable undesirable reactions – may be available, or the value can be calculated. In other words, incompatibilities of the substances that are to be involved in the process need to be addressed.

Much can be learned from past incidents and accidents. Some information is available in databases and some information can be found in the literature, but unfortunately, in companies, much of the information is lost over the years due to poor reporting and incident investigation. Information in the existing literature is no substitute for chemical hazard testing, but it often makes a good starting point for assessing the hazards of a new reaction.

Warning Lack of information about a chemical does not mean that the chemical is benign under all circumstances.

Instructions

The overall sequence suggested involves the following steps:
1. Search for information on potential hazards.
2. Search for incident information.
3. Identifying potential exothermal reactions.
4. Document past incidents and foreseeable reaction hazards.

(1) Search for information on potential hazards

Search for problems and characteristics of potential hazards. Valuable sources include reporting systems, operating experience and past hazard reports.

(2) Search for incident information

There are some databases available in which accident and incident information can be found (see Tool H Supporting Information). Some of these are commercial, while some of them even have restricted access. Books and articles should also be searched. Information on incidents during research and industrial production may also have been found when filling in the "safety" column of the Tool G form.

(3) Identifying potential exothermal reactions

Identify potential exothermal reactions using more than one source if possible (see Tool H Supporting Information). These reactions include the main reaction itself (e.g. heat of reaction, accumulation of reactants), but also competing reactions (e.g. due to reactor materials or impure reagents), decompositions, polymerizations, build-up of unstable substances (e.g. peroxides may build up in redistilled tetrahydrofuran), etc.

Chemical functional groups that can be expected to pose a hazard due to their reactivity are outlined in Tool H Supporting Information.

The importance of addressing chemical incompatibilities cannot be overemphasized when designing inherently safer chemical processes. A section in Tool H Supporting Information deals with this important aspect.

The key parameter in evaluating the hazards of the primary or desired chemical reaction is its heat of reaction (ΔH_r). An initial estimate can be obtained from the literature or calculated from the heats of formation of the reactants and products according to Hess' law:

$$\Delta H_r = \sum \Delta H_{f_{Products}} - \sum \Delta H_{f_{Reactants}} \quad 1$$

The exothermic nature of many industrial reactions is illustrated by typical values for their heats of reaction as given in Tool H Supporting Information.

It is not necessary to have a complete description of the formal kinetics of a chemical reaction in order to evaluate its potential reaction hazards. However, it is important to determine whether, particularly for a semi-batch process, the reaction proceeds rapidly or whether reactant is accumulated during the dosing period. Similarly, sufficient data must be obtained to assess the effect of possible maloperations, for example loss of agitation, temperature/ pressure deviations, reactant charging errors (omissions/overcharging/wrong order), and extended reaction times.

Certain chemical groups are known to reduce the stability and possibly confer explosive properties on a compound. The compound types include:

Aromatic nitro	Azo	Hypochlorite
Aliphatic nitro	Azide	Chlorate
Nitrate ester	Peroxide	Perchlorate
Nitramine	Ozonide	Acetylenic.

However, not all organic compounds containing, for instance, nitro groups and nitrate esters, possess explosive properties. The possession of such properties is dependent on the oxygen balance. This is a measure of a compound's inherent "self-oxidation" ability and can be calculated, ignoring any atoms other than C, H and O, from the substance's empirical formula as follows:

$$C_aH_bO_c + (a + b/4 - c/2)\ O_2 \Rightarrow a\ CO_2 + b/2\ H_2O$$

The oxygen balance is then:

$$\text{Oxygen balance} = \frac{-1600\ (2a + b/2 - c)}{\text{Mol. Wt.}}$$

Compounds that have oxygen balances greater than –100 are likely to be detonating explosives and those with balances between –100 and –150 may show detonation properties under severe confinement. Compounds with oxygen balances less than –200 are not likely to possess explosive properties though they may still be thermally unstable.

If the presence of one of the groups listed above or an oxygen balance of more positive than –200 suggests that a reactant or the reaction mixture may possess explosive properties, then in addition to the evaluation of its thermal stability, it should be tested for explosive properties.

The rate of gas evolution during the normal process and under any envisaged maloperations is required to ensure adequate vent and/or scrubber sizing. The rate of gas evolution is not dependent on scale. Therefore, data obtained from small-scale experiments can be directly related to the plant scale.

Finally, the thermal stability of a reactant or reaction mixture gives a measure of the maximum temperature at which a process can be operated. It can also be used to determine the effects of adding or omitting a solvent, varying the reactant ratios and consequently of possible process maloperations such as overcharging or omitting one of the reactants.

Depending on the results from screening tests (i.e. exotherm size, proximity of decomposition onset temperature to process temperature), secondary testing may be required to more accurately determine:

- the minimum temperature above which the reactor will be unstable on the scale used and the time available to instigate safety measures,
- the consequences of the exotherm – heat of reaction, adiabatic temperature rise/pressure developed/venting requirements.

(4) Document past incidents and foreseeable reaction hazards

A reference to the information gathered should always be made, especially since it is required in *INSET* Stage III when further assessment of the chosen route alternative is done. Also, information on incidents that have been caused by chemicals closely related to those used in the studied alternatives should be noted on the following form.

Tool H form

Project title:

Date: ___ / ___ / ______ **Record of Foreseeable Hazards (Tool H)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Substance/reaction of interest	Short description of the potential hazard	Note	Reference

TOOL I – ISHE PERFORMANCE INDICES

Aim:	To provide a consistent means of ranking and comparing different route options in terms of their inherent SHE performance.
Timing:	The tools require some information or estimates of inventories and equipment but should still be suited for *INSET* Stage II, Chemistry Route Detailed Evaluation. Tool K can be used as an alternative if a rapid screening index is sufficient.
Input:	Basic data available to the project team such as materials and inventories plus physical data generally available on hazard data sheets: - an estimate of the inventory of hazardous materials in the process and their classification in terms of R-phrases (Tool G); - an estimate of the content of the waste streams; - an estimate of the reactivity from Tool L where reaction hazards may be involved. Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). The process block diagram (Tool F).
Output:	Tool I.1 through to I.11 results: separate indices for major accident safety, health and environmental hazards – providing an indication of the "inherent hazard" of the process or plant. These results can be used to compare different chemistry route options and help with the selection of the preferred option, or can be analysed to assess which parts of the process are contributing most to the risks and highlight where efforts to improve the inherent SHE of the process need to be directed. The results can also be fed forward to the multi-attribute evaluation tool (Tool J), to help with decision-making where there is no obvious best option.

Background

Hazards can be generally said to arise from two types of event, acute/catastrophic and chronic. Major hazard safety relates to acute events usually involving the release of energy or material from a process. The effects are therefore generally related to the inventory and hazardous properties of the materials in the process.

Chronic events can take two forms, those from authorized or flowsheet discharges (effluent streams) and those from fugitive emissions arising from non-design weeps and minor leaks, and from activities which breach the process containment (e.g. sampling, charging of raw materials, maintenance, etc.). The latter two aspects can generally be regarded as environmental and health issues respectively.

In the *INSET* Toolkit, indices based on different levels of detail have been developed. The indices that are included, as well as a list of the more detailed indices available from other sources, follow:

Safety, health and environment indices		
Aspect	**Level of assessment**	
	Tool I	**Detailed**

Fire and explosion hazards	Tool I.1 Material hazard classification Inventory	Mond Index Dow Index Consequence assessment Site-specific QRA
Acute toxic hazards	Tool I.2 Material hazard classification Inventory	Consequence assessment Site-specific QRA
Occupational health hazards	Tool I.3 Material hazard classification	
Environmental incident potential	Tool I.4 Material hazard classification Inventory	Consequence assessment Site-specific QRA RASP
Transport incident potential	Tool I.5 Material hazard classification Transport distances	Consequence assessment QRA
Gaseous emissions	Tool I.6 Material hazard classification Gaseous discharges	Detailed site-specific assessment
Aqueous emissions	Tool I.7 Material hazard classification Liquid discharges	Detailed site-specific assessment
Solid and liquid wastes	Tool I.8 Material hazard classification Waste discharges	Detailed site-specific assessment
Energy consumption/ global warming potential	Tool I.9 Energy requirements CO_2 equivalents	
Reaction hazards potential	Tool I.10 Adiabatic temperature rise Onset temperature of decomposition Time to maximum rate	Calorimetry Runaway scenario modelling
Process complexity	Tool I.11 Process steps and boundaries	

Instructions

The overall sequence suggested involves the following steps:
1. Decide on the level of assessment.
2. Select the appropriate tools.
3. Make a representation of the process.
4. Dominant material/equipment approach and alternatives.
5. Assessing material hazards.
6. Absolute vs relative indices.
7. Results.

(1) Decide on the level of assessment

The multi-attribute analysis of the indices derived in this tool may be carried out in a number of ways (see previous table). These range from a simple preliminary assessment which may be completed in a few hours, through to very detailed assessments such as using the Mond Index or doing a QRA. The latter would require a great deal more data and could each take a number of days to complete.

The technique to be used depends on:
- the stage at which the assessment is being carried out,
- the data available,
- the potential impact, and importance, of the effects being considered.

In general, those techniques with more detail will provide a more sound assessment.

It should be noted that many of the assessments involve implications and cannot be considered to be exact. However, it is clear that:
- a process with overall low scores will exhibit better ISHE than one with high scores.
- any individual high score needs to be studied in more detail. This will provide both a better understanding of the critical features as well as ways in which improvements can be made.

If a rapid overview assessment is all that is required, the simple qualitative index in Tool J could be used. For a full analysis, Tools I and J would be used at this assessment stage.

Tool K, the Rapid ISHE Screening Method, could be used where there is only time for a very rapid assessment – this uses simple "judged" evaluations of the chemistry, wastes and feasibility aspects of the different stages of the process.

(2) Select the appropriate tools

The proposed indices will allow the user to assess the route alternatives by allowing the comparison of their safety, health, and environmental aspects. Select those aspects from the previous table which are relevant for your route alternatives and the project scenario. For each aspect chosen, select the suitable level of detail for the tool.

It is recognized that although ISHE is important, other factors will also need to be taken into account. These could include: availability of raw materials, capital costs, novelty of the technology, time to market, etc. As each organization will place the emphasis of the assessment on different aspects, these will need to be developed to meet the company's specific needs.

Note For each aspect, the same, consistent, level of detail should be chosen. In this way, all alternatives can be assessed using the same tool, allowing direct comparisons between process route alternatives.

(3) Make a representation of the process

A schematic representation of the plant is initially required and the Chemistry Route Block Diagram Record (Tool F) is designed for this task. The representation, however, should be completed to the desired and appropriate level of detail as decided upon in Step 1.

The index can be applied to an entire process as one "block", but in most cases it may be useful to split the process into stages or blocks and evaluate the indices for each of these separately. This is particularly true where the dominant material/equipment approach is used, otherwise the entire process is assessed against one material/equipment item only. Although assessing the index for these different stages gives a better appreciation of the safety of the process, it is more time-consuming and can also bring in complications when comparing very different options, since the way the process is split into sections can affect the indices calculated. Again, try to be consistent and break each process option into comparable blocks for the assessment.

Tool G is available to give assistance for classifying the material hazards from a SHE point of view. This is required as the basis for Tool I indices.

(4) Dominant material/equipment approach and alternatives

Most of the Tools I are based on the determination of the indices from the perspective of the dominant material and dominant equipment system. These must be identified and, more importantly, defined. The idea is that it will be very time-consuming and wasteful to apply the indices through the process. Instead, the user should focus on the main areas of concern – the "dominant" ones – and apply the indices to these. The dominant material or equipment may be different for each individual index.

An equipment system is defined as a stage in the process which is isolated from others, or can be in an emergency, for example a distillation column with associated reboiler, condenser, reflux drum, etc. Where an inventory of material is required, this will be either the capacity of the largest single storage tank or the largest equipment system in the process.

Alternatively, the user can choose to evaluate the index for all areas/streams. This would take more effort, but would have the advantages of allowing comparison between the contribution of different areas or streams within each index, and of addressing all the process and taking an overview of its full hazard potential. An intermediate option would be to select a number of materials, streams or equipment items that are likely to be the "most important" even though any one may not "dominate" the situation.

The main point is to be consistent to allow the indices to help identify any important comparisons. So whether you use either the "dominant" approach, the "most important" approach or the "all" approach, keep to it.

For each individual index, look at the various relevant aspects (e.g. inventories, materials, effluent discharges, loads to be transported) and try to assess which stream/inventory/activity is likely to give the worst (highest) index. This may be obvious from the materials/process being considered or may require separate analyses of a number of combinations to find the dominant material.

If there are several contenders, then apply the index to all of these to see which is highest. Remember, the highest index will be from some combination of factors, so do not dismiss one area, for example because it has a low toxicity material – this may be offset by a high inventory. If in doubt, apply the index to a number of plant areas to confirm which is dominant.

Caution should be noted if considering combining the scores for any given index (e.g. adding them together) to get an overall index value for the whole process.

(5) Assessing material hazards

When considering the material hazards, ensure that all the materials involved in the process have been considered, for example:
- feeds,
- catalysts,
- intermediates,
- products,
- by-products,
- impurities,
- refrigerants,
- heat transfer fluids,
- recycles.

It should be noted that in all but a few specific cases, the index treats all types of material the same, be they gas, liquid or solid. This gives a true measure of the inherent hazard, but does not accurately reflect the actual risk and consequences of the hazard. Clearly, a solid in pellet form is likely to present less risk in many accident situations than say in a liquid or gaseous form. Also, if the hazardous material is dissolved or encapsulated in a safer medium, then the risks could be a lot less. Future refinements to the index may allow these factors to be considered systematically. In the meantime, users should bear these factors in mind when using the indices, or devise their own "adjustment factors" to handle these situations.

Where streams or inventories consist of a mixture of materials, then the separate components should be assessed individually, each with their own harm factors and mass flows or mass inventories.

(6) Absolute vs relative indices

Two versions of the indices can be calculated. The absolute index represents the basic inherent hazard of the process, whereas the relative indices are divided by the plant throughput to give a measure of the risk per unit of production (i.e. per unit of product produced), which can be helpful when comparing process options with different throughputs.

Depending on the type of plant/process being considered and the format of any information available, the user may wish to use an alternative basis for comparison with the relative index, for example per batch or per years production instead of per day (which is generally recommended). The objective is to obtain a set of index values per unit (tonne) of product produced. In practice it does not matter which basis is selected, provided it is applied consistently and is relevant to all the options being compared.

The relative indices are the preferred measure where processes or plants of different throughput/batch size are to be compared. The absolute indices are to be used where the absolute degree of inherent SHE needs to be assessed, and where the various options under consideration have the same or similar throughputs. For the majority of applications, the absolute indices will probably be the most appropriate. Further advice on the use of the relative and absolute indices is given in the multi-attribute evaluation tool, Tool J.

(7) Results

It is suggested that only the values from the single dominant parts of the process for each index I.1 to I.11 are presented to aid decision-making – giving a selective "worst case" view of the process.

Where several parts may be important, the values from these can be added under one index. Comparison of the different contributions to the specific index would give a good indication of which areas/units were critical, and whether there was one very dominant area or many areas giving similar problems. However, adding values in some indices and not in others would prevent any consistent comparisons with other options.

An alternative would be to calculate the index values for all process units/transportation/waste streams/etc. and add these together under the relevant index I.1 to I.11. This would take some time to do, but would give a feel for the overall inherent risk of the process, and allow consistent comparisons between process options.

Under no circumstances should the values from different indices be added together (e.g. do not add the result from I.1 to I.2 to get some overall score – this would give an inaccurate picture). The different indices use different bases and scales and are not directly comparable. If you wish to assess the overall impact of the process, use Tool J and the guidance it contains on presenting data and using it to aid decision-making.

Tool I.1 –Fire and explosion hazards index

Aim:	To provide a means of comparing route alternatives on the basis of the potential for fire or explosion.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool F results. Tool G results.
Output:	A semi-quantitative rating of the fire and explosion hazards.

Background

An important facet of any process alternative is its fire and explosion hazard potential. Other indices in Tool I consider the potential for environmental spills, exposure to toxic materials, and inherent health hazard. In addition, it is necessary to consider the potential of fire and explosions to occur within the process.

The assessment needs to take account of those materials with the potential to cause, or be involved in, fires or explosions, their hazard classification and the inventories involved.

There may be occasions where the choice of process routes can either raise or lower the potential for fires and explosions. This needs to be taken into account in the inherent SHE assessment and a simplified assessment procedure has been produced. It must be stressed that this procedure is not suitable by itself for materials of high hazard and must, where appropriate, be supported by a detailed risk assessment.

The design of the plant itself in order to minimize damages due to a fire or explosion is not covered here, but is outlined in Stages III and IV of the *INSET* Toolkit.

Instructions

The overall sequence suggested involves the following steps:

1. Identify flammable and explosive materials.
2. Identify the dominant material(s).
3. Determine the Fire and Explosion Hazard Factor (FEHF).
4. Calculate the Fire and Explosion Hazards Index (FEHI).
5. Refined FEHI calculation.
6. Improve the process.
7. Carry out a more detailed assessment.

(1) Identify flammable and explosive materials

Firstly, based on the list in Tool G, identify all the flammable and explosive materials on the proposed plant which are likely to be stored or exist as significant in-process inventories (e.g. reactors, distillation columns, liquid extraction, etc.). The list should include all likely storage of raw materials, intermediates, etc., including storage associated with transport operations. Use the R-phrases from the chemicals' MSDS to determine the chemicals' safety classification.

(2) Identify the dominant material(s)

For each block in Tool F (or other more suitable units/items) identify the dominant material(s) and make an estimate of the inventory. Document the result using the Tool I.1 form.

(3) Determine the Fire and Explosion Hazard Factor (FEHF)

Look up the Fire and Explosion Hazard Factor (FEHF) for each material from the table below. Document the result using the Tool I.1 form.

Material condition	**FEHF**	
	In building	**Open structure**
Explosive materials (Note 1)	500	500
Unstable material	30	30
Liquefied flammable gases under pressure	50	50
Flammable liquids more than 20°C above their atmospheric boiling point	20	20 (Note 2)
Cryogenically stored liquefied flammable gases	20	5
Flammable gases under pressure	20	5
Highly flammable liquids (flash point < 21°C) below their boiling point	5	5
Flammable liquids (flash point < 55°C)	1	1
Dusty flammable solids	25	10
Flammable solids	0.1	0.1

Note 1: Materials capable of condensed phase explosion without the need to mix with air or oxygen.
Note 2: Only applies where the inventory of an individual system is greater than 1 tonne. In other cases, a value of 5 applies.

(4) Calculate the Fire and Explosion Hazards Index (FEHI)

Calculate the Fire and Explosion Hazards Index (FEHI) based on the inventory of the material and document the result using the Tool I.1 form. The absolute value does not use the plant throughput and the relative value is the index divided by the plant throughput.

$$\text{FEHI} = \frac{\text{FEHF} \times \text{Unit inventory}}{\text{Daily production}}$$

The procedure outlined above is recommended for a first pass. Where the value of the FEHI is seen as significant, a refinement to the procedure is available: see Step 5. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(5) Refined FEHI calculation

For a more accurate assessment the following refinements should be considered:

$$\text{FEHI}_{\text{Ref.}} = \text{FEHI} \times \text{CF1} \times \text{CF2} \times \text{CF3}$$

where the correction factors are determined as follows.

- *CF1 - Heat of combustion*

The FEHF values noted above are relevant for "average" hydrocarbons with a heat of combustion of 44000 kJ/kg calculated on the basis of H_2O as vapour.

Where the actual heat of combustion is significantly lower, the value of the FEHI can be corrected proportionally by using a correction factor (CF1):

$$CF1 = \frac{\Delta H_C \text{ (actual)}}{44000 \text{ kJ/kg}}$$

- *CF2 - Highly reactive/sensitive materials*

The materials included in the table below are either highly reactive or have very low ignition energy levels. The following correction factors (CF2) may be applied.

Material	**CF2**
Carbon disulphide	2
Hydrogen	1.5
Ethylene	1.5
Acetylene	1.5
Weakly flammable materials	0.25 - 0.75

Note Weakly flammable materials should not be given a rating of 200 or 300 since they are unlikely to generate a vapour cloud explosion (VCE) or generate a boiling liquid expanding vapour cloud explosion (BLEVE).

- *CF3 - Liquids more than 20°C above atmospheric boiling point*

The rating given to these materials is based on the potential to cause a VCE. A further refinement may be applied to take account of the likely degree of vapour formation and the minimum value necessary to cause an explosion:

a) For boiling points between 20°C and 50°C above the atmospheric boiling point, the inventory can be refined based on the quantity of vapour likely to be available to participate in an explosion (CF3).

Superheat temperature	**CF3**
20°C	0.3
30°C	0.55
40°C	0.75
50°C	1.00

b) For process plants outside the confines of a building, the cut-off point for a VCE may also be adjusted for the degree of superheat.

Superheat temperature	**Minimum system inventory for VCE [Te]**
20°C	3.3

30°C	1.8
40°C	1.3
50°C	1.0

In the case of inventory values below these for a single system, an FEHF value of 5 should be used.

Document the results using the Tool I.1 form.

(6) Improve the process

Once the FEHI has been calculated, consideration can be given to the way in which improvements could be made. The following main approaches are possible:
1. Elimination of the flammable material.
2. Reduction in the inventory of the material.
3. Changes to the conditions under which the material is kept, in order to reduce the quantity which would be lost in the event of failure, for example by using refrigerated storage instead of pressurized storage.

INSET Tool B can be used to aid the option generation.

(7) Carry out a more detailed assessment

Where the FEHI is high, a more detailed assessment may be carried out using:
- the Dow Index,
- the Mond Index,
- quantified risk assessment (QRA).

Tool I.1 form

Project title:

Date: ___ / ___ / ______ **FEHI: Fire and Explosion Hazards Index (Tool I.1)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Temperature [°C]						
D	Atmospheric boiling point [°C]						
E	Item/inventory [Te]						
F	Fire and Explosion Hazard Factor (FEHF)						
G_a	Absolute FEHI, = E × F						
G_r	Relative FEHI, = E × F / A						
Refinement							
H	Heat of combustion correction (CF1)						
I	Reactivity/sensitivity correction (CF2)						
J	Liquids above b.p. correction (CF3)						
K_a	Refined absolute, FEHI = $G_a \times H \times I \times J$						
K_r	Refined relative, FEHI = $G_r \times H \times I \times J$						

Tool I.2 –Acute toxic hazards index

Aim:	To provide a means of comparing route alternatives on the basis of the acute toxic hazards.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool G results.
Output:	A semi-quantitative rating of the acute toxic hazards.

Background

An important facet of any process alternative is its toxic hazard potential. Other indices in Tool I consider the potential for fire, explosion or the environmental spill potential. In addition, it is necessary to consider the acute toxic hazards of the process alternative due to exposure to any of the toxic materials that are present.

The assessment needs to take account of all toxic materials, their hazard classification and the inventories involved.

There may be occasions where the choice of process routes can either raise or lower the toxic hazard potential of the process. This needs to be taken into account in the inherent SHE assessment and a simplified assessment procedure has been produced. It must be stressed that this procedure is not suitable by itself for materials of high hazard and must, where appropriate, be supported by a detailed risk assessment.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the toxic materials.
2. Identify the dominant material.
3. Determine the Toxic Harm Factor (THF).
4. Calculate the Acute Toxic Hazards Index (ATHI).
5. Improve the process.

(1) Identify the toxic materials

Firstly, based on the list in Tool G, identify all those toxic materials on the proposed plant which are likely to be stored or exist as a significant in-process inventory, for example reactors, distillation columns, liquid extraction, etc. The list should cover all likely storage of raw materials, production and intermediates, etc., including storage associated with transport operations. Use the R-phrases from the chemicals' MSDS to determine the chemicals' safety classification.

(2) Identify the dominant material

Identify the dominant material(s) for each block in Tool F, or other more suitable units/items, and make an estimate of the inventory. Document the result using the Tool I.2 form.

(3) Determine the Toxic Harm Factor (THF)

The Toxic Harm Factor (THF) for the substances in the following table is based on the severity of harm associated with each inventory of a hazardous material. Document the result using the Tool I.2 form.

Safety classification	R-phrase	THF
Very toxic	R26/27/28	1000
Toxic	R23/24/25	100
Harmful	R20/21/22	10
Low hazard	–	1

(4) Calculate the Acute Toxic Hazards Index (ATHI)

The Acute Toxic Hazards Index (ATHI) is calculated as follows:

$$\text{ATHI} = \frac{\text{THF} \times \text{Inventory}}{\text{Daily production}}$$

Note The absolute value of the index does not use the daily production rate whereas the relative value does. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(5) Improve the process

Once the ATHI has been calculated, consideration can be given to the way in which improvements could be made. The three main approaches are:
1. Elimination of the toxic material.
2. Reduction in the inventories of the most hazardous material.
3. Changes to the conditions under which the materials are kept, in order to reduce the quantity which would be lost in the event of failure (e.g. refrigerated storage instead of pressurized storage).

More detailed studies could take into account:
- plant location,
- proximity to populated areas,
- reduction in number of items holding hazardous material (reduction in pipework lengths, etc.),
- gas detection and alarm,
- emergency isolation valves,
- emergency water sprays,
- improved engineering standards,
- dump tanks,
- secondary containment.

INSET Tool B can be used as an aid in the option generation process.

Tool I.2 form

Project title:

Date: ___ / ___ / ______ **ATHI: Acute Toxic Hazards Index (Tool I.2)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Item/inventory [Te]						
D	Toxic Harm Factor (THF)						
E_a	Absolute ATHI $= C \times D$						
E_r	Relative ATHI $= C \times D / A$						

Tool I.3 –Health hazards index

Aim:	To provide a means of comparing route alternatives on the basis of their health hazard performance.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool G results.
Output:	A semi-quantitative rating of the health hazards.

Background

An important facet of any process alternative is its potential health hazard from daily intake/exposure. Other indices in Tool I consider the potential for fire, explosion or the environmental spill potential. In addition, it is necessary to consider the inherent health hazards of the process alternative due to handling procedures and leak points.

The assessment needs to take account of those materials with the potential to cause adverse health effects, their hazard classification and the inventories involved.

There may be occasions where the choice of process routes can either raise or lower the inherent health hazard involved with the process. This needs to be taken into account in the inherent SHE assessment and a simplified assessment procedure has been produced. It must be stressed that this procedure is not suitable by itself for materials of high hazard and must, where appropriate, be supported by a detailed risk assessment.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the dominant materials.
2. Determine the Health Harm Factor (HHF).
3. Estimate the number of locations.
4. Determine the Leak Factor (LF).
5. Calculate the overall Health Hazards Index (HHI).
6. Refined calculation.
7. Improve the process.

(1) Identify the dominant materials

Firstly, based on the "health" column in Tool G, identify the dominant materials which the employees are likely to come into contact with for each part of the plant (see Tool F). The ones that need to be considered include gases, liquids, solutions and powders. Document the result using the Tool I.3 form.

(2) Determine the Health Harm Factor (HHF)

The HHF for the substances in the following table is based on the severity of harm associated with each inventory of a hazardous material. The "health" column in Tool G determines the hazard classification. Document the result using the Tool I.3 form.

Note An aggregate category, representative of the material as a whole, must be done in the case of mixtures.

Hazard classification	HHF
Very high hazard	1000
High hazard	100
Medium hazard	10
Low hazard	1

(3) Estimate the number of locations

For each block in Tool F, estimate the number of locations where routine manual handling operations will need to be carried out for each major equipment item or unit operation (e.g. number of reactors with manual charging, number of filters requiring manual filter change, number of routine manual sampling points, number of tanker filling/emptying stations, etc.). Document the result using the Tool I.3 form.

Note This will only provide a crude indication of the manual handling health hazards as it takes no account of the number, frequency or duration of the tasks.

(4) Determine the Leak Factor (LF)

The Leak Factor (LF) or fugitive release rate, in tonnes/year, for the type of equipment or unit operation concerned then needs to be determined. Estimate the overall contribution to personnel exposure – the Leak Factor (based on generic leak rates for different types of equipment or activities) for each unit operation/stage. Take the category nearest to the characteristics of the unit operation/stage and read off the relevant Leak Factor (LF). Add to this the Leak Factor for manual operations where this applies (i.e.

where a high degree of contact between personnel and the material is likely). Document the result using the Tool I.3 form.

Category	LF
Storage	0.3
Pumping/mixing/heat or mass transfer (clean duty)	0.6
Pumping/mixing/heat or mass transfer or separation (dirty duty)	1.5
Compressors, reactors, etc.	3.0
plus, where applicable: Manual handling operation*	0.6

* e.g. filter change, catalyst change, loading/unloading operations.

"Clean duty" is where the process is generally handling clean gases or free-flowing liquids.
"Dirty duty" covers processes handling slurries, powders, very viscous liquids, or other situations where it is difficult to maintain good housekeeping and a high integrity of process containment.

(5) Calculate the overall Health Hazards Index (HHI)

Calculate the overall Health Hazards Index for all the items of equipment in which the dominant materials are processed.

$$HHI = \frac{HHF \times \Sigma LF}{\text{Daily production}}$$

Note The absolute index is not divided by the throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(6) Refined calculation

For a more accurate assessment, the following refinement should be considered:

$$HHI_{Ref.} = HHI \times CF1$$

where the Leak Shaping Factor CF1 is determined as follows.

Situation	CF1
Hazardous material is a finely divided powder or dust	10
High-integrity seals/gaskets or secondary containment will be provided	0.1
Extract ventilation is to be provided for the "manual handling" operations	0.1
"Manual operation" is essentially enclosed and operated at negative pressure (suction)	0.01

(7) Improve the process

Where the Health Hazards Index of the process is high, consideration can be given to the following measures which will enable improvements to be made.

Equipment

⇓ *Increasing protection*

Minimization of joints/welded construction

High-integrity seals and gaskets

Bellows seal valves

Sealless pumps

Protection of people

⇓ *Increasing protection*

Minimize manual operations

Personal protective equipment

Local exhaust ventilation

High-efficiency "laminar flow" dust and fume extraction

INSET Tool B can be used as an aid in the option generation process.

Tool I.3 form

Project title:

Date: ___ / ___ / _____ **HHI: Health Hazards Index (Tool I.3)** **Page:** ___ / ___
Plant: _______________ **Section:** _______________ **Flowsheet #:** ________ **Revision:** ________
Author: _______________ **Proj. #:** _______________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Health Harm Factor (HHF)						
D	Manual handling/exposure operations [number of manual operations per year]						
E	Equipment/sum of leak factors [Te/year]						
F_a	Absolute HHI $= C \times (0.6 \times D + E)$						
F_r	Relative HHI $= C \times (0.6 \times D + E) / A$						
Refinement							
G	Leak shaping factor (CF1)						
H_a	Corrected HHI $= F_a \times G$						
H_r	Corrected HHI $= F_r \times G$						

Tool I.4 –Acute environmental incident index

Aim:	To provide a means of comparing route alternatives on the basis of the potential to cause acute environmental incidents.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool G results. Major inventories.
Output:	A semi-quantitative rating of the potential for acute environmental incidents of the process.

Background

An important facet of any process alternative is its potential to cause an environmental incident. Other indices in Tool I consider the potential for fire, explosion or the release of toxic gas. In addition, it is necessary to consider the potential to cause acute environmental incidents which could arise if spillages result in the contamination of watercourses, etc.

The assessment needs to take account of those materials, primarily liquids, with the potential to cause adverse environmental effects, their hazard classification and the inventories involved.

There may be occasions where the choice of process routes or plant location can either incur or avoid the potential for an acute environmental incident. This needs to be taken into account in the inherent SHE assessment and a simplified assessment procedure has been produced. It must be stressed that this procedure is not suitable by itself for materials of high hazard and must, where appropriate, be supported by a detailed risk assessment.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the dominant materials.
2. Estimate the inventory.
3. Determine the Environmental Hazard Factor (EHF).
4. Calculate the Acute Environmental Incident Index (AEII).
5. Refined calculation.
6. Improve the process.
7. Evaluate the need for more detailed assessments.

(1) Identify the dominant materials

Firstly, based on the "environment" column in Tool G, identify the dominant materials which could be hazardous to the environment and which are stored or exist as significant in-process inventories, e.g. reactors, distillation columns, liquid extraction, etc. The list should include all likely storage of raw materials, intermediates, etc., including storage associated with transport operations. Document the result using the Tool I.4 form.

(2) Estimate the inventory

For each material, make an estimate of the inventory for each block in Tool F.

(3) Determine the Environmental Hazard Factor (EHF)

Look up the Environmental Hazard Factor (EHF) from the following table. Use the Chemical Hazardous Properties Classification table provided in Tool G to determine the chemicals' hazard classification (using the "environment" column). The Environmental Harm Factor (EHF) for the substances is then given by:

Environmental classification	EHF
Very high hazard	1000
High hazard	100
Medium hazard	10
Low hazard (which includes water and air)	1

Document the result using the Tool I.4 form.

(4) Calculate the Acute Environmental Incident Index (AEII)

The Acute Environmental Incident Index (AEII) is given by the sum of all the above:

$$AEII = \frac{EHF \times Inventory}{Daily\ production}$$

Note The absolute index is not divided by the throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

The procedure outlined above is recommended for a first pass. Where the value of the AEII is seen as significant, a refinement to the procedure is available: see Step 5.

(5) Refined calculation

For a more accurate assessment the following refinement should be considered:

$$AEII_{Ref.} = AEII \times CF1$$

Assess the effect of physical properties on dispersivity from the following table. These factors are based on a simple subjective assessment of the consequences of a spill.

Physical properties	CF1
Liquids miscible with water	1.0
Light immiscible liquids	0.6
Heavy immiscible liquids	0.4
Water soluble powder	0.3
High viscosity/high melting point liquids	0.2
Insoluble powder	0.1

(6) Improve the process

Once the Acute Environmental Incident Index has been calculated, consideration can be given to the way in which improvements could be made through either:
1. Elimination of the material.
2. Using a safer material or a safer form of the material.
3. Reduction in inventory.

Changes in process conditions could also be considered but are less likely to be of value as in the case of toxic materials.

Other factors which need to be considered are:
- secondary containment (i.e. bunding),
- overfill protection,
- emergency isolation valves,
- improved engineering standards.

INSET Tool B can be used as an aid when generating new process options.

(7) Evaluate the need for more detailed assessments

Where the Acute Environmental Incident Index is high, a more detailed assessment that is able to take account of other process features may need to be undertaken. This may include site-specific consequence assessment and quantitative techniques such as ICI's Rapid Assessment of Spill Potential (RASP).

Tool I.4 form

Project title:

Date: ___ / ___ / ______ **AEII: Acute Environmental Incident Index (Tool I.4)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Item/inventory [Te]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute AEII $= C \times D$						
E_r	Relative AEII $= C \times D / A$						
Refinement							
F	Condition factor (CF1)						
G_a	Corrected absolute AEII $= E_a \times F$						
G_r	Corrected relative AEII $= E_r \times F$						

Tool I.5 –Transport hazards index

Aim:	To provide a means of comparing process route alternatives on the basis of their transport hazards (accidental releases of material during transport off-site).
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool G results. Approximate distances between the sources of raw materials and the plant, and between the plant and the destinations for products, by-products and wastes (where these are to be transported in bulk/large quantities).
Output:	A semi-quantitative assessment of the transport risks.

Background

It is a necessary part of industrial activity that materials be moved between manufacturers and users. All transport incurs risks, but in general the transport of hazardous materials in Europe has had a good record. Other indices in Tool I consider the potential for fire, explosion and toxic release from operation of the plant or process. This index addresses these "major hazard" risks during transport to and from the plant/site.

In general it is better to locate the plant or design the process so that the transport of dangerous materials can be avoided or minimized. However, this is not always practicable, and this tool helps provide a simplified procedure to evaluate the transport risks and include these as a consideration when selecting/optimizing a process from an inherent SHE point of view.

The assessment takes account of those materials with the potential to cause adverse effects if released as a result of some transport accident. The inventory of the material and its hazard classification (whether in terms of safety, health or environmental effects) are considered together with the distance these are likely to travel. The tool is aimed at addressing road and rail transport as these are the most common forms used. It must be stressed that this procedure is not suitable by itself for materials or situations of high hazard potential and must, where appropriate, be followed up by or supported by detailed risk assessment.

Transport by air, pipeline or ship has not been included as this is more complex to address and can involve very high quantities of material or special arrangements. If you intend to use these forms of transport, a more detailed assessment should be considered to compare the various options.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the dominant materials.
2. Calculate the transport inventory, distance and number of journeys.
3. Select the relevant Transport Harm Factor.
4. Calculate the Transport Hazards Index (THI).
5. Improve the transportation/process.

(1) Identify the dominant materials

List the materials to be transported. The dominant material from a transport point of view will be the one with the greatest combination of hazard category scale, load/container size and annual distance transported. If it is not clear which will be the dominant one, run the most likely candidates through the calculation. This may be worthwhile in its own right to see how the different transportation activities compare.

(2) Calculate the transport inventory, distance and number of journeys

For the selected (or the few selected) materials to be transported make an estimate of:
- the load size [Te], or the container size [Te] if there are several containers per load.
  Note This is an estimate of the inventory that would "leak" following an accident. A full load would give the worst case, and a single container would give the "minimal" case. If you think more than one container would leak, choose a "load size/container size" to reflect this.
- how far these are to travel per journey [km].
- how many journeys per year are required (annual tonnage/load size).

Document the result using the Tool I.5 form.

(3) Select the relevant Transport Harm Factor

From Tool G, identify the material hazard classification for each material, taking the highest applicable value from the "safety", "health" or "environment" column. Then read off the relevant Transport Harm Factor (THF) from the table below.

Safety, health or environmental classification	**THF**
Very high hazard	1000
High hazard	100
Medium hazard	10
Low hazard	1

Document the result using the Tool I.5 form.

(4) Calculate the Transport Hazards Index (THI)

The Transport Hazards Index (THI) is calculated using:

$$\text{THI} = \frac{\text{THF} \times \text{Load/container size} \times \text{Distance} \times \text{Number of journeys}}{\text{Daily production} \times \text{1E7}}$$

Note The 1E7 factor (10^7) relates to a typical distance, in km, travelled between accidents resulting in some form of leak or puncture of the load. It is generally applicable to road or rail transport. For further advice consult "Major hazard aspects of the transport of dangerous substances – Report and appendices", Advisory Committee on Dangerous Substances, Health and Safety Commission, HMSO, London, 1991.

The absolute index is not divided by the throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(5) Improve the transportation/process

Change the process so:
- the transport of hazardous material is avoided,
  e.g. by onsite generation or locating the process next to a source of raw material.
- a less hazardous material can be transported instead,
  e.g. use safer form of material (pellets vs powder, chlorate vs chlorine), or change the process so less hazardous raw materials are needed (start a step earlier or step later in the process, or use a different route).
- less material needs to be transported,
  e.g. use a concentrated form of the material, recycle material on site.

Change the transport:
- locate plant nearer to source/destination so distances are reduced.
- use a safer route where the chance of an accident is less and/or the consequences of any accident would be less (i.e. quieter roads, avoid towns/cities, avoid environmentally sensitive areas).
- use a more robust container/vehicle so the chance of a leak is smaller.
- would several smaller containers in one load reduce the spill size in an accident?
- use a few large loads or many smaller loads (larger loads – bigger consequences, more loads – more chance of accident, but these are not linear relationships).

Tool I.5 form

Project title:

Date: ___ / ___ / ______ **THI: Transport Hazards Index (Tool I.5)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Daily production [Te/day]						
B	Dominant material						
C	Load/container size (inventory) [Te]						
D	Distance travelled per journey [km]						
E	Number of journeys per year (annual tonnage/load size)						
F	Transport Harm Factor (THF)						
G_a	Absolute THI $= (C \times D \times E \times F) / (1E7)$						
G_r	Relative THI $= (C \times D \times E \times F) / (A \times 1E7)$						

Tool I.6 –Gaseous emissions index

Aim: To provide a means of comparing process condition and plant alternatives on the basis of the potential to cause routine/daily impact on the environment.

Input: Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions).
Tool G results.
Estimates of the quantity of material to be discharged annually.

Output: A semi-quantitative rating of the potential for chronic environmental effects of the process.

Background

The routine waste generated by a process places a burden on the environment which should be avoided or minimized where practicable. This index is intended to assess the inherent impact of the process by looking at the waste streams generated by the process before they are given any remedial/clean-up treatment. Separate indices have been developed for gaseous, aqueous and solid/sludge wastes as these can have very different characteristics and impact potential.

The index is based on a simple load factor, a ratio of the mass flow of waste to product. This is augmented by a factor to account for the hazardous nature of the waste material.

The index is meant to be applied to the process without its effluent treatment facilities to assess the inherent hazard of the process. This will give the best overall picture of which effluents are the most problematic, and enable remedial action to be taken to eliminate or reduce the wastes. The index could also be applied later in design when the effluent treatment facilities are being designed or specified. This would help show which effluents are not being effectively dealt with by the proposed "end-of-pipe" systems.

Instructions

The overall sequence suggested involves the following steps:

1. Identify the dominant material(s).
2. Calculate the waste streams.
3. Determine the Environmental Harm Factor (EHF).
4. Determine the Gaseous Emissions Index (GEI).
5. Improve the process to eliminate/minimize the waste.

(1) Identify the dominant material(s)

List all the "gaseous" waste discharges, i.e all discharges to atmosphere, from the process (pre-effluent treatment). Include air and steam in the gaseous effluents. Note the hazardous materials they contain and the mass flow rates, in tonnes/year, of each of these hazardous materials. The "dominant" waste material will be that with the highest value from a simple multiplication of the annual mass discharged and the Environmental Harm Factor.

(2) Calculate the waste streams

Estimate the *total* mass discharge flow rate, in tonnes/year, for the dominant (or possibly dominant) waste materials from the process, that is, the sum of all discharges of that material from the various streams can then be calculated. If desired an alternative basis to "per year" can be used – but be consistent.

In many cases a single process or effluent stream may contain many different components. Treat each component as a single stream for the purposes of the index, each with its own material classification and mass flow rate.

(3) Determine the Environmental Harm Factor (EHF)

Use the Chemical Hazardous Properties Classification table provided in Tool G to determine the chemicals' hazard classification (using the "environment" column and "health" column – take the higher value). The Environmental Harm Factor (EHF) for the substances then follows from the table below.

Environmental/health classification	EHF
Very high hazard	1000
High hazard	100
Medium hazard (includes ozone-depleting chemicals)	10
Low hazard (includes CO_2 – greenhouse effects)	1
"Inert" (includes water vapour and air)	0.1

(4) Determine the Gaseous Emissions Index (GEI)

The Gaseous Emissions Index (GEI) is given by:

$$\text{GEI} = \frac{\text{EHF} \times \text{Mass discharged per year}}{\text{Annual production}}$$

Note The absolute index is not divided by the throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(5) Improve the process to eliminate/minimize the waste

See the waste minimization sections within Tool B.

Tool I.6 form

Project title:

Date: ___ / ___ / ______ **GEI: Gaseous Emissions Index (Tool I.6)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Annual production [Te/year]						
B	Dominant gaseous emission material						
C	Annual discharge rate [Te/year]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute GEI $= C \times D$						
E_r	Relative GEI $= C \times D / A$						

Tool I.7 –Aqueous emissions index

Aim:	To provide a means of comparing process condition and plant alternatives on the basis of the potential to cause routine/daily impact on the environment.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool G results. Estimates of the quantity of material to be discharged annually.
Output:	A semi-quantitative rating of the potential for chronic environmental effects of the process.

Background

The routine waste generated by a process places a burden on the environment which should be avoided or minimized where practicable. This index is intended to assess the inherent impact of the process by looking at the waste streams generated by the process before they are given any remedial/clean-up treatment. Separate indices have been developed for gaseous, aqueous and solid/sludge wastes as these can have very different characteristics and impact potential.

The index is based on a simple load factor, a ratio of the mass flow of waste to product. This is augmented by a factor to account for the hazardous nature of the waste material.

The index is meant to be applied to the process without its effluent treatment facilities to assess the inherent hazard of the process. This will give the best overall picture of which effluents are the most problematic, and enable remedial action to be taken to eliminate or reduce the wastes. The index could also be applied later in design when the effluent treatment facilities are being designed or specified. This would help show which effluents are not being effectively dealt with by the proposed "end-of-pipe" systems.

Instructions

The overall sequence suggested involves the following steps:

1. Identify the dominant material(s).
2. Calculate the waste streams.
3. Determine the Environmental Harm Factor (EHF).
4. Determine the Aqueous Emissions Index (AEI).
5. Improve the process to eliminate/minimize the waste.

(1) Identify the dominant material(s)

List all the liquid/aqueous waste discharges from the process (pre-effluent treatment), i.e. all discharges to rivers, streams, waterways and the sea from the plant. Include water in the liquid effluents. Note the hazardous materials they contain and the mass flow rates, in tonnes/year, of each of these hazardous materials. The "dominant" waste material will be that with the highest value from a simple multiplication of the annual mass discharged and the Environmental Harm Factor.

(2) Calculate the waste streams

Estimate the *total* mass discharge flow rate, in tonnes/year, for the dominant (or possibly dominant) waste materials from the process, that is, the sum of all discharges of that material from the various streams can then be calculated. If desired an alternative basis to "per year" can be used – but be consistent.

(3) Determine the Environmental Harm Factor (EHF)

Use the Chemical Hazardous Properties Classification table provided in Tool G to determine the chemicals' hazard classification (using the "environment" column and "health" column – take the higher value). The Environmental Harm Factor (EHF) for the substances is then given by:

Environmental/health classification	EHF
Very high hazard	1000
High hazard	100
Medium hazard	10
Low hazard	1
"Inert" (includes water)	0.1

(4) Determine the Aqueous Emissions Environmental Index (AEEI)

The Aqueous Emissions Environmental Index (AEEI) is given by:

$$\text{AEEI} = \frac{\text{EHF} \times \text{Mass discharged per year}}{\text{Annual production}}$$

Note The absolute index is not divided by the throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(5) Improve the process to eliminate/minimize the waste

See the waste minimization sections within Tool B.

Tool I.7 form

Project title:

Date: ___ / ___ / ______ **AEI: Aqueous Emissions Index (Tool I.7)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Annual production [Te/year]						
B	Dominant aqueous emission material						
C	Annual discharge rate [Te/year]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute AEI $= C \times D$						
E_r	Relative AEI $= C \times D / A$						

Tool I.8 –Solid wastes index

Aim:	To provide a means of comparing process condition and plant alternatives on the basis of the potential to cause routine/daily impact on the environment.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool G results. Estimates of the quantity of material to be discharged annually.
Output:	A semi-quantitative rating of the potential for chronic environmental effects of the process.

Background

The routine waste generated by a process places a burden on the environment which should be avoided or minimized where practicable. This index is intended to assess the inherent impact of the process by looking at the waste streams generated by the process before they are given any remedial/clean-up treatment. Separate indices have been developed for gaseous, aqueous and solid/sludge wastes as these can have very different characteristics and impact potential.

The index is based on a simple load factor, a ratio of the mass flow of waste to product. This is augmented by a factor to account for the hazardous nature of the waste material.

The index is meant to be applied to the process without its effluent treatment facilities to assess the inherent hazard of the process. This will give the best overall picture of which effluents are the most problematic, and enable remedial action to be taken to eliminate or reduce the wastes. The index could also be applied later in design when the effluent treatment facilities are being designed or specified. This would help show which effluents are not being effectively dealt with by the proposed "end-of-pipe" systems.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the dominant material(s).
2. Calculate the waste streams.
3. Determine the Environmental Harm Factor (EHF).
4. Determine the Solids Wastes Index (SWI).
5. Improve the process to eliminate/minimize the waste.

(1) Identify the dominant material(s)

List all the solids/slurry discharges from the process (pre-effluent treatment), i.e. those destined for landfill, encapsulation or incineration. Note the hazardous materials they contain and the mass flow rates, in tonnes/year, of each of these hazardous materials. The "dominant" waste material will be that with the highest value from a simple multiplication of the annual mass discharged and the Environmental Harm Factor.

(2) Calculate the waste streams

Estimate the *total* mass discharge flow rate, in tonnes/year, for the dominant (or possibly dominant) waste materials from the process, that is, the sum of all discharges of that material from the various streams can then be calculated. If desired an alternative basis to "per year" can be used – but be consistent.

(3) Determine the Environmental Harm Factor (EHF)

Use the Chemical Hazardous Properties Classification table provided in Tool G to determine the chemicals' hazard classification (using the "environment" column and "health" column – take the higher value). The Environmental Harm Factor (EHF) for the substances is then given by:

Environmental/health classification	EHF
Very high hazard	1000
High hazard	100
Medium hazard	10
Low hazard	1

(4) Determine the Solid Wastes Index (SWI)

The Solid Wastes Index (SWI) is given by:

$$SWI = \frac{EHF \times \text{Mass discharged per year}}{\text{Annual production}}$$

Note The absolute index is not divided by the plant throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(5) Improve the process to eliminate/minimize the waste

See the waste minimization sections within Tool B.

Tool I.8 form

Project title:

Date: ___ / ___ / ______ **SWI: Solid Wastes Index (Tool I.8)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]						
B	Dominant solid waste material						
C	Annual discharge rate [Te/year]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute SWI $= C \times D$						
E_r	Relative SWI $= C \times D / A$						

Tool I.9 –Energy consumption index

Aim:	To provide a means of comparing process condition and plant alternatives on the basis of the potential energy usage and the resultant effect on the global environment.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Estimates of the energy consumption and means of energy production to be utilized.
Output:	A semi-quantitative rating of the potential energy efficiency and global environmental impact from this.

Background

Processes that require less energy to operate are friendlier to the environment, using less of the worlds energy/fuel resources and releasing less pollution into the environment. In particular the burden of CO_2 contributing to global warming will be less. The type of fuel system used can also influence the efficiency of the process.

A simple way of evaluating the "inherent" energy efficiency of the process is suggested that measures the CO_2 burden from the process. This takes into account the amount of energy required and the type of fuel used and should reflect any savings from energy recycling and conservation adopted by the process.

The quality of the estimate of the energy requirements of the process will be fairly crude at the early process development stages. The main factors will be the nature of the reactions (electrochemical, cryogenic, highly endothermic) or the need for "high energy consumption" equipment in the process or ancillaries (e.g. electrostatic precipitators, high-speed rotating equipment, dryers/heaters, refrigeration plant).

Instructions

The overall sequence suggested involves the following steps:
1. Estimate the energy requirements of the process and the sources of this energy.
2. Calculate the amount of CO_2 this is likely to generate.
3. Determine the Energy Factor (EF).
4. Determine the Energy Consumption Index (ECI).
5. Improve the process to minimize the energy consumption and reduce the waste associated with this.

(1) Estimate the energy requirements of the process and the sources of this energy

Make an estimate of the various power and heat requirements of the process [GJ/year], and where this energy is likely to be drawn from, i.e. from electricity, gas, fuel oil or coal.

(2) Calculate the amount of CO_2 this is likely to generate

Use the following table to calculate the amount of CO_2 which will be released into the atmosphere by the energy supply process.

Fuel	**CO_2 factor [Te CO_2 / GJ]**
Gas	0.067
Fuel oil	0.097
Coal	0.126
Electricity	0.214

(3) Determine the Energy Factor (EF)

Calculate the total Energy Factor, i.e. the total amount of CO_2 produced per year by the process in meeting its energy needs. The Energy Factor (EF) is given by:

$$EF = Sum_{\text{for all fuel types}} (CO_2 \text{ factor} \times \text{Energy required})$$

(4) Determine the Energy Consumption Index (ECI)

The Energy Consumption Index (ECI) is given by:

$$ECI = \frac{EF}{\text{Annual production}}$$

Note The absolute index is not divided by the plant throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(5) Improve the process to minimize the energy consumption and reduce the waste associated with this

Tool I.9 – Energy consumption index

See the waste minimization sections within Tool B.

Tool I.9 form

Project title:

Date: ___ / ___ / ______ **ECI: Energy Consumption Index (Tool I.9)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]						
B	Energy usage [GJ/year]						
	Gas Fuel oil Coal Electricity Other						
C	Energy factor (EF) [Te CO_2/year]						
	Gas B_{gas} × 0.067 = Fuel oil $B_{f/oil}$ × 0.097 = Coal B_{coal} × 0.126 = Electricity B_{elec} × 0.214 = Other B_{other} × = Total (Sum of above) =						
D_a	Absolute ECI = C						
D_r	Relative ECI = C / A						

Tool I.10 – Reaction hazards index

Aim:	To provide a means of comparing process condition and plant alternatives on the basis of the potential for runaway reactions.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tool G results. Tool L results (high, medium or low reaction hazard rating). Estimates of the quantity of material in the reactor.
Output:	A semi-quantitative rating of the potential risk from an uncontrollable reaction runaway.

Background

Uncontrolled runaway reactions pose a hazard to the plant and its personnel, and in extreme cases can lead to an accidental release of the reaction material to the atmosphere. The controllability of the reaction and its potential for runaway are key factors. A method to assess these, together with a simple qualitative ranking, is included in Tool L (see the Risk Criteria table in Step 2 of Tool L). Other risk factors relate to the material in the reactor at the time of runaway. The hazard from these is assessed by multiplying the mass of material in the batch/reactor by the Reaction Harm Factor which is derived from the material classifications in Tool G.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the dominant reaction hazard.
2. Identify the appropriate Reaction Risk Factor (RRF).
3. Estimate the mass of material in the reactor.
4. Determine the Reaction Harm Factor (RHF).
5. Determine the Reaction Hazard Index (RHI).
6. Improve the process to eliminate/minimize the risk of runaway.

(1) Identify the dominant reaction hazard

List all the potential runaway scenarios from Tool L. The dominant one will have the greatest combination of Reaction Risk Factor, reaction mass inventory, and Reaction Harm Factor. If in doubt, calculate the index for a few to see which is dominant.

(2) Identify the appropriate Reaction Risk Factor (RRF)

Use the table in Tool L to decide if the reaction is high, medium or low risk in terms of its potential for runaway. Use the classification to determine the Reaction Risk Factor (RRF):

Risk category (from Tool L)	**RRF**
High	100
Medium	10
Low	1
None	0 (tool not required)

(3) Estimate the mass of material in the reactor

Estimate the mass of material [Te] in the reactor or relevant plant section at the time of the runaway.

(4) Determine the Reaction Harm Factor (RHF)

Use the Chemical Hazardous Properties Classification table provided in Tool G to determine the reaction chemicals' hazard classification (using the "safety", "health", or "environment" column – take the higher value of these). Normally there will be a mixture of materials in the reactor, so use your judgement to decide a representative/averaged hazard classification for the batch, or if the hazard is dominated by one material – use the classification and inventory of that material to calculate the index. The Reaction Harm Factor (RHF) for the substances is given by:

Safety/health/environmental classification	**RHF**
Very high hazard	1000
High hazard	100
Medium hazard	10
Low hazard	1

(5) Determine the Reaction Hazard Index (RHI)

The Reaction Hazard Index (RHI) is given by:

$$\text{RHI} = \frac{\text{RRF} \times \text{RHF} \times \text{Mass inventory in reactor}}{\text{Annual production [Te/year]}}$$

Note The absolute index is not divided by the plant throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

(6) Improve the process to eliminate/minimize the risk of runaway

See the advice within Tool L.

Tool I.10 form

Project title:

Date: ___ / ___ / ______ **RHI: Reaction Hazards Index (Tool I.10)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]						
B	Dominant reaction scenario and materials						
C	Reaction Risk Factor (RRF)						
D	Reaction Harm Factor (RHF)						
E	Reactor inventory [Te]						
F_a	Absolute RHI = $C \times D \times E$						
F_r	Relative RHI = $C \times D \times E / A$						

Tool I.11 – Process complexity index

Aim:	To provide a means of comparing process options on the basis of their likely complexity, hence difficulty to control and prevent errors.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Basic process information regarding the various process stages or steps and any changes in pressure, temperature, state and any inputs or outputs from the process.
Output:	A semi-quantitative rating of the potential complexity of the process.

Background

The more complex a process, the more difficult it is likely to be to control and to prevent errors by those who operate or maintain it. A simple process should be inherently safer since it avoids this complexity. Assessing the complexity of a process is difficult and subjective even when detailed information is available. This tool aims to assess complexity at the early stages of process development or concept design, when information is limited. Different types of process and plant will have very different factors affecting complexity. This tool is based on just some of these in an attempt to get a "crude first estimate", and only distinguishes between batch and continuous processes. It should therefore be used with caution and its results interpreted with experience and judgement.

Instructions

The overall sequence suggested involves the following steps:
1. Identify the main characteristics of the process.
2. Calculate the relevant Process Complexity Index (PCI).

(1) Identify the main characteristics of the process

Use a process block diagram or flowsheet to identify the following features which can give an indication of complexity:
- for a batch process – the number of:
  - inputs to the process (raw materials, reagents, solvents, other feeds)
  - outputs from the process (wastes, by-products, products)
  - temperature changes (i.e. where heated or cooled)
  - pressure changes (i.e. where pressure increased or decreased)
  - mixing steps
  - changes in state of the process materials (between solid-liquid-vapour)
  - time-critical operations (where duration or time difference is critical)
  - sequence-critical operations (where vital to ensure correct sequence of operations)
  - any other critical changes or operations that need to be controlled
  - main equipment items in the process (vessels, pumps, reactors, columns, etc).
- for a continuous process – the number of:
  - inputs to the process (raw materials, reagents, solvents, other feeds)
  - outputs from the process (wastes, by-products, products)
  - thermal boundaries (i.e. where process heated or cooled)
  - pressure boundaries (i.e. where pressure increased or decreased)
  - changes in state of the process materials (between solid-liquid-vapour)
  - recycles in the process
  - cross-overs between different trains or sections of the process
  - main unit operations (storage, mixing, transfer, reaction, heat transfer, drying, distillation, etc.).

(2) Calculate the relevant Process Complexity Index (PCI)

Simply add up all the numbers above for the relevant batch or continuous situation to give the total. The absolute index is not divided by the plant throughput, but the relative index is. If desired, a basis other than "per day" could be used, e.g. per batch, per run, or per year – but be consistent so that the index is measured per tonne of final product produced.

Tool I.11 form

Project title:

Date: ___ / ___ / ______ **PCI: Process Complexity Index (Tool I.11)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Annual production [Te/year]						
B	Batch or continuous?						
C_a	Absolute PCI = total of values						
C_r	Relative PCI = C_a / A						

TOOL J – MULTI-ATTRIBUTE ISHE COMPARATIVE EVALUATION

Aim:	To provide a means of evaluating and comparing the ISHE performance of various aspects of the route alternatives as a means to eliminate the more unfavourable process options.
Timing:	To be implemented as an evaluation summary of *INSET* Stage II analysis.
Input:	Dossiers of *INSET* Stage I dominant alternatives (and the engineering-modified versions). Tools I.1 to I.11 indices.
Output:	Diagrammatic semi-quantitative representation of the ISHE performance of each process option aiding the decision-making process. Several alternative means of presentation are suggested, based on a simple comparative assessment and on a more "absolute" scale. Dossier of the remaining route(s) to be passed on to the next stage.

Background

Regulations and safety, health and environmental programmes are increasingly requiring the developers or designers of processes to show that they have selected or designed a process which will not only be "safe", but which also represents current "best technology" or at least improves on what has been done before. Project teams will be expected to be able to show that they have considered all reasonable process options, and that they have adopted a systematic and transparent basis for deciding which option to use. Selecting the "best option" requires many aspects to be considered – including safety, health and environmental performance.

It is obviously easier to do this during the early development stages of a project than to wait until the process is in use or about to start-up and then attempt to justify its operation. The earlier options are identified and evaluated, the easier and cheaper it should be to change or improve the process.

The method outlined below, coupled with a sound hazard identification process, will help to ensure that relevant safety, health and environmental issues are highlighted at an early stage. It will also provide a systematic basis for recording the comparative performance aspects of the options to help with decision-making and demonstrate that options have been considered and screened consistently. In addition, it will assist later discussions with or submissions to the authorities by demonstrating that a systematic approach has been used during process development and that the proposed process represents the best practicable environmental option (BPEO).

This tool has been designed to be straightforward to complete using readily available quantitative and semi-quantitative data where possible. It will provide an initial view of the ISHE performance of a process option to allow comparison between options.

In carrying out the assessment, it is strongly recommended that a multi-disciplinary team is assembled, typically to include:
- a chemist,
- a process engineer,
- an environmental health specialist,
- a safety expert.

This approach will give a broader view on the issues and help to produce consistent decision-making.

Instructions

Two forms of decision aid presentation are provided in the tool.

1) The first presentation method (the qualitative ISHE evaluator) uses a series of "word pictures" to help categorize the process option or plant under consideration for a number of ISHE aspects such as fire and explosion, acute toxicity, etc. (these align with the Tool I indices). Any quantitative index values calculated in Tool I can be used, and some general guidance on the relationship between the absolute numerical index values and the "word pictures" is given in the tool. The tool also includes some suggestions how other business factors can be included with the assessment.

The "word pictures" allow each process option to be assessed against key SHE aspects and then given a rating on a 1 to 5 scale – the lower the number, the inherently safer the process. The results for the different process options under review can then be compared on a consistent basis using the 1 to 5 scores – helping the user to see more clearly the relative advantages and disadvantages of each option, and hence select the best overall to go forward to the next stage of the project.

This qualitative method provides a coarse screen of the options as it is only capable of drawing out substantial differences between the options being considered. If the differences between the options are relatively small, the user could choose to modify the "word pictures" to give a finer screen for that particular series of options. However, if the differences are not substantial it may be better to use the second means of presentation, which looks at the actual index values from Tool I.

2) The second presentation method (the quantitative ISHE evaluator) uses the values of the indices calculated from Tool I. The ratios of the indices for the various process options are then used to see which options offer the best overall performance.

The tool does not provide any advice on weighting factors to allow the index values for the different inherent SHE aspects to be combined to give an overall index. This is because such weightings could differ greatly between one company or process type and another, so it is almost impossible to give advice to suit everyone. Also, some users may prefer to see the relative performance of the different options against each aspect individually. This may give more insight into how these various strengths and weaknesses could be improved or managed. If you wish to apply weightings to the different aspects and hence take the multi-attribute analysis to its full conclusion, then some references and general advice on decision aids is given in Appendix 8 in Part 3.

Detailed instructions for these two presentation methods are given below.

The overall sequence suggested involves the following steps:
1. Decide the level of analysis to be carried out.
2. The qualitative method.
3. The quantitative method.
4. Results interpretation – Assessing the process alternatives.
5. Improve the process.

(1) Decide the level of analysis to be carried out

If a basic analysis of a number of process options that differ considerably in their chemistry or SHE performance is required, then it is suggested that the qualitative inherent SHE evaluation method is applied first. (If this proves to be insufficiently sensitive to the process differences, then you can go on to use the quantitative tool next).

If the process route alternatives to be considered are broadly similar, with only subtle differences in performance, then the quantitative method is suggested, as this should highlight what those differences are more clearly than the qualitative method.

(2) The qualitative method

It is suggested that a multi-disciplinary team is used to determine the appropriate qualitative scores. The team should be familiar with any hazard studies of the process options and the findings from the application of the previous tools in the *INSET* Toolkit.

The team use the "word pictures" method, as given in the table "Qualitative multi-attribute evaluation index – Qualitative scoring method", and consider each of the process options in turn. For each process option the team work down the list of SHE aspects in the method, and at each one try to determine which category (1 to 5) best represents the process being considered. The findings of the assessment should be recorded on the record sheet, Tool J form (3).

Alternatively, you may wish to fill in separate record sheets for each option before bringing these together on one sheet. A record sheet, Tool J form (1), is provided for this purpose, and has the advantage that the score against each aspect can be shaded in to give a clear visual presentation of the SHE performance of the option (shade in the appropriate columns in the 1 to 5 matrix to show the score).

Note that the two economic aspects (CAPEX and OPEX, the capital and operating expenditures respectively) are dealt with in relative, rather than absolute, terms. It is suggested that one option, the benchmark, is set at scale 3 and the others scored accordingly relative to this benchmark option. It is suggested that whichever option is chosen as the benchmark, this is set down on the record sheets as Option A. The prefix "EF" on CAPEX and OPEX indicates that these are economic feasibility indices.

If some or all of the indices from Tool I have been calculated, then these can help determine the qualitative scores. Guidance on the relationship between the absolute index values and the 1 to 5 score is given in the table "Qualitative multi-attribute evaluation index – Qualitative scoring method", but these should not be taken as a strict relationship. We would encourage you to develop the index values so that they better suit your range of SHE performance characteristics.

(3) The quantitative method

The quantitative method uses the values calculated in Tool I as the basis for the evaluation. You need to choose which index values to use, either the "absolute" values or the "relative" values. The absolute values would normally be used where the process options under consideration have the same product capacity. The relative values measure the degree of inherent SHE performance per tonne of product, and so are best used when comparing process options of different throughputs in order to ensure a consistent basis of comparison.

Note that Tools I.1, I.3 and I.4 offer the possibility of a refined index calculation. It is important to apply each of these tools similarly to all options, that is for each tool the index should be calculated either with or without the refinement.

Start by copying the index values from Tool I onto the record sheet provided, Tool J form (2). If you wish to include the technical and economic feasibility aspects, either use the 1 to 10000 values (corresponding to the scale 1 to 5) from the qualitative index ("relative magnitude indicator" values) or use the actual projected costs for CAPEX and OPEX. The economic indices are relative, so set the "benchmark" at value = 100 (Scale 3) and judge the rest from this. There is no quantitative index for technical feasibility (TF).

Normalizing

The index values differ in range and magnitude from one aspect to another. This would make plotting all the values on one sheet very difficult. Instead it is suggested that one of the following ways is used to normalize the values to provide a sensible basis for comparison:

a) Select one of the options to be used as a benchmark against which all the other options can be compared. This makes presentation easier, and also gives a clearer view of the relative strengths and weaknesses of the options relative to each other. Its main problem is that it can hide Option A, or at least make it seem less visible since it always scores 1.0. To apply this method:

- Decide which of the options will be the benchmark – this could be the "favourite", the original idea, or any one selected at random. It is suggested that the benchmark option is set down on the record sheets as Option A.
- For each option, divide its index values for each "aspect" by the corresponding "aspect" value of the benchmark. This results in a ratio of "value (option) **:** value (benchmark)".
- The benchmark option will therefore appear as having ratios of 1.0 for all aspects. The ratios for all the options are then plotted to show the relative strengths and weaknesses of the different options relative to each other. It is suggested that a spreadsheet package is used to do the calculations and present the results.

b) Use the average (arithmetic mean) of the index values (from the different options being considered) for that aspect as the benchmark. This gives a ratio of "value (option) **:** value (average for that aspect)". This method has the advantage that all the options are shown on the presentation. Again, a spreadsheet is the best way to do the calculations and presentation.

c) Establish some typical absolute values (i.e. the index values not divided by the plant throughput) of the indices to use as the benchmark. These will be very industry-specific and situation-specific and should be estimated by reference to past experience. The actual absolute index values are then divided by the relevant "norm" to give the ratio to be presented. The following values are suggested as a start and, where practical, have been broadly based on major hazard inventory criteria.

Suggested normalizing values for the absolute indices	
FEHI	2500
ATHI	1000
HHI	400
AEII	5000
THI	500
GEI	1000
AEI	1000

Suggested normalizing values for the absolute indices	
SWI	1000
ECI	10000
RHI	1000
PCI	70
TF	100
EF CAPEX	100
EF OPEX	100

(4) Results interpretation – Assessing the process alternatives

It is suggested that the index values or ratios calculated above are presented in either a "bar chart" or "spider web" format. Examples of these are given in Support for Tool J, in Part 4, and both formats are generally available as part of a spreadsheet package. One axis of the chart should be the "aspects" of SHE (and any other business factor included), and the other axis should be the scale or the ratio calculated. Several process options can be included on the same chart using different colours or notation to distinguish one from another. If there are a lot of options to be compared, it will probably be worth preparing a separate chart for each and then comparing these side by side – but take care to ensure the charts use the same axes ranges and are at the same scale.

For the qualitative scales presentation, a simple linear scale is recommended with the intersection of the *y*-axis at either "zero" or "2.5", the mid-range point. For the quantitative scale presentation it is suggested that the *y*-axis is a logarithmic scale (to base 10), with the intersection at 1.0.

The presentation charts should be used as an aid to decision-making on the preferred process route. Direct comparison between different aspects may not be possible but some degree of judgement may provide insight between these, for example when comparing safety performance with environmental performance.

It should be noted that at the present time, however, there is no agreed system of weighting which will allow the separate indices to be combined into an overall figure.

You may find it useful to adjust the chart *y*-axis format depending on the values for the options being considered, so that it is easier to see which are high and which are low.

In the "bar chart" presentations, look for options that consistently show low scores, i.e. are inherently safer than the others. If there are one or two high scores in an otherwise "good" option, ask how significant these are (you may be confident that you can deal with the hazard concerned by "add-on" means), or whether there are ways in which they can be reduced.

The "spider web" diagrams provide a different presentation. Here the area within the envelope gives a visual indication of the inherent SHE performance – the smaller the area the better. If you are looking at lots of options, then it will be impractical to put them onto one chart. Consider making charts for each individual option, then laying these side by side to see which gives the smaller area. If there is a high score, look to see which aspect this relates to and ask if it can be reduced or managed better.

(5) Improve the process

Using the results presentations as a guide to where the major deficiencies lie in each particular process alternative, attempt to determine how the process alternative could be improved. The option generation and challenging of Tool B may be of assistance in this stage of proceedings.

Qualitative multi-attribute evaluation scoring method

Note The absolute index ranges suggested in this table are indicative only. The range of values between different types of plant will be considerable, and it is suggested that users adapt these ranges to suit there particular needs. For example, the values from a large petrochemical plant will be very different from those for a fine chemical or speciality chemicals manufacturer. Users should use their experience to adjust the ranges to span the range of situations they are likely to meet and hence allow the indices to provide useful distinction between the various options being considered.

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method

Index	**Aspect**	**1**	**2**	**3**	**4**	**5**
FEHI	Fire and explosion hazards (Use "safety" column in Tool G for hazard classifications.)	No hazardous materials being used, or only small quantities (<1 Te) of low/medium-hazard materials in use.	Modest (1-10 Te) use of low/medium-hazard materials and/or some small quantities of high-hazard materials.	Large quantities (tens of tonnes) of low/medium-hazard materials, modest quantities of high-hazard materials or small quantities of very-high-hazard materials in use.	Large quantities of high-hazard materials in use, or modest quantities of very-high-hazard materials. Use of modest quantities of flammable liquids above boiling point.	Large quantities of very-high-hazard materials in use. Use of large quantities of highly flammable liquids above boiling point.
	Absolute index range	0-10	11-100	101-500	501-2000 for process (501-5000 for storage)	>2000 for process (>5000 for storage)

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method

Index	Aspect	1	2	3	4	5
ATHI	Acute toxic hazards (Use "health" column in Tool G for hazard classifications.)	No hazardous materials being used, or only small quantities of low/medium-hazard in use.	Modest use of low/medium-hazard materials and/or some small quantities of high-hazard materials.	Large quantities of low/medium-hazard materials, modest quantities of high-hazard materials or small quantities of very-high-hazard materials in use.	Large quantities of high-hazard materials in use, or modest quantities of very-high-hazard materials.	Large quantities of very-high-hazard materials in use.
	Absolute index range	0-10	11-100	101-1000	1001-10000 for process (1001-20000 for storage)	>10000 for process (>20000 for storage)
HHI	Health hazards (Use "health" column in Tool G for hazard classifications.)	No hazardous materials being used, or only low-hazard materials in a low-mobility form (solid or liquid – not dust or vapour) or inside a well-contained plant.	Little or no manual handling of low/medium-hazard materials, or some high-hazard materials in a low-mobility or dilute form or inside a well-contained plant.	Some manual handling of low-hazard materials. Medium-hazard materials in plant which does not have high containment integrity.	Frequent/routine manual handling of low-hazard materials, or occasional contact with some medium-hazard or high-hazard materials. Very-high-hazard materials in low-mobility form or inside a well-contained plant.	Frequent/routine manual handling of medium-hazard materials, or occasional contact with high-hazard materials. High-hazard materials processed in plant which does not have high containment integrity.
	Absolute index range	0-10	11-100	101-500	501-2000	>2000

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method

Index	Aspect	1	2	3	4	5
AEII	Acute environmental incidents (Use highest of "health" or "environment" column in Tool G for hazard classifications.)	No hazardous materials being used, or only small quantities of low/medium-hazard materials in use.	Modest use of low/medium-hazard materials and/or some small quantities of high-hazard materials.	Large quantities of low/medium-hazard materials, modest quantities of high-hazard materials or small quantities of very-high-hazard materials in use.	Large quantities of high-hazard materials in use, or modest quantities of very-high-hazard materials. High-hazard materials in a very mobile form such as dust, vapour or pressurized liquid above its boiling point.	Large quantities of very-high-hazard materials in use or modest quantities in a very mobile form such as dust, vapour or pressurized liquid above its boiling point.
	Absolute index range	0-10	11-100	101-1000	1001-10000 for process (1001-20000 for storage)	>10000 for process (>20000 for storage)
THI	Transport hazards (Use highest of "safety", "health" or "environment" column in Tool G for hazard classifications.)	Little or no need for transport of hazardous materials in or out of the plant. Occasional small transfers (few kg) of low-hazard materials.	Infrequent (less than monthly) transport of significant quantities of low/medium-hazard materials over short journeys (less than 100 km).	Weekly transport of significant quantities of low/medium-hazard materials, monthly transport of high-hazard materials over short/medium journeys (up to 500 km).	Daily transport of significant quantities of medium-hazard materials, weekly transport of significant quantities of high-hazard materials over long distances.	Daily transport of significant quantities of high-hazard materials or regular transport of significant quantities of very-high-hazard materials.
	Absolute index range	0-0.20	0.21-10	11-1000	1001-5000	>5000

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method

Index	Aspect	1	2	3	4	5
GEI	Gaseous emissions (Use "health" column in Tool G for hazard classifications.)	Little or no gaseous effluent from the process.	Some gaseous effluent, but mainly air or steam with only trace quantities of low/medium-hazard material.	Significant gaseous effluent containing low/medium-hazard material or large quantities of CO_2 or other greenhouse or ozone-depleting chemicals.	Significant gaseous effluent containing high-hazard material, or very large quantities of effluent containing medium-hazard material.	Significant gaseous effluent containing very-high-hazard material, or very large quantities of effluent containing high-hazard material.
	Absolute index range	0-10	11-100	101-500	501-2000	>2000
AEI	Aqueous emissions (Use highest of "health" or "environment" column in Tool G for hazard classifications.)	Little or no liquid effluent from the process.	Some liquid effluent, but mainly water with only trace quantities of low/medium-hazard material.	Significant liquid effluent containing low/medium-hazard material, or high BOD/COD or discoloured material (BOD/COD = biological/chemical oxygen demand).	Significant liquid effluent containing high-hazard material, or very large quantities of effluent containing medium-hazard material.	Significant liquid effluent containing very-high-hazard material, or very large quantities of effluent containing high-hazard material.
	Absolute index range	0-10	11-100	101-500	501-2000	>2000

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method

Index	Aspect	1	2	3	4	5
SWI	Solid wastes (Use highest of "health" or "environment" column in Tool G for hazard classifications.)	Little or no solid or landfill-type wastes from the process.	Some solid effluent, but mainly inert material with only trace quantities of low/medium-hazard material.	Significant solid effluent containing low/medium-hazard material.	Significant solid effluent containing high-hazard material, or very large quantities of effluent containing medium-hazard material, or containing medium-hazard material in a very mobile form (liquid or vapour).	Significant solid effluent containing very-high-hazard material, or very large quantities of effluent containing high-hazard material, or containing high-hazard material in a very mobile form (liquid or vapour).
	Absolute index range	0-10	11-100	101-500	501-2000	>2000
ECI	Energy consumption/global warming	Very-low-energy process – power only needed for lights, control and some minor low-power process operations.	Low-energy process – power only used for some low-demand transfer and mixing-type operations.	Medium-energy process with some heat transfer or medium-energy mechanical or transfer operations.	High-energy process with significant heat transfer, distillation, evaporation or high-energy mechanical or transfer operations.	Very-high-energy process involving electrolysis, large-scale drying or heat transfer, or large-scale very-high-energy mechanical or transfer operations.
	Absolute index range	0-100	101-1000	1001-10000	10001-100000	>100000

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method

Index	Aspect	1	2	3	4	5
RHI	Reaction hazards	No potential for reaction hazards.	Tool L – low-risk reactions. Reaction generally stable and straightforward to control but could become unstable in extreme situations.	Tool L – medium-risk reactions. Reaction susceptible to runaway unless close control is kept on process, but any runaway would start slowly giving some time to react and recover.	Tool L – high-risk reactions, with only modest quantities of material involved (few tonnes). Reaction very susceptible to runaway unless close control is kept on process, and runaway would be very rapid leaving little time to react and recover.	Tool L – high-risk reactions, with large quantities of material involved (tens of tonnes). Process involves very exothermic reactions with large quantities of unstable materials very prone to rapid runaway. Or process includes more than three stages with medium/high-risk reactions.
	Absolute index range	0	≤10	11-500	501-10000	>10000
PCI	Process complexity	Very simple plant requiring little control or maintenance.	Simple plant requiring some control, but with reasonable time to react. Modest, below-average maintenance requirements.	Moderately complex plant with some "time"-critical or "setting"-critical controls. Average maintenance requirements.	Complex plant with many critical control requirements, or complex operations or sequences. Above-average maintenance requirements.	Very complex plant, with complex interactions between plant areas and process stages, and difficult control requirements. Very high maintenance requirements.
	Absolute index range	0-10	11-25	26-50	51-100	>100

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method
Other (non-SHE) factors you may wish to include in the assessment

Index	Aspect	1	2	3	4	5
TF	Technical feasibility	Very feasible, little or no technical risk. Use of well-established technology within company experience.	Feasible, small technical risk. Mostly using established technology, but some technology or application new to the company – but not new to the industry.	Needs some development, modest technical risk. Modest use of technology or application new to that company, but not new to that industry.	Needs significant development, significant technical risk. Significant new technology to company, or some technology new to that industry.	Unlikely to be feasible at current time, major technical risk. Largely new technology to the company or significant technology new to that industry.
	Relative magnitude indicator	1	10	100	1000	10000
EF CAP EX	Economic feasibility CAPEX	Significant reduction in capital cost.	Small reduction in capital cost.	Cost-neutral, no increase or decrease overall.	Slightly higher capital costs, but could be worthwhile if this brings significant SHE or other advantages.	Significantly higher capital costs.
	Relative magnitude indicator	1	10	100	1000	10000

Inherent SHE (Tool J) Qualitative Multi-Attribute Evaluation Index – Qualitative Scoring Method

Other (non-SHE) factors you may wish to include in the assessment

Index	Aspect	1	2	3	4	5
EF OPEX	Economic feasibility OPEX	Significant improvement in operating, maintenance, decommissioning, transport or raw-material costs.	Small improvement in operating, maintenance, decommissioning, transport or raw-material costs.	Cost-neutral or any gains offset by losses elsewhere.	Slightly higher operating, maintenance, decommissioning, transport or raw-material costs, but these may be worthwhile if they bring significant SHE or other advantages.	Significantly higher operating, maintenance, decommissioning, transport or raw-material costs.
	Relative magnitude indicator	1	10	100	1000	10000

Tool J form (1) – Qualitative inherent SHE evaluation: Single option summary sheet

Project title:

Date: ___ / ___ / ______ **Inherent SHE Single Option Summary Sheet (Tool J)** ☐ **Word picture** **Page: ___ / ___**
Process option: ________________ ☐ **Index range**
Author: ________________ **Proj. #: ________________** **Ref. #: _________**

Index	Aspect	Dominant factor	1	2	3	4	5	Comments
FEHI	Fire and explosion hazards							
ATHI	Acute toxic hazards							
HHI	Health hazards							
AEII	Acute environmental incidents							
THI	Transport hazards							
GEI	Gaseous emissions							
AEI	Aqueous emissions							
SWI	Solid wastes							
ECI	Energy consumption/ global warming							
RHI	Reaction hazards							
PCI	Process complexity							
TF	Technical feasibility							
EF CAPEX	Economic feasibility CAPEX							
EF OPEX	Economic feasibility OPEX							

Tool J form (2) – Quantitative inherent SHE evaluation: Single option index values record sheet

Project title:

Date: ___ / ___ / ______ **Inherent SHE Single Option Index Value Summary Sheet (Tool J)** **Page: ___ / ___**
Process option: _______________
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Index	Aspect	Dominant factor	Absolute index value	Relative index value	Comments
FEHI	Fire and explosion hazards				
ATHI	Acute toxic hazards				
HHI	Health hazards				
AEII	Acute environmental incidents				
THI	Transport hazards				
GEI	Gaseous emissions				
AEI	Aqueous emissions				
SWI	Solid wastes				
ECI	Energy consumption/ global warming				
RHI	Reaction hazards				
PCI	Process complexity				
TF	Technical feasibility				
EF CAPEX	Economic feasibility CAPEX				
EF OPEX	Economic feasibility OPEX				

Tool J form (3) – Inherent SHE multi-attribute evaluation: Option comparison record

Project title:

Date: ___ / ___ / ______ **Inherent SHE All Options Summary Sheet (Tool J)** ☐ **Word picture** **Page: ___ / ___**
Process option: ________________ ☐ **Index range**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Index	Aspect	Index values/qualitative score for the different options						Comments
		Option A	Option B	Option C	Option D	Option E	Option F	
FEHI	Fire and explosion hazards							
ATHI	Acute toxic hazards							
HHI	Health hazards							
AEII	Acute environmental incidents							
THI	Transport hazards							
GEI	Gaseous emissions							
AEI	Aqueous emissions							
SWI	Solid wastes							
ECI	Energy consumption/ global warming							
RHI	Reaction hazards							
PCI	Process complexity							
TF	Technical feasibility							
EF CAPEX	Economic feasibility CAPEX							
EF OPEX	Economic feasibility OPEX							

TOOL K – RAPID ISHE SCREENING METHOD

Aim: Fast-track alternative approach to Stage II, to rapidly assess each route alternative with respect to its ISHE performance, by considering the chemicals involved and the unit operations.

Timing: To be used when time restrictions make it impossible to use the more rigorous methods of the *INSET* Toolkit or when there only is a need to check alternative processes in a very brief way.

Input: Dossiers of *INSET* Stage I dominant alternatives (*and* the engineering-modified versions). Data from MSDSs.

Output: Chemistry Materials Hazards Classification form.
Process Hazard Index Classification form.

Background

This tool is designed to be a fast alternative to other more rigorous tools in the *INSET* Toolkit. Basically the tool aids in making a record of the normal assessment process carried out by chemists and engineers whenever they have to evaluate the advantages and disadvantages of different alternatives.

The tool is based on:

- classic inherent safety: substitution, intensification, attenuation, simplification;
- the concept that it is better to deal with known technology/problems than unknown ones;
- perhaps the radical idea that where S, H and E conflict, we should choose the better E option, since E is most sensitive/public concern at present, its technology is less well understood than that of major hazard and health control, and a company has more direct control over S and H than it does over E (little control once effluents have left the factory).

Instructions

The overall sequence suggested involves the following steps:
1. Draw up process block diagram.
2. List the chemicals involved.
3. Consider the hazardous properties of the chemicals.
4. Consider any hazardous unit operations.
5. Generate options and select the best alternative.

(1) Draw up process block diagram

Draw up the process/chemistry stages in diagrammatic form showing each stage in turn, with its inputs and outputs. Tool F is suggested for this exercise.

(2) List the chemicals involved

List all chemicals involved in the chemical route, i.e. raw materials, intermediates, by-products/wastes and utilities, on Tool K form (1), the Chemistry Materials Hazards Classification.

(3) Consider the hazardous properties of the chemicals

If you only wish to ensure that the SHE aspects of the chemicals involved in the route alternative have been "considered", Tool K form (1) could be filled in using the following system:

Symbol	Description
K	known hazard
–	not a hazard
?	unknown

Used in this way, Tool K becomes a rapid SHE analysis indicator.

Alternatively, Tool K form (1) may be used to record the actual safety, health and environmental values for each chemical. This type of intensive analysis could be done in *INSET* Stage III, for example.

Various terms have been defined in order to classify the many properties of the substances. For example, a chemical's toxicity is often categorized into acute or chronic, and even the dose and to what part of an environment the substance is applied, are important to the way the data can be interpreted. Although there may be difficulties in interpreting the data, this information is valuable and may be needed when considering the process route alternatives' chemicals.

Only the most important chemical properties affecting inherent SHE can be included in the paper-based matrix. A computerized system should be considered when trying to do a more detailed analysis.

The data required is often available from the MSDS forms of the chemical substances (see Tool G Supporting Information), but it will not be available for all chemicals. Structure-activity relationship (SAR) estimations may be used to supplement the information.

(4) Consider any hazardous unit operations

Use the second part of the tool if a rapid screening of the alternatives with respect to the inherent SHE aspects of the unit operations is required. This could provide an indicator of how ISHE a route alternative is, and some form of challenging added to this stage (Tool B) would bring inherent SHE into the selection process.

Start by dividing the whole process into unit operations based on the block diagram. The level of detail in the study is dependent on the amount of unit operations (in some cases the process can be considered as one entity). Use Tool K form (2), the Process Hazard Index Classification, for documentation.

Assess initially each individual unit in the flowchart using the proposed index. Record the results on the Tool K (2) form together with a justification for the assessment when it is deemed necessary.

Index	Description
1	Benign process *and* effluents[2] using established technology
2	Some process hazards[1] but of low severity/scale and well understood[3], *and* effluents[2] benign
3	Significant process hazards[1] but well understood[3] *or* effluents[2] contain some hazardous materials but these are easy to treat/handle[3]
4	Significant process hazards[1] *or* hazardous effluents[2], either of which may be awkward to manage or not well understood[3]
5	Very high process hazards *or* hazardous effluents[2] that are poorly understood[3] or difficult or manage, or involve the use of materials that are seen as "unacceptable" in SHE terms or with respect to the objectives of the project as defined by Tool A.2.

(1) Process hazards include thermal runaway/reaction instability, the use, or creation, of significant inventories or concentrations of flammable, explosive or toxic materials, or hazardous operations involving dangerous equipment, conditions or materials.

(2) The reference to "effluents" means those waste streams from the process prior to any clean-up/recovery. Treating/handling refers to the clean-up, recovery or "making safe" of these effluents.

(3) Understood/easy to handle are terms which are intended to relate to the specific company/division in question and its skills and experience (i.e. not the industry as a whole, since one company may be used to handling a material or process, whereas another may not).

(5) Generate options and select the best alternative

Use Tool B, the option generation tool, to challenge, initially the worst rated process stages and then the process as a whole. Use the information gathered to select the best route to be taken to further optimization, even though a direct comparison with another route may be difficult.

Tool K form (1)

Project title:

Date: ___ / ___ / ______ **Chemistry Materials Hazards Classification (Tool K)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Chemical	Safety values				Health values				Environmental values			
	Explos. & fire	Stability	React.	Physical prop.	Chronic	Acute (skin)	Acute (inhal.)	Acute (eyes)	Toxicity	Degrada bility	Bioaccu mulation	Physical prop.

Tool K form (2)

Project title:

Date: ___ / ___ / ______ **Process Hazard Index Classification (Tool K)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Stage/unit operation	Index	Comments

TOOL L – CHEMICAL REACTION REACTIVITY – STABILITY EVALUATION

Aim:	To identify any chemical process that may have runaway potential or in which other hazardous situations may occur due to chemical reactions.
Timing:	These are part of the vital information that needs to be considered during the more detailed investigation of the process.
Input:	Dossiers of *INSET* Stage II. Laboratory tests.
Output:	Chemical Reaction Reactivity – Stability Evaluation Record.

Background

Many chemical reactions that are operated on the industrial scale involve the release of heat, that is they are exothermic. In addition, even greater amounts of heat can be released when decomposition reactions are initiated through unsuitable operating conditions. The consequences of a violent exothermic runaway reaction can be as severe as those from the ignition and explosion of a fuel/air mixture.

It is important, therefore, that any exothermic reactions which could arise are identified and that possible chemical reaction hazards are considered. This should be carried out at an early stage of reactor or process design. The effect of scale-up is particularly important. A reaction, which is apparently innocuous on the laboratory or even the semi-technical scale, can be disastrous on the manufacturing scale. Similarly, a large quantity of gas produced by, for example, the sudden decomposition of a diazonium compound can be vented easily on the laboratory scale, but the same decomposition on the large scale could pressurize and rupture a plant vessel.

In addition to the above, the consequences of possible process maloperation must be considered, for example overcharging or omission of one of the reactants, agitation failure, or poor temperature control.

Chemical reaction hazards principally arise from:
- rapid exothermic reactions which can raise the temperature to the decomposition temperature or cause violent boiling of the reactants,
- thermal instability of reactant mixtures and products,
- rapid gas evolution which can pressurize and possibly rupture the plant.

Instructions

The overall sequence suggested involves the following steps:
1. Evaluate the thermal hazards.
2. Determine the risk levels.

(1) Evaluate the thermal hazards

Evaluate the thermal risk potential of different chemical processes or operations (e.g. distillations) by determining the severity of a potential incident that may occur and the probability with which it may occur. In the case of chemical reaction hazards, the energy release potential of the reaction or decomposition can be used as a measure of the severity while the onset temperature of a decomposition reaction (T_{onset}) and initiation or accumulation problems can be used to indicate the probability of the event occurring.

As a preliminary screening tool, the potential hazards arising from both the desired reaction and also from possible decomposition reactions have been combined. More detailed evaluation of the chemical reaction hazards of a process, taking into account the influence of the plant, will be needed if further development of the process occurs.

Severity

In order to evaluate the severity, the following data is required:
- Reaction energy potential, ΔH_r [kJ/kg], of the desired process reaction. This can be obtained from estimation/calculation, measured using differential scanning calorimetry (DSC) or more accurately using reaction calorimetry.
- Decomposition energy potential, ΔH_d [kJ/kg], of the most energetic decomposition reaction of the reactants, reaction mixture or products. This can be obtained from estimation/calculation, or measured using DSC.
- Heat capacity, C_p [kJ/Kg.K], of the reaction mass. This can be calculated from the individual heat capacities of the reactants and products, or where these are not known a typical value of 1.7 kJ/kg.K for organic substances can be used.
- Adiabatic temperature rise, ΔT_{ad} [K], resulting from the release of the energy potential of the decomposition reaction. This is simply calculated from $\Delta H_d / C_p$.
- Maximum temperature of the synthesis reaction, MTSR [°C]. In the initial screening procedure, this should be taken as either the process temperature T_p plus the adiabatic temperature rise of the desired reaction (MTSR = $T_p + \Delta H_r / C_p$) or the maximum temperature of the heating medium, whichever is the greater.
- Boiling point, Bp [°C], of the reaction mass. Where this is not known, the boiling point of the most volatile component should be used.
- Gas evolution [l/kg] occurring during the desired process. The majority of decomposition reactions also liberate gas; however, in these cases the data is only required when designing an emergency relief system.

Probability

Initiation, accumulation or autocatalytic behaviour information (yes/no/unknown) on problems resulting from difficulties of initiation of the desired reaction is sometimes available in the literature (e.g. the problems of initiating Grignard reactions are well reported). These problems also become evident during initial laboratory studies, e.g. a long work-off time is required to allow the reaction to go to completion.

In order to evaluate the probability, the following data is required:
- Onset temperature of decomposition reaction, T_{onset} [°C], is the temperature at which exothermic activity is first detected in small-scale screening tests, e.g. DSC.

- Time to maximum rate under adiabatic conditions, TMR_{ad} [hr], gives an indication of the time available, at a particular temperature, to take corrective actions. The TMR_{ad} at the maximum temperature of the synthesis reaction, MTSR, should be made.

See Tool L Supporting Information for a more detailed description.

(2) Determine the risk levels

Where multi-step processes are being compared, the stage with the highest thermal risk should be used in the initial evaluation.

Use a simple three-level criteria system (high, medium, low) for the initial assessment of the thermal risk of a process as shown in the following table:

Risk criteria	**Severity**	**Probability**
High	$\Delta T_{ad} > 200$ K *or* MTSR – $T_p > 200$ K *or* Bp surpassed	$T_{onset} - T_p < 50$ K *or* $TMR_{ad} < 8$ h *or* initiation/accumulation
Medium	50 K < $\Delta T_{ad} < 200$ K *or* 50 K < MTSR – $T_p < 200$ K *or* gas evolution	100 K > $T_{onset} - T_p > 50$ K *or* 8 h < $TMR_{ad} < 24$ h
Low	$\Delta T_{ad} < 50$ K *or* MTSR – $T_p < 50$ K	$T_{onset} - T_p > 100$ K *or* $TMR_{ad} > 24$ h

Irrespective of the risk level determined in this preliminary assessment of the thermal hazards of the process, a more complete assessment of the chemical reaction hazards associated with the process should be carried out before the process is operated on the plant scale.

Tool L form

Project title:

Date: ___ / ___ / ______ **Chemical Reaction Reactivity – Stability Evaluation Record (Tool L)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Ref. #	Reaction studied	Method used	Severity	Probability	Risk	Reference

TOOL M – PROCESS SHE ANALYSIS/PROCESS HAZARDS ANALYSIS AND RANKING

Aim: The aim of this tool is to provide a simple method to identify and rank any hazards in the proposed process. These should be recorded and used as a focus for seeking out inherently SHE engineering alternatives. The tool focuses on the fundamental sources of hazard in the process rather than operational deviations such as in a HAZOP. For processes that have been assessed by using the more rigorous tools of the *INSET* Toolkit, this tool probably reveals little new information. The tool can, however, be valuable as a means to make designers familiar with a process developed by the company's development chemists, or one bought from an external source.

Timing: The tool is designed to be applied at a stage where no significant development of the chosen process can be obtained by generating new process conditions and consequently, improved inherent SHE is obtained mainly by better engineering solutions. The tool should also be used as a first means to assess those parts of a process system that have been developed outside the company and where changes to the process conditions are not feasible.

Input: Dossier of dominant process condition alternatives.

Output: A record of the main hazards associated with the process and an assessment of these (list of hazards with priorities assigned on 1-to-5 scale of severity).

Background

The tool can be used by an individual, but is best suited to a study team of the type used for other hazard identification studies. Typical team members could include a leader and secretary, process engineers and chemists working on the project, and a SHE specialist.

The tool includes a hazard prompt list which is intended to be used to aid a preliminary hazards assessment or other hazard identification study to identify the hazards that need to be managed, and provide a focus for identifying areas where inherently safer approaches would be most effective. Alternatively, a conventional PHA, HAZOP or "What-If" analysis could be used.

The prompt list is intended to be applied by a study team or individual to each area of a plot plan or section of a process flow diagram (see Tool F) to identify the hazards to safety, health and the environment. The objective is to identify the *sources of hazard.* These should include those for both accidental scenarios (acute events) and non-accidental scenarios (chronic events), e.g. accidental loss of containment, fugitive emissions and "flowsheet" emissions.

Ranking of the hazards permits a more effective prioritization, that is where to start first in terms of looking for inherently safer engineering alternatives. Ranking is complicated by the many different effects on safety, health and the environment, by the way the hazard is realized and by its effects which can be acute or chronic or both.

Several ranking systems have been developed to address the acute effects of accidental events, often to assist with HAZOPs or other hazard studies. However, these do not address the longer-term effects or deal with occupational health effects or long-term releases into the environment. The following system is offered to try to bring these together.

The priority classification is based on a 1-to-5 rating of severity in terms of the consequences of the hazards as judged by the person(s) using the tool.

It is suggested that the ranking system is applied by someone with some experience in safety and environmental risk assessment to ensure hazards are suitably classified. One way of achieving this would be to hold a separate session following the hazard identification study to rank the hazards. The team present at this could include someone from the hazard identification study and expert advisors on safety, health, environmental and business risks.

By also ranking the hazards of the process in terms of their likely consequences for safety, health and the environment (and, where relevant, business loss prevention), it provides one means to target the more serious hazards when seeking inherently SHE alternatives.

Instructions

The overall sequence suggested involves the following steps:
1. Draw up process flowsheet/flow diagram.
2. Identify materials, articles or conditions with potential to cause harm.
3. Rank hazards.

(1) Draw up process flowsheet/flow diagram

If not already done so, draw up the process/chemistry stages in diagrammatic form (the block diagram/flowsheet, see Tool F), showing each stage in turn, with its inputs, outputs and conditions. Each stage could be shown as a box on the diagram, with arrows showing the transfer (and direction of flow) of material to/from one box from/to another. Key process conditions can be shown inside the box (temperature, pressure, pH, concentrations, etc.). There should also be a brief description of the process to accompany the flowsheet, stating the main process objectives, limiting conditions/constraints, the purpose (function or functions) of each stage and feed/reagent, etc., and how the process is expected to work/operate.

It is recommended that the function list used in the tools is used for the flowsheet, that is select functions from: mix, separate, size change, store, heat/cool, transfer, reaction.

Use the method below also to analyse ancillary parts of the process and plant such as transport, reagent preparation/storage/feed systems and utilities (especially heat transfer and effluent systems as well as treatment processes). These often contain hazardous materials, or involve complex processes which can cause a hazard themselves or trigger hazards in the main process.

(2) Identify materials, articles or conditions with potential to cause harm

Go through the diagram stage by stage, stream by stream, to identify the hazards associated with the materials, conditions, reactions or type of equipment likely to be involved, and list these. The prompt list and hazard study record sheet provided may be used to structure this study. It may be useful to also record any known causes or effects of these hazards, or conditions (e.g. temperature limits) that initiate/prevent them. The study should not attempt to solve the problems/hazards as this is done later, but in these studies the acceptability of non-inherently SHE solutions should be considered. This gives the chemical engineers an opportunity to concentrate on the, from an inherent SHE point of view, most important parts of the process.

Alternatively, use the results of existing company hazard studies or hazard check-lists to draw up a list of the key hazards associated with the process.

Note Remember to consider all the operating modes when you carry out the study, including, for example, start-up and maintenance.

Flowsheet Hazard Identification Study Prompt List	
Internal hazards	Toxic Eco-toxic Explosive Flammable Hazardous combustion products Prone to thermal runaway reaction Unstable material or condition Corrosive/erosive material Strong oxidant/reductant Incompatible materials/processes

	High speed or dangerous machinery High pressure or vacuum High temperature or cryogenic Prone to leaks, spills Hazardous operation or location Manual handling of hazardous materials Deliberate breaches of containment (sampling, maintenance, etc.)
External hazards	Transport hazards Natural hazards (weather extremes, flooding, lightning, earthquake, etc.) Security breach

(3) Rank hazards

It may be useful to rank the hazards listed to see which ones deserve most attention. To do this, review the hazards identified either at the end of or during the hazard identification study to assess their relative importance.

The priority classification is based on a 1-to-5 rating of severity in terms of the consequences of the hazards as judged by the person(s) using the tool. Separate classes are given for safety and health, environment and business hazards. Each hazard should be assessed against each of these classes and the level of severity determined.

Determine the priority of the hazards by looking for those hazards with the highest scores for safety, health, and environment (and business if you wish to include this). For example, the worst hazards would score a 5 in all three categories.

You may wish to apply your own "weightings" to these class scores. For instance, if the environment is your key concern, you could use the environmental class score as the main basis for setting the priorities, and only use the safety, health and business scores as secondary and tertiary factors.

The results of the ranking should be recorded for use later on when searching for inherently SHE alternatives. Provision has been made on the Process Hazard Identification Record Sheet for this. You may also wish to produce a list of hazards in descending order of priority.

Flowsheet Hazard Ranking					
HAZARD CATEGORY	**(5) Catastrophic**	**(4) Major**	**(3) Severe**	**(2) Appreciable**	**(1) Minor**
Safety and health					
On-site people – acute events	Many fatalities	Several fatalities	Single fatality *or* major permanent disability	Multiple injuries with return to work	Minor injury
Off-site people – acute events	Fatalities	Major injuries or fatalities	Some hospitalization for screening	Discomfort	None
On-site people – chronic events	Exposure to very toxic materials or toxic biological agents with chronic or accumulative effects or which can	Exposure to very toxic materials or toxic biological agents	Exposure to toxics, irritants and harmful materials	Exposure to irritants	None

Flowsheet Hazard Ranking					
HAZARD CATEGORY	**(5) Catastrophic**	**(4) Major**	**(3) Severe**	**(2) Appreciable**	**(1) Minor**
	grow in the environment				
Environment					
Environment – acute events	Major incident with significant loss of species or habitat; threat to air quality could result in local evacuation of people	Significant short-term damage or minor long-term damage requiring clean-up action; air pollution could result in local people being asked to stay indoors	Minor short-term damage to adjacent land or water courses	Discolouration of water or air; noise	None
Environment – chronic events	Potential for major pollution incident if process control or clean-up systems were to suffer a minor failure or loss in performance	Potential for major pollution incident if process control or clean-up systems were to suffer a major failure	Process problems could lead to some discharges exceeding limits for short periods	Some discharges close to acceptable limits	All discharges well within accepted discharge limits
Environment – global effects	Process produces very large quantities of CO_2, or VOCs, or makes significant use of materials harmful to the ozone layer	Potential to release significant VOCs and/or some ozone-depleting chemicals	Significant CO_2, minor VOCs	Minimal CO_2 discharge	None
Business (loss prevention)					
Public reaction	Severe pressure to cease operation	National media coverage	Local media coverage	Minor local complaint	None
Off-site damage	Serious structural damage	Damage to windows, tiles, cladding	Superficial damage, e.g. to paintwork	None	None
On-site damage	Company-specific	....	....	....	....
Production loss	Company-specific	....	....	....	....

Tool M form

Project title:						
Date: ___ / ___ / ______ Author: ________________	Process Hazard Identification Record Sheet (Tool M) Proj. #: ________________		Ref. #: ________		Page: ___ / ___	For hazard review use only
Stage/input/outpu t	Hazard/problem	Causes	Effects	Hazard ranking	Comments	New ranking after changes

TOOL N – EQUIPMENT INVENTORY FUNCTIONAL ANALYSIS METHOD

Aim: To provide an understanding of why inventory is required on a plant, leading to the generation of ideas on how it might be minimized.

Timing: Where it has been identified that the release of a particular material could result in serious consequences, the detailed design will need to consider ways in which the inventory can be further minimized. The greatest benefit is likely to come from the use of this technique on a *selective* basis when the equipment and inventory have been identified. This tool could probably be applied concurrently with Tool O, where the complexity of the equipment is addressed.

Input: Stage III dominant alternative dossier.
A description of the basic unit operations and proposed equipment is required. A P&ID, initial plant layout plot plan, equipment data sheets, information on the process and equipment hazards may also be useful.
Proposed inventory, including in-process inventory.

Output: Functional analysis of inventories of selected hazardous materials.
List of suggestions on how inventories could be further reduced.

Background

Earlier parts of this toolkit will have identified which materials, if released, could result in harm to people or the environment. During the detailed design stage, consideration will need to be given to the ways in which these inventories could be minimized even further.

Reducing the inventory of hazardous materials in the process or ancillary systems is a key factor in achieving an inherently safer plant. As an example, if inventory is required because of the unreliability of upstream equipment, ideas may be generated on how the reliability could be improved, thus reducing the need for inventory. In these cases, it is proposed that a structured technique, inventory functional analysis (IFA), be applied.

By challenging the basis of the plant equipment selection with the aim of reducing the inventory of the hazardous materials, the tool helps prompt ideas for more inherently SHE equipment and gives some background information on the different types of equipment to help with the selection.

This process involves a *team* approach. It is *not* a HAZOP, but the results could lead to some simplification of the HAZOP. The IFA will only be required in those areas where a problem is seen to exist and inventory reduction is seen to be necessary.

A team comprised of the following members is suggested:
- team leader,
- process engineer,
- machines engineer,
- control engineer,
- operations representative (optional).

In addition, when considering reaction systems, a chemist should be included in the team.

Past experience has shown that the HAZOP technique is most effective when applied to final P&ID's. The IFA should, therefore, be carried out before the HAZOP. A different leader (who was not present in the IFA) should be used for the HAZOP and it may be appropriate to change other members of the team (i.e. a junior process engineer could be used in the IFA study with a more experienced senior engineer assisting in the HAZOP).

Instructions

The overall sequence suggested involves the following steps:

1. Select the plant section.
2. Identify the function.
3. Function consideration.
4. Generate ideas on how the inventory could be minimized.
5. Develop the minimization ideas.

(1) Select the plant section

A specific section of the plant, where inventory reduction is required, must be selected. Either each major equipment item or pipeline is taken in turn, or only the most hazardous sections could be considered. Alternatively, merely considering the equipment and pipelines containing the highest inventories may be sufficient. The material being handled and the likely inventory must be known. These could be identified from the ELDs or a preliminary P&ID of the plant.

(2) Identify the function

Using the guidewords given below, identify *functions* for which inventory is relevant to the section being considered. (See examples in Support for Tool N, in Part 4.)

Guidewords	Inventory analysis
Ensure stable operation	Control systems Distillation/reboilers Reactor Pumps Other
Isolate from up-stream processes	Up-stream off-line time/breakdown Up-stream batch operations Up-stream receipt (road/rail/ship) Uncertainties of supply Other
Isolate from down-stream processes	Downstream off-line time/breakdown Down-stream batch operations Material despatch (road/rail/ship) Uncertainties of consumption Other
Provide residence time for	Reaction Settling/separation Control Analysis Blending Other
Hold-up	Mass transfer operations Heat transfer operations Pipework Other
Prevent breakthrough	Gas/vapour Liquids

Note The guidewords are used to promote thinking and should not be used mechanically.

(3) Function consideration

For each *function,* consider the other heading:
(a) What is the critical parameter?
e.g. head or liquid height, volume, mass.
(b) What is the datum level/reference point against which the parameter is measured?
e.g. the critical dimension might be the liquid head (parameter) above the pump centre line (datum).
(c) Is the inventory or head specific to that function or is it shared with other functions?
(d) What is the total volume/mass?

(4) Generate ideas on how the inventory could be minimized

Generate ideas on how the inventory could be minimized. These ideas should then be developed into workable proposals outside of the meeting. It is suggested that the findings of the studies are recorded to provide an audit trail for decision-making.

A prompt list describing the prime factors involved with inventory levels follows. It is offered in order to challenge the inventory of materials in key process equipment and pipework to see why the inventory is required, and prompt the designer to consider ways of reducing the inventory by eliminating or changing these requirements.

The prompt list should identify *why* the inventory is required, and then challenge this need to see if it can be eliminated or changed.

(5) Develop the minimization ideas

The aim is to reduce inventory to an optimum by challenging the designer to change the basis of these requirements so that a smaller (or no) inventory is needed. The following list gives examples of options that are available when one considers how to minimize the inventory of vessels, tanks or other "inventory"-containing equipment items based on a prime factor and underlying factor.

Prime factor	Underlying factors	Options
Residence time	Control	Increase speed of controller. If level control, make vessel tall and thin.
	Heat transfer	Improve mixing, heat transfer area, LMTD. Change vessel geometry.
	Mass transfer	Improve mixing. Use premix stage.
	Reaction to progress	Improve mixing, raise temperature.
	Sample turn around	Use on-line analysis. Prioritize sampling regime.
Buffer capacity	Quality control	As above.
	Mis-match in input/output flow rates	Change upstream/downstream throughputs. Make process so throughput can be altered easily to match that needed.
	Mis-match in input-output availability	Improve reliability/availability.
Batch size	Complete number of batches	Do you need to hold more than one batch at a time?
Physical dimensions	Vessel size set by physical requirements such as internal cooling coils, demisters or other column/vessel internals, etc.	Change vessel geometry, e.g. by use of narrow base to reduce inventory, or tall and thin rather than short and squat. Look for other means of achieving function of internals.
Any or all of above	Combine functions and share inventory	Consider combining unit operations so overall inventory is reduced, e.g. combine reaction and heat transfer in one vessel, or combine buffer capacity and pH control in one vessel. Use an in-line mixer for mixing of a reagent and for reaction. Use pipework for heat transfer (simple co-axial heat exchanger).

The following chart gives examples that can be applied to each main pipe section in order to identify means of reducing pipework and pipeline inventories.

Main factors	Underlying factors	Options
Need for pipework Eliminate non-essential pipework	Main process transfer	Carry out both stages in same place.
	Vent, drain	Use larger plant sections for vent and drains based on maintenance requirements.
	Flexibility/optional routing	Is this essential? If rarely used, and low hazard would a temporary hook-up provision be better than a permanent connection?
	By-pass lines	Is by-pass needed? Check availability of plant and maintenance regime.
Length Decreasing pipe length reduces inventory and pipework costs	Separation of units	Bring units nearer together (balance with access, escalation considerations).
	Routing to suit layout/pipe ducts, etc.	Optimize runs of pipe supports, trenches, banks, etc. to minimize distances. Place high-hazard lines on short runs.
Diameter Decreasing the pipe diameter reduces inventory (by square of diameter)	Product shear damage – need for low velocity	Avoid sharp bends and in-line fittings so velocity can be kept reasonably high.
	Solids handling – need to prevent blockages	Smaller diameter will increase velocity and help prevent settling.
	Self venting – need for venting space	Operate line fully flooded with only enlarged entry section.
	Allowable pressure drop – need to increase diameter for given flow rate	Reduce number of fittings or other flow restrictions. Increase allowable pressure drop – bigger pump, increased head difference, operate upstream or downstream plant at different pressures, reduce viscosity of material or surface roughness of pipe.

Tool N form

Project title:

Date: ___ / ___ / ______ **Inventory Functional Analysis Record Sheet (Tool N)** **Page:** ___ / ___
Plant: ________________ **Item:** ________________ **Material:** ________________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________ **Meeting #:** ________

Function	Critical parameter	Datum	Specific/shared	Volume	Ideas to minimize

TOOL O – EQUIPMENT SIMPLIFICATION GUIDE

Aim: To challenge the need for valves, instruments, flanges and other pipework or equipment fittings that can increase the complexity of the plant and maintenance requirements.

Timing: The tool is best applied at the early stages of detailed design when the preliminary P&IDs or ELDs are available. By the time detailed design stage has been reached, most of the opportunities for inherent safety design will have passed. The basic materials, reactions, process conditions and inventories will have been fixed. However, there are many opportunities during detailed design where it is possible to minimize the number of potential leak sites (which often also reduces capital cost and maintenance requirements) and to make the plant more friendly to build, operate, maintain, and decommission. This tool could probably be applied concurrently with Tool N, where the inventory of the equipment is addressed.

Input: Stage III dominant alternative dossier.
Engineering Line Diagrams (ELDs) or Piping and Instrument Diagrams (P&IDs) of the plant.

Output: List of suggestions for making the plant less complex by reducing the need for or complexity of fittings.

Background

Pipework and equipment fittings increase the complexity of the plant and maintenance requirements. The safety implications are that more fittings may mean a higher chance of leaks due to maintenance activities and equipment failure. A more complex plant may also be more prone to operating error.

The inventory functional analysis (IFA) technique (see Tool N) may be extended to identify potential sources of release (e.g. flanges, pressure tappings, etc.), with the objective of identifying how these could be minimized during design by simplification or elimination.

Instructions

The overall sequence suggested involves the following steps:
1. Select a plant section.
2. Identify the function.
3. Minimization of potential leak sites.
4. Develop the minimization ideas.

(1) Select a plant section

A specific section of the plant, where simplification may be possible, must be selected. Either each major equipment item or pipeline is taken in turn, or only the most hazardous sections could be considered. Alternatively, merely consider the equipment and pipelines judged to be most prone to problems/leaks. The material being handled must be known. These could be identified from the ELDs or a preliminary P&ID of the plant.

(2) Identify the function

Using the guidewords given below, identify *functions* for which potential leak sources are relevant to the section being considered. The tool provided is to be used to challenge the need for fittings such as valves, instruments, flanges, etc., and help the designer reduce the need to incorporate such items.

The following guidewords may assist in the identification of the hazardous areas.

Guidewords	Potential for release	
Operations	Sampling Venting Draining Purging	Flushing Loading Unloading Blockage removal
Equipment	Flanges Gaskets Sight glasses Valves Pumps Compressors	Stirrers Seals Bellows Pressure tappings Analysers

Note The guidewords are used to promote thinking and should not be used mechanically.

(3) Minimization of potential leak sites

Generate ideas on how potential leak sites could be minimized. These ideas should then be developed into workable proposals which would then be reassessed in order to evaluate whether they have in fact increased the inherent safety.

(4) Develop the minimization ideas

The aim is to reduce leak sites to an optimum by challenging the designer to change the bases of these requirements. The following item list with the corresponding functions gives examples of options to minimize the need for different items that may leak.

Item	Function	Options
Control valve	Process control (flow)	Use restriction orifice. Control elsewhere – upstream pressure, liquid level, etc.
Manual valve	Block valve (open/close) for maintenance/plant isolation, venting and draining	Consider having larger plant sections for isolation – if this section is taken out, do other adjacent sections also have to be shut down? If so treat these as one section for isolation. Does the equipment need to be drained? Can it be designed to drain via the adjacent equipment? Can the plant be vented via adjacent equipment? Are other means of isolation available? – other valves in the process Make sure valve has clear indication that it is open or closed. Ball and plug valves have handles that do this better than gate or diaphragm valves.
	For switching between plant sections, by-passes	Is this flexibility needed? Can you operate using the by-pass anyway? Improve reliability of plant section or equipment, and make it easier to repair/replace so outages are no longer significant.
Instrumentation	Main process control sensors	Are these necessary or just for convenience? Can they be replaced by a more reliable or non-intrusive sensor (e.g. ultrasonic level detector, pipewall thermocouple)?
	Local instrumentation	As above. Consider what operations are expected to be done, hence information required on plant rather than via the control room.
Bellows connections/joints	Thermal expansion handling	These are prone to leak/failure and should be avoided. Use more flexible pipe run/layout or expansion loops instead.
Sight glasses	Local flow detection	These should be avoided, they are prone to leak and rarely offer good visibility.
Sample points	To check quality, or material type/content	Can main process sampling be replaced by in-line instrumentation? Can the need for sampling be reduced by improving instrumentation or process control? Is this the best place to take a sample? Use a narrow sample line where possible (hypodermic type where sample small and not prone to blockage – this reduces leak rate if sample valve fails).
Blanks/blinds	To isolate or restrict flow	Spectacle blinds are easy to see if the "blank" is open or closed.
Flow-direction-sensitive fittings and in-line items	E.g. pumps, non-return valves, some instrumentation	Make sure flow direction is clearly and permanently shown on the fitting and on the associated pipework. Consider using different connection or pipe bore at inlet and outlet so item cannot be wrongly fitted.
Equipment identification	For construction, operation and maintenance	Ensure all items are clearly labelled. Names related to their function are easier to remember and less prone to mistakes than a pure alphanumerical tag reference. Ensure a logical and consistent approach to labelling that reflects the process and the layout.

Tool O form

Project title:

Date: ___ / ___ / ______
Plant: ________________
Author: ________________

Equipment Simplification Assessment Record Sheet (Tool O)
Section: ________________
Proj. #: ________________ **Ref. #: ________**

Page: ___ / ___

Guideword	Item	Function	Options	Comments

TOOL P – HAZARDS RANGE ASSESSMENT FOR GASEOUS RELEASES

Aim: The tool is intended to provide engineers with an easy-to-look-up indication of the magnitude of major accident hazards based on either the process inventory or the size of typical leak sites. This information can be used, for instance, for siting and plant layout purposes, but this should also encourage the reduction in key inventories and the minimization of the size and number of key potential leak sites by allowing the user to quickly establish which areas of the plant/release scenarios are of most concern. In particular, it shows how the magnitude of the hazard can be expected to increase or decrease as the inventory or release rate is changed.

Timing: This tool can be used when siting or layout of the plant is first discussed, but can naturally be applied at any stage where the basic materials and inventories in the process are available or can be estimated (e.g. when considering incidents in connection with transporting hazardous substances). The tool is probably of most relevance when inventories and flows are being decided.

Input: Stage III dominant alternative dossier.
List of estimated plant inventories (tonnes) of materials classified as explosive, flammable gas/liquified gas, flammable liquid or toxic. Alternatively, release rates can be used (kg/second) as the basis of the assessment. The release rates can be calculated by conventional methods.

Output: A crude assessment of the likely severity of the hazard presented by the accidental release of the material involved in terms of the likely hazard range and/or area of land affected.

Background

The hazard range tool is a series of simple nomographs which provide an order of magnitude indication of the hazard range and area affected for some common hazards arising from the release of flammable or toxic process materials.

The data is based on relatively crude hazard models and has required many simplifying assumptions to be made, and so should be used with this in mind. The nature of many of these hazards is complex and this tool can only present a very simplified assessment of the hazard ranges. Any critical aspects of the hazard or the design should be checked using specific models and calculations at an appropriate level of detail and accuracy.

Note The tool is not appropriate for use with dusts or solids.

Instructions

The overall sequence suggested involves the following steps:
1. List and classify the materials.
2. Estimate the inventory of the hazardous materials.
3. Assess the basic hazard from a *flammable/explosive gas or vapour.*
4. Assess the basic hazard from a *toxic gas or vapour.*
5. Assess the need for more detailed modelling.

(1) List and classify the materials

For the part of the process or plant to be studied, list those materials that will exist as gases or may vaporize during the hazardous event studied. The list produced in Tool G may provide a useful basis. Add to this those gaseous or vaporized substances that might be formed in the proposed process or plant under special circumstances, such as unintended reaction between two raw materials or runaway reactions (hints might be found, for instance, in Tool H and Tool L).

Classify the identified substances according to the classification given in the EEC Directive 84/449/EEC on the one hand into: extreme risk of explosion, risk of explosion, extremely flammable, highly flammable, or flammable, and on the other hand into: very toxic, toxic, or harmful. Some substances may fall outside this classification.

(2) Estimate the inventory of the hazardous materials

Estimate the inventory of each material on the list. If the tool is used at the process selection stage or at a very early concept design stage, these inventory estimates may be very crude. At this stage, and as a worst case scenario, assume that all the inventory of a material is released in a single event.

At the later stages of design, the inventory estimates should be better. At this stage you probably wish to consider the inventories, for example, in the tank farm, in the process, or different isolatable parts of the process separately. This will enable the more hazardous sections of the plant to be identified. We would still recommend that all the inventory of a given material in that part of the process is taken as being released in the single event.

If the plant includes pipelines or small-size/high-throughput equipment, you may also wish to assess the relative consequences of leaks based on the likely leak size. This could be based on typical leak sizes (say 25 mm or 50 mm diameter hole size) or on full bore rupture.

(3) Assess the basic hazard from a flammable/explosive gas or vapour

Assess the type of basic hazard from the flammable/explosive material concerned. Consider if both instantaneous and continuous release options are possibly relevant or if only one of these is. It will then be assumed that the total amount of the substance in an isolatable part of the process takes part in the event and that the flammable substance will ignite at or close to the leak source.

For flammable gases, the hazards could be a vapour cloud explosion (VCE), flash fire or jet fire. For liquified flammable gases, or other flammable liquids held above their boiling point at atmospheric pressure, the hazards could be a boiling liquid expanding vapour explosion (BLEVE), VCE, flash fire or jet fire.

In the above cases, the actual hazard will depend on the nature of the leak and the timing of ignition. In general, flash fires and BLEVEs will involve the largest hazard range to people, VCEs will cause most damage to the plant or buildings, and jet fires can cause severe localized damage to a plant.

For flammable liquids, the hazard will generally be a pool fire, but if the liquid is very volatile, consideration of the flash fire range to estimate what could happen if the liquid evaporated and formed a drifting gas cloud would also be necessary.

Use the tables provided to estimate the hazard range and/or area affected:

- hazard ranges for instantaneous flammable releases,
- area affected by hazard for instantaneous flammable releases,
- hazard ranges for continuous flammable releases,
- area affected by hazard for continuous flammable releases.

The hazard range gives an indication of how far the hazard can extend, the area affected gives a better indication of the magnitude of the hazard.

List and compare the hazard ranges and areas affected for the different release scenarios to determine which are the most severe. This can then be used to focus efforts on minimizing inventory within the process or to seeing where substitution of materials may be useful. You can also use the tables provided to see how the hazard range or affected area changes if the inventory is, for example, reduced by half.

The record sheet provided should be completed in order to record the assessment results.

Consult Tool P Supporting Information (Part 4, Support for Tool P) for more information regarding the basis for the tool.

Note Some materials are both toxic and flammable, so you may need to assess both aspects.

(4) Assess the basic hazard from a toxic gas or vapour

For toxic materials, use the toxic hazard charts based on the amount of material that becomes airborne. The proportion of the material released that becomes airborne will depend on the type of release and material properties. Assume all the material released becomes airborne for materials held in the process as gases and vapours, or materials held as liquid under pressure in the process but which are gas/vapour at normal temperature and pressure. For other liquids it will be necessary to calculate the flash fraction (F) to estimate how much becomes airborne:

$$F = C_p\,(T_s - T_b)\,/\,H_v$$

where: T_b = normal boiling point [K]
T_s = operating temperature of material [K]
C_p = average heat capacity of the liquid [J/kg.K]
H_v = heat of vaporization of the liquid [J/kg].

If C_p and H_v data are not available, then the value of C_p/H_v can be approximated to 0.0044 for typical liquids.

As flashing of the vapour occurs, some of the liquid will be entrained as droplets. These can be small and evaporate in the resulting vapour cloud. As an approximation for this effect take the total proportion of the material released that becomes airborne to be twice the flash fraction:

Proportion of material that becomes airborne = 2F.

This approximation holds for low values of F. If the flash fraction is more than 0.2, then the entrainment will be considerable, and it would be wise to assume that all the material released becomes airborne.

Use the tables provided to estimate the hazard range and/or area affected:

- hazard ranges for instantaneous toxic releases,
- area affected by hazard for instantaneous toxic releases,
- hazard ranges for continuous toxic releases,

- area affected by hazard for continuous toxic releases.

The hazard range gives an indication of how far the hazard extends, the area affected gives a better indication of the magnitude of the hazard. The lines for harmful, toxic, etc. on the gas dispersion charts represent the range/area at which that category starts, i.e. the minimum hazard range/affected area to fall within that category. The "harmful" category therefore extends from the "harmful" line on the chart to the "toxic" line on the chart, and similarly for the other categories.

The fourth line (ppm level) does not relate to any harm level, but simply shows the hazard range to 1 ppm based on the simulation runs.

List and compare the hazard ranges/areas affected for the different release scenarios to determine which are the most severe. Use this to focus attempts to minimize inventory in the process or to see where substitution of materials may be useful. You can also use the tables to see how the hazard range or affected area changes if the inventory is, for example, reduced by half.

The record sheet provided should be completed in order to record the assessment results.

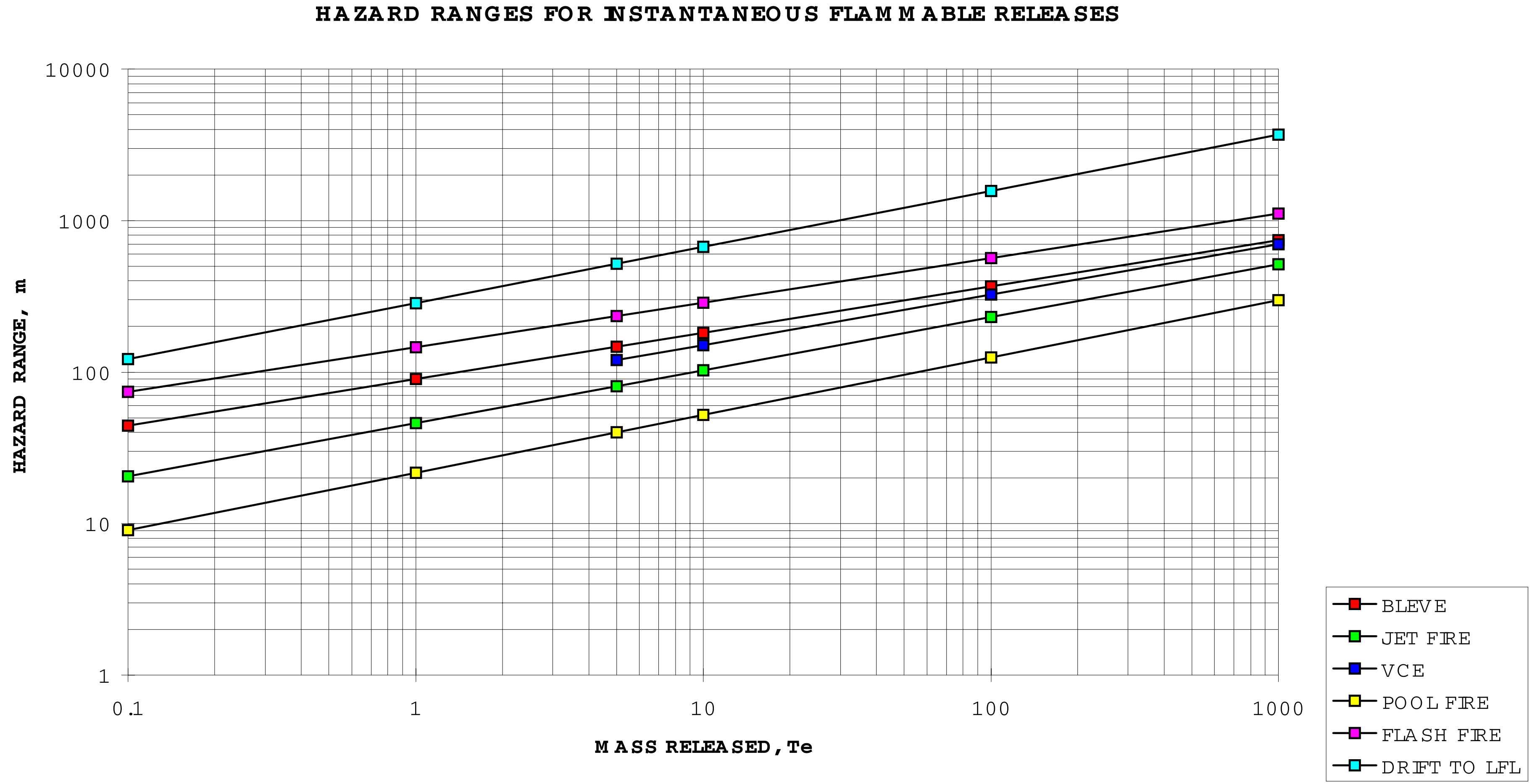
Consult Tool P Supporting Information (Part 4, Support for Tool P) for more information regarding the basis for the tool.

Note As some materials are both toxic and flammable, you may need to assess both of these aspects separately.

(5) Assess the need for more detailed modelling

If there is a need for more detailed modelling of the consequences of a leak, commercially available software packages should be used. It is recommended that the consequence analysis is carried out by a person who is familiar with the limitations of the models used.

Note An explanation of the terms and the fields in the Process Hazards Range Assessment Record Sheet follows in Tool P Supporting Information (Part 4, Support for Tool P).


HAZARD RANGES FOR INSTANTANEOUS FLAMMABLE RELEASES
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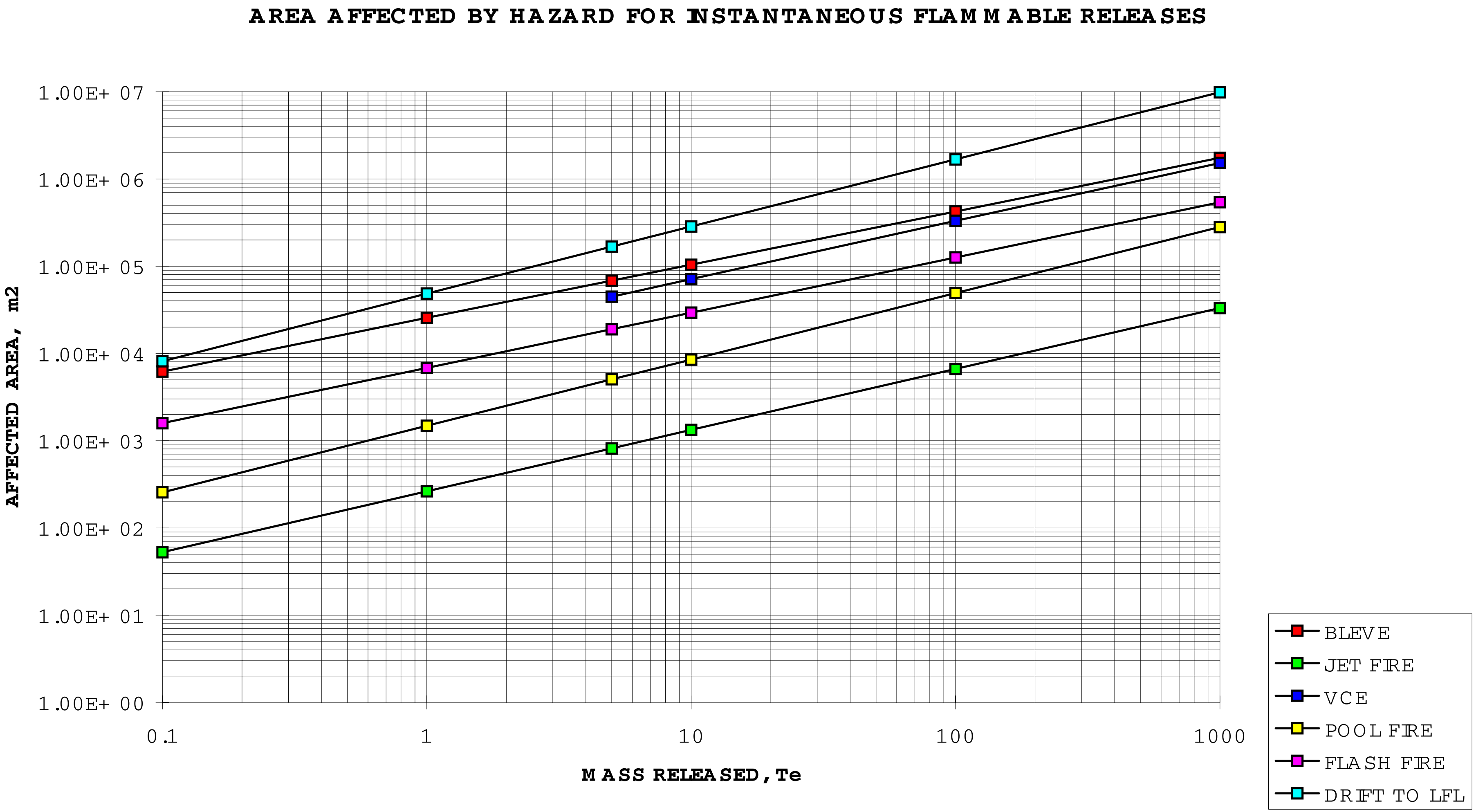
FLASH FIRE
DRIFT TO LFL


AREA AFFECTED BY HAZARD FOR INSTANTANEOUS FLAMMABLE RELEASES
AFFECTED AREA, m2
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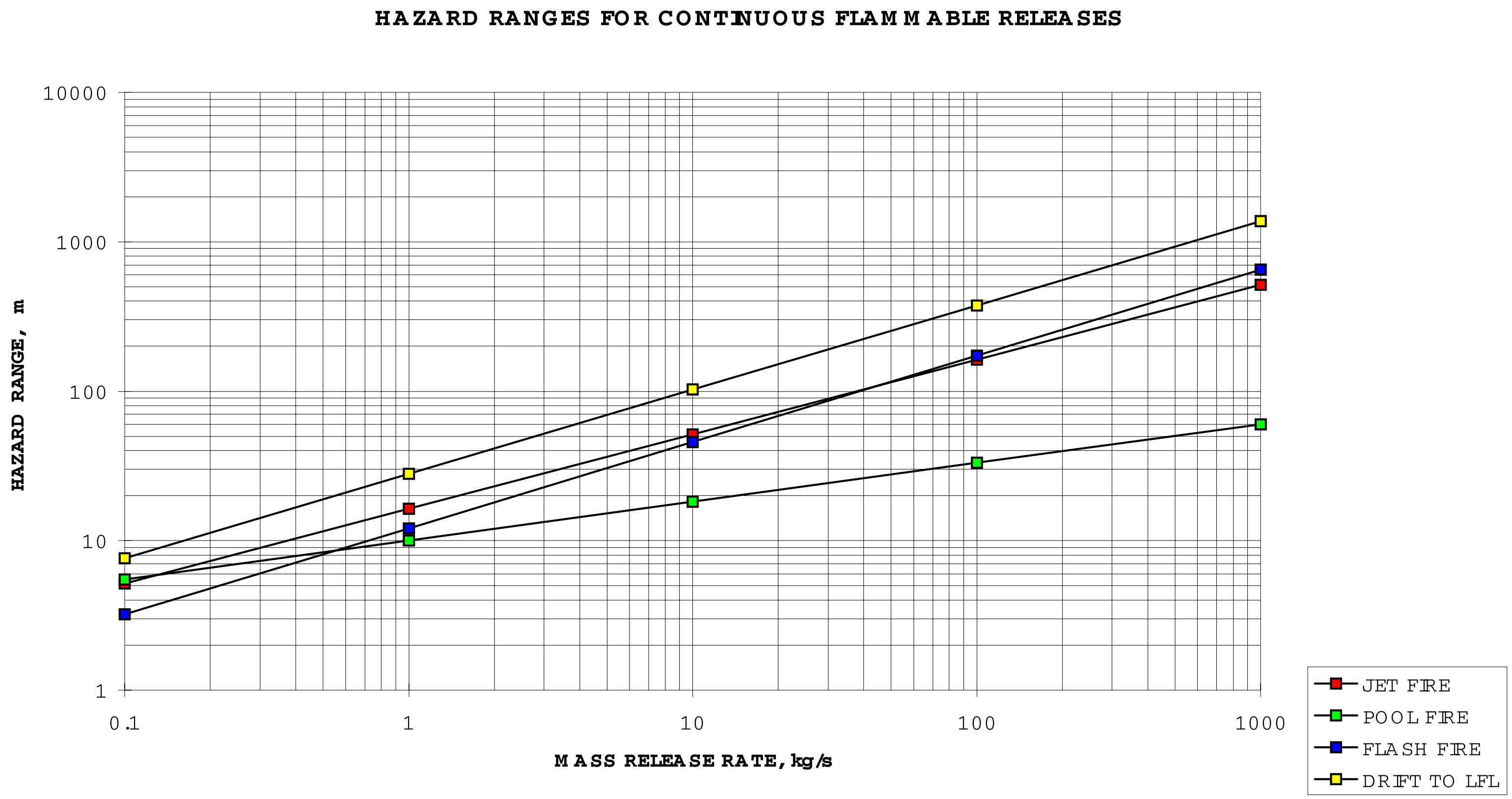
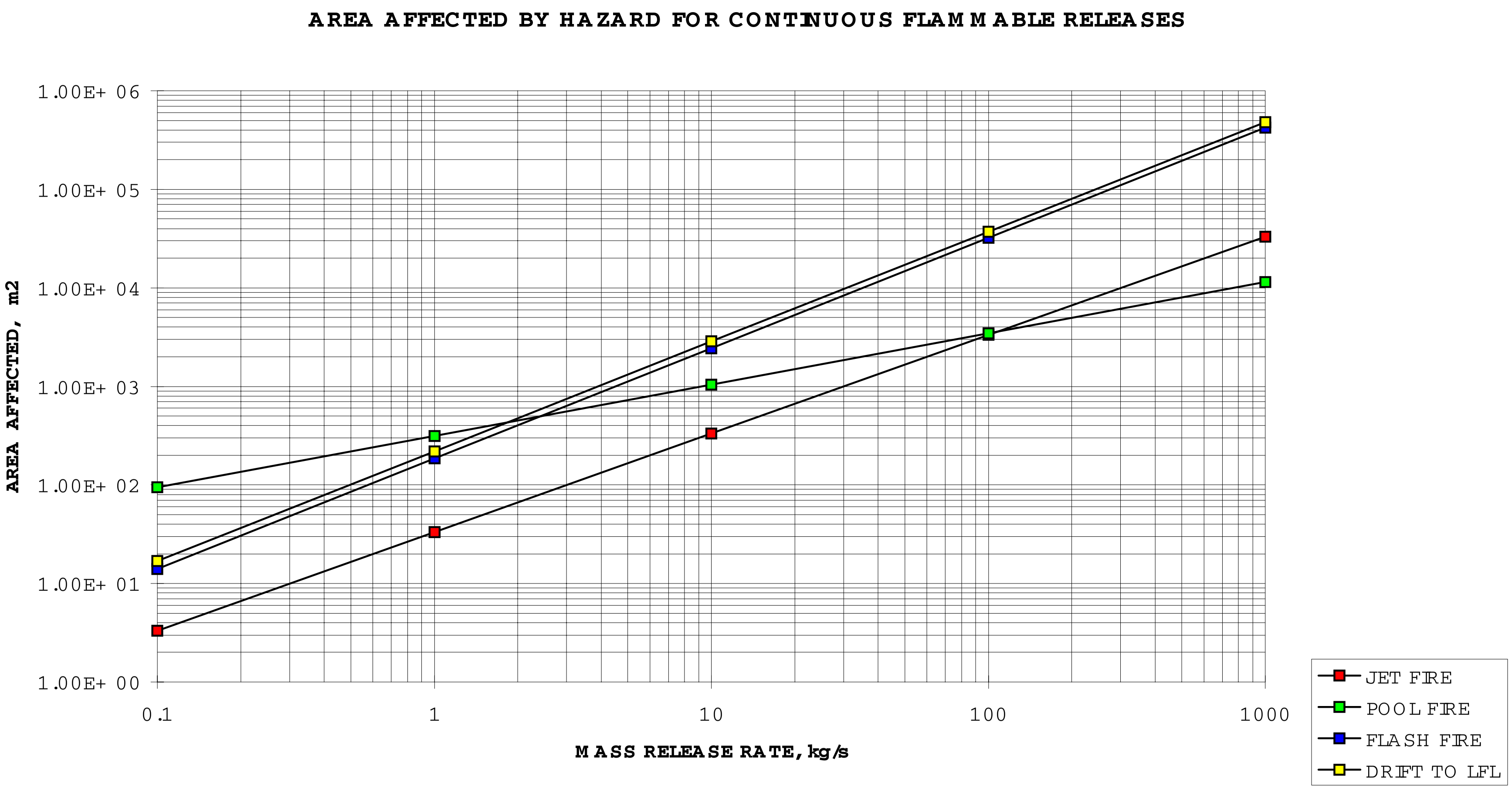
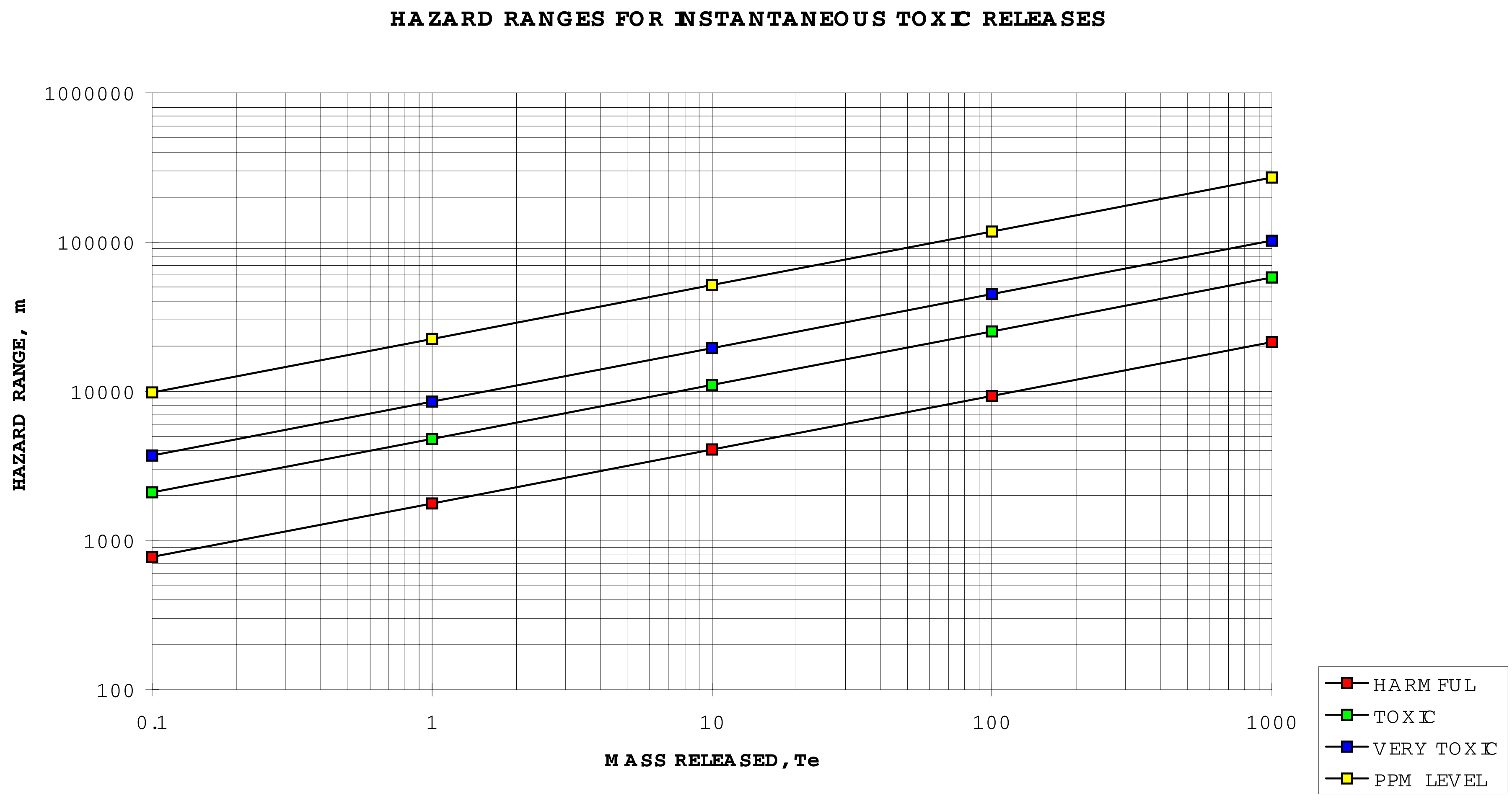
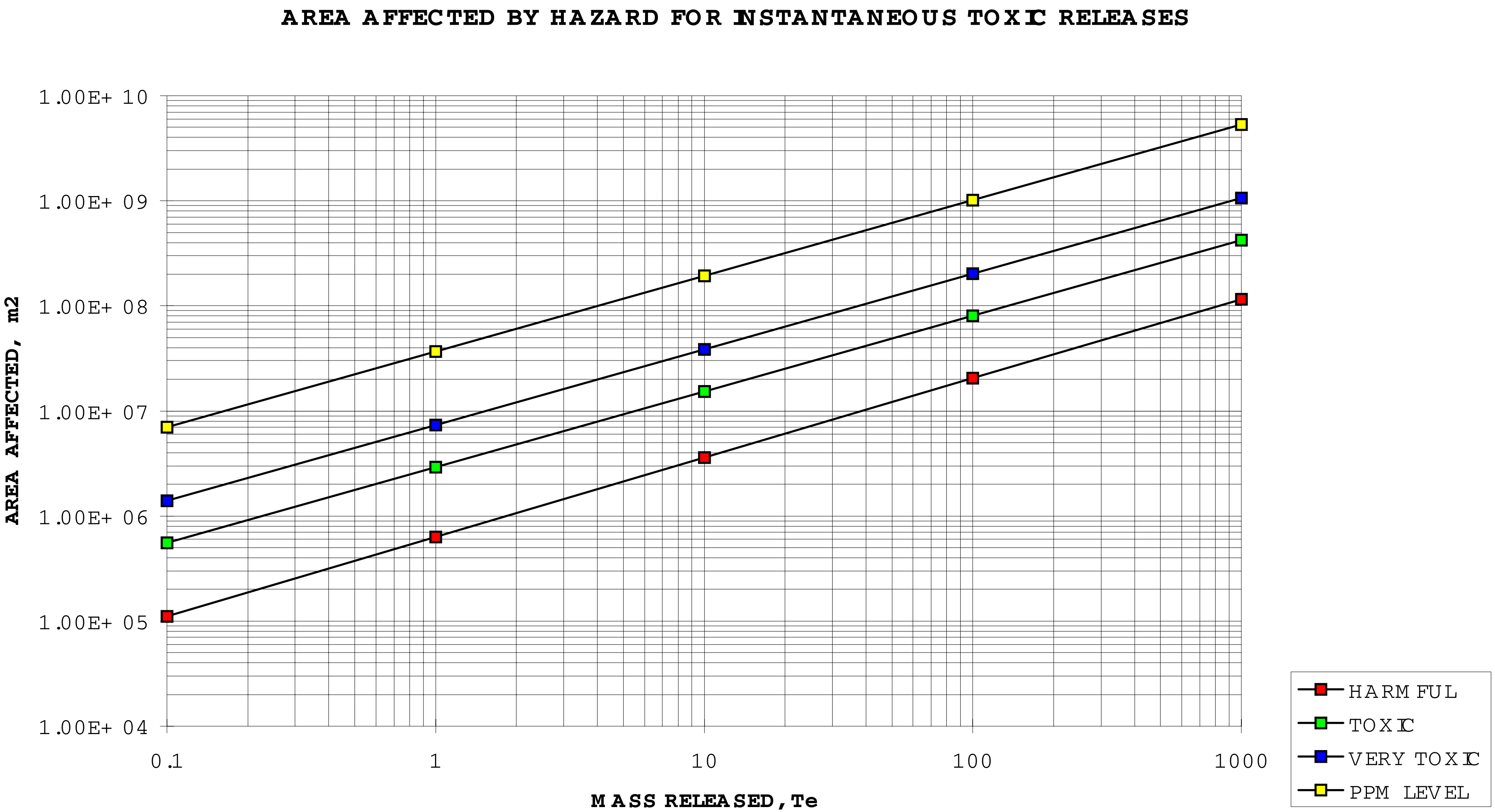
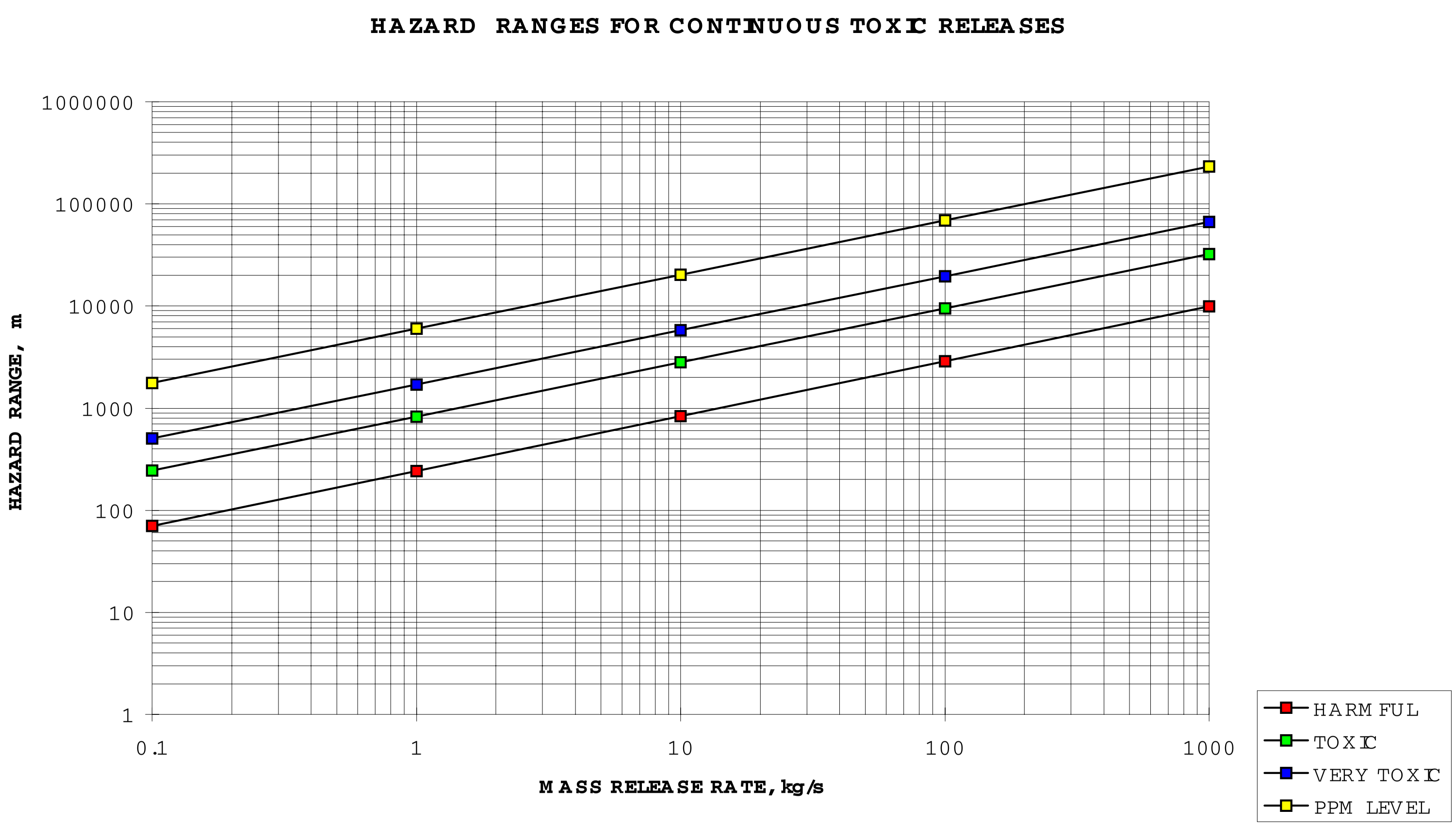
POOL FIRE
FLASH FIRE
DRIFT TO LFL

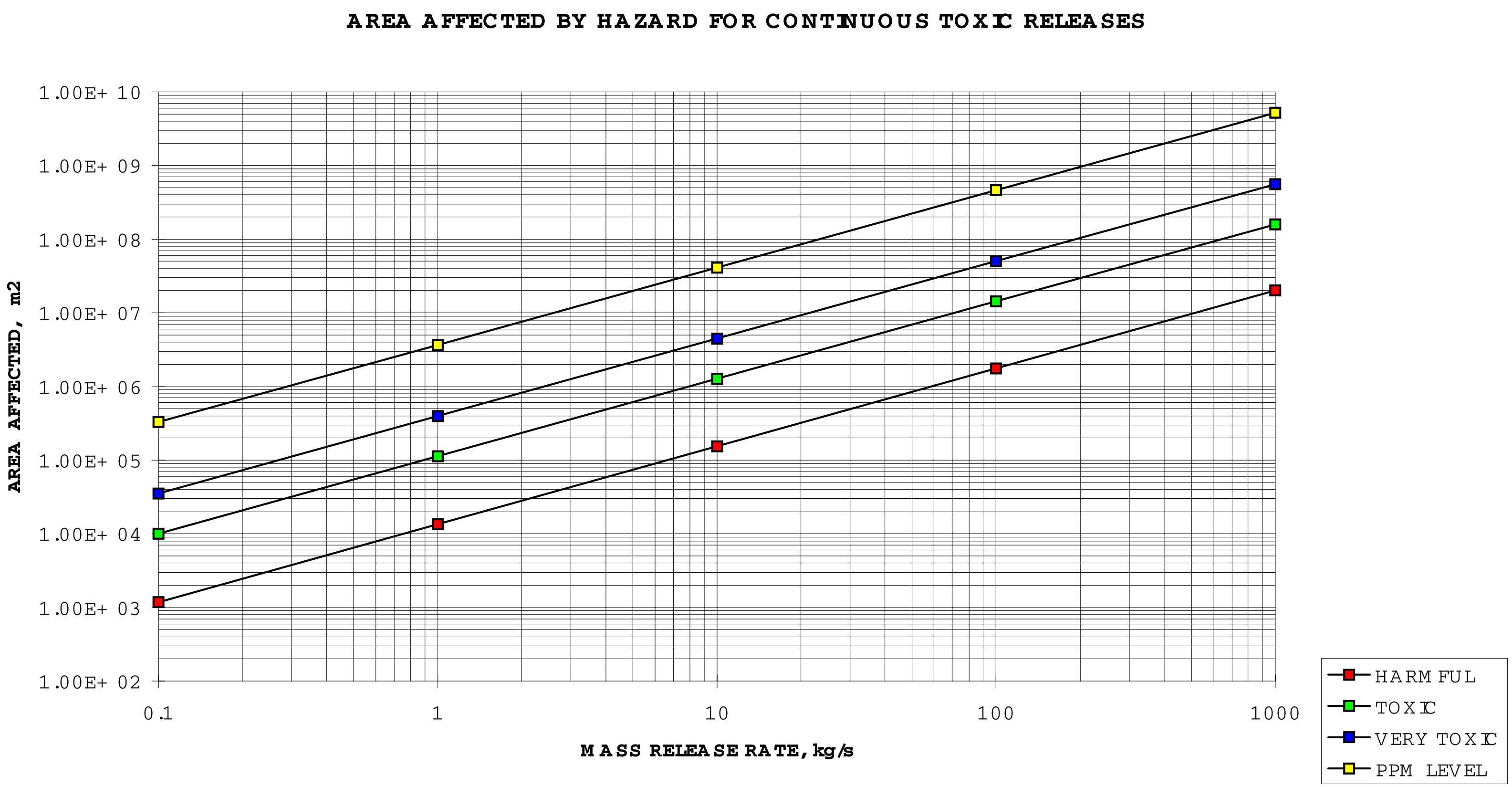

HAZARD RANGES FOR CONTINUOUS FLAMMABLE RELEASES
HAZARD RANGE, m
10000
1000
100
10
1
0.1
1
10
100
1000
MASS RELEASE RATE, kg/s
JET FIRE
POOL FIRE
FLASH FIRE
DRIFT TO LFL


AREA AFFECTED BY HAZARD FOR CONTINUOUS FLAMMABLE RELEASES
AREA AFFECTED, m2
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
0.1
1
10
100
1000
MASS RELEASE RATE, kg/s
JET FIRE
POOL FIRE
FLASH FIRE
DRIFT TO LFL


HAZARD RANGES FOR INSTANTANEOUS TOXIC RELEASES
HAZARD RANGE, m
1000000
100000
10000
1000
100
0.1
1
10
100
1000
MASS RELEASED, Te
HARMFUL
TOXIC
VERY TOXIC
PPM LEVEL


AREA AFFECTED BY HAZARD FOR INSTANTANEOUS TOXIC RELEASES
AREA AFFECTED, m2
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
0.1
1
10
100
1000
MASS RELEASED, Te
HARMFUL
TOXIC
VERY TOXIC
PPM LEVEL


HAZARD RANGES FOR CONTINUOUS TOXIC RELEASES
HAZARD RANGE, m
1000000
100000
10000
1000
100
10
1
0.1
1
10
100
1000
MASS RELEASE RATE, kg/s
HARMFUL
TOXIC
VERY TOXIC
PPM LEVEL


AREA AFFECTED BY HAZARD FOR CONTINUOUS TOXIC RELEASES
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
AREA AFFECTED, m2
0.1
1
10
100
1000
MASS RELEASE RATE, kg/s
HARMFUL
TOXIC
VERY TOXIC
PPM LEVEL

Tool P form

Project title:

Date: ___ / ___ / ______ **Process Hazards Range Assessment Record Sheet (Tool P)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Material	Location/function	Inventory [Te]	Leak rate [kg/s]	Hazard type	Hazard range [m]	Affected area [m^2]	Comment/priority

TOOL Q – SITING & PLANT LAYOUT ASSESSMENT

Aim: To challenge the basis of the plant layout at the early stages of its development, in order to see how changes to the layout could improve segregation and make the layout more inherently SHE.

Timing: The tool is best applied once the initial process flowsheets and equipment selection have been identified and one or more possible layouts sketched out. This would normally coincide with the early stages of project scoping or concept design.

Input: Stage III dominant alternative dossier.
A description of the basic unit operations and equipment proposed is required, preferably in the form of a process diagram or P&ID, initial plant layout plot plan and equipment datasheets. Information on the process and equipment hazards would also be useful, e.g. in the form of a hazard file or data sheets (e.g. from Tool M) to help focus on the main problem areas.
Approximate location of potential raw material suppliers, destinations for by-products and wastes.
The location of key customers (where product is hazardous).

Output: A revised layout or list of suggestions for improving the layout to make it inherently safer. The tool could also be applied at the very early stages of layout to determine the layout strategy and any key objectives to be used when developing the layout.

Background

A necessary part of industrial activity is that materials be moved between manufacturing facilities and from the manufacturing site to the customer. All transportation incurs risk. For example, even serious accidents have occurred where lorries containing non-hazardous materials have run out of control. Against this background, the record for the transport of hazardous materials within Europe is a good one.

The location of the facility, then, is an important consideration in the design of any chemical process plant.

There may be occasions where the choice of process routes/choice of plant location can either incur or avoid the transport of hazardous materials. This needs to be considered in the inherent SHE assessment, and a simplified assessment procedure has been produced as part of Tool Q. It must be stressed that this procedure is not solely suitable for materials of high hazard and must, where appropriate, be supported by a detailed risk assessment.

In some cases, materials may be transported by pipeline or by ship. Usually these cases are unique and involve high tonnages of material. No attempt has been made to produce a general method for these. Similarly, transport by air has not been considered.

After a decision on the location of the facility has been made, an equally important aspect to be considered is the layout of the site itself.

Segregation by distance or the use of buffer zones or barriers can play a key role in the mitigation of hazards. These aspects are addressed by EEC Directive 82/501/EEC, on major industrial accidents. The basic layout of the plant itself, and its relationship with other plant and vulnerable areas around it, can provide an inherent means of mitigating hazards such that risks are avoided or minimized.

This tool provides a prompt list that ensures the user considers the inherent hazards that are involved with the proposed plant design and would be best applied in a layout review meeting or by an experienced layout specialist.

Instructions

The overall sequence suggested involves the following steps:
1. Make a representation of the plant.
2. Assess the layout.
3. Assess the risk from transportation.

(1) Make a representation of the plant

A plot plan or other layout schematic will be required for the layout inherent SHE study. Information on the layout of the site (topography) and any relevant adjacent features (other plants, housing, public roads and paths, watercourses, environmentally sensitive areas, climatic conditions, etc.) is necessary.

(2) Assess the layout

A simple prompt list is provided to be used to structure a review of the conceptual plant layout to identify the main problems and find inherently safer ways of tackling these. The guidewords in the tool should be applied to question each section or aspect of the layout.

It is suggested that the findings of the studies are recorded to provide an audit trail for decision-making.

Apply the following prompt list to the proposed layout at the early stages of the design, or use it to develop layout options and then assess these.

Plant Layout Assessment Prompt List	
hazard avoidance	Site away from sources of external hazards Site away from sensitive areas – people, environment, amenity Site close to supplies of raw material Site close to users of product Site away from severe environmental hazards Site where landscape/geography favourable
segregation	Hazards from other hazards Hazards from people and environment Plant from plant Process from storage from loading/unloading areas Control room from plant hazards Administration block from plant/hazards Workshops from plant/hazards Public from plant Materials from environment – access routes, roads, paths, rivers, adjacent land, air Materials from other materials (process or common, e.g. water) where these could interact to cause a hazard (especially in storage areas) Materials from conditions that could cause a hazard (e.g. humidity, cold, heat, shock/shaking, sunlight, corrosive conditions) Flammables from sources of ignition
hazard prevention	Access for maintenance Logical layout Clear, logical and consistent plant labelling Design to allow good housekeeping
hazard control	Drains/bunds - carry or contain spills from process - cope with fire fighting water/runoff - prevent spread of hazard via drains Good ventilation Passive better than active protection Emergency systems can survive hazards? (detection, ESD, blowdown, alarms, communications)
mitigation	Clear, safe escape routes Safe muster areas Access for emergency/rescue services Access to protective equipment Access to fire fighting/safety equipment Alarms and communications effective, accessible Consider adjacent plants, industrial activities, public activities, environment (air, land, water, species, etc.) Effluents/discharges (normal and emergency) compatible with materials from *other users* of watercourses, air, sewers, etc.
hazard scenarios	Use realistic hazard scenarios – talk through to check layout is adequate
other issues	Fire fighting water supply Security Visitors Noise levels – plant and transport Smells/odours Appearance Discolouration of air/water Illumination and "light pollution"

(3) Assess the risk from transportation

Unacceptable risks during transportation of chemicals to or from the plant may require that parts of the process are moved to an other site or that additional units are needed to either produce a hazardous raw material on site, or transform a waste product to something less dangerous, for example through reaction, incineration or dilution.

Firstly, list the materials which will be transported to and from the site. These include:
- raw materials,
- intermediates,
- products,
- wastes.

Secondly, identify the likely suppliers and users, and the approximate distances over which the material is likely to travel. Where necessary, direct "as the crow flies" distances can be used and multiplied by 1.3 to allow for normal road/rail divergencies. Also identify the likely means of transportation.

Note In the case of products distributed to many customers, it may be appropriate to consider only the key distribution points.

Thirdly, for each of the materials, use the hazard classification from Tool G to assess the risk involved with each substance. Special consideration should be given to any special properties of the material being transported, for example materials which react violently with water or air. Where the transport risks are high, consideration can be given to alternatives (see also Tool B):

Transport Inherent SHE Option Identification Guideword List

Keyword	**Option**
avoid	Use of less hazardous materials Safer location of plant – reduce distance, avoid routing near sensitive areas Splitting the production so that a less hazardous material is transported (transport in a more benign form)
more of/less of	Evaluation of larger or smaller container sizes
protect	Different type of container/transporter (see Tool Q Supporting Information, in Part 4, Support for Tool Q)

It should be remembered that transport may often be the dominant factor in determining on-plot storage. Once the size of a unit load is determined, there will be a need to store an amount greater than this both at the despatching and the receiving end.

Where loss of containment would result in serious consequences, it is recommended that a more detailed assessment of transport is undertaken. This may make use of quantified risk assessment.

Tool Q form

Project title:

Date: ___ / ___ / ______ **Plant Layout and Siting Assessment Record Sheet (Tool Q)** **Page: ___ / ___**
Plant: ________________ **Section: ________________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Guideword	Aspect of layout/siting	Options	Comments

TOOL R – DESIGNING FOR OPERATION

Aim: To provide a simple aide-mémoir or check-list for those involved in the detailed design of plant to prompt them to consider ways in which to make the plant easier to operate and maintain. It could also be used when preparing the plant control, operation and maintenance philosophies, or when writing the procedures associated with these. Use of this tool to analyse some of the more hazardous tasks to see how these could be made safer is also possible.

Timing: Possibly used at various times throughout the design process, the tool is best applied once the initial process flowsheets and equipment selection have been identified and one or more possible layouts sketched out. This would normally coincide with the early stages of project scoping or concept design.

Input: Stage III dominant alternative dossier.
List/schedule and description/knowledge of manual operation or maintenance tasks required, especially those that are considered to be particularly hazardous.

Output: Suggestions for improving or eliminating these tasks so that the plant is made inherently friendlier – reducing the chance of making an error, or making the consequences of an error easier to recover or less severe.

Background

Within the *INSET* Toolkit, various tools that enable the user to consider various aspects of chemical process development with inherent SHE aspects as the central issue have been developed. The various preceding tools cover the entire project development, from identifying the various possible alternatives, right up to siting and layout of the plant. Although probably indirectly covered at various stages during the *INSET* Toolkit analysis, the actual operation of the plant would not have been directly addressed (for example, aspects that concern the safety of the plant personnel with regard to their working conditions, procedures and habits). By also designing for operation using inherent SHE aspects, the inherently safer plant becomes a reality.

The simple aide-mémoir check-list presented in this tool could be used to consider ways in which to make the plant easier to operate and maintain. It could also be used when preparing the plant control, operation and maintenance philosophies, or when writing the procedures associated with these. Use of this tool to analyse some of the more hazardous tasks to see how these could be made safer is also possible.

Instructions

The overall sequence suggested involves the following steps:
1. Challenge control, operation and maintenance tasks.
2. Option generation.

(1) Challenge control, operation and maintenance tasks

Use the main headings from the Designing for Operation Guideword List as prompts to identify alternative designs, equipment, layout or practices to reduce the need for manual activities or to make those activities easier to perform, or to make them less prone to error. The guidewords could be included in a check-list for design reviews, or as supplementary guidewords in a HAZOP or other hazard/operability study. You may wish to seek the advice of an ergonomist or human factors expert for some of the more critical tasks.

(2) Option generation

Apply the following guidewords to identify problems and generate alternative options where there are interactions between people and the process plant (a simple summary of the guidewords is provided).

Designing for Operation Guideword List – to challenge control, operation and maintenance tasks
Eliminate task
Substitute task
Reduce tasks
Simplify task
Make status clear
Allow for error detection & recovery
Make error "impossible"
Make conditions easier
Segregate from hazards
Minimize exposure
Simplify procedure

Tool R Supporting Information (see Part 4, Support for Tool R) contains examples of typical questions that may be encountered while using Tool R. Note that the list is not exhaustive!

Further challenging of the entire process could be done using Tool B.

Tool R form

Project title:

Date: ___ / ___ / ______ **Designing for Operation Assessment Record Sheet (Tool R)** **Page: ___ / ___**
Plant: ________________ **Section: ________________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Plant area	Task/aspect	Guideword	Options	Comments

BLANK FORMS - CHEMICAL HAZARDOUS PROPERTIES CLASSIFICATION TABLE AND BLANK TOOL FORMS

CONTENTS

Chemical Hazardous Properties Classification
Tool A.1 form (1)
Tool A.1 form (2)
Tool A.2 form (1)
Tool A.2 form (2)
Tool B form
Tool C form
Tool D form (1)
Tool D form (2)
Summary sheet for *INSET* stage I
Tool E form
Tool F form
Tool G form
Tool H form
Tool I.1 form through to Tool I.11 form
Tool J form (1)
Tool J form (2)
Tool J form (3)
Tool K form (1)
Tool K form (2)
Tool L form
Tool M form
Tool N form
Tool O form
Tool P form
Tool Q form
Tool R form

Chemical Hazardous Properties Classification

Class	Safety	Health	Environment
Very high hazard **VH**	Materials which present hazards that endanger life at a large distance from the source of the material or in very small concentrations/amounts	Materials which present hazards that endanger life on contact with the source or following short-term exposure in the working environment	Materials which present hazards that could result in a significant loss of habitat or species
	Very toxic **R26/27/28** Category 1 carcino/muta/teratogenic Extreme risk of explosion **R3**	Very toxic **R26/27/28** Category 1 carcino/muta/teratogenic	Aquatic very toxic **R50** Very toxic **R26/27/28** Category 1 carcino/muta/teratogenic
High hazard **H**	Materials which present hazards that endanger life, or could result in serious injuries some distance from the source of the material or in small concentrations/ amounts	Materials which present hazards that could cause serious injury, or cause serious long-term adverse effects on contact with the source material or following short-term exposure in the working environment, or endanger life following prolonged exposure in the working environment	Materials which present hazards that could result in significant long-term damage to habitat or to certain vulnerable species
	Toxic **R23/24/25** Risk of explosion **R2** Extremely flammable **R12/13** Highly flammable **R11** Oxidizing **R9/11**	Toxic **R23/24/25** Category 2 carcino/muta/teratogenic Corrosive – severe burns **R35**	Aquatic toxic **R51** Non-aquatic toxic – various species Toxic **R23/24/25** Category 2 carcino/muta/teratogenic
Medium hazard **M**	Materials which present hazards that could result in injuries or long-term adverse effects close to the source of the material, or flammable materials of low flashpoint (21-55°C)	Materials which present hazards that could cause injury or long-term adverse effects on contact with the source or following prolonged exposure in the working environment	Materials which present hazards that could result in some slight loss of habitat or species or long-term adverse effects on habitat or species
	Harmful **R20/21/22** Flammable **R10** Oxidizing **R8**	Harmful **R20/21/22** Category 2 carcino/muta/teratogenic Corrosive – burns **R34** Irritant	Aquatic harmful **R52** Aquatic adverse effects **R53** Dangerous to ozone layer **R59** General adverse effects **R58** Harmful **R20/21/22** Category 2 carcino/muta/teratogenic
Low hazard **L**	Materials which present no hazard, or which present hazards that are unlikely to result in serious injury or long-term adverse effects	Materials which present no hazard, or which present hazards that are unlikely to result in serious injury or long-term adverse effects	Materials which present no hazards, or which present hazards that are unlikely to result in long-term adverse effects
	Not classified as "dangerous" under the 84/449/EEC Directive	Not classified as "dangerous" under the 84/449/EEC Directive	Not classified as "dangerous" under the 84/449/EEC Directive

Tool A.1 form (1)

Project title:

Date: ___ / ___ / ______ **General Constraints of the Project Sheet (Tool A.1)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

ID	Constraint	Date
C_{G1}		
C_{G2}		
C_{G3}		
C_{G4}		
C_{G5}		
C_{G6}		
C_{G7}		
C_{G8}		
C_{G9}		
C_{G10}		
C_{G11}		
C_{G12}		
C_{G13}		
C_{G14}		
...		

Tool A.1 form (2)

Project title:

Date: ___ / ___ / ______ **Project-Specific Constraints Sheet (Tool A.1)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

ID	Constraint	Date
C_{P1}		
C_{P2}		
C_{P3}		
C_{P4}		
C_{P5}		
C_{P6}		
C_{P7}		
C_{P8}		
C_{P9}		
C_{P10}		
C_{P11}		
C_{P12}		
C_{P13}		
C_{P14}		
...		

Tool A.2 form (1)

Project title:

Date: ___ / ___ / ______ **General Objectives of the Project Sheet (Tool A.2)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

ID	Objective	Attribute	Date
O_{G1}			
O_{G2}			
O_{G3}			
O_{G4}			
O_{G5}			
O_{G6}			
O_{G7}			
O_{G8}			
O_{G9}			
O_{G10}			
O_{G11}			
O_{G12}			
O_{G13}			
O_{G14}			
...			

Tool A.2 form (2)

Project title:

Date: ___ / ___ / ______ **Project-Specific Objectives Sheet (Tool A.2)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

ID	Objective	Attribute	Date
O_{P1}			
O_{P2}			
O_{P3}			
O_{P4}			
O_{P5}			
O_{P6}			
O_{P7}			
O_{P8}			
O_{P9}			
O_{P10}			
O_{P11}			
O_{P12}			
O_{P13}			
O_{P14}			
...			

Tool B form

Project title:

Date: ___ / ___ / ______ | **Process Option Generation Record Sheet (Tool B)** | **Page: ___ / ___**
Stage/input/output: ______________________________
Author: ________________ | **Proj. #: ________________** | **Ref. #: ________**

Guideword	Effect of options in terms of SHE performance	Inherent SHE benefit (note as + , 0, or –)			Feasibility	Other benefits or disadvantages (e.g. cost)	Comments/ recommendations
		Safety	Health	Env.			

Tool C form

Project title:

Date: ___ / ___ / ______ **Preliminary Chemistry Route Options Record (Tool C)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________ **Route for:** ___________________________________

Source: **Lead to new ref.:**

Reaction conditions		Overall yield	Possible variations	Other comments	Reason for failure
Step					
Temp.					
Pressure					
Time					
Yield					

Tool D form (1)

Project title:

Date: ___ / ___ / _____ **General Screening Questions List (Tool D)**

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Compulsory questions		Additional questions	
Q1	Are any of the materials on the EU "Black list" (banned)?	**Q11**	Are "greenhouse effect" chemicals involved?
Q2	Are any of the materials on the EU "Grey list" (dangerous)?	**Q12**	Are persistent toxic chemicals or heavy metals involved?
Q3	Are carcinogenic/teratogenic materials involved?	**Q13**	Does the process use raw materials that are limited or under threat?
Q4	Are any ozone-depleting chemicals involved?	**Q14**	Does the process introduce hazards that are new to the company/site?
Q5	Are any highly toxic materials involved?	**Q15**	Are there likely to be problems during the site decommissioning?
Q6	Are unstable/explosive materials involved?	**Q16**	____________________ ?
Q7	Do any of the materials react violently with air or water?	**Q17**	____________________ ?
Q8	Will the wastes need further treatment?	**Q18**	____________________ ?
Q9	Is the ultimate fate of any the materials unknown?	**Q19**	____________________ ?
Q10	Will hazardous materials need to be imported/exported?	**Q20**	____________________ ?

Tool D form (2)

Project title:

Date: ___ / ___ / ______ **General Screening Questions Results Sheet (Tool D)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Ref. #	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	...	Reason	Decision
A_1															
A_2															
A_3															
A_4															
A_5															
A_6															
A_7															
...															

Summary sheet for *INSET* stage I

Project title:

Date: ___ / ___ / _____ **Dominant Alternatives Record (Tool D/Tool E)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Alternative Ref. #	Grounds for favourable assessment

Tool E form

Project title:

Date: ___ / ___ / ______ **Criteria Screening Matrix (Tool E)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Alternative Ref. #	**Constraints**										**Meets constraints**	**Objectives**										**Passes initial screen**
	C_{G1}	C_{G2}	C_{G3}	...	C_{P1}	C_{P2}	C_{P3}	C_{P4}	C_{P5}	...		O_{G1}	O_{G2}	O_{G3}	O_{G4}	O_{G5}	...	O_{P1}	O_{P2}	O_{P3}	...	
A_1																						
A_2																						
A_3																						
A_4																						
A_5																						
A_6																						
A_7																						
A_8																						
A_9																						
A_{10}																						
Footnote 1																						
Footnote 2																						
Footnote 3																						

Tool F form

Project title:

Date: ___ / ___ / ______ **Chemistry Route Block Diagram Record (Tool F)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________** **Block diagram for: __________________________**

Source: **Lead to new ref.:**

Possible variations	Other comments	Reason for failure

Tool G form

Project title:

Date: ___ / ___ / ______ **Chemical Function & Hazards Classification (Tool C/Tool G)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Chemical	Function	Comments	Safety	Health	Environment

Tool H form

Project title:

Date: ___ / ___ / ______ **Record of Foreseeable Hazards (Tool H)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Substance/reaction of interest	Short description of the potential hazard	Note	Reference

Tool I.1 form

Project title:

Date: ___ / ___ / ______ **FEHI: Fire and Explosion Hazards Index (Tool I.1)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Temperature [°C]						
D	Atmospheric boiling point [°C]						
E	Item/inventory [Te]						
F	Fire and Explosion Hazard Factor (FEHF)						
G_a	Absolute FEHI, = E × F						
G_r	Relative FEHI, = E × F / A						
Refinement							
H	Heat of combustion correction (CF1)						
I	Reactivity/sensitivity correction (CF2)						
J	Liquids above b.p. correction (CF3)						
K_a	Refined absolute, FEHI = $G_a \times H \times I \times J$						
K_r	Refined relative, FEHI = $G_r \times H \times I \times J$						

Tool I.2 form

Project title:

Date: ___ / ___ / ______ **ATHI: Acute Toxic Hazards Index (Tool I.2)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Item/inventory [Te]						
D	Toxic Harm Factor (THF)						
E_a	Absolute ATHI $= C \times D$						
E_r	Relative ATHI $= C \times D / A$						

Tool I.3 form

Project title:

Date: ___ / ___ / _____ **HHI: Health Hazards Index (Tool I.3)** **Page:** ___ / ___
Plant: _______________ **Section:** _______________ **Flowsheet #:** ________ **Revision:** ________
Author: _______________ **Proj. #:** _______________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Health Harm Factor (HHF)						
D	Manual handling/exposure operations [number of manual operations per year]						
E	Equipment/sum of leak factors [Te/year]						
F_a	Absolute HHI $= C \times (0.6 \times D + E)$						
F_r	Relative HHI $= C \times (0.6 \times D + E) / A$						
Refinement							
G	Leak shaping factor (CF1)						
H_a	Corrected HHI $= F_a \times G$						
H_r	Corrected HHI $= F_r \times G$						

Tool I.4 form

Project title:

Date: ___ / ___ / ______ **AEII: Acute Environmental Incident Index (Tool I.4)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Item/inventory [Te]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute AEII $= C \times D$						
E_r	Relative AEII $= C \times D / A$						
Refinement							
F	Condition factor (CF1)						
G_a	Corrected absolute AEII $= E_a \times F$						
G_r	Corrected relative AEII $= E_r \times F$						

Tool I.5 form

Project title:

Date: ___ / ___ / ______ **THI: Transport Hazards Index (Tool I.5)** **Page: ___ / ___**
Plant: ________________ **Section: ________________** **Flowsheet #: ________** **Revision: ________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]						
B	Dominant material						
C	Load/container size (inventory) [Te]						
D	Distance travelled per journey [km]						
E	Number of journeys per year (annual tonnage/load size)						
F	Transport Harm Factor (THF)						
G_a	Absolute THI $= (C \times D \times E \times F) / (1E7)$						
G_r	Relative THI $= (C \times D \times E \times F) / (A \times 1E7)$						

Tool I.6 form

Project title:

Date: ___ / ___ / ______ **GEI: Gaseous Emissions Index (Tool I.6)** **Page: ___ / ___**
Plant: ________________ **Section: ________________** **Flowsheet #: ________** **Revision: ________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]						
B	Dominant gaseous emission material						
C	Annual discharge rate [Te/year]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute GEI $= C \times D$						
E_r	Relative GEI $= C \times D / A$						

Tool I.7 form

Project title:

Date: ___ / ___ / ______ **AEI: Aqueous Emissions Index (Tool I.7)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Annual production [Te/year]						
B	Dominant aqueous emission material						
C	Annual discharge rate [Te/year]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute AEI $= C \times D$						
E_r	Relative AEI $= C \times D / A$						

Tool I.8 form

Project title:

Date: ___ / ___ / ______ **SWI: Solid Wastes Index (Tool I.8)** **Page: ___ / ___**
Plant: ________________ **Section: ________________** **Flowsheet #: ________** **Revision: ________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Annual production [Te/year]						
B	Dominant solid waste material						
C	Annual discharge rate [Te/year]						
D	Environmental Harm Factor (EHF)						
E_a	Absolute SWI $= C \times D$						
E_r	Relative SWI $= C \times D / A$						

Tool I.9 form

Project title:

Date: ___ / ___ / ______ **ECI: Energy Consumption Index (Tool I.9)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]						
B	Energy usage [GJ/year]						
	Gas Fuel oil Coal Electricity Other						
C	Energy factor (EF) [Te CO_2/year]						
	Gas B_{gas} × 0.067 = Fuel oil $B_{f/oil}$ × 0.097 = Coal B_{coal} × 0.126 = Electricity B_{elec} × 0.214 = Other B_{other} × = Total (Sum of above) =						
D_a	Absolute ECI = C						
D_r	Relative ECI = C / A						

Tool I.10 form

Project title:

Date: ___ / ___ / ______ **RHI: Reaction Hazards Index (Tool I.10)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Annual production [Te/year]						
B	Dominant reaction scenario and materials						
C	Reaction Risk Factor (RRF)						
D	Reaction Harm Factor (RHF)						
E	Reactor inventory [Te]						
F_a	Absolute RHI = $C \times D \times E$						
F_r	Relative RHI = $C \times D \times E / A$						

Tool I.11 form

Project title:

Date: ___ / ___ / ______ **PCI: Process Complexity Index (Tool I.11)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________ **Flowsheet #:** ________ **Revision:** ________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]						
B	Batch or continuous?						
C_a	Absolute PCI = total of values						
C_r	Relative PCI = C_a / A						

Tool J form (1) – Qualitative inherent SHE evaluation: Single option summary sheet

Project title:

Date: ___ / ___ / ______ **Inherent SHE Single Option Summary Sheet (Tool J)** ☐ **Word picture** **Page: ___ / ___**
Process option: ________________ ☐ **Index range**
Author: ________________ **Proj. #: ________________** **Ref. #: _________**

Index	Aspect	Dominant factor	1	2	3	4	5	Comments
FEHI	Fire and explosion hazards							
ATHI	Acute toxic hazards							
HHI	Health hazards							
AEII	Acute environmental incidents							
THI	Transport hazards							
GEI	Gaseous emissions							
AEI	Aqueous emissions							
SWI	Solid wastes							
ECI	Energy consumption/ global warming							
RHI	Reaction hazards							
PCI	Process complexity							
TF	Technical feasibility							
EF CAPEX	Economic feasibility CAPEX							
EF OPEX	Economic feasibility OPEX							

Tool J form (2) – Quantitative inherent SHE evaluation: Single option index values record sheet

Project title:

Date: ___ / ___ / ______ **Inherent SHE Single Option Index Value Summary Sheet (Tool J)** **Page:** ___ / ___
Process option: ________________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Index	Aspect	Dominant factor	Absolute index value	Relative index value	Comments
FEHI	Fire and explosion hazards				
ATHI	Acute toxic hazards				
HHI	Health hazards				
AEII	Acute environmental incidents				
THI	Transport hazards				
GEI	Gaseous emissions				
AEI	Aqueous emissions				
SWI	Solid wastes				
ECI	Energy consumption/ global warming				
RHI	Reaction hazards				
PCI	Process complexity				
TF	Technical feasibility				
EF CAPEX	Economic feasibility CAPEX				
EF OPEX	Economic feasibility OPEX				

Tool J form (3) – Inherent SHE multi-attribute evaluation: Option comparison record

Project title:

Date: ___ / ___ / ______ **Inherent SHE All Options Summary Sheet (Tool J)** ☐ **Word picture** **Page: ___ / ___**
Process option: _______________ ☐ **Index range**
Author: _______________ **Proj. #: _______________** **Ref. #: ________**

Index	Aspect	Index values/qualitative score for the different options						Comments
		Option A	Option B	Option C	Option D	Option E	Option F	
FEHI	Fire and explosion hazards							
ATHI	Acute toxic hazards							
HHI	Health hazards							
AEII	Acute environmental incidents							
THI	Transport hazards							
GEI	Gaseous emissions							
AEI	Aqueous emissions							
SWI	Solid wastes							
ECI	Energy consumption/ global warming							
RHI	Reaction hazards							
PCI	Process complexity							
TF	Technical feasibility							
EF CAPEX	Economic feasibility CAPEX							
EF OPEX	Economic feasibility OPEX							

Tool K form (1)

Project title:

Date: ___ / ___ / ______ **Chemistry Materials Hazards Classification (Tool K)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Chemical	Safety values				Health values				Environmental values			
	Explos. & fire	Stability	React.	Physical prop.	Chronic	Acute (skin)	Acute (inhal.)	Acute (eyes)	Toxicity	Degrada bility	Bioaccu mulation	Physical prop.

Tool K form (2)

Project title:

Date: ___ / ___ / ______ **Process Hazard Index Classification (Tool K)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Stage/unit operation	Index	Comments

Tool L form

Project title:

Date: ___ / ___ / ______ **Chemical Reaction Reactivity – Stability Evaluation Record (Tool L)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Ref. #	Reaction studied	Method used	Severity	Probability	Risk	Reference

Tool M form

Project title:

Date: ___ / ___ / ______ **Process Hazard Identification Record Sheet (Tool M)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________ **For hazard review use only**

Stage/input/output	Hazard/problem	Causes	Effects	Hazard ranking	Comments	New ranking after changes

Tool N form

Project title:

Date: ___ / ___ / ______ **Inventory Functional Analysis Record Sheet (Tool N)** **Page: ___ / ___**
Plant: ________________ **Item: ________________** **Material: ________________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________** **Meeting #: ________**

Function	Critical parameter	Datum	Specific/shared	Volume	Ideas to minimize

Tool O form

Project title:

Date: ___ / ___ / ______ **Equipment Simplification Assessment Record Sheet (Tool O)** **Page:** ___ / ___
Plant: ________________ **Section:** ________________
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

Guideword	Item	Function	Options	Comments

Tool P form

Project title:

Date: ___ / ___ / ______ **Process Hazards Range Assessment Record Sheet (Tool P)** **Page: ___ / ___**

Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Material	Location/function	Inventory [Te]	Leak rate [kg/s]	Hazard type	Hazard range [m]	Affected area [m^2]	Comment/priority

Tool Q form

Project title:

Date: ___ / ___ / ______ **Plant Layout and Siting Assessment Record Sheet (Tool Q)** **Page: ___ / ___**
Plant: ________________ **Section: ________________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Guideword	Aspect of layout/siting	Options	Comments

Tool R form

Project title:

Date: ___ / ___ / ______ **Designing for Operation Assessment Record Sheet (Tool R)** **Page: ___ / ___**
Plant: ________________ **Section: ________________**
Author: ________________ **Proj. #: ________________** **Ref. #: ________**

Plant area	Task/aspect	Guideword	Options	Comments

The *INSET* Toolkit

INherent **S**HE **E**valuation **T**ool

Volume 2

The *INSIDE* Project Team Partners:

AEA Technology

Eutech Engineering Solutions

INBUREX

Kemira Agro

TNO

VTT Manufacturing Technology

The *INSIDE* Project

The *INSET* Toolkit

INherent **S**HE **E**valuation **T**ool

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The *INSET* Toolkit is divided into four parts which are presented in two volumes. Each volume contains two parts of the toolkit. Detailed contents of the four parts are given on the following pages.

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Part 4 – Supporting material for the tools

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1.2 Overall framework for hazard management in design, including ISHE management strategy
1.3 Classic ISHE conflicts
1.4 The *INSET* Toolkit
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2.2 Where should you start in the *INSET* Toolkit?
2.3 When should you use the tools?
2.4 How to find your way around the *INSET* Toolkit?

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H Record of foreseeable hazards
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Chemical hazardous properties classification table *(from Tool G)*

Blank tool forms

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1. PRESENTATION PACKAGE

This appendix contains overheads and notes on the *INSET* Toolkit which are intended to assist in presenting the toolkit to colleagues or management. The presentation was prepared using MS PowerPoint, and the computer file in question is included on the floppy disc which is part of the toolkit.

(The presentation is not inluded in this version of the Toolkit, but is contained within a stand alone Powerpoint file INSET Toolkit 3_1_pres.ppt)

2. IMPLEMENTATION IN YOUR ORGANIZATION

This appendix is concerned with suggestions and ideas that may be helpful in achieving an increased use of inherent SHE principles in your organization.

2.1 Integration of inherent SHE

Inherent SHE, as introduced in Chapter 1 of Part 1, and the importance of its application within the chemical process industry, is self-evident. The fact that it is not integrated as a primary aspect of consideration in the design of new chemical process facilities can be attributed to many factors, and one aim of the *INSIDE* Project was to rectify this anomaly.

From the preliminary stages of the *INSIDE* Project, various initiatives have been proposed that may encourage the integration of inherent SHE and improve the use of inherent SHE in industry. It has been recognized that, in practice, some form of systematic method would be needed to integrate inherent SHE into the development and design activities, and that this integration would have to start at a very early stage in a project to be worthwhile.

The *INSET* Toolkit has been developed to assist companies integrate inherent SHE into their organizations, initially as an awareness tool, but also as a guide to inherently safer solutions.

2.2 How to integrate inherent SHE into the development and design process

The incorporation of inherent SHE principles in the development and design stages of any project, although recognized as vitally important, is not usually rigorously applied. The reasons for this vary from lack of awareness of the benefits to the lack of tools and methodologies.

Various initiatives have been proposed and the findings to date highlight a number of current practices and ideas in industry that are helping to encourage the use of inherent SHE (ISHE) in its R&D and design teams. The fundamentals seem to be:

- management commitment and support to the adoption of ISHE and the implications this may have for training programmes, project organization, etc.
- introducing and maintaining a good level of awareness of the ISHE principles and applications amongst the chemists and design engineers.
- setting aside time in the development and design programme to identify and evaluate alternatives, recognizing that this should save time later by reducing the need for changes.
- providing opportunities for the chemists, designers and operators to discuss and analyse ideas at all stages of the development and design process.
- providing some methods or tools to help lateral thinking and encourage innovation.
- addressing SHE aspects in an integrated way to establish the trade-offs and conflicts these can bring.

Together, these activities should help foster a culture that rewards good innovation and clear thinking, and one which recognizes the importance of doing things well and early. It would also appear that these initiatives need to go hand-in-hand, and companies who have just tackled one or two of these together have found that it has not been very effective, either having limited effect or quickly losing impetus. Table 1 shows how to approach the various stages of hazard management, while Table 2 gives an overview of the general principles of ISHE.

Table 1 Overall approach to hazard management

<table>
<tr><th colspan="2">Approach</th><th>Stage</th></tr>
<tr><td colspan="2">Identify all hazards and causes of these
– materials, actions, conditions</td><td>IDENTIFY HAZARDS
↓</td></tr>
<tr><td colspan="2">Assess hazards*, their causes and effects and how these interact with the design</td><td>UNDERSTAND HAZARDS
↓</td></tr>
<tr><td rowspan="3">APPLY INHERENT SAFETY PRINCIPLES</td><td>Avoid or eliminate hazard by design</td><td>AVOID HAZARD
↓</td></tr>
<tr><td>Intensify, attenuate or substitute to reduce the severity of the hazard</td><td>REDUCE SEVERITY
↓</td></tr>
<tr><td>Simplify the process or plant to reduce the likelihood of the hazard occurring</td><td>REDUCE LIKELIHOOD
↓</td></tr>
<tr><td colspan="2">Use distance, or use sections of the plant itself as barriers, to segregate/protect people and emergency systems from effects of hazards</td><td>SEGREGATE
↓</td></tr>
<tr><td rowspan="2">APPLY "ADD-ON" SAFETY</td><td>Use safeguards that do not need initiation, and hence have high availability</td><td>APPLY PASSIVE SAFEGUARDS
↓</td></tr>
<tr><td>Use active systems, but note that these depend on timely hazard detection and initiation</td><td>APPLY ACTIVE SAFEGUARDS
↓</td></tr>
<tr><td colspan="2">Operator and maintenance procedures should be the last resort, especially for control and mitigation, where the chance of error or failure is high.</td><td>APPLY PROCEDURAL SAFEGUARDS
↓</td></tr>
<tr><td colspan="2">* Use the findings of the hazard assessment to estimate the risks, and target and implement inherent → segregation → add-on safeguards until risks are tolerable or as low as reasonably practicable (ALARP)</td><td>RISKS TOLERABLE/ALARP</td></tr>
</table>

2.3 How to implement ISHE into your organization

Implementation and integration of inherent SHE within your organization and its procedures is of paramount importance to the development of inherently safer plants. Mentioned previously as a fundamental aspect, the commitment of management is vital. Some of the more practical tips once commitment has been ensured include:

- having an enthusiastic senior manager appointed to "champion" ISHE.
- including ISHE in the safety introduction training package for new recruits.
- having regular informal "lunchtime sessions" on issues relevant to work, and occasionally including ISHE issues.
- including ISHE objectives in the kick-off meeting on new projects.
- asking for a statements at various stages of the project on how ISHE principles have been incorporated into the process route development, concept design and detailed design.
- including a review of ISHE as part of the end of project appraisal, and passing on any lessons or suggestions onto the design and development team.
- setting up a development team at the early stages of process development which includes an experienced process engineer and operator (preferably those who will go on to design and operate the plant), so design and operation implications can be discussed as the process develops.
- appointing a SHE specialist to each development and design project with the time and remit to co-ordinate SHE aspects and promote the adoption of ISHE.
- using check-lists or HAZOP style guidewords to identify process or design alternatives at various stages of each project. These could form part of the design SHE procedures, and take the form of formal study groups or be used by small teams or individuals as part of their ongoing work. Similarly some indices could be used to measure the improvement in inherent SHE, or to compare options.
- reviewing existing plants and processes to look for good examples of ISHE which can be copied, and to provide any evidence of benefits to support the case for ISHE.

This list is by no means exhaustive, but should give a flavour of how ISHE can be encouraged within your organization.

Table 2 The most common ISHE principles and their possible application

Principle: Eliminate or reduce the hazard at source	
Application	**Possible methods/examples**
Change to a less hazardous material.	Use less hazardous raw materials, reagents and utilities.
Use a safer form of the hazardous material.	Use hazardous "dust" as a slurry or in pellet form. Use a reactive chemical in a dilute or "safe" form. Use in a different state (vapour, liquid, solid, gel, paste).
Change to a less hazardous reaction.	Change the reaction, its feeds or reagents. Change the sequence or timing of the stages. Change the reaction conditions, temperature, pressure, pH, etc.
Modify the process or plant – to eliminate or reduce the hazard at source.	Provide sufficient heat transfer capability to prevent thermal runaway. Use in-line mixers in tube reactors, hence reduce chance of "mixer failure".
Modify the process or plant – to reduce the amount of hazardous waste products it produces.	Seek out processes which minimize the amount of waste they produce, and minimize the hazardous material in those wastes. Can these "wastes" be re-used, or changed so they can be re-used? – as another product, as feed to another process.
Modify the process or plant – to reduce the inventory of hazardous materials.	Generate hazardous raw materials on-site "on demand", or pipe them in from an adjacent facility. Use pipe reactors instead of pot reactors. Use continuous or semi-continuous processing rather than batch. Use equipment and unit operations that are compact. Minimize storage requirements.

Principle: Design the plant to make it more tolerant of failures – to withstand the hazards or reduce their effects at source	
Application	**Possible methods/examples**
Change the process conditions to reduce or dilute the effects of the hazard.	Avoid need for holding liquids above normal boiling point. Use refrigerated storage for liquified gases.
Modify design envelope to withstand hazards.	Design process to take maximum possible pressures, temperatures, acidity, levels, etc. *or* restrict pressures in feeds *or* change process parameters so the pressure cannot exceed the design pressure of the process. Limit utility supply conditions so that critical temperatures, heat transfer fluxes, etc. cannot be exceeded.
Improve the containment integrity.	Use all welded connections. Use double containment. Reduce the need for maintenance or other intervention activities. Reduce the number of possible leaks sites, or design the leak site and its location to minimize the leak rate (e.g. spiral wound gasket vs CAF gasket, 50 mm connection rather than 100 mm connection).

Principle: Design the process and plant to reduce the chance of the hazard occurring	
Application	**Possible methods/examples**
Make the plant less prone to failure.	Use simple, reliable, "fit for purpose" equipment. Ensure the plant and process is ergonomically designed to reduce chance of human error.
Design plant to be tolerant of failures.	Design the plant so no single failure causes a hazard (idea of defence in depth). Use smaller pipeline sizes so the leak rate from any failure is restricted.

Principle: Design to limit the consequences of the hazard	
Application	**Possible methods/examples**
Reduce the mobility (escape from containment) of the hazardous material.	Low-pressure non-volatile liquids will not travel as far as high-pressure vapours. Pellets or slurries will not spread as easily as dust.
Improve the means of detecting, controlling and retrieving hazards including unintentional releases.	Design the plant so the main hazards can be quickly identified. Provide suitable control and containment measures (e.g. vent capture systems, bunds/drains).
Design the process and treatment systems to reduce the impact of effluents and other intentional plant emissions.	Consider whether a given material is best discharged to the air, water, or land. Optimize the process and treatment options in an integrated way so the effluents produced are minimized (it could be better to use a process that produces more effluent but which can be effectively treated, rather than one that produces less effluent but which cannot be effectively treated).
Reduce the exposure of those at risk to the hazards.	Minimize handling and intervention requirements (e.g. by reducing the need for maintenance; using engineered handling, loading and unloading systems; using ventilation systems to prevent hazardous materials entering the workplace).
Locate the hazards away from sensitive targets.	Locate hazardous plant suitable distances from other plant areas, control rooms, workshops, offices and emergency access routes. Locate the site a suitable distance from public areas, environmentally sensitive areas, or other plants or installations with potential for escalation or hazardous interaction.

Principle: Control residual hazards as simply as possible	
Application	**Possible methods/examples**
Control of residual hazards – use passive rather than active systems.	Use control and emergency systems that do not need to be "turned on" to work.

Principle: Make add-on systems simpler and more effective	
Application	**Possible methods/examples**
Passive and active systems – make these inherently simpler/effective.	Keep systems simple and reliable. Minimize need for operator intervention.

3. *INSET* INDUSTRIAL TRIALS

This appendix summarizes the industrial trials which were carried out as part of the *INSIDE* Project to test the practicality and usefulness of the *INSET* Toolkit. The following three applications are reported:

- a series of trials on process development for small-scale batch-wise fine chemicals manufacture, by VTT Manufacturing Technology in conjunction with Kemira Agro,
- a trial on a plant design for large-scale continuous production of bulk chemicals, by Eutech Engineering Solutions in conjunction with an ICI business, and
- a small trial on a plant modification, by INBUREX with a German company.

3.1 An application on *INSET* Stages I and II from the fine chemicals industry

A series of trials have been carried out at Kemira Agro Oy's Espoo Research Centre, Finland. The trials were carried out to test the effectiveness of the *INSET* Toolkit to promote the adoption of inherently SHE alternatives during the chemistry route selection and evaluation stages of a project. This section summarizes the trials carried out and their findings.

The Espoo Research Centre is the Kemira Group's largest research site. The research centre's activities play an essential role not only within Kemira Agro, but also in the development of profitable business for the other divisions of the Kemira Group. Its objectives include the development of new products and production methods, improved use of raw materials, and environmental care. The research staff includes experts in organic and inorganic chemistry, biochemistry, biology, physical chemistry, physics, mathematics, polymer chemistry and agricultural sciences.

The trials were carried out by organic chemists and chemical engineers involved in the development of processes for Kemira Fine Chemicals Oy's fine chemicals plant located in Kokkola on the Finnish west coast. The work during these trials was led by a safety expert from VTT Manufacturing Technology. VTT is the largest research organization in the Nordic countries.

These trials, from the fine chemicals industry, show how the *INSET* Toolkit can be used from the earliest possible stage of process development, i.e. the selection of the chemical route to be tested and optimized in the process development laboratory, in order to come up with a process alternative that is (i) economical, (ii) leads to a product of the required quality, and (iii) which includes inherent SHE (ISHE) aspects within the chemistry of the process itself. The aim of the trials was on one hand to refine the methods proposed in the *INSET* Toolkit and on the other to demonstrate the usefulness of some of the tools. These trials comprised the assessment of route alternatives for three different organic compounds.

Applying *INSET* Stage I in practice to preliminary chemistry route selection

To achieve a basis for the integrated safe, environmentally responsible, economical and quality-oriented manufacturing of a desired chemical product, all the criteria relating to the manufacturing process and the product must be established. Usually, the product constraints are defined by the customer which, in turn, affects the inherent properties of the product. Besides the requirements set by the customers, many other criteria exist for every process development project. For example, the processes studied at Kemira were to be carried out in an existing plant, and consequently the plant itself placed certain constraints on the process alternative chosen.

As it may not always be clear to the chemist what the predefined criteria are for any given new project or product, it is useful to have a systematic way of collecting information on these to establish criteria for each process and provide the basis for the elimination of unfavourable process routes. A framework specifically developed for gathering this information is provided in Tool A, Detailed Constraints and Objectives Analysis. Ideally, the input from the management, the sales department, the plant, the maintenance department, and from safety, health and environmental experts, should be recorded on the Tool A forms. However, in the trials carried out at the Espoo Research Centre, these forms were filled in by an experienced synthesis chemist who knew the general and project-specific criteria set by the company as well as the relevant national legislation. Some of the constraints and objectives identified for the studied processes can be found in the examples given in Part 4 of the toolkit.

In Kemira, as in most – if not all – other industrial organizations, it is inevitable that only one (or a few) chemical routes can actually be tried out more thoroughly in the laboratory. It is, however, important that all possible chemical routes, no matter how difficult, unusual or esoteric some may at first seem, are identified and then evaluated with regards to SHE, ISHE and other criteria so that the most "promising" routes (about five) are selected for further evaluation and optimization. In some cases, tens of route ideas will easily be generated in a short time. Evaluation of the routes is often the most difficult task and this is where the experience and literature knowledge of the chemist comes into play. It is also where the *INSET* Toolkit can provide useful tools and guidance.

The information gathered from the previously mentioned sources was found to be quite varied with respect to both details and relevance for the particular projects at hand. Ideally, all identified reaction schemes should have been documented. In these trials, however, the chemists left the most unattractive routes undocumented. The suggested way of documenting the alternatives is presented in Tool C and the form in this Preliminary Chemistry Route Options Record Tool was found to be a useful and effective means to document the route options and draw out some of the inherent SHE aspects.

The trials clearly showed, however, that all the alternatives must be presented in a similar way to ensure that the decisions are not in any way biased due to inconsistent presentation of the data. There were even cases where simplifications of the detailed information that was available were needed in order to obtain comparable presentations. In some cases, alternatives were initially grouped together, thus reducing the amount of resources needed for the documentation.

During the iterative decision-making process the rejected alternatives were reassessed. A need for more detailed investigations/presentations for some of the alternatives arose at that stage. The Process Option Generation Tool (Tool B) would have provided a good basis for this, presenting a systematic way to challenge the alternatives that have been identified, but in the trials at Kemira, this tool was only used in some carefully selected areas.

The Preliminary Chemistry Route Rapid ISHE Evaluation Method (Tool D) was initially used to screen the alternatives. This consists of a standard set of questions regarding inherent SHE aspects of the process. These standard questions would normally be supplemented with questions that are deemed relevant to the specific project. However, supplementary questions were not added in the trials and consequently it was found that the compulsory questions were not sufficient to effectively rank the alternatives.

The more rigorous assessment method in Tool E (Preliminary Chemistry Route Detailed ISHE Evaluation Method) includes a challenging procedure which enables the more ISHE route alternatives to be identified. The recommended way of proceeding through Tool E was to initially only use the constraints criteria from Tool A.1. The use of the project objectives in addition to the constraints is left optional. In all cases studied here, the more comprehensive lists of objectives were required to make well-informed judgements and satisfactory conclusions in obtaining a set of realistic alternatives. The sole use of the list of constraints proved to not be limiting enough to help the elimination of alternatives.

The shortcomings of every alternative were assessed and solutions to improve the suggested process were sought. For example, a route alternative was not discarded if it merely involved a "black list" material as this substance may actually be substituted by a safer chemical or solvent, and the particular route alternative may then be more inherently safe than the others.

The alternatives that have not been eliminated were subsequently ranked to yield a candidate set of a few alternatives. It became obvious that it is not an easy task to assess the various alternative routes based solely on the information at hand at this stage, especially as the level of detail varies from one route to another. Since the criteria are mainly non-SHE issues at this stage, the *INSET* Toolkit can only address a fraction of all aspects that have to be considered during the decision-making process.

The results of the decision-making were summarized on the Dominant Alternatives Record (Tool D/Tool E). The tools enabled the reasoning behind the screening and ranking to be well documented in each case. In some cases, the reason for the rejection was also documented.
At the conclusion to *INSET* Stage I, the following documents had been prepared:
- lists of the constraints of the project (General Constraints of the Project Sheet and Project-Specific Constraints Sheet, Tool A.1)
- lists of the objectives of the project (General Objectives of the Project Sheet and Project-Specific Objectives Sheet, Tool A.2)
- modified route alternatives for the project (Process Option Generation Record Sheet, Tool B)
- a set of alternative synthesis routes and improved versions of these (Preliminary Chemistry Route Options Record, Tool C)
- a result sheet for the general set of question prompts (General Screening Questions Results Sheet, Tool D)
- an analysis matrix of the alternative routes with regard to the constraints and objectives of the project (Criteria Screening Matrix, Tool E)
- documented grounds for the decisions taken in selecting the candidate set of alternative routes (Dominant Alternatives Record, Tool E).

Applying *INSET* Stage II in practice to detailed chemistry route evaluation

The next task was to further reduce the number of candidate routes to one or two that could be taken to the laboratory for a more detailed examination. Considering the importance of the decision-making at this stage of the project, the necessity of having all the relevant information at hand became apparent.

Operation and design of the production plant in Kokkola contributes to the overall SHE performance of a process, and Kemira's chemist could not overlook this aspect even at this early stage. The complexity of a process alternative is usually determined by the operation steps, for example phase separations, recyclings with distillations, filtrations, washings, dryings. These require time and equipment, and so have a considerable influence on the production costs and the SHE aspects of a process. Alternatives can rapidly be analysed and compared when presented in the form of process block diagrams which include the reaction and operation steps. In the trials, these block diagrams/flowsheets were drawn by the chemists.

The diagram as described in Tool F, the Chemistry Route Block Diagram Record, is intended to show the supply, reaction equipment, etc. and the interconnectedness of the respective vessels (which could represent piping or other transference means). It was realized later in the trials that the same level of detail is needed for all alternatives in order to obtain comparative results.

In *INSET* Stage II, preliminary information on the chemicals and their hazardous reactions must be collected for each of the remaining alternative synthetic routes. The same was subsequently done for the corresponding engineering-modified alternatives that are generated. A general classification of chemical hazards from a SHE point of view was carried out to provide the basis for the assessment. Tool G, the Chemical Hazards Classification Method, was used for this. The properties of the chemicals and their mixtures were estimated if they were not otherwise available.

If possible, the evaluation of the routes should be carried out in a uniform way and by considering all aspects of every remaining alternative. In these trials, both the rapid screening tool and the more complex index tools were tested.

Should a rapid screening tool be sufficient at this stage, the simplistic Rapid ISHE Screening Method (Tool K) could be used. However, in these trials it became evident that the decisions had to be based on a more detailed analysis of the operations involved. Most of the ISHE Performance Indices in Tool I were found to be relevant and therefore used in the trials. Figure 1 shows the results from the first calculation of one of the indices, the Acute Toxic Hazards Index (Tool I.2), for the synthesis of 2-chloro-nicotinic acid from nicotinic acid.

The common experience was that a computer-based system would have drastically reduced the time needed for the calculations. It was also discovered that some of the results of the indices were not totally in line with the experience of the chemists involved in the trials. For instance, the toxicity of methanol was thought to be overemphasized by some of the indices (see Figure 1).

Project title: *CNA*							
Date: *26/ 03/ 1997* **ATHI: Acute Toxic Hazards Index (Tool I.2)** **Page:** *01 / 01* **Plant:** ____________ **Section:** __________ **Flowsheet #:** *_1 & 2__* **Revision:** *_1__* **Author:** ____________ **Proj. #:** __________ **Ref. #:** _______							
		Option A	**Option B**	**Option C**	**Option D**	**Option E**	**Option F**
A	Daily production [Te/day]	6	5	1.6			
B	Dominant material	NAO	$POCl_3$	MeOH			
C	Item/inventory [Te]	6	39	10.5			
D	Toxic Harm Factor (THF)	1	1	100			
E_a	Absolute ATHI = C × D	6	39	1050			
E_r	Relative ATHI = C × D / A	1	8	660			

Figure 1 Calculation of the Acute Toxic Hazards Index for the synthesis of 2-chloro-nicotinic acid from nicotinic acid

The qualitative part of the Multi-attribute ISHE Comparative Evaluation (Tool J) was subsequently used to pool the calculated indices in a way which allowed a direct comparison of the alternatives to be made.

Table 1 presents the results obtained from Tool J based on the index shown in Figure 1. Again, it can be seen in the last column that the tool based on the absolute index range gives a high score (4) for the process step where methanol is used. The tool based on the word picture gives a slightly lower score (3), but based on the assessment of the chemists the score should be even lower (2).

Table 1 Results from the use of Tool J on the process given in Figure 1

	Step A	**Step B**	**Step C**
Absolute ATHI (from Tool I.2)	6	39	1050
Qualitative inherent SHE evaluation (word picture)	2	3	3
Qualitative inherent SHE evaluation (index range)	1	2	4
Subjective score given by the chemists	1	3	2

Note The last row shows the subjective assessment made by the chemists taking part in the study.

Compared with the other indices the score obtained from the Fire and Explosion Hazards Index was found to be surprisingly low. The reason for this was not assessed.

In practice, it was shown that most process alternatives did not fulfil all the criteria set, and therefore, the shortcomings of every alternative needed to be challenged and solutions to improve the suggested process needed to be sought. The modified alternative should then again be compared with the previously best ranked alternative. Due to time constraints, the challenging and comparison was not carried out at this stage of the trials.

At the conclusion to *INSET* Stage II, the following additional documents had been prepared in these trials:

- a set of guideword-modified alternative routes for the project (Process Option Generation Record Sheet, Tool B)
- a preliminary process block diagram for each alternative (Tool F)
- chemical lists that include its function and comments (follows from Tool C) and the S, H, and E hazard classification (Tool G)
- Rapid ISHE Screening Method result sheets (Tool K)
- inherent S, H, and E performance indices evaluation result sheets (Tool I)
- Multi-attribute ISHE Comparative Evaluation result sheets (Tool J).

Lessons learnt

The screening and ranking of alternatives should be a fast and non-resource intensive method of reducing the basic set of alternatives to a feasible set of alternatives which will later be subjected to more formal scrutiny. By using the forms provided in the *INSET* Toolkit this procedure took longer than usual but can be justified by the improved documentation of available route alternatives. It is believed that the importance of an improved record-keeping is growing and may be required when quality assurance issues (e.g. ISO 9000, GMP) and pollution prevention issues (e.g. IPPC, BAT) are handled in the company.

Of the two ISHE evaluation methods suggested in the toolkit, Tool D turned out to be too general and needed to be complemented with more process-specific questions to reduce the amount of alternative routes significantly. The value of the alternative method, Tool E, depends on the degree of detail of the lists of "musts" and "wants" to which the route alternatives are compared.

It was shown that the block diagrams produced in Tool F were crucial for the subsequent analyses, and it was found to be important that the different alternatives are drawn carefully and with the same level of detail. This exercise was found to be very useful as it revealed operations that were not evident from the reaction sequence schemes. The experienced chemists taking part in the trials had no problems in drawing the initial versions of the preliminary block diagrams, but even then it is recommended that engineers are given an opportunity to make their comments on the diagram as early as possible. It is also very important to note that if the level of detail differs greatly from one route alternative to the other, the results of the indices calculated in Tool I may be misleading.

The use of the Chemical Function & Hazards Classification form (Tool G) is simple, but the "environment" classification may need to be reassessed when more information on the fate of chemicals in the environment becomes available.

As mentioned earlier, the calculation of the indices in Tool I took more time than was considered appropriate, and a computer-based system would have been preferred. Based on the limited amount of experience gained in these trials, it is too early to say if the indices give reliable results, but the first impression is that most of the scores reflected the view of the experienced chemists involved in the trials.

How to get the best from Stages I and II of the *INSET* Toolkit

The trials showed that the tools for Stages I and II of the *INSET* Toolkit provided a practical and useful means of addressing inherent SHE and recording the decision-making processes at Kemira's Espoo Research Centre. Documenting the data on the suggested forms substantially improves the transfer of information from the researchers in Espoo to the designers working for Kemira Engineering and the plant operators of Kemira Fine Chemicals.

Experience of using the tools can be used to refine the toolkit further. In the future, Kemira may customize the toolkit to reflect its own needs and the safety and environmental policy of the company. Due to the modular structure of the toolkit, company-specific tools can easily be added. It may be beneficial, if, for instance, traditional tools for the calculation of costs for the raw materials, the investment and the plant operation, were added to the toolkit (these were outside the scope of the *INSIDE* Project and were therefore not included in or developed for the *INSET* Toolkit).

With the Intranet capabilities now available, chemical companies such as Kemira may prefer that the record sheets used for documentation could be filled in by using the computer and stored in an electronic form. On the other hand, drawing reaction sequences and block diagrams can probably still be carried out faster on paper than by using a computer.

The *INSET* Toolkit has given the synthesis chemists at Kemira, for the first time, a set of tools that can be used at the early stages of a process development to systematically assess and record the SHE performance of the proposed chemical route and process.

3.2 Application of the *INSET* Toolkit for chemistry route selection for a large continuous processing plant

This section describes how the *INSET* toolkit as developed by the *INSIDE* project team was applied to a project within an ICI international business. It describes how individual tools were tailored into an overall process to suit the chemistry route screening exercise that was being carried out. Some of the difficulties in applying these techniques are identified and the ways in which these were overcome. Significant findings from the work are described plus the key learning points about applying inherent SHE principles to this type of project.

This work was carried out on a real project which is subject to commercial sensitivities. The information contained in this paper is therefore restricted to the inherent SHE process which was carried out. The learning points are however of a generic nature which would apply in most situations. The trials were carried out by development chemists and chemical engineers from the ICI business, led by a process SHE consultant from Eutech Engineering Solutions Ltd, a wholly owned subsidiary of ICI plc, who provide a range of engineering consultancy services.

The project

The ICI business involved are undertaking a fundamental review of the technology options for increasing the capacity for one of their main intermediate products. This is seen as a key project by the business, and a cross-functional team has been set up charged with clear objectives including a target date for completion of a budget estimate.

A number of factors such as capital costs and operating costs were considered as important issues on which the project team needed to deliver. The importance of safety, health and environmental (SHE) issues was also given a high prominence. This was partly due to ICI corporate standards requiring that inherent SHE factors should be considered early during a project life-cycle. The business also recognized that to maintain competitiveness in a world market with ever tightening legislation, plants being designed today would need to reach at least the most stringent world-wide standards. In areas such as environment impact where legislation is developing rapidly, the direction of change would need to be anticipated and taken into account.

Literature searches had been carried out to identify potential chemical routes, and this had revealed a number of options. The status of these ranged from full-scale proven processes through pilot plant scale to patented ideas, some with technology familiar to ICI and others less commercially available and potentially requiring considerable development effort.

Gaining commitment

Before attempting to carry out an inherent SHE assessment it was considered essential that commitment was first achieved at senior manager level, in order that time and resources are made available at the earliest opportunity in the project. On this occasion there was the benefit that the senior SHE manager for the ICI business was a firm supporter of inherent SHE principles and had been involved from the outset with the *INSIDE* project team.

With this senior support in place, a session was held with the project team to introduce the concepts of inherent SHE, describe the *INSET* Toolkit in outline and explore the ways in which these tools could be applied. This exercise proved to be very successful in gaining the commitment and co-operation of the project team, and identifying the most appropriate tools for the assessment. Key team members such as the development chemist and chemical engineer would play a key role in preparing information, and it was essential that they were fully committed to this work, by understanding the benefits that could be achieved.

Proposed process

Inherent SHE principles can be applied at most stages in a project life-cycle, although it is likely that the scale of the benefits will reduce as the design progresses and the degrees of freedom for change become more limited. Individual projects will vary widely in their starting points and the type of process technology involved.

For the above reasons the *INSET* Toolkit has been designed to be applied flexibly, and it is not anticipated that all tools would be required for a specific project. A process was developed which selected the most appropriate tools for this assessment, and combined these into an overall process which also identified the information which would be required in advance.

The team were initially very interested in Tool J, the multi-attribute ISHE comparison of the alternative chemistry routes, based on some earlier work in ICI using a similar technique. This tool produces semi-quantitative indices for a number of performance indicators allowing a comparison between options to be made. To carry out this exercise some detailed information is required for each option, such as main inventories and processing conditions. It was recognized that to achieve this level of detail considerable progress would need to be made along the development route, and opportunities for introducing alternative ISHE improvements may well be lost.

The *INSET* tools must be applied as early as possible to derive maximum benefit, but account needed to be taken of the level of information readily available at the early stages. The following process was proposed, recognizing that this may well require adaptation as the work progressed:

1. Using Tool C, prepare chemical route options records for each route, identifying the chemical conversion undertaken, the reaction conditions and the expected yield and selectivity of the reaction.
2. Using Tool G, prepare a list of all the chemicals involved in the process listed as reactants, solvents, products, wastes, catalysts, etc., and classify these materials on their hazard potential to safety, health or the environment.
3. By combining Tool A and Tool D, carry out a team analysis of the constraints and objectives for the project, and compare each process option with these constraints/objectives to identify any routes which could be eliminated at this stage.
4. For each chemistry route option, develop a block diagram showing the main process sections with processing conditions and estimates of dominant inventories. Indicate main flows into

and out of each block with flow rates and a breakdown of components by percentage present.
5. Using the guidewords and record sheets in Tool B, generate process options to improve inherent SHE by challenging each section and line on the block diagram. Consider if any options can be eliminated at this stage.
6. Prepare further information on each option such as dominant inventories, stream flow rates, boiling points, flash points, etc.
7. Using Tool I, calculate ISHE performance indices for each option and present the results using Tool J (Multi-attribute ISHE Comparative Evaluation). The objective is to aid the decision-making process by identifying the preferred process route, putting inherent SHE considerations alongside process economics.

Preparation challenges

In preparing the data a number of issues arose which needed to be addressed to avoid a lot of unnecessary work. The level of detail varied widely on the options under consideration, and it was necessary to bring these to a common standard. In general it was found that the level of detail in the technical literature was adequate at this stage.

There were a large number of chemicals involved which required classification of their hazards against risk phrases. It was necessary to restrict the list of chemicals to the significant streams, in general ignoring minor impurities. Laboratory chemical suppliers catalogues were found to be a good source of the risk phrases required to classify the chemical hazards.

Difficulties were found with the classification for environmental hazards, partly due to lack of information on the waste streams post-final treatment, and partly due to the risk phrases being incomplete descriptors of the hazard to the environment.

The block diagram records would be very detailed if broken down to each unit operation with flow rates on all the main process streams shown. It was decided to only show the main process sections and quantify only those streams which exited the process, which included all product, by-product, recycle and waste streams.

Tool A – Detailed constraints and objectives analysis

A brainstorming session was held to identify the constraints and objectives for the project. Constraints were defined as those issues which had to be addressed by the project, objectives as those issues which were important but could be traded off against other considerations. For each chemistry route option, each constraint and objective was considered and a decision made on whether the option was generally positive, negative or neutral relative to the other options. The results were recorded on the standard sheet with the tool, with supporting reasons for the decision.

This exercise proved of great value for the project team as it addressed issues beyond the scope of inherent SHE. Issues were categorized as company/project-critical or SHE-critical. The number of issues in the latter category indicated the importance of the inherent SHE approach.

The team leader acted as a facilitator for this exercise. A checklist of issues had been prepared in advance, partly based on Tool D; this was referred to at the end of the brainstorming session.

One of the process routes was shown to be the best known to ICI and therefore the easiest in terms of meeting time scales, but it had hazardous waste streams which would require careful consideration. A patented variation on this process gave a significant improvement but required technology not readily available to ICI, and an extended development time. Another route had relatively-low-hazard waste streams but was highly inefficient and involved a large internal recycle stream of flammable materials.

It was felt that the findings of the exercise were very valuable in focusing the thoughts of the team on the key issues, and recognizing the areas on each process which required further development. It is possible that in other situations a clear favourite would emerge at this stage, avoiding the need to progress to a more detailed level on a number of alternatives. For example, it may be identified that a waste stream contains a black-listed substance which cannot be avoided, making this route a liability which would give problems with the anticipated tightening legislation.

Tool B – Process option generation

Each chemistry route option was reviewed in turn, initially challenging all the waste streams from the process to identify ways in which these could be avoided, substituted for a less hazardous alternative or reduced in size. Where available, more detailed process flow diagrams were used as a reference document to identify where the streams originated and help with generating options for improvements. Finally, each block was considered to identify the dominant inventory of hazardous material and consider ways in which this could be reduced.

The results of this exercise were recorded in terms of their separate effects on safety, health and environment as ++, +, 0, – or ––. In a number of cases there were trade-offs where for example a positive effect on the environment was offset by a negative effect on safety. As an example, a change in catalyst technology eliminated a waste stream and the need for handling of a hazardous powder catalyst, but required the process to be operated at considerably higher pressure and temperatures.

The focus on waste streams proved to be very effective, as it identified some of the difficult treatment requirements which would need solutions for the process to be viable. On this project the capital cost estimates in the process economics comparison had not included for these treatment facilities on one of the options. The needs for positioning of the plant close to the sea for instance for waste disposal, or close to integrated plants to take by-products or recycle streams was also identified. Some of the key improvements to the process to reduce wastes at source were also identified.

It was felt by the project team that the exercise had identified and prioritized the development work which was required to optimize the ISHE performance. It was stated by the project leader that objectives for the team members for the next year had been set by the process.

Next steps

The analysis carried out to date has been done on a sub-selection of the possible chemistry options. Having proven the value of the *INSET* tools, the process will be repeated on all the options to see if a clear favourite route can be established. If none or only a few of the options can be eliminated at this stage, the next step will be to use Tools I and J as planned.

It is clear that the process being followed has a number of decision points at which a favoured route may emerge, dependent on the results of the assessments. If a favourite cannot be established, then more detailed information needs to be gathered on the range of alternatives that remain. This methodology clearly makes sense in terms of minimizing the amount of work, but does require an early start to the process.

Once a route has been established as the favourite by the screening process, further tools from the *INSET* Toolkit can be used to improve the inherent SHE performance, by challenging the function of each unit operation and looking in particular for reductions in inventory.

Key learning points

1. It is important to make a start on the inherent SHE process as soon as possible to get maximum benefit. If you wait while development of the process is carried out to produce more detailed information, the opportunities for improvement will pass.

2. It is a good idea to map out a process at the start to give an idea of the path to be followed, but recognize that this may require adaptation based on the findings. Use the process to help, don't become a slave to the process.

3. At the early stages there are complex issues involved in identifying which process options are preferred. The tools for such situations should be simple and act as an assist to decision-making. Elaborate tools which go into excess detail are likely to cause further confusion.

4. In most practical situations there will be a vast difference between the levels of detail on the process options being considered. It is important to anticipate this and to ensure that all options are brought to a similar level of detail to allow meaningful comparisons to be made.

5. The process described here involves key individuals such as the development chemist and process engineer in considerable extra work at this early stage. The commitment to the process is vital for its success and there needs to be an appreciation that the effort will lead to much greater savings later. This is achieved by avoiding the need for re-design or design of systems which could have been avoided.

6. Once established as a process it can be repeated for further chemistry route options which may only appear later in the project. A consistent approach can be taken, where records are kept of the key issues at each stage. These records are likely to be extremely valuable if later on in the project government agencies require evidence that the best available technology has been selected.

7. Highlighting the key issues on the chemistry route assists in dealings with technology licensers or in-house company experts, by helping to ensure that the correct questions are asked. Research work can also be targeted at solving the main concerns identified.

8. Whereas decisions on process options are usually dominated by economic factors at the early stages, these techniques allow the SHE factors to be considered in a structured way. It was felt that the exercise also allowed a more balanced estimate of plant costs to be made, allowing for example for equivalent levels of waste treatment between options. It was considered that the improvements identified would generally reduce capital and operating costs by the focus on elimination, avoidance and reduction.

9. The focus of this exercise was much greater on environmental issues than safety and health issues. This was considered to be consistent with the current pressures exerted on the process industry, and reflects a perceived over-emphasis on safety and health in the past. Design of process plant is generally well-developed in controlling the hazards due to flammable or toxic materials, but less so with minimizing the environmental impact.

10. The project team felt that the level of data collection for the tools was appropriate and had considerable benefit in helping the team to identify and understand the hazards. They were convinced of the value of the methodology, and this should allow continuing efforts to be made throughout the project cycle to apply inherent SHE principles.

11. In conclusion the team would definitely use the techniques on future projects, and cited further benefits such as improved communication between the project team members and greater opportunity for innovation and ideas generation using the structured approach in the toolkit.

3.3 Application of the *INSET* Toolkit to a process upgrade

A small trial of the *INSET* Toolkit was carried out during the design of a new unit to improve the throughput of a process for the manufacture of aluminium alkyls. Most of the major decisions relating to the choice of unit operation and process conditions had already been taken, but the toolkit was used successfully to optimize some of the more detailed aspects of the design.

Situation

A continuous process for the manufacture of aluminium alkyls involved a purification stage in which the process stream was distilled under vacuum to produce pure product using a pot boiler. The residues from the distillation are recycled.

Aluminium alkyls are extremely hazardous. They are spontaneously flammable in air, react violently with water to form hydrogen, and are also prone to decomposition at elevated temperatures yielding reactive aluminium. During the distillation phase, deposits are formed in the boiler and column which have to be manually removed. This is an extremely hazardous operation which is carried out after steaming in an attempt to passivate the residues. This cleaning process involves significant down-time and to improve throughput a replacement distillation unit is being designed.

It had already been decided to use an evaporator rather than a pot boiler, an intrinsically much safer alternative. For the same throughput, the evaporator has a lower inventory and residence time and operates with lower heating medium and process temperatures. The lower temperature and shorter residence time will further minimize any decomposition of the product and the design will help prevent the deposition of solid residues and thus reduce the need for frequent cleanouts.

Preliminary plant drawings were available, and these were used as the basis for the trial. In an attempt to see if the inherent SHE aspects of the proposed design could be further improved, parts of Tool N (Equipment Inventory Functional Analysis Method) and Tool O (Equipment Simplification Guide) were used to question and develop alternatives in a meeting with the process engineer and the plant safety specialists.

Outcome

By questioning both the function of the individual plant items and also the reason for the inventories involved it was found that:

- The quantity of the flammable heating medium had been left the same as was used for the pot boiler. This could be significantly reduced considering the demand of the evaporator.
- The possibility of using direct condensation as the first condensation stage rather than traditional tube condensor would be investigated. This would further reduce the likelihood of deposit formation and subsequent need for removal.

- Connections would be provided to allow the immediate introduction of nitrogen in the event of a process upset.
- The design strength of the complete unit would be slightly increased to allow it to be completely flooded with dilute alkali solution. This is one of the few certain methods to deactivate the deposits before they are manually removed.

Conclusions

This limited trial demonstrated the practicality, flexibility and adaptability of the *INSET* Toolkit, and showed how it can be used effectively to challenge the basis of design and help identify "inherently better" ways of achieving the design function. It also showed the benefits of applying the *INSET* Toolkit to plant modifications, even fairly late on in the design stages. Use of the toolkit enables a number of significant improvements to be made which should improve the safety of the unit and improve plant operability and availability.

4. INHERENT SHE: EXAMPLES & SUGGESTED FURTHER READING

4.1 List of ideas and examples

A list of inherent SHE ideas and examples, as found in the literature, is given below. They are classified according to the four *INSET* stages:

- Stage I: Chemistry route selection,
- Stage II: Chemistry route detailed evaluation,
- Stage III: Process design optimization, and
- Stage IV: Process plant design,

and within each stage according to the following ISHE principles:

- substitution,
- intensification,
- moderation,
- simplification, and
- segregation.

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Stage I – Substitution	
1	Replace combustible solvents with non-combustible ones.
1	Replace anhydrous ammonia with aqueous ammonia.
1	Replace anhydrous hydrochloric acid with aqueous hydrochloric acid.
1	Replace oleum with sulphuric acid.
1	Replace concentrated fuming nitric acid with dilute nitric acid.
1	Replace dry benzoyl peroxide with wet benzoyl peroxide.
3	Choose processes with wastes that are biodegradable.

Stage II – Substitution	
1	Reduce or eliminate the need for solvents, diluents or other "carriers".
1	Can valuable by-products be recovered from waste streams?
2	Methyl methacrylate (MMA) production alternatives – comparison of inherent safety of these, see this reference for comparison of six alternative routes.
3	Replace chlorine gas with common salt or chlorate.
3	Replace catalysts based on heavy metals with homogeneous catalysts without heavy metals to reduce effluent and disposal problems.
4	Check that changes to one part of a process do not reduce hazards at the expense of increased hazards elsewhere, e.g. at feed stock manufacturers or product finishing.
4	Replace hydrogen peroxide (hazardous and problematic) with air (cheap and stable) and a catalyst for oxidation reactions.
4	Gaseous hydrogen may be a safer alternative to hydrazine for reduction reactions in some situations where catalyst failures or other problems could lead to hydrazine accumulation.
4	Use high boiling point solvents to prevent these boiling off if the reaction runs away (e.g. toluene instead of acetone).
6	Replace volatile organic solvents and cleaning agents with less volatile aqueous-based solvents/cleaning agents.
7	Replace flammable solvents with non-flammable ones.
9	Use carbon dioxide to control the pH of water rather than a conventional acid (e.g. sulphuric). This has the advantage that the solution cannot be overdosed since any excess carbon dioxide would not dissolve.
9	Consider the use of electro-chemistry methods of treating toxic wastes to render them harmless.
13	Replace toxic or flammable heat transfer media with non-hazardous ones such as water or steam.
19	Use magnesium hydroxide slurry instead of concentrated sodium hydroxide solution to control pH. Sodium hydroxide is much more hazardous to store and handle.
19	Transport methanol instead of methane, ethylene dibromide instead of bromine, and ethyl benzene instead of ethylene.
24	Would the use of high-purity feeds and reagents avoid or reduce any hazards or the need for additional processing, e.g. reduce the chance of runaway, or reduce the amount of wastes produced, or simplify waste treatment?
Stage II – Intensification	
1	Replace batch operations with continuous or semi-continuous operations.
1	Replace co-current operations with counter-current operations.
2	Use high-yield reactions that can go to completion to minimize recycle and wastes.
3	Replace pot reactors with more efficient electrochemical reactors, fuel cells, pressure swing units, temperature swing units or membrane units.
5	Keep energy densities low in reactors by avoiding unnecessary accumulation of exothermically reacting compounds or by increasing heat capacity.
6	Recycle solvents by recovering by-products/impurities from them. These by-products often have value in themselves as feeds to other processes or as products.
13	Reduce inventories by making the reaction more rapid (reduce residence time) and with improved conversion (reduced recycle). Large recycles and residence times are indicators of an inefficient process.

Stage II – Moderation	
1	Design washing operations to minimize the waste produced. Can this waste be fed back into the process?
1	Would increasing the concentration of by-products in waste streams make the recovery of these more feasible?
3	Consider carrying out exothermic gas phase reactions in modified turbines – to extract the energy as electricity/power.
4	Optimize reagent addition times and profiles to exothermic reactions so that loss of cooling would not lead to thermal runaway.
4	Ensure external heat sources or heat transfer media are not at temperatures which could initiate exothermic decomposition of the reactor contents.
5	Use low boiling point/volatile solvents or other reaction components in situations where these could boil off if the reaction temperature increased above normal, providing a means of evaporative cooling to slow down any runaway. Solvents could be selected to give the appropriate boiling point. Limitations to this method are any resulting pressure rise or loss of vacuum due to vaporization, the effect this may have on the boiling point, and dealing with this material in the reactor vent system.
5	Use variable feed rates to reactors to allow the reaction to progress quickly but avoiding triggering thermal runaway (the maximum safe addition rate will change as the reaction progresses, and may be especially critical during the middle stages when the heat transfer capacity limits the rate at which the reaction should be allowed to proceed). If a variable feed rate is not practicable, the feed could be controlled in several time steps, each of a different but fixed feed rate.
7	Use materials at low concentrations to reduce their hazardous effects.
7	Use very volatile substances dissolved in solution to reduce vaporization.
7	Where very hazardous substances are involved, consider providing some means of chemically converting any excess material to a safer form.
7	Ensure the compatibility of feedstocks.
9	Add solid feeds to processes as slurries to reduce manual handling (or keep it to a specially designed reagent make-up area) and avoid the need to manually discharge material into the reactor or main process.
10	Use explosive powders in the form of slurries to ease handling and reduce chance of dust explosion.
10	Use reactants in dilute form to provide better reaction control and reduce the chance of runaway.
13	Can the reaction temperature be lowered to make runaway less likely?
13	Can we lower the temperature to below the material's atmospheric boiling point, or dilute it in a solvent to make any leaks less of a problem?
13	Use materials and services below their boiling point to prevent phase changes.
21	Consider the following options for effluent treatment: reduction, attenuation (e.g. noise – acoustic covers), regeneration, recycling, absorption, adsorption, neutralization, biotreatment, combustion (consider effects of combustion products), dilution (with air or water), or dumping.
Stage II – Simplification	
1	Recycle "waste" streams, back into the process or as feed to another process.
2	Reduce the number of processing steps.
2	Reduce the number of reaction stages.
4	Consider changing the sequence of addition of the initial reactor charge and subsequent reagents to make the process safer in the event of cooling, heating or mixing failure.
Stage II – Simplification (cont'd)	
4	Use catalysts that become deactivated under process fault conditions, where this would bring the

	reaction to a halt safely.
13	Is it possible to mix (some or all) reactants together thoroughly under conditions such that the reaction cannot proceed, and then initiate the reaction (e.g. by raising the temperature or pressure, or by adding a key catalyst or final ingredient)? This could ensure better reaction or conversion by ensuring good mixing. If the conversion is high, there will be less need to recycle and less effluent to deal with.

Stage III – Substitution	
5	Avoid the use of utilities and services fluids that could react dangerously with the process fluids.
5	Avoid the use of materials in the process that could react dangerously with common contaminants, e.g. air, nitrogen, water, steam, iron oxide (rust), oils, greases or hydraulic fluids.
6	Replace steel pipe with glass-lined or plastic-lined pipe for corrosive duty.
6	Replace conventional pumps with canned motor or sealless pumps.
6	Use filter bags made of conducting material or with built-in metallic fibres to prevent the build-up of static electricity.
8	Consider the use of direct steam injection for heating of aqueous-based fluids, where contamination by heat transfer fluids (such as oils) could be a problem, and the resulting dilution is acceptable. The steam could also be used via an ejector to heat and transfer the material, or to provide the pumping power to circulate and mix the contents as during the injection heating period (use in-vessel ejector).
8	Replace tray columns for distillation and separation with packed columns or film trays to reduce the liquid inventory (hold-up per theoretical stage for conventional tray is 40-100 mm, for packed column 30-60 mm and for film tray less than 20 mm).
12	Silica gel was used to replace carbon as an absorber for the purification of helium. The silica was less efficient, but would not explode if it absorbed oxygen (this change was made following an incident involving a carbon bed).
13	Could liquified nitrogen or carbon dioxide be used as a refrigerant rather than ammonia, hydrocarbons or fluorinated hydrocarbons?
13	Replace pumps with gravity flow or compressed air pressurization (air lifts) or ejectors, especially if the material is subject to degradation or can present a shock hazard when handled roughly.
Stage III – Intensification	
1	Replace distillation columns or continuous still pots with wiped film stills.
1	Replace extraction columns with centrifugal extractors.
1	Replace tray dryers with flash dryers.
1	Replace stirred tank reactors with plug-flow reactors.
1	Replace mixing vessels with in-line mixers.
1	Replace liquid feeds with gas feeds in pipework or pipelines to reduce the inventory and leak rate if a leak occurs.
1	Replace hazardous material imports and storage with in-situ production on demand.
2	Use a high-pressure, low-inventory equipment/pipework/reactor *or* low-pressure, high-inventory equipment/pipework/reactor. A "compromise" design of medium inventory and pressure gives the worst leak scenario.
3	Replace conventional separation units with high-g units (rotating, cyclonic, fluidic etc).
3	Replace shell and tube exchangers with plate and "compact" heat exchangers.
3	Optimize the size of loads for transportation taking account of the hazards and containment/packaging options (large bulk tanker or drum or small concentrated packages).
3	Replace mixer-settler trains with a counter-current packed column to reduce inventory and the number of interface control units required.
3	Replace conventional packed columns with pulsed columns or compact fluidic devices to improve mass transfer and reduce inventory.

Stage III – Intensification (cont'd)	
3	Use membrane technology such at ICI's FM21sp™ to generate chlorine on demand from common salt.
4	Use a jet mixing device for the rapid mixing and reaction of hazardous materials (as for nitroglycerine manufacture using glycerine, nitric acid and sulphuric acid) to minimize the inventory and ensure rapid progression of the reaction.
5	Use back mixing devices to ensure good mixing and distribution (avoid hot spots) in plug-flow reactors.
7	Reduce need for storage and transport of hazardous materials.
8	Consider replacing distillation and separation columns with membrane separation or liquid-liquid extraction (these may need larger inventories, but can often be carried out at ambient pressures or temperatures).
8	Can two columns be combined into one to reduce (halve) the inventory held in the bottom, bottoms pumps, reboiler and condenser.
9	Replace pot reactors with tube reactors.
9	Replace conventional heat exchangers with "printed circuit" type etched plate exchangers.
10	Replace high-pressure liquid phase reactors with vapour reactors to lower the inventory and potential leak rate.
11	The inventory of a pot reactor for gas-liquid reaction was reduced by using a down-pumping impeller to draw gas into the liquid from the gas phase above the liquid, rather than using conventional sparging. The reaction was more efficient because any excess gas was recirculated by the impeller system back into the liquid.
11	Vortex mixing can reduce the inventory of membrane separators.
11	A centrifugal fluidized bed drier contains lower inventories than a conventional drier.
11	Can the need for buffer storage be eliminated or reduced by providing more reliable plant, better planned inspections or adopting "just in time" repair strategies?
12	Use thin-film evaporators instead of conventional evaporators to reduce inventory.
13	Reduce storage inventory by increasing plant availability.
13	Reduce storage inventory by manufacturing raw material on site or using a product already on site.
13	Combine reaction steps to avoid the need for intermediate storage.
20	Design process systems so they can be rapidly isolated in an emergency, with only small locked-in inventories.
22	Replace conventional oily water clean-up systems with hydrocyclones to reduce inventory by an order of magnitude. Hydrocyclones could also be used in other applications for physical separation based on density difference.
23	Consider using fluidic contactors for solvent recovery, gas cleaning, distillation and steam stripping. These are simpler and more compact than conventional columns, with typically one fifth the active volume of a column, and no need for any packing.
Stage III – Moderation	
1	Limit maximum and minimum temperatures for equipment containing material which becomes unstable above or below a given temperature.
1	Design equipment to take maximum possible pressure.
1	Design equipment to contain materials if temperature control fails and contents reach ambient or surrounding process temperature.
Stage III – Moderation (cont'd)	
1	Divide up multi-step processes, where different steps are carried out at various sites, to minimize the need to transport hazardous materials.
5	Recirculating temperature-controlled fluid heat transfer systems try to bring the process to the

	same temperature, and can provide heating or cooling (so for example if the process temperature goes too high, the "heating" system would cool the process and limit the temperature excursion).
5	Replace steam or electrical heat transfer/heating systems with those based on temperature-controlled liquid recirculation in cases where it is important to keep the process within a narrow temperature range.
6	Use high humidity (by steam injection) to dissipate static electricity build-up on dust particles in air.
6	Avoid the need for direct contact by, or exposure of, operators to hazardous materials or operations by designing for automatic or remote operation.
7	Use inert fluid heat transfer media to transfer heat between two streams that may cause a hazard if they were to come into contact (i.e. use secondary heat transfer system rather than direct contact in the same exchanger).
7	Use vent capture systems such as blowdown tanks to retain material from relief vents.
10	Hold liquified gases at ambient pressure by use of refrigeration.
13	Store materials at low pressure and temperature to minimize the potential leak rate.
13	Store materials in a different chemical or physical form to reduce the hazard (e.g. dust as slurry or solid).
13	Limit temperature rises by using lower temperature heating media.
13	Design vessels to withstand the maximum foreseeable pressure and avoid the need for a relief vent system.
13	Design pipework and downstream tanks to withstand pump closed-head delivery pressure so as to avoid the need for a relief valve or kick-back line.
13	Design vessels in a train to take the full upstream pressure, and so avoid the need for several pressure relief systems.
13	Design vessels to withstand full vacuum where this is a problem, and avoid the need for a vacuum relief system (these can draw air into systems containing flammable materials, and even nitrogen systems can fail).
13	Select materials of construction that can withstand both normal and deviation conditions such as high temperature, acidity, concentration, and contamination by other materials in the process.
17	Design reactors with excess cooling capacity to maintain sufficient heat transfer even when circulation fails (i.e. design to cool by natural convection).
17	Make the heat capacity of the reactor high to slow down any heat rise so it can be detected early enough to control it.
19	Refrigerated storage of liquified gases or highly volatile liquids is generally safer than pressurized storage since the consequences of a leak are greatly reduced. However in some situations refrigeration may pose some material integrity problems and mean that the chance of a leak could be high, in this case pressurized storage at ambient temperature may be preferable.
Stage III – Simplification	
1	Replace a multipurpose vessel with separate specific function vessels to reduce complexity.
5	Electrical heaters can deliver heat at any temperature and so provide a controllable source of heat, but they cannot cool.

Stage III – Simplification (cont'd)	
5	Steam heaters will deliver heat up to a given temperature (which may be above its saturation temperature).
5	Avoid dead ends or other dead spots/poorly mixed areas in reactors, pipework or buffer storage where heat accumulation could occur triggering thermal decomposition or runaway.
7	Carefully match plant section capacities, modes of operation, turndown ratios, and availabilities to minimize or eliminate the need for intermediate buffer storage.
8	Use jet mixing nozzles to rapidly mix hazardous materials, and to provide an inherent means of ensuring one material can only flow if the other is, and for keeping the ratio of one flow to another approximately constant. In an ejector the suction side will only flow when the pressure side is flowing, and the flow rate of the pressure side fluid also determines the suction side flow.
9	Could gas required at pressure be produced at pressure to avoid the need for gas compression equipment which is prone to leaks and need a lot of maintenance.
13	Internal heat transfer systems (e.g. cooling coil inside a vessel) can be more efficient than external heat exchange systems, and have the advantage that any leak from the system is contained within the vessel.
14	Use fluidic pumping devices since they have no moving parts, no seals and can be welded into the pipework.
15	Challenge the need for sampling. Sample points are hazardous and a potential leak site. Can the sampling arrangement be designed to eliminate the need for contact between the operator and the material, and prevent the material from escaping to atmosphere?
16	Design the reactor or main process vessel to withstand overfilling/overflow and avoid the need for a separate overflow vessel or catchpot.
19	Reducing the inventory of storage tanks may have little effect on safety. Leaks are more likely from pipework and fittings, or from the process (these may also be more hazardous due to higher temperatures and pressures). Time spent looking at the process and piping will be of most benefit. It may be better to have a few large tanks rather than lots of smaller ones, since this may reduce the likelihood of a leak.
20	Select materials of construction that will not fail suddenly or catastrophically.
24	Design the plant to avoid undesired backflow or syphoning, by using height, syphon breaks, anti-syphon loops.

Stage IV – Substitution	
12	In cryogenic operations brass and aluminium packings can ignite in the presence of oxygen, copper will not.
Stage IV – Intensification	
8	Use a narrow bottom on distillation or separation columns to reduce the liquid inventory (this practice is often used where the product is susceptible to degradation).
8	Consider putting the bottoms pump, condenser and reboiler inside a distillation or separation column to reduce the liquid inventory by taking up space otherwise occupied by liquid. This also reduces the potential leak sites since this equipment is now inside the main column pressure vessel.
24	Reduce pipework inventories by reducing the line length and diameter but note that small bore pipework, less than 25 or 50 mm diameter, is more vulnerable to damage than large pipework.
Stage IV – Moderation	
7	Design pressure-containing equipment so that it "leaks before breaks".
7	Provide double containment with interspace monitoring for hazardous materials, especially if leaks may not be otherwise easily detected, such as from the base of underground or skirted tanks.
10	Design tanks or other containment with engineered weak seams or sections to ensure that failures result in the least damage or spillage (e.g. weak tank roof seams so lid fails rather than seams below the liquid level, preventing failure causing a liquid spill).
14	Use fully flooded drains for flammable materials as these have no vapour space and so are less likely to suffer an explosion.
14	Use submerged pumps to avoid the need for pump rooms (any leaks just go back into the surrounding liquid).
19	Design flammable liquid storage so spills and leaks do not accumulate under the tanks or other process equipment to reduce the chance of an escalating fire.
19	Consider totally enclosing toxics plant to prevent leaks to the atmosphere, especially if the materials cannot catch fire or explode.
19	Consider the use of double-wall containment to reduce the chance of leaks. Interspace monitoring allows timely detection of inner-wall leaks.
19	Ensure the venting of explosions or overpressure is routed to a "safe" area where it cannot cause further damage.
24	Use deep drains and bunds for volatile materials to minimize the open surface of any spill and so reduce evaporation/dispersion.
Stage IV – Simplification	
3	Minimize the need for flanges, gaskets and other connections that present potential leak sites.
7	Replace conventional valves with bellow valves to reduce the chance of leaks.
7	Replace conventional pumps with canned motor or magnetically coupled pumps.
7	Use all (or mainly) welded connection pipework to reduce the number of potential leak sites (and maintenance requirements).
7	Ensure systems are of "fail-safe design".
7	Design and install plant and instrumentation to avoid the possibility of confusion or ambiguity during connection or operational monitoring of the plant status.

Stage IV – Simplification (cont'd)	
9	Place valves or other equipment that needs to be operated at the same time or in careful sequence next to each other so they can be carried out by the same person (from a case where a valve on one floor had to be operated at the same time as one on another floor, which needed two people and had to rely on good communications between these two people).
10	Use fixed pipework rather than flexible hoses for hazardous materials to reduce chance of a leak due to hoe or coupling failure or operator error.
10	Challenge the need for installed spares and associated piping, valves, etc., and the need for by-passes and instrumentation – hence reduce complexity and the number of potential leak sites.
10	Ensure non-return valves (check valves) and other directional equipment clearly shows the correct orientation so as to ensure they are not fitted the wrong way around.
10	Replace conventional gaskets with high-integrity gaskets such as spiral wound or ring-tied joints, or better still use a welded connection to reduce the potential for, and size of, any leaks.
10	Beplace expansion bellows with expansion loops which are more tolerant of poor installation and need less maintenance.
10	Use bolted joints in preference to quick release couplings, as these give the opportunity to remake the joint if the plant is still pressurized when the joint is opened (better chance of safe recovery). Some types of quick release coupling can also give a "second chance" for recovery if the line is pressurized when it is opened up.
15	Use valves which clearly show whether they are open or shut (e.g. rising spindle, ball valve with tee handle).
15	Use spectacle blinds rather than simple line blanks since these show whether the line is open or blanked/restricted.
25	Avoid the use of sight glasses and other weak links in the containment.
25	Design vessel inlets to avoid splash when flammable liquids are involved which can generate static electricity (e.g. by dipping the inlet line below the liquid level – but take care to make sure this cannot back-syphon).
26	Try to avoid the need to store large quantities of materials which could form strata or set up thermal layers. These can "roll over" in certain conditions, placing stresses on a tank which could cause it to rupture.
Stage IV – Segregation	
7	Use good plant siting and layout to reduce risks to people and other plants.
10	Build plants handling explosive or flammable materials in the open to allow leaks to safely disperse (you need several tons to produce an explosion in an open area compared with perhaps a few kilograms in a confined building). This option may not be suitable for materials that are also very toxic or damaging to the environment at even low concentrations.
18	Locate loading and unloading areas away from the main process inventories.
18	Consider the slope of the ground and the prevailing wind direction when laying out the plant, as these will affect the dispersion and spread of any leaks.
19	Take account of emergency planning and response requirements in the original plant design and layout.
19	Locate plants away from centres of population or environmentally sensitive areas.
25	Use buffer zones in the plant layout to protect people and the environment from the effects of hazards (these could be open spaces or low-hazard plant such as non-essential services and utilities).

Part 3

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5. INFORMATION ON DATABASES

Major databases that contain information on chemical synthesis routes are listed in Table 1. Information regarding the use of patented materials and methods is now, more than ever, a very important aspect in the search for new chemicals and synthesis routes. Table 1 also lists various databases which allow the chemist to find previously patented synthetic routes as well as information regarding patent restrictions.

The use of "Information Services" providers who have experience at searching these massive databases may provide an efficient means of accessing the required data.

These services, amongst others, may be available directly to the chemist if the organization has links to the Internet. Sites providing this type of information and on how to access it include http://www.fiz-karlsruhe.de/ which has all the necessary information you need about the **STN®** databases, and http://info.cas.org/ which provides quite an extensive amount of information about the **CAS®** databases. Derwent, the "scientific and patent information" people also have valuable information and links available at http://www.derwent.co.uk/.

Table 1 A wealth of information is available from various database sources

Category	Comments	Information on types
Databases that contain chemical syntheses	These databases are commonly and most efficiently searched using electronic methods, although GMELIN, BEILSTEIN and CHEMICAL ABSTRACTS are available in paper-based form.	ChemInformRX GMELIN BEILSTEIN CHEMICAL ABSTRACTS (CA) CHEMICAL ABSTRACTS PLUS (CAplus) CASREACT CHEMREACT (and STS – Synthesis Tree Search) ORAC (Organic Reactions Accessed by Computer)
Patent databases	Electronic searching has made these databases very accessible.	PATOSEP WORLD PATENT INDEX INPADOC (EPO) ESPACE (EPO) INPAMONITOR MARPAT JAPIO CLAIMS
Chemical accidents	Reports of major chemical accidents.	FACTS MHIDAS
Chemical properties	MSDSs are widely available in electronic form nowadays.	See Table 2.

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Many other services are also currently available via the Internet, although with varying degrees of usefulness. Due to the dynamic nature of the Internet/WWW, however, sites that were available one day may not be valid the next. Upon finding a particularly useful site, it is very important to "bookmark" it for future reference. The Internet provides a rich source of chemical information in the form of MSDSs. Further background information is supplied in Appendix 7.

The open literature also provides the chemist with a wealth of synthesis information via journals and text books. The advent of receiving journals electronically will provide the chemist with access to novel syntheses even sooner than before, although much of the older information will probably remain available only in the literature.

Various databases that allow the chemist to search many journals for these possible new production route alternatives are now becoming available. CAS SciFinder and KR ScienceBase are perhaps the most talked about services as they promise an efficient means to sieving through the "mountains" of information that are available nowadays. CS ChemOffice has a similar setup which also allows searches of the BEILSTEIN database via CROSSFIRE™. Various computer-based databases that allow citation searches of the abstracts of many journals include CURRENT CONTENTS Chemistry Citation Index and CHEMKEY. Others, such as CEABA, provide enormous abstracts listings. SATIS Products offer the MSDIS program that allows the user to find the sources, about 100 different ones, for many properties, etc. of chemicals. A database such as ACD (Available Chemicals Directories) from MDL Information Systems Inc. could also be a useful reference source; this was previously implemented in OSAC (Organic Structures Accessed by Computer), but is being replaced by an ISIS (Integrated Scientific Information System) version.

IPCS INCHEM consolidates a wide variety of information produced by a number of international bodies (UNEP, ILO, WHO) whose goal is to assist in the sound management of chemicals and provides a means of rapid access to information on chemicals commonly used throughout the world (http://www.inchem.org/).

Various chemical property databases are listed in Table 2, and although only those in English are listed, some databases are even available in various languages.

Table 2 Some of the more well-known databases on chemical properties and safety, health and environment information

Database name	Contents
CESARS [2]	chemical information
CHEM (EC chem.labelling)	risk/safety information
ChemAdvisor	chemical information
CHEMINDEX [2]	chemical information
CHEMINFO [2]	chemical information, MSDSs
CHEMLIST [1]	chemical inventory
CHEMSAFE [1]	chemical safety information
CHEMTOX	chemical information
CHRIS [2]	chemical information
CISDOC (CISILO)	OSH information
CISINFO	chemical information
DETHERM [1]	chemical property data
DIPPR [1]	chemical property data
ECDIN	chemical information
EINECS and ELINCS	chemical inventory
EPACHEM	chemical data
EXPOSURE LIMIT VALUES	exposure limits
HSDB [1,2]	chemical safety information
HSELINE	OSH information
IPCS CHEM SAFETY CARDS	chemical information
IRPTC/UNEP	OSH information
MSDS-OHS and MSDS-CCOHS [1]	MSDSs
NIOSHTIC [1,2]	chemical information
OHMTADS	toxicology
OSHA databases	OSH information
RTECS [1,2]	toxicology
TOXLINE [1,2]	toxicology
UN Chemical databases	chemical safety

(1) Available through STN International (http://www.fiz-karlsruhe.de/)
(2) Available through Canadian Centre for Occupational Health and Safety (http://www.ccohs.ca/)

6. COMPUTER-AIDED SYNTHESIS DESIGN PROGRAMMES

Computer-aided synthesis and molecular modelling are valuable tools for the identification of chemical routes. A means of obtaining reaction pathway alternatives is nowadays often required, in an attempt to perhaps discover novel synthesis routes, and also to identify those reactions that may have escaped the chemist's notice.

A model programme may simply be defined on the basis of a connection table and a Gibbs energy minimization routine. However, computer determination of a structure must be guided by not only a comprehensive set of rules, but spectroscopic information must also be considered, for example.

Many programmes follow the retrosynthetic approach since there are few general problem-solving strategies available that "invent" chemical reactions, but this generally leads to limitations due to combinatorial explosions. The evaluation of these possible routes to sieve out realistic alternatives is then also a limitation of this type of approach. (Kirk-Othmer Vol. 7, p. 115)

- The CAOS/CAMM (Computer-Assisted Organic Synthesis/Computer-Assisted Molecular Modelling) in the Netherlands are an important group in this field.

- CAMEO (Computer-Assisted Mechanistic Evaluation of Organic reactions) is mainly for reactivity evaluation and exothermicity calculation, while EROS is a mainframe-based multi-step reaction simulator.

- LHASA (Logic and Heuristics Applied to Synthetic Analysis) and CHIRON (CHIRal synthON) are synthesis planning systems, as is CASP (Computer-Assisted Synthesis Planning). CHIRON actually consists of five modules:
  - CARS-2D (Computer-Assisted Reaction Schemes and Drawings),
  - CASA (Computer-Assisted Stereochemical Analysis),
  - CAPS (Computer-Assisted Precursor Selection),
  - CARS-3D (3-Dimensional drawing and simulation), and
  - REAL-TIME (Real-time 3D molecule manipulation).

- IGOR is also a computer-aided reaction planning and discovery program, whereas SYNCHEM2 is an expert system for organic discovery.

- CONGEN (CONformation GENerator) is a program performing conformational searches on segments of proteins.

7. INTERNET ADDRESSES FOR CONTACTING EXTERNAL EXPERTS

The Internet is a powerful tool especially in the hands of a well-instructed chemist, but also for engineers, as it can accommodate the very valuable communications links often needed in the area of research. It can be a very useful tool for contacting experts in the field of chemistry and engineering. In addition, up-to-date information on relevant conferences, upcoming and new publications, etc. can be accessed relatively easily and from a large interested audience.

Many organizations can exploit this resource fully be means of the WWW, although others may be slightly restricted by the fact they only have a simple e-mail connection. These connections often allow the user to access previously relatively inaccessible sources of information.

A list of useful Internet addresses is now a very important part of any research done using the Internet. Some helpful advice on this is given in the table below.

	Comments	More information
WWW Browser	Very useful programme that allows a researcher to view a multitude of valuable Internet resources.	Various comparable browsers are available.
E-mail	Although not easily, e-mail still allows a researcher to contact many of the same resources. The most basic form of electronic communication is, however, still very powerful and important.	FTP, Gopher, Archie, Veronica, Finger, Usenet, Whois, Netfind, WAIS, WWW pages, mailing lists, etc. are all available to the experienced e-mailer.
Search engines	Are very, if not the most, useful facilities on the WWW. These allow the user to quickly find relevant information to any query at hand.	The Yahoo Site (http://www.yahoo.com/) contains an extensive listing of sites on the WWW. Many search engines exist, and it is advisable to not only search using one specific search engine.
Bookmarks	Useful, and often necessary facility to keep reference of valuable sites.	Most browsers and e-mail facilities include some means for saving this electronic address data. Bookmarks will need to be kept up-to-date.
Note Once a search engine has been mastered, the following information could be relatively easily found.		
Chemistry sites	Many sites exist which are well set up. These usually have been organized into categories that allow easy link-up to the desired field of interest.	Use a search engine to look for *chemistry* on the Internet, and make bookmarks.
Also: Correspondence by e-mail to various other research institutions is very important and similarly, one should make it a precedent to establish a "contact" list from the following sectors.		
Colleges and universities	To make contacts to researchers and projects in the fields you are interested in or involved with.	Use a search engine to find the relevant *universities* and/or *research groups* on the Internet, and make bookmarks.
Companies	Many company listing sites are available.	Use your favourite search engine to search for the particular *company name.*
Newsgroups	Can be very useful when requiring assistance. Questions of all sorts are raised, and even good advice is given.	Search for relevant *newsgroups.*
Mailing lists	By subscribing to various mailing lists, one can obtain regular updates on virtually anything.	Search for relevant *mailing lists.*

Beware: As always, the reliability of any Internet sources needs to be scrutinized.

8. DECISION AIDS

Efforts have been taken throughout the *INSIDE* Project to ensure that a common approach is applied at each stage in the search for the most inherently SHE design. Each tool therefore helps the user to assess and challenge designs and to promote the search for better alternatives. Eventually, a decision must be made to progress with one option. In practice, each option needs to be assessed against a number of different aims and requirements, both for SHE and other economic and business factors. This can be done either in a qualitative or quantitative way. Some factors will be easy to assess whereas others may be less tangible or more judgemental, e.g. the "quality" of the product, the public image. Also, each option may have different strengths and weaknesses, so simple comparisons may be difficult to do.

To overcome some of the potential difficulties in selecting best options, the *INSET* tools include some criteria and measures for key SHE aspects of performance. These criteria and measures provide a basis for consistent and justifiable decision making. However, these may need to be augmented with formal decision aids, especially where there is no clear "best option". A key objective of these decision aids is to help the user decide what factors need to be considered and how important these are relative to each other (their weightings). This appendix gives a brief overview of some of the more common decision aids and suggests which are suitable for use with the *INSET* Toolkit.

Decision techniques vary from quick "rough-and-ready" approaches to formal methods that are quantitative and based upon sound theoretical principles. There are many factors that influence the type of approach that is selected, including the importance of the decision, familiarity with the techniques, information that is available, and time and cost.

It is important to realize that there are two types of decision that might be made. The ideal is the optimal decision, the choice that maximizes whatever objectives have been set given the best available information. This is often not a realistic goal (owing to a lack of resources or information) and decision makers are then faced with making a good and robust decision which, if necessary, can be tested and scrutinized. Risk assessments provide a useful analogy. Full, quantified assessments are preferred but experience shows that most of the benefits arise from working through a problem in a systematic and transparent way, and in particular from the insights into the problem that the assessor gains from this process, rather than the production of an accurate measure of risk.

There are many textbooks devoted to decision-making. Many of these are of an academic nature, or devoted to decision-making in a commercial environment (e.g. whether to drill for oil, the timing of an entry of a new product into the market). The Center for Chemical Process Safety of the American Institute of Chemical Engineers have published a book entitled "Tools for making acute risk decisions with chemical process safety applications" [1]. This is a useful compendium of decision-making techniques and has been used to form the basis of this appendix. It is worth noting that the book makes few references to real situations where decision techniques have been used in the consideration of process design options. This will reflect in part the commercial sensitivity of such decisions. However, it is even more likely that the factors affecting the decision-making process are complex, difficult to unambiguously define, and possibly contradictory. The benefit of adopting formal methods is that these difficulties are raised and challenged, and that choices are agreed, even if there can be no reassurance that the optimal course of action is finally selected.

There are many decision aids from which to choose. A discussion of how to select the technique most appropriate to the decision under consideration is deferred until later. First, some of the more important techniques are considered.

8.1 Overview of decision techniques

The CCPS present an interesting taxonomy of techniques which reflect different approaches and philosophies [1]. Five categories are distinguished which are introduced below.

8.1.1 Decision techniques which consider competitive responses

Decisions involving S, H and E do not tend to have a competitive nature and are therefore of only passing interest to *INSET*. There are formal decision techniques that may be used for circumstances where people or companies compete, and therefore have conflicting objectives. Game theory is a branch of mathematics that attempts to discover successful strategies for those involved in a competitive situation.

8.1.2 Decision techniques which address many of infinite alternatives

Three techniques are discussed in the CCPS guide. All are based on mathematical programming, a quantitative technique that attempts to allocate resources as effectively as possible given well-defined objectives and constraints:

- Mathematical programming is best applied when the problem can be clearly defined. One often cited application is the balancing of a petrochemical plant, where there are multiple feeds, various processing options, and a variety of customers requiring a complexity of products. Mathematical programming can help to ensure that the plant is balanced as best as possible, often with the objective of minimizing costs or maximizing profits.
- Goal programming replaces one objective function with a number of goals which need to be balanced. Whilst it is more closely allied to commercial reality, and attempts to balance possibly competing goals, it is more difficult to apply than mathematical programming.
- Compromise programming is a further extension of goal programming. It is an interactive technique, and recognizes that it may be necessary to modify the objective functions in order to balance possibly competing goals.

8.1.3 Decision techniques which require objective inputs

Cost-benefit analysis (CBA) is the most commonly encountered technique which falls into this classification. The technique requires the assessor to include costs and benefits as criteria, usually expressed as monetary values. The decision rule is then to maximize the ratio of benefits against costs. An assignment of monetary value can be difficult, especially for criteria which do not have a ready market (e.g. value of a human life, valuation of environmental harm), and has led to techniques such as hedonic pricing and willingness-to-pay as indirect approaches for the assignment of values.

CBA aims to objectively assess decisions by ensuring that the analysis is made for, and not with, the decision maker; qualitative or value judgements are avoided. CBA therefore provides the decision maker with specific information but no more. When assessing the complex environmental issues involved with pollution, for example, the decisions that need to be made are not simple and the methodology that lies behind the analysis can be obscured. Often the decision maker is excluded from the experience of proceeding through the problem in a structured and methodical manner, a process which can frequently be more informative than the numerical results which are produced.

Major difficulties may be encountered when extending the technique to SHE-type projects, for example:

- The method attempts to avoid value judgements. However, attributing costs to SHE benefits often involves value judgements.
- Future projections are more complex and uncertain since SHE time horizons are usually longer than commercial horizons.
- Money is assumed to be the preferred numerical measure – this can be difficult to apply to intangible SHE assets.
- Account of uncertainty is rarely or poorly made.
- Time preferences are assumed to have simple discounting behaviour.

To quote French: "Cost-benefit analysis does not make objective value judgements; it makes subjective ones obscure" [2].

8.1.4 Decision techniques which do not treat uncertainty and value separately

The techniques that fall into this class are most likely to be of interest to users of the *INSET* Toolkit. These techniques do not distinguish between the inputs (or values) and the uncertainties (or risks) associated with them. Some of the techniques require quantitative inputs, whereas others can function on more subjective inputs.

Voting methods

Voting methods help groups to decide among alternatives. There are a number of variations upon the theme of voting, including: plurality, where the option with the most votes wins (also known as "first past the post"), and the Borda count method, where the voter ranks the alternatives and the rankings may then be combined in a variety of ways to select the winner.

Voting methods have the advantage that they are quick to use, simple to understand, and do not require extensive resources. The disadvantages are that the steps by which the decision was made become obscure, sensitivities are unknown, and the systems can be manipulated by informed voters.

Group decision-making can be difficult. Not only can informed decision makers manipulate the result but there is also the problem that groups can become dominated by individuals who distort outcomes by force of personality or through seniority. The nominal group technique (NGT) tries to overcome some of these problems by limiting the interaction between members of the group. Ideas are generated silently, anonymously and in writing. Following the opportunity for the group to clarify the ideas through discussion, members then vote in secret, from which the options are ranked. The preliminary vote is presented and discussed. Finally, the group conducts another, but more sophisticated vote, from which the idea or strategy is selected.

Weighted scoring methods

There are a number of variants, but all are based on a common approach:
1. Select the decision criteria.
2. Weight the criteria according to their relative importance to the overall decision.
3. For each alternative, assign scores for all criteria.
4. Determine the overall score for each alternative by combining the individual scores and weights.
5. Select the alternative with the highest combined score.

Although these methods are not based on sound theoretical foundations (i.e. the scores do not usually have any physical meaning), they are commonly used because of their ease of application and because they do not necessarily demand detailed information that can be difficult to obtain. The techniques force the decision makers to make value judgements explicit through the quantification of the weights. However, uncertainty cannot be addressed explicitly and results can be manipulated through the selection of criteria.

The analytic hierarchy process (AHP) is a weighted scoring method which requires decision makers to explicitly make comparisons between criteria. At a simple level the decision is defined by identifying goals, criteria, and options. Pairwise comparisons are made between all criteria, to determine how well the alternatives meet the goals. The comparisons can then be combined to determine which option best meets the goal. (More complexity can be added by introducing extra layers, or hierarchy, into the process.) Whilst AHP is favoured because of its speed of operation and demands for explicit comparisons, it has the disadvantage that it cannot take account of risk or uncertainty.

Kepner-Tregoe decision analysis is another weighted scoring method. The objectives are divided into "musts" and "wants". "Musts" are not weighted: these are pass/fail criteria which the alternatives must satisfy. "Wants" are additional factors which influence the decision: these are weighted to express relative desirability. Once again the method is quick to use and does not call upon extensive resources. The technique has also been refined to take account of risks by asking the analyst to consider the negative consequences of the preferred option. However, whilst making explicit judgements, the technique again cannot make proper account of risk or uncertainty.

Other methods

Other decision support methods which fall into this class include:

- Outranking methods, where the aim is to order preferences, recognizing that some choices are clear whilst others are not. Refinements to the approach include measures to take account of the decision maker's comfort (concordance) or discomfort (discordance) when making preferences for one option against another.
- Screening/ranking methods are very simple techniques which work on pass/fail criteria. Any option which does not pass is rejected. Ranking techniques are then used to prioritize those options which pass the first screen.

8.1.5 Decision techniques that treat uncertainty and value separately

The techniques that fall into this category are based upon firm theoretical foundations. They are rigorous and logical, which makes them well suited to decision-making under situations where the final selection might need to be justified. The downside is that they require a better quality of both information and people experienced in the application of the techniques.

Pay-off matrices

Pay-off matrices are relatively simple, using a two-dimensional matrix to describe the essence of a problem. The matrix is one of actions against outcomes together with the probability of each outcome. Analysis of the combination of entries in the matrix allows the preferred action to be selected.

Decision analysis

Both decision analysis and multi-attribute utility analysis (see below) draw upon the important concept of utility which was first developed by Von Neumann and Morgenstern in the 1940's. The concept of utility is important because it makes it possible for the decision analyst to measure the relative value to a decision maker of the pay-offs (or consequences), neither of which have to be monetary, in a decision problem. The decision maker is then set the objective of maximizing the expected utility.

Decision analysis is very much like quantified risk analysis, being founded upon the concepts of consequence and likelihood. Actions, uncertainties, outcomes and values are identified and constructed into a decision tree. The problem can then be analysed to select the course of action which maximizes the expected utility. The analysis can be taken further, by measuring the response of the model to changes in the probabilities associated with various outcomes. This is known as uncertainty analysis and is a powerful way of assessing the confidence that the decision maker should place on the preferred scenario.

Multi-attribute utility analysis

Multi-attribute utility analysis (MUA) is an extension of decision analysis that allows the decision maker to address multiple, and possibly competing, objectives. The main differences are that MUA requires that (i) multiple objectives must be identified which determine the goals of the decision, (ii) attributes and measurement schemes must be set so that the success with which each alternative can meet the objective can be estimated, and (iii) a multi-attribute utility function is defined that accounts for the trade-offs between different objectives (this is in addition to the utility function that characterizes each attribute).

Although rigorous and defensible, MUA is demanding on resources, requiring time, good information and experienced practitioners.

8.2 Characteristics and applicability of various decision aids

The CCPS guide summarizes the various decision aids in terms of six important characteristics, namely: resource requirements (time, experience, depth of information), complexity of analysis, logical rigour, group focus, quantitativeness, and track record of the technique in the process industry. A simplified summary is reproduced in Table 1.

Table 1 Summary of characteristics of various decision aids

	Resource needs	Complexity of analysis	Logical rigour	Group focus	Quantitat-iveness	Track record
Analytic hierarchy process	moderate	moderate	moderate	moderate	moderate	limited
Cost-benefit analysis	moderate	moderate	moderate	limited	extensive	extensive
Decision analysis	extensive	extensive	extensive	moderate	extensive	moderate
Kepner-Tregoe decision analysis	moderate	moderate	moderate	moderate	moderate	moderate
Mathematical programming	extensive	extensive	moderate	limited	extensive	limited
Multi-attribute utility analysis	extensive	extensive	extensive	moderate	extensive	limited
Pay-off matrix analysis	moderate	moderate	moderate	moderate	moderate	limited
Screening/ranking methods	limited	limited	moderate	moderate	limited	limited
Voting	limited	limited	limited	extensive	limited	limited

Table 1 shows that the use of most decision support techniques in the context of industrial design/SHE is limited. The exception is cost-benefit analysis. The reasons for the popularity of CBA are not clear, but may include CBA's similarity with budget appraisal techniques such as discounted cash flow and its characteristic that all contributory factors are expressed as monetary values. Decision analysis has received moderate usage; it is the most rigorous and logical of the decision support tools but is time-consuming and can require extensive resources. Kepner-Tregoe decision analysis has also received moderate usage within the process industry; the important elements of the technique are easy to understand and participants do not require extensive training. Table 2 shows the types of decision aid that are most suitable for a range of problem types.

Table 2 Summary of applicability of various decision aids

Decision problem class	Distinguishing problem aspects					Well-suited decision aids
	Resource availability	**Problem complexity**	**Importance**	**Group involvement**	**Need for quantification**	
Quick Simple	Low	Low	Low	Low	Low	Screening and ranking
Quick Group dec.	Low	–	–	High	Low	Voting
More thorough Group dec.	High	–	–	High	Low	Nominal group technique
Quick Highly quantitative Non-group decision	Low	–	–	Low	High	Analytic hierarchy process Kepner-Tregoe decision analysis Pay-off matrix Outranking
Quick Highly quantitative Group dec.	Low	–	–	High	High	Pay-off matrix Analytic hierarchy process Kepner-Tregoe decision analysis
Complex Quantitative High importance Resource availability	High	High	High	–	High	Cost-benefit analysis Mathematical programming (and variants), Decision analysis Multi-attribute utility analysis

8.3 Application within *INSET*

Aids that are quick and easy to use will most likely attract the attention of users of the *INSET* Toolkit since they more closely match the style of the toolkit. (The decision support process must help, and not dominate, more traditional design functions. Complex, resource-intensive techniques such as multi-attribute utility analysis are best used in cases where the importance of the decision warrants the extra effort.) Decision aids that are distinguished by their ability to help make quick, quantitative decisions include the analytic hierarchy process, Kepner-Tregoe decision analysis, and pay-off matrices.

Tools I (Inherent SHE Performance Indices) and J (Multi-attribute ISHE Comparative Evaluation) within the toolkit suggest ways in which design attributes, such as factors contributing to safety, health and the environment, may be individually characterized and combined to produce preliminary SHE rankings. In some circumstances the *INSET* tools may be sufficient to allow selection of the most inherently friendly option. In other circumstances the distinctions between options may be less clear, in which case decision support aids can be useful. (Tools within the toolkit do not explicitly address how the various attributes should be balanced or traded-off against each other, since this is the subject of decision analysis.) Analysis of the example presented in Tool J Examples in Part 4 indicates, placing equal weighting on all attributes, the following descending ordering of options:

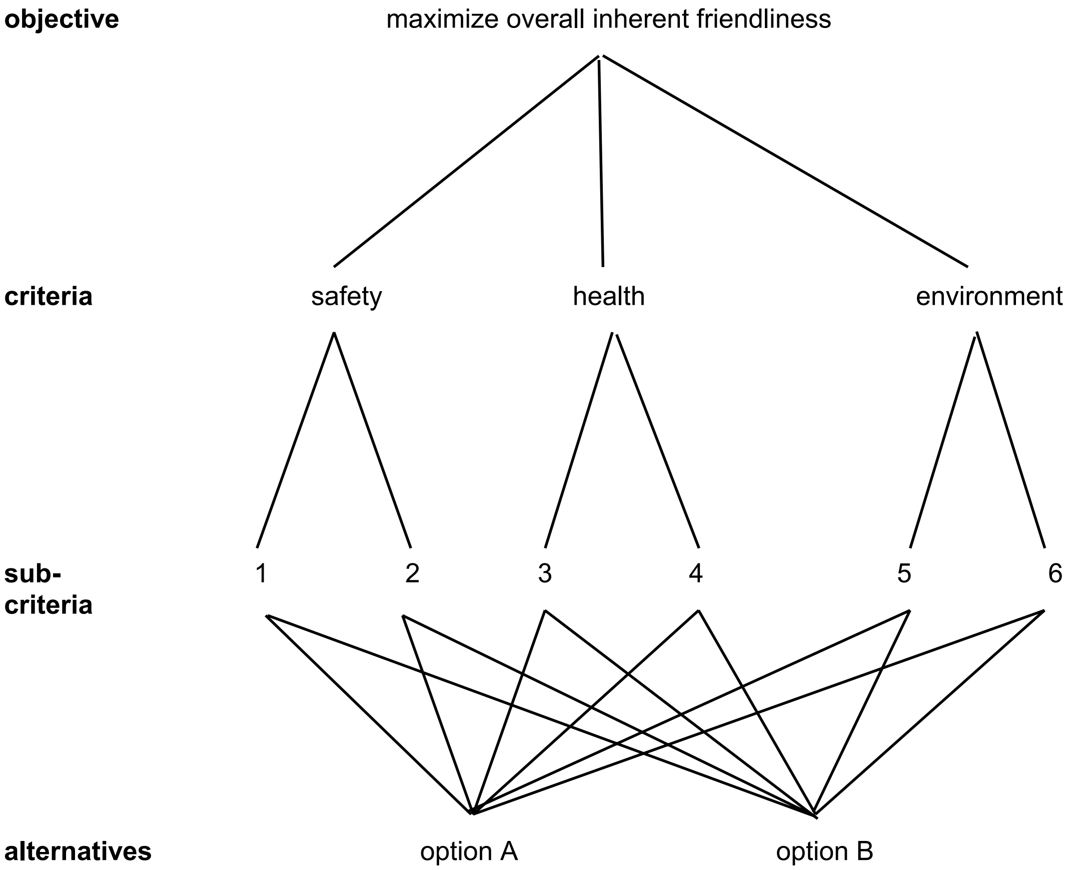
$$A \approx C > D \geq B.$$

However, more formalized decision support methods are useful in circumstances where decision makers consider that equal weightings are inappropriate.

The analytic hierarchy process (AHP) usefully illustrates how decision aids may be used to support users of the *INSET* Toolkit. AHP is favoured by some decision makers because it is structured, it has mathematical elegance, and calculations are quick. One disadvantage, however, is an absence of underlying logic, a point that should not be obscured by the method's elegant mathematical structure.

Figure 1 shows how AHP structures the decision by (i) identifying criteria that contribute to the objective, (ii) identifying sub-criteria (if any), and (iii) linking the criteria to the alternatives. The hypothetical problem illustrated in Figure 1 breaks the decision down into a restricted set of sub-criteria/attributes used in Tools I and J. For example, performance against the fire and explosion sub-criterion/attribute is measured using the Fire and Explosion Index (FEHI) of Tool I.

AHP requires pairwise comparisons to be made between the criteria (sub-criteria) for each level of the problem. Pairwise comparisons are strictly required at only the lowest level above the options. However, comparisons of pairwise comparisons between higher levels will show where inconsistencies lie. This can be important since one of the AHP's recognized disadvantages is that it can be very difficult to ensure perfect consistency – examination for consistency can show where pairwise comparisons might need to be reassessed. In this example, comparisons were made for level 2 criteria (1 vs 2, 1 vs 3, ... 5 vs 6). Comparisons can initially be qualitative but must eventually be translated to a numerical score; in this example, scores ranging from 1 (no preference can be assigned) to 9 (extreme importance) were used. AHP therefore forces the decision maker(s) to consider the relative importance of each attribute, even if the attributes are seemingly dissimilar. This distinguishes decision-making methodologies from the toolkit aids, where no attempt has been made to weight attributes.



where sub-criteria may, for example, include:
1 - Fire & explosion (FEHI)
2 - Reaction hazards (RHI)
3 - Occupational hygiene (HHI)
4 - Acute human toxicity (ATHI)
5 - Gaseous effluent (GEI)
6 - Aqueous/liquid effluent (AEI)

Figure 1 Structure of decision criteria for hypothetical AHP analysis of various options

Tables 3 and 4 illustrate how AHP works, based on the Tool J example. The illustration shown here has been based on a comparison between options A and C for a restricted set of attributes, i.e. two each for safety (FEHI, RHI), health (HHI, ATHI) and environment (AEI, GEI).

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Table 3 Pairwise comparisons of S, H and E attributes

	FEHI	RHI	HHI	ATHI	GEI	AEI
FEHI	1	5	4	9	6	6
RHI	0.2	1	9	4	5	5
HHI	0.25	0.11	1	0.5	4	4
ATHI	0.2	0.25	2	1	3	3
GEI	0.167	0.2	0.25	0.33	1	0.5
AEI	0.167	0.2	0.25	0.33	2	1

Table 3 is the pairwise comparison table for the attributes based on scores ranging from 1 (no preference) to 9 (high preference). Table 4 shows the normalized scores, together with the calculated priorities. In this example, the priorities show that safety attributes have more importance than health and environmental attributes.

Table 4 Normalized pairwise comparisons of S, H and E attributes (weighted so that S > H > E)

	FEHI	RHI	HHI	ATHI	GEI	AEI	Priority
FEHI	0.50	0.74	0.24	0.59	0.29	0.31	0.45
RHI	0.10	0.15	0.55	0.26	0.24	0.26	0.26
HHI	0.13	0.02	0.06	0.03	0.19	0.21	0.11
ATHI	0.10	0.04	0.12	0.07	0.14	0.15	0.10
GEI	0.08	0.03	0.02	0.02	0.05	0.03	0.04
AEI	0.08	0.03	0.02	0.02	0.10	0.05	0.05
	1	1	1	1	1	1	1

Table 5 shows how well options A and C meet the various S, H & E attributes. The comparisons have been based upon the scores assigned in Tool J qualitative example. In the absence of a suitable scoring method such as that provided by the *INSET* Tools I and J, the decision maker would need to estimate scores for each option against each attribute, for example using a system ranging from 1 to 9.

Table 5 Comparison of S,H & E attributes with options A and C

	FEHI	RHI	HHI	ATHI	GEI	AEI
Option A	0.6	0.6	0.6	0.5	0.5	0.6
Option C	0.4	0.4	0.4	0.5	0.5	0.4

Entries in Tables 4 and 5 can then be combined to give final scores of 0.59 and 0.41 for options A and C respectively. These would indicate that option A is preferable to option C.

Finally, the AHP analysis is summarized for the full set of attributes which are identified in the Tool J example. The more extensive analysis illustrates how easily the technique handles more complex problems. However, the more extensive analysis also provides a warning, showing how the results can change as attributes enter/leave the analysis and how a numerical approach can sometimes confuse unless used with care. Table 6 shows the normalized pairwise comparisons for the *full* set of S, H & E attributes and options given in the Tool J example. Non-SHE attributes such as capital and operating expenditures (CAPEX and OPEX) were included. Once again the attributes were skewed so that S > H > E.

Table 7 shows how well the options meet the attributes, again based on numbers produced for the *INSET* Tool J example.

Table 6 Normalized pairwise comparisons of S, H and E attributes (weighted S > H > E)

	FEHI	ATHI	HHI	AEII	THI	GEI	AEI	SWI	ECI	RHI	PCI	TF	CAPEX	OPEX	Priority
FEHI	.19	.34	.38	.30	.04	.25	.27	.28	.18	.17	.08	.08	.04	.07	.19
ATHI	.06	.11	.15	.18	.04	.18	.20	.20	.07	.13	.08	.08	.04	.07	.11
HHI	.04	.06	.08	.18	.04	.11	.12	.12	.07	.13	.08	.05	.04	.07	.09
AEII	.04	.04	.03	.06	.04	.11	.20	.16	.07	.08	.08	.05	.04	.07	.08
THI	.09	.06	.04	.03	.02	.01	.01	.01	.11	.01	.01	.08	.01	.01	.03
GEI	.03	.02	.03	.02	.09	.04	.01	.01	.11	.08	.13	.08	.13	.11	.06
AEI	.03	.02	.03	.01	.14	.12	.04	.02	.11	.08	.13	.08	.13	.11	.07
SWI	.03	.02	.03	.02	.14	.12	.08	.04	.02	.08	.13	.08	.13	.11	.07
ECI	.04	.06	.04	.03	.01	.01	.01	.08	.04	.13	.01	.14	.09	.07	.05
RHI	.05	.04	.03	.03	.11	.02	.02	.02	.01	.04	.08	.08	.13	.11	.05
PCI	.06	.04	.03	.02	.11	.01	.01	.01	.18	.01	.03	.01	.09	.07	.05
TF	.06	.04	.04	.03	.01	.01	.01	.01	.01	.01	.13	.03	.01	.07	.03
CAPEX	.19	.11	.08	.06	.11	.01	.01	.01	.02	.01	.01	.14	.04	.04	.06
OPEX	.09	.06	.04	.03	.11	.01	.01	.01	.02	.01	.01	.01	.04	.04	.04
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table 7 Comparison of S,H & E attributes with options A, B, C and D (based on *INSET* Tool J qualitative example)

	Option A	Option B	Option C	Option D
FEHI	0.40	0.27	0.26	0.08
ATHI	0.30	0.13	0.18	0.39
HHI	0.38	0.31	0.14	0.17
AEII	0.20	0.20	0.55	0.06
THI	0.32	0.26	0.23	0.19
GEI	0.13	0.65	0.15	0.07
AEI	0.52	0.23	0.17	0.08
SWI	0.36	0.16	0.36	0.13
ECI	0.22	0.05	0.27	0.47
RHI	0.40	0.40	0.10	0.10
PCI	0.17	0.19	0.35	0.29
TF	0.05	0.01	0.47	0.47

CAPEX	0.08	0.01	0.83	0.08
OPEX	0.08	0.83	0.08	0.01
Score	0.29	0.25	0.29	0.17

The AHP analysis for the full set of attributes, using weightings where S > H > E, ranked the options:

$$A \approx C > B \geq D.$$

However, when attributes are weighted approximately the same, the AHP order of priorities becomes C > A > B > D. This is in contrast to the other AHP analyses and also differs from the more simplistic ranking obtained by inspection of the Tool J qualitative scores where the order was $A \approx C > D \geq B$.

These illustrative examples highlight two important benefits: the ease of using AHP and the ease of manipulating the analysis to investigate the sensitivity of the answers. However, the illustration also highlights the care that needs to be taken when using decision tools. Seemingly conflicting results can be obtained as attributes enter/leave the analysis and as weightings change. The resolution of conflicts/confusion can be a time-consuming distraction. Therefore, whilst decision support tools can help designers identify the most inherently SHE option, care must also be taken to ensure that the tool does not become an unnecessary distraction or that the manipulation of numbers does not become an end in itself.

Part 3

In conclusion:

- Additional effort is required to use decision support tools with the *INSET* Toolkit.
- The additional effort may be unnecessary for simple decisions (e.g. one clear winner, few options and/or attributes).
- A methodological approach allows the decision maker to understand the ways in which attributes combine to favour certain options.
- The use of decision support methodologies forces decision makers to consider how attributes such as S, H and E should be traded-off against each other.
- Methodological decision approaches, such as AHP, can identify where conflicts exist. The pairwise comparisons A>B *and* B>C *and* A>C are inconsistent, and analysis will identify the inconsistencies and provide insights to remedy the inconsistencies.
- The robustness of the decision can be examined by performing "what-if" studies, to see how re-scoring/re-weighted comparisons effect the final decision.
- Numbers can sometimes confuse the decision-making process.
- Formal decision support techniques should be used for complex and/or important decisions.

References

1. "Tools for making acute risk decisions with chemical process safety applications", Center for Chemical Process Safety, American Institute of Chemical Engineers, 1995.

2. French S., "Decision theory: An introduction to the mathematics of rationality", Ellis-Horwood, 1988.

9. GLOSSARY

Abbreviations

ALARP	As Low As Reasonably Practicable
BLEVE	Boiling Liquid Expanding Vapour Explosion
BPEO	Best Practicable Environmental Option
CAPEX	CAPital EXpenditure
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
ELD	Engineering Line Diagram
HAZOP	HAZard and OPerability study
INSET	**IN**herent **S**HE **E**valuation **T**ool
INSIDE	**IN**herent **S**HE **I**n **DE**sign
ISHE	Inherent Safety, Health & Environment
LCA	Life-Cycle Analysis
MSDS	Material Safety Data Sheet
OPEX	OPerating EXpenditure
PHA	Process Hazard Analysis
P&ID	Piping and Instrument Diagram
QRA	Quantitative Risk Assessment
RASP	Rapid Assessment of Spill Potential
SHE	Safety, Health & Environment
US EPA	United States Environmental Protection Agency
VCE	Vapour Cloud Explosion
VOC	Volatile Organic Compound
WWW	World-Wide Web

Definitions

Active safeguard
An "add-on" engineered system or provision to prevent, control or mitigate a hazard or hazards which needs to be activated to come into effect. Such systems rely on timely hazard detection and regular testing to ensure they operate.

Add-on safeguard
An engineered safeguard which is only there to ensure safety and has no function in the normal operation of the plant or process.

Detection system
A system or provision to enable a hazard or hazard initiation sequence, or the realization of a hazard to be identified. These systems do not prevent, control or mitigate the hazards themselves, but are vital to the initiation of active and procedural safeguards, and consequently form an integral part of these safeguards.

Hazard
A chemical or physical condition or activity that has the potential for causing damage to people, property or the environment.

Hazard avoidance
Measures taken in the design of the process or plant to eliminate or avoid the hazardous material, condition or action, i.e. by removing it completely.

Hazard control
Measures taken to limit the severity of a hazard before it is realized (reduce the consequences) or recover the situation before the hazard is realized (reduce the likelihood) – especially actions or measures that interfere with the chain of events leading to the realization of the hazard which would limit the effects of the hazard or enhance/enable recovery.
Note Active control (and mitigation) measures need to be initiated before they can start to have an effect and so rely on the timely detection of the developing chain of events. Detection therefore plays key role in hazard management. (See "detection system".)

Hazard mitigation
Measures taken to limit the effects or spread (consequences) of the hazard once it has been realized. These can include emergency response actions such as escape and evacuation arrangements.

Hazard prevention
Measures taken to prevent, or reduce the likelihood of the hazardous situation or action arising, or to reduce the chance of a hazard being realized. In practice, the only way of totally preventing the hazard is to avoid/eliminate it. Prevention is therefore to do with reducing the chance/likelihood of the hazard arising or being realized.

Inherent safeguard
The design or adaption of a process, engineered system, plant or provision to avoid, prevent, control or mitigate a hazard or hazards. The safeguard is achieved by the basic functionality or attributes of the process, plant or system.

Inherent safety design
An approach to plant and process design whereby the hazards are avoided or reduced to such trivial levels that the plant and process pose no threat of harm to people, property or the environment on-site or off-site, and as a result there is no need for additional engineered or procedural safeguards.

Inherently safer design
An approach to design that recognizes that hazards cannot always be avoided or reduced to trivial levels, but which avoids or reduces the hazards at source, or simplifies the process or plant to minimize the likelihood of the hazards being realized so far as is reasonably practicable. The residual risks are then dealt with, so far as is reasonably practicable, by an appropriate combination of engineered and procedural safeguards, but with a preference for those measures that are simpler and more likely to be effective, e.g. passive safety systems rather than active ones.

Passive safeguard
An "add-on" engineered system or provision to prevent, control or mitigate a hazard or hazards which does not need to be activated or has no moving parts. Such systems should have a high availability since they do not rely on timely hazard detection to operate.

Procedural safeguard
A system, procedure or action undertaken by personnel to prevent (proactive), control or mitigate (reactive) a hazard or hazards.

Part 4 - Supporting material for the tools

Part 4 – Table of contents

A Detailed constraints and objectives analysis
A.1 - Detailed constraints analysis
A.2 - Detailed objectives analysis
B Process option generation (incl. Process waste minimization guide)
C Preliminary chemistry route options record
D Preliminary chemistry route rapid ISHE evaluation method
E Preliminary chemistry route detailed ISHE evaluation method
F Chemistry route block diagram record
G Chemical hazards classification method
H Record of foreseeable hazards
I ISHE performance indices
I.1 - Fire and explosion hazards index
I.2 - Acute toxic hazards index
I.3 - Health hazards index
I.4 - Acute environmental incident index
I.5 - Transport hazards index
I.6 - Gaseous emissions index
I.7 - Aqueous emissions index
I.8 - Solid wastes index
I.9 - Energy consumption index
I.10 - Reaction hazards index
I.11 - Process complexity index
J Multi-attribute ISHE comparative evaluation
K Rapid ISHE screening method
L Chemical reaction reactivity - stability evaluation
M Process SHE analysis/process hazards analysis and ranking
N Equipment inventory functional analysis method
O Equipment simplification guide
P Hazards range assessment for gaseous releases
Q Siting & plant layout assessment
R Designing for operation

SUPPORT FOR TOOL A.1 – DETAILED CONSTRAINTS ANALYSIS

Tool A.1 examples

Used in the initial stages of chemical process route assessment, Tool A of the *INSET* Toolkit is invaluable as it provides the foundation for the assessment stages that follow. The basis of Tool A.1 is to delimit the particular project.

Example A.1.1 shows the constraints for the production of a fictitious substance "Insetol" and how the two forms of Tool A.1 have been used to record these.

Example A.1.2 shows how Tool A.1 could have been used if it had been available to those involved in the real project described in the example. The information in the referenced article has been used as input.

Example A.1.1: Insetol

A fictitious Finnish company intends to start developing a process to produce the fictitious chemical substance "Insetol". The General Constraints of the Project Sheet was used to list the various constraints that are appropriate to all projects undertaken by the company. The subsequent Project-Specific Constraints Sheet was used to list the particular restrictions that have been deemed to be required for the "Insetol" project.

Project title: *INSETOL*

Date: *01/ 06/ 1995* **General Constraints of the Project Sheet (Tool A.1)** **Page:** *01/ 01*

Author: _*E.S.*___________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

ID	Constraint	Date
C_{G1}	*Black-listed chemicals forbidden*	*1.6.95*
C_{G2}	*Finnish laws must be obeyed*	*1.6.95*
C_{G3}	*"Responsible Care" obligation*	*25.9.95*
C_{G4}		
C_{G5}		
C_{G6}		
C_{G7}		
C_{G8}		
C_{G9}		
C_{G10}		
C_{G11}		
C_{G12}		
C_{G13}		
C_{G14}		
...		

Project title: *INSETOL*

Date: *09/ 02/ 1996* **Project-Specific Constraints Sheet (Tool A.1)** **Page:** *01/ 01*

Author: _*E.S.*___________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

ID	Constraint	Date
C_{P1}	*Known reagents (mentioned in the EINECS list)*	*9.2.96*
C_{P2}	*Starting materials must be available in Finland*	*9.2.96*
C_{P3}	*The production process must not be covered by patents*	*9.2.96*
C_{P4}	*Major investments not allowed*	*9.2.96*
C_{P5}	*Production capacity must exceed 0.7 Tonnes per month*	*9.2.96*
C_{P6}	~~*Cost from starting materials and waste treatment: 300 FIM/kg of product*~~	~~*9.2.96*~~
C_{P7}	*Cost from starting materials and waste treatment: 250 FIM/kg of product*	*19.2.96*
C_{P8}		
C_{P9}		
C_{P10}		
C_{P11}		
C_{P12}		
C_{P13}		
C_{P14}		
...		

Example A.1.2: Constraints of an inherently safer design of an LPG process

Adopted from an article by J.C.A. Windhorst (Novacor Chemicals Ltd).
(Windhorst J.C.A., "Application of inherently safe design concepts, fitness for use and risk-driven design process safety standards to an LPG project", Proceedings of 8th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Volume II, Elsevier, 1995, pp. 543-554.)

The problem

Because of changing market conditions, a business opportunity arose for the development of a project that would convert a by-product Liquefied Petroleum Gas (LPG) stream into a plastics co-monomer stream. The facility was planned for the Joffre site in Alberta, Canada, a region where the temperature can drop to –40°C during the winter months. Two world-scale ethylene plants, a polyethylene plant, utilities, loading and unloading and other support facilities are located at the site.

The ethane feedstock arrives by pipeline. Product ethylene storage at the site is minimal and spec ethylene is shipped immediately by pipeline to the customers. Butene-1, used as a co-monomer for the production of polyethylene, is imported by rail. The co-monomer is stored in two bullets and in railcars which are being used as temporary storage. The unloading station, storage facilities and railcars are located near the polyethylene plant. The typical site storage is two weeks.

By-products from the ethylene plant are a C4 stream that contains significant amounts of butadiene, C3 and C5+ streams. C4 by-product from the ethylene plants goes to two large spheres located in the storage area where a butadiene stabilizer is added. From there, the C4 by-product is pumped to the by-product loading area for shipping to the customers. The normal mode of operation is to operate one sphere with C4 by-product and use the partially filled other one as a backup. All the by-products are shipped out by railcars from the loading station. In terms of the C4 movements, there is a flow of C4 by-product by rail from Joffre to the Southern US, and another flow of butene-1 co-monomer in the opposite direction.

The requirements

The main aims were to reduce rail transport exposure and to optimize inherent process and environmental protection by making it part of the conceptual design specification development. The main deliverables were a design based on:

- a partial and selective hydrogenation of C4 by-product stream to a mixture of butenes,
- the separation of a stream of co-monomer quality butene-1 from the mixture of butenes.

Early on, it was realized that inherent safety, as applied to the existing process operation, could be improved by:

- reducing the overall inventory of butene-1 co-monomer through more precise inventory management,
- replacing the temporary butene-1 co-monomer rail storage with deluge-protected fixed storage, and
- reducing the total inventory of the C4 by-product through more precise inventory management.

The inherent safety features of the new by-product upgrading unit could be improved by selection of a process that:

- requires small process inventories, albeit at moderate pressures, dictated by the need to use cooling water for condensation (this was considered simpler and safer than the use of a vapour recompression compressor), and
- did not require a complicated process control system for bringing the plant back to a safe operating mode in case of an upset.

Inherent environmental protection/safety of the new by-product upgrading unit could be improved by selection of a process that:

- minimized the creation of waste products and did not require new disposal methods of, until now, unknown waste products, but

- allowed disposal of waste product(s) in existing by-product stream(s),
- does not require the import and site storage of new chemicals, e.g. reactants, and
- utilized a catalyst that could be readily handled before as well as after use and that could be disposed of, preferably through reactivation.

Constraints

Requirements for the product are based on the constraints ("musts") defined by the customer and the inherent properties that come with the product as proposed by the supplier. The customer's requirements are met when the inherent properties are acceptable to the customer. All requirements should be ranked into "musts" and "wants" (see also Example A.2.2) and cover plant requirements, economics, process safety, occupational safety and environmental goals.

If Novacor Chemicals had had access to the *INSET* Toolkit, the project-specific constraints mentioned in the article, could have been listed on the form as shown on the next page.

(See Example A.2.2 for the objectives, as well as for the engineering solutions the company selected to fulfil their requirements.)

Project title: *LPG*

Date: ___ / ___ / *1995* **Project-Specific Constraints Sheet (Tool A.1)** **Page:** *01* / *01*

Author: _*YM*____________ **Proj. #:** _*LPG2*__________ **Ref. #:** ________

ID	Constraint	Date
C_{P1}	*Existing C4 stream as starting material*	*D.M.YY*
C_{P2}	*Separation of a stream of co-monomer quality butene-1*	*D.M.YY*
C_{P3}	*Location of the process is Joffre, Canada*	*D.M.YY*
C_{P4}		
C_{P5}		
C_{P6}		
C_{P7}		
C_{P8}		
C_{P9}		
C_{P10}		
C_{P11}		
C_{P12}		
C_{P13}		
C_{P14}		
...		

Tool A.1 supporting information

Included in this section are the EEC List I and List II Chemicals, the UK "Red list", and the Helcom lists. These may be useful when trying to identify potential problems with the chemical route alternatives. The "Standard list of risk phrases" is also presented.

EEC List I Chemicals - "Black list" - 129 substances

1,1,1-Trichloroethane
1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane
1,1,2-Trichlorofluorethane
1,1-Dichloroethane
1,1-Dichloroethylene
1,2,4,5-Tetrachlorobenzene
1,2,4-Trichlorobenzene
1,2-Dibromomethane
1,2-Dichloroethane
1,2-Dichloroethylene
1,2-Dichlorobenzene
1,2-Dichloropropane
1,3-Dichlorobenzene
1,3-Dichloropropane-2-ol
1,3-Dichloropropene
1,4-Dichlorobenzene
1-Chloro-2,4-dinitrobenzene
1-Chloro-2-nitrobenzene
1-Chloro-3-nitrobenzene
1-Chloro-4-nitrobenzene
1-Chloronaphthalene
2,3-Dichloropropene
2,4,5-T (and salts & esters)
2,4-D (and salts & esters)
2,4-Dichlorophenol
2-Amino-4-chlorophenol
2-Chloro-p-toluidine
2-Chloroaniline
2-Chloroethanol
2-Chlorophenol
2-Chlorotoluene
3-Chloroaniline
3-Chlorophenol
3-Chloropropene
3-Chlorotoluene
4-Chloro-2-nitroaniline
4-Chloro-2-nitrotoluene
4-Chloro-3-methylphenol
4-Chloroaniline
4-Chlorophenol
4-Chlorotoluene
Aldrin
Anthracene
Arsenic & inorganic compounds
Arsenic pentoxide
Arsenic trioxide
Azinophos-ethyl
Azinophos-methyl
Benzene
Benzidine
Benzylchloride
Benzylidinechloride
Biphenyl
Cadmium & compounds
Cadmium sulphide
Carbontetrachloride
Chloroalhydrate
Chlorobenzene
Chlordan
Chloronaphthalenes (tech. mixture)
Chloronitrotoluenes (m.4-chl.-2-nitr.tolu)
Chloroacetic acid
Chloroform
Chloroprene
Chlorotoluidines (m.2-chloro-p-tolu.)
Coumaphos
Cyanurchloride
DDT (and metabolites DDD & DDE)
Demeton
Dibutyltin salts (m. oxide & chloro.)
Dibutyltinchloride
Dibutyltinoxide
Dichlorodiisopropylether
Dichloromethane
Dichloronitrobenzenes
Dichloroanilines
Dichlorobenzidines
Dichlorprop
Dichlorvos
Dieldrin
Diethylamine
Dimethoate
Dimethylamine
Disulfoton
Endosulfan
Endrin
Epichlorhydrin
Ethylbenzene
Fenitrothion
Fenthion
Heptachloro (& heptachloroperoxide)
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexanes
Hexachloroethane
Isopropylbenzene
Linuron
MCPA
Malathion
Mecoprop
Mercury & compounds
Methamidophos
Mevinphos
Monolinuron
Naphthalene
Omethoate
Oxydemeton-methyl
PCB (and PCT= cas 61788-33-8)
Parathion (+ cas 298-00-0)
Pentachlorophenol
Phoxim
Polyaromatic carbonhydrid.(3,4-bpy,bfl.)
Propanil
Pyrazon
Simazine
Tetrabutyltin
Tetrachloroethylene
Toluene
Triazophos
Tributylphosphate
Tributyltinoxide
Trichlorobenzene (tech.mixture)
Trichloroethylene
Trichlorfon
Trichlorophenols (+ cas 88-06-2)
Trifluralin
Triphenyltinacetate
Triphenyltinchloride
Triphenyltinhydroxide
Vinylchloride
Xylenes (o-, m-, p-, mixed)

In 1976, the Council of EEC adopted a Directive on pollution caused by certain dangerous substances discharged into the aquatic environment (76/464/EEC). The aim of the Directive was to eliminate pollution of water by a number of listed dangerous families and groups of substances. Each member state had to establish emission standards for discharges that must not exceed certain limit values.

Following the adoption of the Directive, EEC commissioned several studies to select individual chemicals from the listed families and groups of chemicals in the Directive. About 1500 substances were listed based on toxicity, persistence and bioaccumulation. Another 500 chemicals produced or used in quantities greater than 100 tons per year within the Community were also examined by means of a mathematical model to evaluate the risk to the aquatic environment. Several other lists (e.g. US Environmental Protection Agency list of toxic pollutants, the Canadian list of priority chemicals and the German catalogue of substances constituting a risk to the aquatic environment) were also considered. From these candidate substances, this list of 129 priority pollutants was produced.

UK "Red list" - 23 substances

1,2-Dichloroethane
Aldrin
Atrazine
Azinphos-methyl
Cadmium & its compounds
DDT
Dichlorvos
Dieldrin
Endosulfan
Endrin
Fenitrothion
Hexachlorobenzene
Hexachlorobutadiene
Lindane (gamma-hexachlorocyclohexane (HCH))
Malathion
Mercury & its compounds
Polychlorinated biphenyls (PCBs)
Pentachlorophenol & its compounds
Simazine
Tributyltin compounds
Trichlorobenzene
Trifluralin
Triphenyltin compounds

A conference of ministers representing North Sea littoral countries, held in 1987, agreed on certain initiatives to reduce inputs of potentially dangerous substances to the North Sea from land-based sources. The UK Government responded by proposing reductions of some of these substances. For this purpose, a "Red list" of 23 substances was selected on the basis of toxicity, persistence, potential for bio-accumulation, carcinogenicity and estimated concentration in the aquatic environment.

As a base for selection of the "Red list" substances, the Department of the Environment used EEC List I candidate substances and substances on Annex ID of the Ministerial Declaration of the Third International Conference on the Protection of the North Sea.

The selection procedure was based on four different scenarios reflecting the significance of acute toxic effects (short-term scenario), chronic toxic effects (long-term scenario), carcinogenic, mutagenic or teratogenic properties (carcinogenicity scenario) and toxicity to higher organisms (food-chain scenario). Each scenario involved a decision tree with parameters designated high, medium or low significance.

The selection procedure finally led to the "Red list" consisting of 23 substances, which were considered to represent a particularly high risk to the aquatic environment.

HELCOM: Priority harmful substances - 46 substances

Arsenic
Atrazine
Azinphos-ethyl
Azinphos-methyl
Cadmium
Carbontetrachloride
Chloroform
Chlorpicrin
Chromium
Copper
Dichloroethane, 1,2-
Dichlorvos
Dioxins
Endosulfan
Fenitrothion
Fenthion
Halogenated org subst measured as AOX
Hexachlorobenzene
Hexachlorobutadiene
Lead
Malathion
Mercury
Nickel
Nonylphenolethoxylate
PAH
Parathion
Parathion-methyl
Pentachlorophenol
Simazine
Tetrachloroethylene
Tributyltin compounds
Trichlorobenzene
Trichloroethane
Trichloroethylene
Trifluralin
Triphenyltin compounds
Xylenes
Zinc

The Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea was first signed in 1974 by the countries with coastlines on the Baltic Sea.

Work concerning substances listed by the Final Declaration of the Third International Conference on the Protection of the North Sea has continued within the Helsinki Commission (HELCOM). With slight amendments, the lists from the 3rd North Sea Conference have been adopted by HELCOM.

At its 12th meeting, in February 1991, HELCOM adopted the "Baltic Sea list of priority harmful substances other than nutrients for immediate action in order to reach the 50% reduction goal by 1995" (Annex 6 to the report of the 12th meeting). Forty-six substances were included on the list; certain metals and their compounds, biocides as well as other organic substances. Discharges during the year 1987 serve as a basis for the reductions.

HELCOM is also working on a waiting list of chemicals for further selection of candidates for reduction.

In April 1992, a diplomatic conference was held in Helsinki. The participating parties agreed to prevent and eliminate pollution of the marine environment of the Baltic Sea area caused by harmful substances. Broadly identified chemicals groups, such as heavy metals and their compounds; organohalogen compounds; organic compounds of phosphorus and tin; nitrogen and phosphorus compounds; radioactive substances, including wastes, etc., shall be given priority in the preventive measures. Some thirty substances (most of which are pesticides) designated for total or partial prohibition of use, were listed.

HELCOM: Waiting list - 190 substances

2,3,4,5-tetrachlorophenol
2,3,4,6-tetrachlorophenol
2,3,5,6-tetrachlorophenol
2,4,6-trichlorophenol
acenaphthene
acetic acid, 2,4-dichlorophenoxy- (2,4-d)
acetic acid, chloro-
acetic acid, trichloro-
aldicarb
amitrol (3-amino-1,2,4-triazole)
aniline, 2-chloro, 4-nitro-
aniline, 2-chloro-
aniline, 3-chloro-
aniline, 4-chloro-
anthracene
anthraquinone, 2-chloro-
arsine, diphenylchloro-
arsine, ethyldichloro-
bentazon
benz(a)antrhracene
benzene
benzene, 1,2,4,5-tetrachloro-
benzene, 1,2-dichloro-
benzene, 1,3-dichloro-
benzene, 1,4-dichloro-
benzene, 1-(1-methylethyl)-4-nitro-
benzene, 1-chloro, 2,4-dinitro-
benzene, 1-chloro, 3-nitro-
benzene, 1-chloro, 4-methyl-
benzene, 1-fluoro-4-isothiocyanato-
benzene, chloro-
benzene, chlorodinitro- (mixed isomers)
benzene, ethyl-
benzene, isopropyl- (cumene)
benzene, nitro-
benzene, nitro-, 2-chloro-
benzene, pentachloro-
benzene, m-dinitro-
benzenedicarbonic acid, 1,2-
benzoamine,4-(2,4-dichlorophenoxy)-
benzonitril, 2,6-dichloro-
biphenyl
bis(2-chloroisopropyl)ether
butadiene, 2-chloro-1,3- (chloroprene)
captan
carbazole
carbofuran
carbonic acid, diphenylester
chlorpyrifos
cobalt
cumafos
cyclohexane
cyclohexane, methyl-
cyclohexylamine
decanol-1, n-
demeton
diazinon
dicofol
diethylamine
dihydrazinesulphate
dimethoate
dimethylamine
dinoseb
diphenyl, 4,4'-diamino- (benzidine)
diphenylamine, n,n-
diphenylether
disulfoton
dithiocarbamates
epichlorhydrine
ethanal, trichloro- (chloral,trichloroacetaldehyde
ethane, 1,1,2-trichloro-, 1,2,2-trifluoro-
ethane, 1,1,2,2-tetrachloro-
ethane, 1,1,2-trichloro-
ethane, 1,1-dichloro-
ethane, pentachloro-
ethane, hexachloro-
ethanediamine, 1,2-, n-(4-bromophenyl)methyl-
ethanol, 2-chloro-
ethene, 1,1-dichloro-
ethene, 1,2-dichloro-
ethene, chloro- (vinylchloride)
fluoranthene
foxim
guanidine, cyano-
hexane, 1,6-dichloro-
hexane, 1-chloro-
hexanol, 2-ethyl-
hexanol, 1-, 3,5,5-trimethyl-
isodecyl alcohol
isononanol
isoxazolamine, 5-
lead, tetraethyl-
linuron
methamidophos
methane, dichloro-
methane, diphenyl-
methane, tetrabromide-
mevinphos
mineral oil
mirex
monolinuron
naphthalene
naphthalene, hexachloro-
nickel tetracarbonyl
nitrobenzotrifluorides-m
nitrobenzotrifluorides-o
nitrobenzotrifluorides-p
norbornadiene, 1,2,3,4,7,7-hexachloro-
octane, n-
octanol, 1-
omethoate
oxydemeton-methyl

pentane
phenanthrene
phenol, 2,3-dichloro-
phenol, 2,4-dichloro-
phenol, 2-amino-4-chloro-
phenol, 2-benzyl-, 4-chloro-
phenol, 2-chloro-
phenol, 2-methoxy-, 4-propenyl-
phenol, 2-methyl-
phenol, 3-chloro-
phenol, 3-methyl, 4-chloro-
phenol, 4,4'(methylethylidene)bis-
phenol, 4-chloro-
phenol, 4-nonyl-
phenol, dinitro-2-methyl- (dinitro-o-cresol, dnoc)
phenol, dodecyl- (mixed isomers)
phenol, trichloro-
phenol, p-butyl-, 1,1,3,3-tetramethyl-
phenoxyacetic acid, 2-methyl-4-chloro- (mcpa)
phenoxypropanoic acid, 2,4-dichloro- (dichlorprop)
phenoxypropanoic acid, 2-methyl-4-chloro- (mcpp)
phosphate, cresyldiphenyl-
phosphate, tributyl-phosphate, tricresyl-
phosphate, trioctyl -
phosphate, triphenyl-
phosphate, tris (2,3-dibromo-1-propyl)-
phosphate, trixylenyl-
phthalate, butylbenzyl-
phthalate, di-n-octyl-
phthalate, dibutyl-
phthalate, diethyl-
propachlor
propane, 1,2-dichloro-
propanil
propanol, 1,3-dichloro-2-
propene, 1,3-dichloro-
propene, 2,3-dicloro-
propene, 3-chloro- (allylchloride)
propionic acid, 2,2-dichloro-
pyrazone (chloridazon)
sulfotep
thiram
tin, dibutylbis(lauroyloxy)-
tin, dibutyldichloro-
tin, dibutyloxo-
tin, tetra-n-butyl-
toluene
toluene, 2,3-dinitro-
toluene, 2,4-dinitro-
toluene, 2-chloro-
toluene, 3-chloro-
toluene, 4-t-butyl-
toluene, alpha,alpha-dichloro- (benzylidenchloride
toluene, alpha-chloro- (benzylchloride)
toluene, ethyl- (mixed isomers)
triazine, 2,4,6-trichloro-1,3,5-(cyanuric chloride
triazophos
trichlorfon
xylene, m-
xylene, o-
xylene, p-

EEC List II Chemicals (Dangerous substances) - "Grey list"

- approximately 1200 substances

Annex I is a list of substances classified according to health hazards and physico-chemical properties. The list consists of dangerous substances with information concerning classification and labelling (danger symbols, risk phrases and safety phrases). The classification is binding on the manufacturers/importers. The aim of the classification and labelling is to protect the general public and the environment from the identified hazards.
Note The fact that a substance is not placed on the list does not imply that it is not hazardous.

The list was originally prepared in 1967 as a consequence of Article 4 of Directive 67/548/EEC. Annex I is revised when required. The object of classification is to identify the substances' inherent properties (toxicological, physico-chemical, etc.) which could constitute a risk when the substances are handled or used. The labelling is then a consequence of the classification. Since 1967 the directive (and Annex I) has been modified several times. Individual concentration limits for substances, to be used for the classification of preparations, have also been included in Annex I. After the fifteenth technical adaptation, to which this text refers, also ecotoxicological properties of substances are considered in the classification (sixteenth technical adaptation).

The definitions on which the classification is based – as well as the requirements on packaging and labelling – are stated in Directive 67/548/EEC.

Standard risk phrases of health hazards

There are 64 standard risk phrases (R-phrases) expressing the health hazards (in words) in the European Community regulations. In substance databases, the numbers of the pertinent phrases are separated by dashes (-). When similar R-phrases are specified, they are combined in a single phrase. The number of a combined phrase is given by writing the numbers of the original phrases separated by slashes (/).

The complete list of R-phrases follows (see 67/548/EEC Article 2.2):

1. Explosive when dry.
2. Risk of explosion by shock, friction, fire or other sources of ignition.
3. Extreme risk of explosion by shock, friction, fire or other sources of ignition.
4. Forms very sensitive explosive metallic compounds.
5. Heating may cause an explosion.
6. Explosive with or without contact with air.
7. May cause fire.
8. Contact with combustible material may cause fire.
9. Explosive when mixed with combustible material.
10. Flammable.
11. Highly flammable.
12. Extremely flammable.
13.† Extremely flammable liquefied gas.
14. Reacts violently with water.
15. Contact with water liberates extremely flammable gases.
16. Explosive when mixed with oxidizing substances.
17. Spontaneously flammable in air.
18. In use, may form flammable/explosive vapour-air mixture.
19. May form explosive peroxides.
20. Harmful by inhalation.
21. Harmful in contact with skin.
22. Harmful if swallowed.
23. Toxic by inhalation.
24. Toxic in contact with skin.
25. Toxic if swallowed.
26. Very toxic by inhalation.
27. Very toxic in contact with skin.
28. Very toxic if swallowed.
29. Contact with water liberates toxic gas.
30. Can become highly flammable in use.
31. Contact with acids liberates toxic gas.
32. Contact with acids liberates very toxic gas.
33. Danger of cumulative effects.
34. Causes burns.
35. Causes severe bums.
36. Irritating to eyes.
37. Irritating to respiratory system.
38. Irritating to skin.
39.* Danger of very serious irreversible effects.
40.* Possible risk of irreversible effects.
41.* Risk of serious damage to eyes.
42. May cause sensitization by inhalation.
43. May cause sensitization by skin contact.
44. Risk of explosion if heated under confinement.
45. May cause cancer.
46. May cause heritable genetic damage.
47.† May cause birth defects.
48.* Danger of serious damage to health by prolonged exposure.
49. May cause cancer by inhalation.
50. Very toxic to aquatic organisms.
51. Toxic to aquatic organisms.
52. Harmful to aquatic organisms.
53. May cause long-term adverse effects in the aquatic environment.
54. Toxic to flora.
55. Toxic to fauna.
56. Toxic to soil organisms.
57. Toxic to bees.
58. May cause long-term adverse effects in the environment.
59. Dangerous for the ozone layer.
60. May impair fertility.
61. May cause harm to the unborn child.
62. Possible risk of impaired fertility.
63. Possible risk of harm to the unborn child.
64. May cause harm to breast fed babies.

* means there is additional information on the pairing possibilities.
† means that the phrase is no longer used.

The commonly used combination phrases follow:

R14/15	Reacts violently with water liberating highly flammable gases.
R15/29	Contact with water liberates toxic, highly flammable gas.
R20/21	Harmful by inhalation and in contact with skin.
R20/22	Harmful by inhalation and if swallowed.
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed.

R21/22	Harmful in contact with skin of if swallowed.
R23/24	Toxic by inhalation and in contact with skin.
R23/25	Toxic by inhalation and if swallowed.
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed.
R24/25	Toxic in contact with skin and if swallowed.
R26/27	Very toxic by inhalation and in contact with skin.
R26/28	Very toxic by inhalation and if swallowed.
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed.
R27/28	Very toxic in contact with skin and if swallowed.
R36/37	Irritating to eyes and respiratory system.
R36/38	Irritating to eyes and skin.
R36/37/38	Irritating to eyes, respiratory system and skin.
R37/38	Irritating to respiratory system and skin.
R39/23	Toxic: danger of very serious irreversible effects through inhalation.
R39/24	Toxic: danger of very serious irreversible effects in contact with skin.
R39/25	Toxic: danger of very serious irreversible effects if swallowed.
R39/23/24	Toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R39/23/25	Toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if swallowed.
R39/23/24/25	Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R39/26	Very toxic: danger of very serious irreversible effects through inhalation.
R39/27	Very toxic: danger of very serious irreversible effects in contact with skin.
R39/28	Very toxic: danger of very serious irreversible effects if swallowed.
R39/26/27	Very toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R39/26/28	Very toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R39/27/28	Very toxic: danger of very serious irreversible effects in contact with skin and if swallowed.
R39/26/27/28	Very toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R40/20	Harmful: possible risk of irreversible effects through inhalation.
R40/21	Harmful: possible risk of irreversible effects in contact with skin.
R40/22	Harmful: possible risk of irreversible effects if swallowed.
R40/20/21	Harmful: possible risk of irreversible effects through inhalation and in contact with skin.
R40/20/22	Harmful: possible risk of irreversible effects through inhalation and if swallowed.
R40/21/22	Harmful: possible risk of irreversible effects in contact with skin and if swallowed.
R40/20/21/22	Harmful: possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.
R42/43	May cause sensitization by inhalation and skin contact.
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation.
R48/21	Harmful: danger of serious damage to health by prolonged exposure in contact with skin.
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed.

R48/20/21	Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.
R48/21/22	Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation.
R48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin.
R48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed.
R48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

SUPPORT FOR TOOL A.2 – DETAILED OBJECTIVES ANALYSIS

Tool A.2 examples

Used in the initial stages of chemical process route assessment, Tool A of the *INSET* Toolkit is invaluable as it provides the foundation for the assessment stages that follow. The basis of Tool A.2 is to further delimit the particular project.

Example A.2.1 shows the objectives for the production of a fictitious substance "Insetol" and how the two forms of Tool A.2 have been used to record these.

Example A.2.2 shows how Tool A.2 could have been used if it had been available to those involved in the real project described in the example. The information in the referenced article has been used as input.

Example A.2.1: Insetol

A fictitious Finnish company intends to start developing a process to produce the fictitious chemical substance "Insetol". The General Objectives of the Project Sheet was used to list the various objectives that are appropriate to all projects undertaken by the company. The subsequent Project-Specific Objectives Sheet was used to list the particular boundaries that have been deemed to be required for the "Insetol" project.

Project title: *INSETOL*

Date: *09/ 02/ 1996* **General Objectives of the Project Sheet (Tool A.2)** **Page:** *01/ 01*

Author: _*E.S.*___________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

ID	Objective	Attribute	Date
O_{G1}	*Grey-listed substances should be avoided*		*9.2.96*
O_{G2}	*Carcinogenic substances should be avoided*		*9.2.96*
O_{G3}	*Ozone-depleting substances should be avoided*		*9.2.96*
O_{G4}	*Highly toxic substances should be avoided*		*9.2.96*
O_{G5}	*Unstable/explosive substances should be avoided*		*9.2.96*
O_{G6}	*Substances reactive with air or water should be avoided*		*9.2.96*
O_{G7}			
O_{G8}			
O_{G9}			
O_{G10}			
O_{G11}			
O_{G12}			
O_{G13}			
O_{G14}			
...			

Project title: *INSETOL*

Date: *09/ 02/ 1996* **Project-Specific Objectives Sheet (Tool A.2)** **Page:** *01/ 01*

Author: _*E.S.*___________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

ID	Objective	Attribute	Date
O_{P1}	*Environmentally sound processes for the starting materials*		*9.2.96*
O_{P2}	*Cost from starting materials and waste treatment less than 100 FIM/kg of product*		*9.2.96*
O_{P3}	*Chemistry known to the company where possible*		*9.2.96*
O_{P4}	*Rapid process development to achieve rapid access to markets*		*9.2.96*
O_{P5}	*Easy to produce in a multi-purpose plant*		*9.2.96*
O_{P6}	*Minimum amount of new chemicals, e.g. solvents*		*19.2.96*
O_{P7}			
O_{P8}			
O_{P9}			
O_{P10}			
O_{P11}			
O_{P12}			
O_{P13}			
O_{P14}			
...			

Example A.2.2: Objectives of an inherently safer design of an LPG process

Adopted from an article by J.C.A. Windhorst (Novacor Chemicals Ltd).
(Windhorst J.C.A., "Application of inherently safe design concepts, fitness for use and risk-driven design process safety standards to an LPG project", Proceedings of 8th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Volume II, Elsevier, 1995, pp. 543-554.)

The problem and the requirements

See Example A.1.2.

Objectives

If Novacor Chemicals had had access to the *INSET* Toolkit, the project-specific objectives mentioned in the article could have been listed on the form as shown on the last page of this example. (See also Example A.1.2 regarding the constraints of the project.)

The solution chosen by the company

The selected process satisfied the environmental requirements. This resulted in "spin-off" benefits in the process safety area – such as the reduction of "material" traffic at and around the site and the fact that staff would not handle unfamiliar chemicals.

The process would convert the C4 by-product into the butene-1 co-monomer via a selective hydrogenation step followed by a fractionation step. The product, the butene-1 co-monomer, butene-2, could be sold locally with a small amount of heavies which could be blended with the C5+ stream. Two butene-1 co-monomer daytanks (bullets) would be installed and used on an alternating basis, i.e. butene-1 would be pumped from the fractionation unit to one of two daytanks and sent to a sphere after a quality check. For this purpose, one of the C4 by-product spheres would be converted to butene-1 co-monomer service. Butene-2 product would be sent to a tank (bullet) before shipment.

Storage safety would be maximized by partial mounding of new storage vessels, thereby reducing deluge requirements. Mounding was a viable option in Joffre, Alberta, since the water table is low (minimizing buoyancy forces on vessels) and the climate would not cause excessive corrosion to mounded vessels.

Further gains were possible by locating some facilities in the by-product storage area, thereby reducing the process storage of hydrocarbons. Simulations of leaks and spills in the storage area and from the process equipment were done as part of the conceptual design, before any process simulation, in order to develop timely design specifications for the next design stages. The simulations showed that:

- liquid spills could be ruled out in the process area,
- liquid spills could occur in the storage area under low-pressure conditions. These low-pressure conditions can happen during the winter months when the temperature drops to temperatures as low as –40°C.

Since liquid spills in the reactor area were unrealistic, it would be served by a regular runoff (storm water) sewer except in the location(s) where heavy ends were produced/handled or lubricants for rotating equipment were to be used. A specially designed containment pit was envisioned for the storage area.

Analysis of the expected flare load indicated that the existing flares could handle this load. Venting of the hydrocarbons to the atmosphere would be minimized.

Three teams were interested in assuming responsibility for the by-product upgrader: Poly, E1 and Shipping, the latter being responsible for storage and by-product handling but not co-monomer unloading. An analysis of the territorial risks suggested that the upgrading facility would be best located in the area that fell under the responsibility of Shipping. This conclusion was based on consequence analyses (using similar database failure frequencies) for the different siting options. The result was driven by the capital investments in the different areas. After an analysis of human factors, however, it was concluded that locating the entire facility in Shipping could not be supported. Human factors considered were the level of Shipping operator experience with reactive systems and sophisticated process control. Based on plot plan, flaring and other considerations, the decision was made to locate the reactor section in the process facility nearest to the storage area, which resides under Shipping, away from the process.

As C4 spills were possible in the storage area, a vehicular ignition of a potential vapour cloud was considered a distinct possibility. The main reason for this is the fact that the main access road runs along the storage area. This busy road serves all main buildings. Day-staff levels in these buildings can reach hundred persons or more. A vapour cloud ignition would result in a flash fire or an explosion that might cause further knock-on effects. Since such an event would be relatively high risk to the staff, it was decided to design the storage area with a containment pit to minimize the vaporization of C4's. Had the storage area been in a remote area of the site, increased vaporization would have been considered the lowest-risk option and the preferred operating mode. Since the containment pit had to be available year round, heat tracing was required to ensure that the pit would not fill with snow and ice during the winter months.

The final process selection was done based on these safety and environmental factors.

Conclusions drawn by the company

1. Researchers', developers' and designers' prime responsibility is to build safe facilities.
2. Process safety and environmental risk criteria should be reconciled and unified.
3. Environmental protection/safety and process safety should be integrated into research, development and design activities from the very beginning.

4. Researchers, developers and designers (engineers) should review codes, regulations and rules critically to see if they are appropriate or apply.
5. Research, development and design should be done by knowledgeable cross-functional teams or individuals.
6. Spill and release simulations should be done at the conceptual design stage to establish the basis for a cost-effective and responsible environmental design and a sound cost estimate.

Project title: *LPG*

Date: ___ / ___ / *1995* **Project-Specific Objectives Sheet (Tool A.2)** **Page:** *01* / *01*

Author: _*YM*___________ **Proj. #:** _*LPG2*__________ **Ref. #:** ________

ID	Objective	Attribute	Date
O_{P1}	*Partial and selective hydrogenation*		*D.M.YY*
O_{P2}	*Reduction of the overall inventory of butene-1 co-monomer through more precise inventory management*		*D.M.YY*
O_{P3}	*Replacement of the temporary butene-1 co-monomer rail storage with deluge-protected fixed storage*		*D.M.YY*
O_{P4}	*Reduce rail transport exposure*		*D.M.YY*
O_{P5}	*Develop philosophy for dealing with vents and drains*		*D.M.YY*
O_{P6}	*Selection of a process with small inventories*		*D.M.YY*
O_{P7}	*Selection of a process with moderate pressures, in order to be able to use cooling water for condensation*		*D.M.YY*
O_{P8}	*Selection of process that does not require complicated process control systems*		*D.M.YY*
O_{P9}	*Minimization of waste products*		*D.M.YY*
O_{P10}	*No new disposal methods of, until now, unknown waste products*		*D.M.YY*
O_{P11}	*Allowing disposal of waste product(s) in existing by-product stream(s)*		*D.M.YY*
O_{P12}	*No new chemicals required, e.g. reactants*		*D.M.YY*
O_{P13}	*Utilization of a catalyst that can be readily handled before as well as after use*		*D.M.YY*
O_{P14}	*Utilization of a catalyst that can be disposed of, preferably through reactivation*		*D.M.YY*

SUPPORT FOR TOOL B – PROCESS OPTION GENERATION

Tool B supporting information

Process waste minimization guide

1. Introduction

The protection of the environment (together with the concept of environmentally sustainable development) is seen to be an important objective. However, issues of safety, health, and the environment are indivisible, and the *INSET* tools aim to encourage R&D scientists and design engineers to address concurrently all three aspects as a project progresses from its infancy to detailed final designs.

The *INSET* tools encourage all involved with the design of chemical processes and plant to consider the effects that their decisions will have on the environment during all stages of a design project. Once the likely impacts and issues have been identified, designers are then encouraged to search for environmentally better alternatives.

Waste minimization has not been directly addressed by the *INSET* tools. The decision was taken that the tools, which first help to identify environmentally hazardous or undesirable materials and which then challenge their use, should naturally promote the adoption of processes which minimize the production of wastes. For example, the environmental index will be of great assistance in focusing the designer's attention on the main streams which contribute to waste. Calculation of the environmental index will quantify the amounts and types of waste produced and encourage the process design team to seek ways in which the index may be further reduced.

The objective of this guide is therefore to provide an initial source of material which will help the design team to consider ways in which the production of wastes may be minimized.

Just as it has been recognized that conflicts are likely to exist between safety, health and environmental issues, it is also understood that the complete elimination of waste is unlikely to be a realistic goal.

2. The benefits of waste minimization

The benefits to a company which successfully minimizes waste are becoming increasingly apparent and include:
- cost savings – achieved by reducing raw materials costs, operating costs, waste treatment costs and waste disposal costs,
- better compliance with regulatory standards and targets,
- reduced potential for environmental liabilities,
- better protection of people's health and safety,
- better environmental protection,
- improved image.

Many of the benefits listed above are associated with the realization that the true costs of environmental harm had previously not been borne by the waste producer. Many societies are attempting to correct this imbalance by establishing a combination of regulatory and economic approaches to ensure that all the environmental costs are paid by the waste producer.

3. Some definitions

Process industry waste has been defined by the IChemE to be "a loss of raw materials, intermediates, by-products or main products which require time, manpower and money to manage". Tighter legal definitions may be found in European Commission definitions and national laws.

Waste minimization involves any technique, process or activity which either avoids, eliminates or reduces a waste at source, usually within the confines of the production unit, or allows re-use or recycling of the waste for benign purposes. Synonymous terms include:
- waste minimization,
- waste reduction,
- clean or cleaner technologies, engineering or processing,
- pollution prevention/reduction,
- environmental technologies,
- low and non-waste technologies.

4. An overview of waste minimization techniques

The European Community have established a hierarchy of waste management options:

Prevention *Best option*

⇑

Minimization

Recycling

Disposal *Worst option*

The list is presented in descending order of acceptability: prevention of waste generation at source is the preferred option, waste disposal is the least desirable option.

It must be stressed that waste minimization is concerned with prevention, minimization and recycling of wastes. End-of-pipe techniques are undesirable since they do not prevent the unwanted generation of waste but instead offer management some method of control by altering the form of the waste and/or the final disposal route of the waste. The desire to prevent the generation of waste at source closely matches the philosophy of inherent safety.

Of importance to a manufacturer is the fact that end-of-pipe treatments of wastes often involve a significant and on-going cost.

5. Approach to waste minimization studies

It is useful to first understand where process wastes may be generated. The origins of waste in the process industry have been succinctly described by Smith and Petela. Two main types of waste are identified:

1. process waste

⇑

   a. reactor waste — *First efforts*
   b. separation and recycle waste
2. utility waste
   a. waste from heat exchanger network
   b. utilities waste — *Last efforts*

There is a hierarchy of wastes; the arrow indicates the order of importance and where waste minimization efforts should be devoted to ensure the best savings.

The reaction dictates many of the other waste streams. Once the reaction route has been decided much of the flexibility to make savings in the areas of separation, recycle, utilities, etc. are constrained. The *INSET* Toolkit encourages chemists and those involved with the initial selection of the chemical route to also consider the engineering and process implications (from the perspective of safety, health and the environment) in order to design out potential problems as early as possible.

Having understood in a generic manner the origins of waste, a methodical study may be designed so that waste minimization measures may be identified and implemented as effectively and efficiently as possible. The US Environmental Protection Agency have recommended a structured approach to the identification of waste minimization opportunities:

- *Phase I - Planning and organization*
  This phase of the project involves obtaining management commitment, defining the project goals, and assembling a project team with the required blend of skills.
- *Phase II - Assessment*
  This phase of the project should involve the collection of data, design reviews, site inspections, prioritization and selection of waste minimization issues, generation of waste minimization options, and selection of options for further study.
- *Phase III - Feasibility and analysis phase*
  This phase involves technical evaluation, economic evaluation, and the selection of options for implementation.
- *Phase IV - Implementation*
  Obtaining the commitment and resources necessary to proceed, installation of any equipment, implementation of any procedures, and finally evaluation of performance.

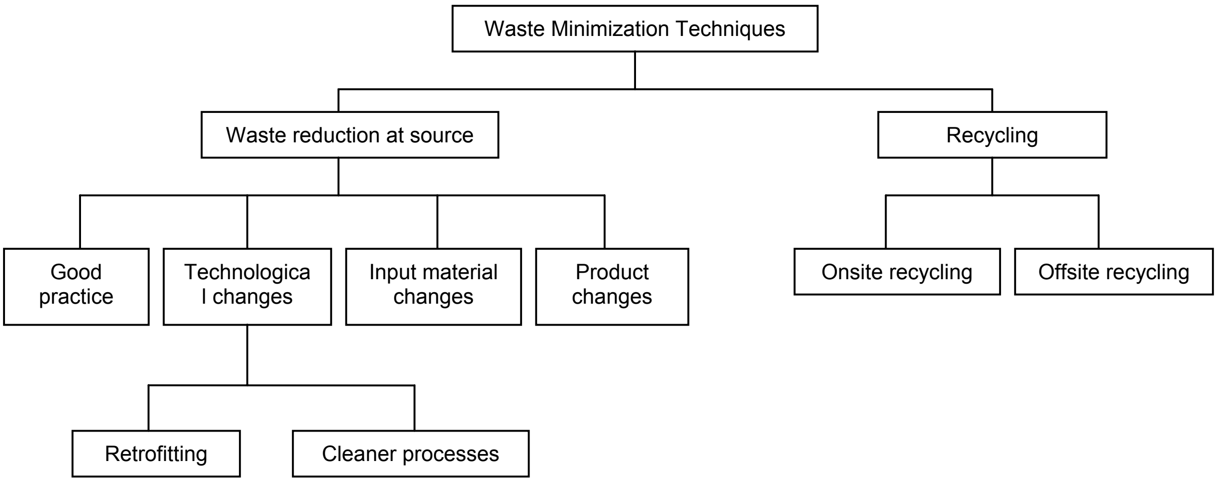
It is important to establish effective goals. It is much better to set measurable, quantifiable goals since qualitative goals can be interpreted ambiguously.

In common with many new things there can be barriers to the establishment of waste minimization projects despite the reduced costs and improved environmental performance that can be achieved. Conflicts between various departments may impair efforts to introduce new methods (production bottlenecks may be established, production may have to be halted, marketing functions may have to reassure customers, financing may be awkward, etc.). Such barriers should be identified and action taken to resolve any uncertainties as early as possible.

6. Assessment of other waste minimization opportunities

The approach recommended by the US EPA for the assessment of waste minimization opportunities is very similar to those described in the *INSET* Toolkit for the assessment of more inherently SHE alternatives: i.e. first, understand the issues and problems; second, generate alternatives/solutions; and finally, rank the alternatives.

Two broad types of waste minimization techniques may be identified, namely waste reduction at source and recycling:



Source reduction is preferred to recycling of wastes.

The reader is referred to the original reports for a more detailed description of the various waste minimization techniques. Just a few of each are listed below to illustrate what is meant by each technique.

6.1 Source reduction

Good practice

The positive action of ensuring that all waste production steps are identified and understood is the first step to successful waste minimization. Relatively simple actions may then be taken to minimize waste by implementing good management practices such as good housekeeping, good operations and good maintenance.

The effort required is typically of an operational and administrative nature which may be quickly set up and show relatively quick pay-backs.

Technology changes

An assessment of the wastes arising may indicate that wastes can be minimized by technological changes. Technological changes could include: changes in the production process; changes to equipment, layout or piping; the use of automated procedures; and changes in operating conditions (flow rates, temperature, pressure, residence times, sequencing).

The reactor should be considered to be the heart of the process and is frequently the root cause of most waste. There are five major sources of waste production from reactors:
1. difficulties recycling unreacted feed material back into the reactor.
2. primary reactions producing waste.
3. secondary reactions of the desired product leading to waste by-products.
4. impurities in the feed becoming wastes or undergoing reactions to produce additional waste by-products.
5. degradation of catalysts or the need to replace catalysts in a way that they have to be disposed of.

Smith and Patela have identified a number of areas in the design and operation of chemical reactors where unwanted wastes may be generated. Techniques based upon an understanding of reaction kinetics and thermodynamics are suggested to help reduce the waste produced by both single and multiple reaction systems.

Technological changes may be made to process and/or equipment specifications. The scale of the technological changes can range from no/low cost modifications to those which require substantial modifications and cost.

Input material changes

As discussed above, wastes may arise from the choice of the input material. The wastes may be inherent in the choice of raw material and can be avoided only by finding alternative inputs (e.g. aqueous-based paint systems rather than solvent-based systems). Alternatively, wastes may be impurities in the input material and may be avoided by:
- purification.
- substitution for a better-specified alternative supply.
- substitution for a completely different material.

Product changes

A manufacturer may implement changes to the final product with a view to minimizing wastes during either manufacture and/or upon final disposal by the end-user. Options available to the manufacturer include:
- product substitution (e.g. replacement of solvent-based systems by aqueous alternatives),
- product conservation (e.g. changing/reducing the amounts of packing), and
- changes to the product composition (e.g. reformulations of primary batteries to avoid the use of mercury).

6.2 Recycling

Wastes may be recycled by:
- *use* as an input in another process;
- *re-use* as an input in the originating process; or
- *reclamation* of valuable material. Recycling may be performed on-site or off-site. (Reclamation is normally performed off-site.)

It must be emphasized that the reduction of waste at source is preferable to recycling. Whilst recycling is better than disposal, it is likely to consume more resources (energy and management time) than methods which reduce waste at source.

7. Waste minimization in the context of inherent SHE

The generation of waste is known to be an inefficient and wasteful use of resources.

Historically, waste minimization efforts were devoted mainly to areas which directly impacted upon profits, often with little regard to effects beyond the factory fence. This type of attitude is no longer acceptable and failure to address the causes of waste production could jeopardize a company's future success and well-being. Waste minimization as a self-contained exercise has been recognized by, for example, the US EPA and the IChemE as an important and valuable activity. Waste minimization is also considered to be an important component of the design of chemical plant and processes. However, waste minimization cannot be considered as an isolated part of the design process and for this reason strenuous efforts have been made to incorporate aspects of inherent safety, health and the environment into the design process. Accordingly, waste minimization should be a natural consideration when using the *INSET* tools to first select the chemical route and in the subsequent stages of process design.

7.1 Best environmental option

The options for waste disposal that are available to industry are becoming increasingly restricted and unattractive as the environment becomes more heavily regulated. Where the generation of process wastes is unavoidable, a decision must be made regarding the most suitable final destination for the waste. This can be an extremely difficult decision to make, especially since man's understanding of the environment remains relatively primitive and the data which would be required to make a fully informed selection are rarely available.

Her Majesty's Inspectorate of Pollution in the UK have attempted to help define the best environmental option in terms of an index which takes into account pollution loads to various environmental compartments and which then assigns weights so that the total environmental burden may be estimated. This calculation may be performed for a number of process configurations and the best alternative then identified. Whilst such an approach provides a clear framework in which decisions may be made, it has received criticism since it sums the effects from various environmental compartments in a manner which cannot be justified on purely scientific grounds.

The position with regard to best environmental option calculations is further complicated when financial considerations are taken into account. It is clearly unreasonable to expect a company to invest what may be large sums of money to achieve the best option, when an alternative which is nearly as good may be achieved at a fraction of the cost. Arguments of degree then come into play. Methods of cost-benefit analysis could be used to resolve the problem by identifying the point at which additional costs are not offset by environmental benefits. However, the information required by cost-benefit techniques are rarely available.

Thus, whilst recognizing the need to select the best environmental option, it cannot be emphasized too strongly that waste prevention is the best way to proceed. The approaches encouraged by the *INSET* Toolkit will help to eliminate waste and, if that cannot be achieved, identify the waste disposal options.

7.2 Life-cycle design

The concept of life-cycle analysis or life-cycle design has received increased attention over recent years. Behind the titles lie the common idea that the environmental burdens should be considered at all stages of the project, ideally including the burdens of winning raw materials, through power generation and transport, up to final disposal of all items used in the manufacture and use of the product. Such concepts are in the spirit of the *INSET* Toolkit.

Consideration of the wastes that are generated, and how they may be best disposed, are of direct relevance to designers of plant.

Life-cycle design - Strategies

Life-cycle design strategies for waste disposal focus on the concept of *waste modification:*
- could the waste be made into a product or by-product?
- could the waste be made reusable/recyclable?
- could the waste be made easier to recover?
- could the waste be made easier to treat?
- could the waste be made easier to dispose or render harmless?
- could the waste be made more/less mobile in the environment, perhaps by aiding or hindering dispersion in the environment?

Life-cycle design - Some techniques

Techniques suitable to modify waste could include changing:
- concentration
- chemical composition
- pH
- pressure and/or temperature
- the state (solid, liquid, vapour, slurry)
- particle size/distribution
- water content (hydrate/dehydrate)
- solubility
- boiling point
- reactivity.

No strict guidelines can be made regarding the direction of the change. For example, if a waste had been identified as suitable for recovery or secondary processing then it might be appropriate to make the waste more reactive (or less inert). Alternatively, final disposal to landfill might be most suitable in which case it would be likely that modifications to make the waste less reactive (or more inert) would be most appropriate.

Other approaches may also help with waste management and the design team should consider:
- separating or combining waste components,
- combining with other additives, reagents or carriers,
- encapsulation of wastes.

7.3 Waste minimization techniques

Finally, in an effort to help designers to seek and implement waste minimization approaches, some methods and lists are included as aids to stimulate the search for alternatives and/or solutions to problems:
- Step 5, in the Tool B Instructions, lists waste minimization keywords which may be used within a waste minimization brainstorming session.
- Table 1 lists techniques by which environmental releases may be managed. These should be thought of as methods of last resort, and whilst it is recognized that the use of some in a design may be

inevitable, it must be appreciated that their use in a process is at odds with the philosophy of inherent SHE.

- Table 2 reproduces a list produced by the US EPA which highlights the types of waste typical of plant operations. The US EPA also produced a list of causes and controlling factors in waste generation for which the reader is referred to the original reports for further details.

All the approaches identified in this discussion of waste minimization are consistent with those developed during the *INSIDE* Project, namely the identification of alternatives followed by an assessment of each alternative and finally informed option selection.

References

Crittenden B. and Kolaczkowski S., "Waste minimization – A practical guide", IChemE, Rugby, UK, 1995.

European Community Waste Framework Directive (91/156/EEC)

HMIP, "Environmental, economic and BPEO assessment principles for integrated pollution control", Draft Technical Guidance Note E1 (Environment), 1995.

Keoleian G.A. et al., "Product life-cycle assessment to reduce health risks and environmental impacts", Noyes Data Corporation, 1994.

SETAC, "A conceptual framework for life-cycle impact assessment", Society of Environmental Toxicology and Chemistry, 1993.

Smith R. and Petela E., "Waste minimization in the process industries – (1) The problem", The Chemical Engineer, 31 October 1991, pp. 24-25.

Smith R. and Petela E., "Waste minimization in the process industries – (2) Reactors", The Chemical Engineer, 12 December 1991, pp. 17-23.

US Environmental Protection Agency, "Waste minimization opportunity assessment manual", US EPA Hazardous Waste Engineering Research Laboratory, Office of Research and Development, Cincinnati, Ohio, USA, 1988.

Table 1 Release minimization – Abatement techniques
(1) Techniques suitable for the minimization of airborne releases

Point of release	**Abatement techniques**
Pressurized releases	phase separation (e.g. two-phase flow) scrubber flare vent dump tank knock-out drum parallel release with two pressure settings total containment vs venting
Storage	floating-roof tanks internal floating covers venting (combustion, condensation, absorption, adsorption)
Transfer (loading/unloading)	sub-surface filling filling to bottom of vessel vapour balance lines (= closed loop?) extraction to arrestment plant
Transfer (e.g. to cooling/washwaters)	carry-over phase separation intermediate stripping drainage to effluent plant discharge to vessels with suitable treatment (e.g. drum storage, filters) vent and stream vessels to flare
Secondary releases (e.g. of washwater)	cooling/quenching water steam ejectors carrier media (e.g. for catalysis, neutralizing agents) water formed as a by-product consider pre-stripping
Particulates	cyclones fabric filters ceramic filters wet collection devices electrostatic precipitators dust suppression equipment
Gaseous matter	condensation absorption adsorption biofiltering and scrubbing thermal decomposition

Table 1 (cont'd) Release minimization – Abatement techniques
(2) Techniques suitable for the minimization of waterborne releases

Option/alternative	**Abatement techniques**
Reduce wastewater discharges	recycle (to process, to secondary uses) segregate (process water, secondary water, storm water) minimize washing consider dry-cleaning wipe PINCH analysis
Pre-treatment	in-plant pre-treatment of *heavy metals* (oxidation/reduction, precipitation/filtration) in-plant pre-treatment of *organics* (oxidation, air/steam stripping, GAC (granular activated carbon), ion-exchange, reverse osmosis, electrodialysis) primary treatment (neutralization, coagulation/flocculation, flotation/sedimentation/filtration, biological roughing, trickle filter, anaerobic treatment) secondary treatment (aerated lagoon, rotating biological contactors, activated sludge) tertiary treatment (filtration, ozonation, GAC, powdered activated carbon, denitrification/nitrification, sludge dewatering, gravity thickening, dissolved-air flotation, filtration, drying, centrifugation, sludge digestion sludge disposal (land, lagoon, incineration, encapsulation)
Separate organics	American Petroleum Institute (API) separators tilted plate separators electrostatic coalescers dissolved and induced air floatation use of acceptable physical coalescing systems
Steam stripping	e.g. for removal of sulphurous contaminants
Neutralization	
Solids removal	settlement floatation precipitation dewatering filtration
Biological treatment	
Activated carbon	
Ion exchange	
Electrolytic exchange	
Membrane processes	ultrafiltration reverse osmosis membrane filtration pervaporation
Oxidation techniques	wet air advanced (peroxides, ozone-promoted (UV, semi-conductor photocatalysts))
Thermal destruction	

Table 1 (cont'd) Release minimization – Abatement techniques
(3) Techniques suitable for the minimization of releases to land

Option	**Abatement techniques**
Disposal of solids	incineration solidification encapsulation biological composting landfill
Dusty solids	use flakes weigh under extraction use flexible fabric seals (e.g. for transfer) enclose automatic equipment dissolve (sacks into vessel contents) fill from bottom to top
Packaging	minimize use bio-degradable products

Table 2 Typical wastes from plant operations (source: US EPA, IChemE)

Plant function	Location/operation	Potential waste material
Material receiving	Loading docks, incoming pipelines, receiving areas	Packaging materials, off-spec materials, damaged containers, inadvertent spills, transfer hose emptying
Raw materials and product storage	Tanks, warehouses, drum storage yards, bins, storerooms	Tank bottoms, off-spec/excess materials, spill residues, leaking pumps/valves/tanks/pipes, damaged containers, empty containers
Production	Melting, curing, baking, washing, coating, formulating, reaction, materials, handling	Washwater, rinse water, solvents, still bottoms, off-spec products, catalysts, empty containers, sweepings, duct work clean-out, additives, oil, filters, spill residue, excess materials, process solution dumps, leaking pipes/valves/hoses/tanks/process equipment
Support services	Laboratories	Reagents, off-spec chemicals, samples, empty sample/ chemical containers
	Maintenance shops	Solvents, cleaning agents, degreasing sludges, sand blasting waste, caustic, scrap metal, oils, greases
	Garages	Oils, filters, solvents, acids, caustics, cleaning bath sludges, batteries
	Powerhouses/boilers	Fly ash, slag, tube clean-out material, chemical additives, oil, empty containers, boiler blowdown
	Cooling towers	Chemical additives, empty containers, cooling tower blowdown, fan tube oils

SUPPORT FOR TOOL C – PRELIMINARY CHEMISTRY ROUTE OPTIONS RECORD

Tool C examples

Example C.1: Documentation of a synthetic route for the production of Z-Pro-OMe

Adopted from an article by K. Takeda et al. (Kitasato University).
(Takeda K. et al., "Dicarbonates: convenient 4-dimethylaminopyridine catalysed esterification reagents", Synthesis 1994, pp. 1037-1042.)

The project

The result of the search to find a synthetic route for the production of Z-Pro-OMe included a route alternative from *Synthesis* from the October 1994 issue.

The write-up of the reaction is exactly as follows:

Methyl Benzyloxycarbonylprolinate (6); General Procedure:
To a solution of Moc_2O (40 mg, 0.28 mmol) **(1a)** and Z-Pro (53.3 mg, 0.2 mmol) in dry THF (2 ml) was added DMAP (2.5 mg, 0.02 mmol) at r.t. After 5 min, the solvent was removed in vacuo and the residue was purified by preparative TLC (silica gel; benzene/acetone, 15:1) to give Z-Pro-OMe **(6)**[8] (54.1 mg, 96%) (Table 1, run 4).

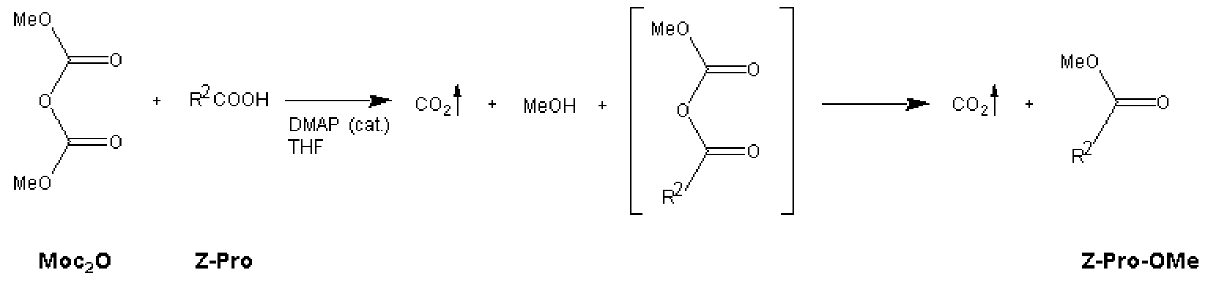
The following data-sheet was filled in with the information obtained from the "recipe" given.

This recipe, displayed in the form of a graphical chemical reaction scheme, allows the chemist to visualize the amount of steps involved with the synthetic route.

Project title:

Date: ___ / ___ / ______ **Preliminary Chemistry Route Options Record (Tool C)** **Page:** ___ / ___

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________ **Route for:** ____________________



DMAP = 4 - dimethylaminopyridine

1

Source: *Synthesis 10, October 1994, p. 1063* **Lead to new ref.:**

Reaction conditions		Overall yield	Possible variations	Other comments	Reason for failure
Step	*A-D*	*96%*	*A suggested variation uses the DMAP catalyst on polystyrene. Reaction time: 96 hr, yield: 93%.*	*Purified on silica gel, with benzene/acetone @ 15:1. Product is an oil.*	
Temp.	*RT*				
Pressure	*n/a*				
Time	*5 min.*[+]				
Yield	*96%*				

SUPPORT FOR TOOL D – PRELIMINARY CHEMISTRY ROUTE RAPID ISHE EVALUATION METHOD

Tool D examples

Used in the initial stages of chemical process route assessment, Tool D of the *INSET* Toolkit enables a rapid evaluation of route alternatives in order to limit the number of alternatives needing more thorough analysis.

Example D.1 shows the answers obtained for the general screening questions when applying Tool D to some of the alternative routes that lead to the fictitious substance "Insetol".

Example D.2 shows how Tool D could have been used if it had been available to those involved in the project described. The information in the referenced article has been used as input.

Example D.1: Insetol

A company intends to start developing a process to produce the fictitious chemical "Insetol". The preliminary chemistry route rapid ISHE evaluation method was used to rapidly screen the many alternatives found. The records for three of these are shown at the end of the example.

It can be seen from this example that none of the three alternatives can be found to be dominant. However, by working through the set of questions, the chemist has realized that the wastewater formation in alternative 3 is at an unacceptable level, and a better option should be sought (e.g. by challenging the process alternative, using Tool B). If no better alternative can be found, alternative 3 should be abandoned. If a major change is required to alterna-
tive 3 in order to make it acceptable, it would be better to introduce this process as a new alternative with its own reference number.

Project title: *INSETOL*

Date: *09/ 02/ 1996* **General Screening Questions Results Sheet (Tool D)** **Page:** *01/ 01*

Author: _*E.S.*___________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

Ref. #	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	...	Reason	Decision
A_1	?	?	?	Yes	No	Yes	No	Yes	Yes	Yes				Recognized that there may be SHE problems, BUT: this alternative is probably commercially available	+
A_2	?	?	?	Yes	No	Yes	Yes	Yes	Yes	Yes				Closely related to a commercial alternative	+
A_3	?	?	?	No	?	Yes	Yes	Yes	Yes	No				Waste from the diazotization operation	–
A_4															
A_5															
A_6															
A_7															
...															

Example D.2: Rapid ISHE evaluation of synthetic routes for the production of methyl methacrylate

Adopted from an article by D.W. Edwards and D. Lawrence (Loughborough University of Technology). (Edwards D.W. and Lawrence D., "Assessing the inherent safety of chemical process routes: Is there a relation between plant costs and inherent safety", Trans IChemE, Vol. 71, 1993, pp. 252-258.)

The project

If Loughborough University of Technology had had access to the *INSET* Toolkit, the comparison of the alternatives mentioned in the article could have been made as shown on the last page of this example.

Based on the information given in Table 8 of the referenced article, the General Screening Questions Results Sheet has now been filled in by a chemical engineer who had no experience with the production of methyl methacrylate. This is often the case when new alternatives are sought. The correctness of the answers has not been checked, which also reflects normal practice.

The engineer also identified two possible alternatives when using Tool B to challenge two of the original alternatives.

The abbreviations used to identify the alternatives are based on those used in Table 8 of the article. This table is also given here for ease of reference.

Route/Step	Reactants	Products	Temp. [°C]	Pressure [psia]	Yield [%]
ACH	**Acetone cyanohydrin**				
1	methane ammonia oxygen	hydrogen cyanide	1200	50	80
2	acetone hydrogen cyanide	ACH	29-38	15	91
3	ACH sulphuric acid	HMPA/HMPASE	130-150	103	98
4	HMPA/HMPASE methanol	MMA	110-150	103	100
5	sulphuric acid ammonium bisulphate oxygen fuel gas	sulphur dioxide carbon dioxide nitrogen	980-1200	15	100
6	sulphur dioxide oxygen	sulphur trioxide	405-440	15	100
	HMPA = 2-hydroxy-2-methyl propionamide HMPASE = 2-hydroxy-2-methyl propionamide sulphate ester				
C2/PA	**Ethylene-based via propionaldehyde**				
1	ethylene carbon monoxide hydrogen	propionaldehyde	130	220	91
2	propionaldehyde formaldehyde	methacrolein	160-185	720	98
3	methacrolein oxygen	methacrylic acid	350	–	58
4	methacrylic acid methanol	MMA	70-100	100-110	75
C3	**Propylene-based**				
1	propylene carbon monoxide hydrogen fluoride	isobutyl fluoride	70	1322-1469	95
2	isobutyryl fluoride water	isobutyric acid	40-90	147	96
3	isobutyric acid oxygen	methacrylic acid	320-354	37-44	61
4	methacrylic acid methanol	MMA	70-100	100-110	75

C2/MP	**Ethylene-based via methyl propionate**				
1	ethylene carbon monoxide methanol	methyl propionate	100	1469	89
2	methanol oxygen	methylal	–	–	–
3	methyl propionate methylal	MMA	350	–	87
i-C4	**Isobutylene-based**				
1	isobutylene oxygen	methacrolein	395	–	42
2	methacrolein oxygen	methacrylic acid	350	54	58
3	methacrylic acid methanol	MMA	70-100	100-110	75
TBA	**Tertiary butyl alcohol (TBA)-based**				
1	TBA oxygen	methacrolein	350	71	83
2	methacrolein oxygen	methacrylic acid	350	54	58
3	methacrylic acid methanol	MMA	70-100	100-110	75

Project title: *MMA*

Date: *23/ 08/ 1996* **General Screening Questions Results Sheet (Tool D)** **Page:** *01/ 01*

Author: _*H.K.*___________ **Proj. #:** _*MMA1*___________ **Ref. #:** ________

Ref. #	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	...	Reason	Decision
A_1 (ACH)	No	No	Yes	Yes	Yes	Yes	Yes	Yes	No	No	Yes	?		Several hazardous chemicals involved	–
A_2 (C2/PA)	No	No	Yes	No	Yes	Yes	Yes	No	No	No	Yes	?		C_2H_4 , CO, H_2 , propionic aldehyde, formaldehyde, methacrolein	–
A_3 (C2/MP)	No	No	?	No	Yes	No	Yes	No	No	No	Yes	No		C_2H_4 , CO	–
A_4 (C3)	No	No	?	Yes	Yes	No	No	No	No	No	Yes	No		CO, HF	–
A_5 (TBA)	No	No	?	No	Yes	No	No	No	No	No	No	No		Methacrylate may pose a problem	+
A_6 (i-C4)	No	No	?	No	Yes	No	No	No	No	No	No	No		Methacrylate may pose a problem	+
A_7 (A_1 mod)	No	No	Yes	Yes	Yes	Yes	Yes	No	No	No	Yes	?		Several hazardous chemicals involved	–
A_8 (A_2 mod)	No	No	No	No	No	No	No	No	No	No	Yes	?		CO	+

SUPPORT FOR TOOL E – PRELIMINARY CHEMISTRY ROUTE DETAILED ISHE EVALUATION METHOD

Tool E examples

Used in combination with Tool A at the initial stages of chemical process route assessment, Tool E of the *INSET* Toolkit enables a detailed evaluation of route alternatives in order to limit the number of alternatives needing more thorough analysis.

Example E.1 shows how the Criteria Screening Matrix has been used on some of the alternative routes to a fictitious substance "Insetol".

Example E.1: Insetol

A company intends to start developing a process to produce the fictitious chemical "Insetol". The forms of Tool A were filled in earlier and were now used as criteria. The records for three of the many alternatives found are shown at the end of this example.

As no dominant alternative can be identified based on the constraints, this example emphasizes the need to complete both Tools A.1 and A.2 – identifying as many relevant criteria as possible. Since the objectives are negotiable, the amount of "–" ratings only gives an indication of how unattractive a certain alternative is.

Project title: *INSETOL*

Date: *09*/ *02*/ *1996* **Criteria Screening Matrix (Tool E)** **Page:** *01*/ *01*

Author: _*E.S.*___________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

Alternative Ref. #	Constraints										Meets constraints	Objectives										Passes initial screen
	C_{G1}	C_{G2}	C_{G3}	...	C_{P1}	C_{P2}	C_{P3}	C_{P4}	C_{P5}	...		O_{G1}	O_{G2}	O_{G3}	O_{G4}	O_{G5}	O_{G6}	O_{P1}	O_{P2}	O_{P3}	...	
A_1	+?	+			+	+?					+?	+	+?	−	+?	−	+	+	−			
A_2	+?	+			+	+?					+?	+	+?	−	+?	−	−	+	+?			
A_3	+?	+			+	+?					+?	+	+?	+	+?	−	−	+	+?			
A_4																						
A_5																						
A_6																						
A_7																						
A_8																						
A_9																						
A_{10}																						
...																						

Footnote 1	
Footnote 2	
Footnote 3	

SUPPORT FOR TOOL F – CHEMISTRY ROUTE BLOCK DIAGRAM RECORD

Tool F examples

This tool, while being the logical next step following the completion of *INSET* Stage I, can also be implemented as the initial step in cases where the route alternatives to a particular product are limited in number and already defined. This will, in reality, be the case for many projects that are already at a particular level of development.

Example F.0 – although not showing the use of Tool F itself – is included here to illustrate a typical case where the decision-making tools presented in *INSET* Stage I are not needed. An initial screening by using *INSET* Tools D or E was not necessary due to the small amount of alternatives identified. The chemist responsible for the search had no problems in deciding which dominant route alternatives to study further.

Example F.1 shows the block diagram of the isolation and purification stages for one of the alternative routes to the fictitious chemical substance "Insetol".

Example F.0: Heterocyclic compound – Alternatives generation, constraints & objectives, and identification of the most feasible alternatives as an input to Tool F

Adopted from internal reports of one of the members of the *INSIDE* consortium.

The problem

A business opportunity arose for the development of a chlorinated heterocyclic compound. The problem was to develop a competitive process within the time frame given by the potential customer.

Alternatives generation

Alternatives were generated in the following ways:

1. Published information
A search for published methods to synthesize the compound in question was carried out. The search covered information found from the following sources:
- Chemical Abstracts (recent publications by a data search, older publications searched manually),
- Beilstein (database),

- ORAC-programme,
- handbooks and textbooks.

2. Computer-assisted synthesis
No retrosynthetic analysis was carried out.

3. Experts
Ideas were generated by the chemist responsible. These ideas were mainly based on knowledge gained from analogous processes. The ideas presented can be subdivided into:
- the "ideal" process,
- alternatives not mentioned in the literature but still "theoretically" possible with regards to the basic chemistry, and
- innovative alternatives (no knowledge of whether they actually will work in reality).

The ideas were validated by searching for the suggested reactions in the open literature.

The results of the steps above were summarized by the chemist in a report including short comments on the different alternative concepts – separate literature searches were carried out for the intermediates and these were reported in a similar fashion.

The *INSET* approach

According to the *INSET* approach, the form presented in Tool A.1, to summarize the constraints of the project, and the form presented in Tool A.2, to list the desired objectives, have been used (as shown on the next pages). The constraints and objectives for the project were not explicitly defined, but the chemist involved in the screening of the synthesis alternatives was aware of the general limitations.
Note In this example, we have categorized neither the constraints nor the objectives into the "general" or "project-specific" types.

The initial screening was based on the following aspects:
- synergy with existing processes,
- processes that are not accepted or not wanted by the production plant,
- economically impossible processes (regardless of yield, etc.) and curiosities.

In this case, only six feasible route types to the desired compound were identified.

Of the following production principle categories, categories 1, 2 and 5 (of which 1 and 2 make up a synthesis route) are covered in more detail by the literature. Alternatives 1 and 2 include synergy to starting materials A and B already used by the company. Methods in category 5 may include the cheapest route.

Category	Production method
1	Chlorination of the hydroxyl group of the starting material: typical reagents are PCl_5, $POCl_3$ and $SOCl_2$.
2	Rearrangement followed by chlorination: typical reagents are PCl_5 and $POCl_3$ ($SOCl_2$ is not among the reagents mentioned in the literature!).
3	Oxidation of an alkyl group (the oxidizer can even be chlorine), followed by hydrolysis of the chlorinated compound.
4	Hydrolysis of side-chain halogenated and ring-chlorinated starting material.
5	Synthesis of the heterocyclic ring from non-cyclic starting materials.
6	Miscellaneous procedures.

Subsequently, these alternative routes were documented as block diagrams in Tool F. Later, other *INSET* Stage II tools were used according to the instructions given (including option generation by using Tool B).

Project title: *HETCOMP1*

Date: *08/ 04/ 1996* **Constraints of the Project Sheet (Tool A.1)** **Page:** *01/ 01*

Author: _*E.S.*___________ **Proj. #:** _*HC1*____________ **Ref. #:** ________

ID	Constraint	Date
C_1	*Raw material costs must be less than X ECU/kg*	*8.4.96*
C_2	*The production process must not be covered by patents*	*8.4.96*
C_3	*Known reagents (mentioned in the EINECS list)*	*8.4.96*
C_4	*Major investments not allowed*	*8.4.96*
C_5	*Production capacity must exceed Y tons per month*	*8.4.96*
C_6		
C_7		
C_8		
C_9		
C_{10}		
C_{11}		
C_{12}		
C_{13}		
C_{14}		
...		

Project title: *HETCOMP1*

Date: *08/ 04/ 1996* **Objectives of the Project Sheet (Tool A.2)** **Page:** *01/ 01*

Author: _*E.S.*___________ **Proj. #:** _*HC1*____________ **Ref. #:** ________

ID	Objective	Attribute	Date
O_1	*Chemistry known to the company where possible*		*8.4.96*
O_2	*Rapid process development to achieve rapid access to markets*		*8.4.96*
O_3	*Easy to produce in a multi-purpose plant*		*8.4.96*
O_4	*Acceptable amount of waste*		*8.4.96*
O_5	*Minimum amount of new chemicals, e.g. solvents*		*8.4.96*
O_6			
O_7			
O_8			
O_9			
O_{10}			
O_{11}			
O_{12}			
O_{13}			
O_{14}			
...			

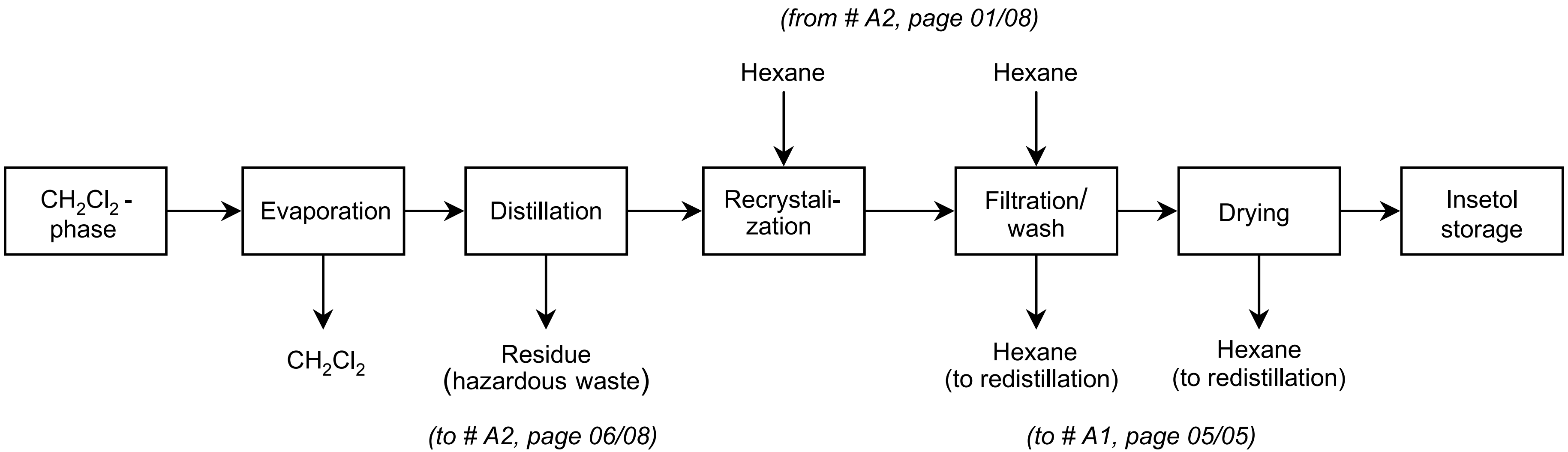
Example F.1: Insetol

A company has identified three potential chemical routes to produce the fictitious chemical substance "Insetol". Later, using Tool B, Process Option Generation, a modified version of alternative 2 was identified. This version was called alternative 4. The block diagram at the end of this example is for the isolation and purification stage of the product using the new alternative design.

Project title: *INSETOL*

Date: *03/ 08/ 1996* **Chemistry Route Block Diagram Record (Tool F)** **Page:** *03/ 03*

Author: _*YM*_____________ **Proj. #:** _*IT1*____________ **Ref. #:** _*A4*_____ **Block diagram for:** _*Isolation and purification*



Source: **Lead to new ref.:**

Possible variations	Other comments	Reason for failure

SUPPORT FOR TOOL G – CHEMICAL HAZARDS CLASSIFICATION METHOD

Tool G examples

Example G.1: Chemistry material hazards classification of synthetic routes for the production of methyl methacrylate

Adopted from an article by D.W. Edwards and D. Lawrence (Loughborough University of Technology). (Edwards D.W. and Lawrence D., "Assessing the inherent safety of chemical process routes: Is there a relation between plant costs and inherent safety", Trans IChemE, Vol. 71, 1993, pp. 252-258.)

The project

If Loughborough University of Technology had had access to the *INSET* Toolkit, a classification of the chemical hazard inherent in the alternatives mentioned in the article could have been made as shown on the last page of this example.

Based on the information given in Table 8 of the referenced article, and together with MSDS information, the Tool G form, Chemical Function & Hazards Classification, has now been completed for two process alternatives for methyl methacrylate.

In order to identify the alternatives, the abbreviations are as used in Table 8 of the article. This table is also given here for ease of reference.

Route/Step	Reactants	Products	Temp. [°C]	Pressure [psia]	Yield [%]
ACH	**Acetone cyanohydrin**				
1	methane ammonia oxygen	hydrogen cyanide	1200	50	80
2	acetone hydrogen cyanide	ACH	29-38	15	91
3	ACH sulphuric acid	HMPA/HMPASE	130-150	103	98
4	HMPA/HMPASE methanol	MMA	110-150	103	100
5	sulphuric acid ammonium bisulphate oxygen fuel gas	sulphur dioxide carbon dioxide nitrogen	980-1200	15	100
6	sulphur dioxide oxygen	sulphur trioxide	405-440	15	100
	HMPA = 2-hydroxy-2-methyl propionamide HMPASE = 2-hydroxy-2-methyl propionamide sulphate ester				
C2/PA	**Ethylene-based via propionaldehyde**				
1	ethylene carbon monoxide hydrogen	propionaldehyde	130	220	91
2	propionaldehyde formaldehyde	methacrolein	160-185	720	98
3	methacrolein oxygen	methacrylic acid	350	–	58
4	methacrylic acid methanol	MMA	70-100	100-110	75
C3	**Propylene-based**				
1	propylene carbon monoxide hydrogen fluoride	isobutyl fluoride	70	1322-1469	95
2	isobutyryl fluoride water	isobutyric acid	40-90	147	96
3	isobutyric acid oxygen	methacrylic acid	320-354	37-44	61
4	methacrylic acid methanol	MMA	70-100	100-110	75

C2/MP	**Ethylene-based via methyl propionate**				
1	ethylene carbon monoxide methanol	methyl propionate	100	1469	89
2	methanol oxygen	methylal	–	–	–
3	methyl propionate methylal	MMA	350	–	87
i-C4	**Isobutylene-based**				
1	isobutylene oxygen	methacrolein	395	–	42
2	methacrolein oxygen	methacrylic acid	350	54	58
3	methacrylic acid methanol	MMA	70-100	100-110	75
TBA	**Tertiary butyl alcohol (TBA)-based**				
1	TBA oxygen	methacrolein	350	71	83
2	methacrolein oxygen	methacrylic acid	350	54	58
3	methacrylic acid methanol	MMA	70-100	100-110	75

Project title: *MMA*

Date: *02/ 09/ 1996* **Chemical Function & Hazards Classification (Tool C/Tool G)** **Page:** *01/ 01*

Author: _*H.K.*___________ **Proj. #:** _*MMA1*____________ **Ref. #:** _*A2 (C2/PA)*_

Chemical	Function	Comments	Safety	Health	Environment
Ethylene	*R*		*H*	*H*	*L*
Carbon monoxide	*R*		*VH*	*VH*	*VH*
Methanol	*R*		*H*	*H*	*H*
Methyl propionate	*Int.*		*H*	*VH*	*M*
Air	*R*	*Could be replaced by oxygen*	*L*	*L*	*L*
Methylal	*Int.*		*H*	*H*	*H*
Water	*W*	*May contain minor amounts of methanol and metylal*	*L*	*L*	*L*
Purged air	*W*	*May contain minor amounts of methanol and metylal*	*?*	*?*	*?*
Zr/P-mixed oxide	*C*		*?*	*?*	*?*
Co/Rh	*C*	*Heavy metals (Co)*	*?*	*?*	*?*
Methyl methacrylate	*P*		*M*	*M*	*L*
Bottoms from product distillation	*W*	*Might be used as fuel in the refinery*	*?*	*?*	*?*

Project title: *MMA*

Date: *02/ 09/ 1996* **Chemical Function & Hazards Classification (Tool C/Tool G)** **Page:** *01/ 01*

Author: _*H.K.*___________ **Proj. #:** _*MMA1*___________ **Ref. #:** _*A5 (TBA)*_

Chemical	Function	Comments	Safety	Health	Environment
t-Butyl alcohol	*R*		*H*	*H*	*M*
Air	*R*	*Could be replaced by oxygen*	*L*	*L*	*L*
Methacrolein	*Int.*		*H*	*VH*	*VH*
Water	*S*		*L*	*L*	*L*
Methacrylic acid	*Int.*		*H*	*M*	*?*
t-Butyl acetate	*S*	*Flammable liquid, irritant*	*M*	*L*	*L*
Methanol	*R*		*M*	*M*	*M*
MoBiSb	*C*		*?*	*?*	*?*
P-Mo	*C*		*?*	*?*	*?*
Carboxylic acid	*C*		*?*	*?*	*?*
Waste water	*W*	*Contains small amounts of organic chemicals*	*?*	*?*	*?*
Purged air	*W*	*Contains small amounts of organic chemicals*	*?*	*?*	*?*
Methyl methacrylate	*P*		*M*	*M*	*L*

Tool G supporting information

Material safety data sheets

The MSDS, sometimes called the CSDS (chemical safety data sheet), has been developed through the necessity to provide hazard information on various chemical substances.

The modern MSDS contains not just information on the hazardous properties of the chemicals involved in a particular preparation, but also information from first-aid measures right through to disposal and regulatory information.

Categories/sections of the MSDS

The following 16 items are generally regarded to be sufficient for a modern MSDS:

- *(a)* chemical product and company identification (including trade or common name of the chemical and details of the supplier or manufacturer).
- *(b)* composition/information on ingredients (in a way that clearly identifies them for the purpose of conducting a hazard evaluation).
- *(c)* hazards identification.
- *(d)* first-aid measures.
- *(e)* fire-fighting measures.
- *(f)* accidental release measures.
- *(g)* handling and storage.
- *(h)* exposure controls/personal protection (including possible methods of monitoring workplace exposure).
- *(i)* physical and chemical properties.
- *(j)* stability and reactivity.
- *(k)* toxicological information (including the potential routes of entry into the body and the possibility of synergism with other chemicals or hazards encountered at work).
- *(l)* ecological information.
- *(m)* disposal considerations.
- *(n)* transport information.
- *(o)* regulatory information.
- *(p)* other information (including the date of preparation of the chemical data sheet).

SUPPORT FOR TOOL H – RECORD OF FORESEEABLE HAZARDS

Tool H examples

Tool H of the *INSET* Toolkit provides a simple sheet for recording foreseeable hazards. New entries should be added during the whole lifetime of the project.

Example H.1 shows how the form of Tool H has been used to record foreseeable hazards involving hydrazine.

Example H.1: Past incidents and foreseeable hazards involving hydrazine

Adopted from the internal reports of one of the *INSIDE* consortium members.

The problem

The decision as to what strength hydrazine to be used in a process had to be made. Past incidents data was used to find out what type of hazards could be foreseen.

The search

Databases, books and articles were used to find any information regarding the hazards, the accidents and incidents, that were related to hydrazine usage.

Documentation

The results were documented using the form included in *INSET* Tool H. The results summarized on the first page of the form are shown at the end of this example.

Project title: *TS*

Date: ___ / ___ / _____ **Record of Foreseeable Hazards (Tool H)** **Page:** *01* / *03*

Author: _*H.A.*___________ **Proj. #:** _*TS1*____________ **Ref. #:** _*TS5*____

Substance/reaction of interest	Short description of the potential hazard	Note	Reference
Hydrazine hydrate, water solution	*Warehouse fires.* *Cause of the hazard: heat, air, alkali metals, halogens, oxidizing agents.* *Hazard, reaction products:* N_2H_4 , NO_x , *explosion, heat formation.*	*No references given to the original sources.*	*Kallonen R. and Murronmaa I., 1989 Kemikaalivarastojen paloissa syntyviä vaarallisia aineita. Technical Research Centre of Finland, Research Notes 999, Espoo.*
Hydrazine, solution	*Freight train derailed due to jammed axle bearing. Cars derailed contained military fuel and drummed hydrazine. 8 to 10 hydrazine drums were crushed giving toxic fumes. Residents evacuated & rail services & road traffic severely disrupted.* *Material hazard: Fire.*	*No references given to the original source. Accident happened in Sea Cliff, Ca., USA.*	*MHIDAS database*
Hydrazine hydrate	*Hydrazine hydrate reacts with stannous cloride to give a compound, stannous dihydrazinechloride. When this substance is heated, it decomposes explosively.*	*Manual of Hazardous Chemical Reactions, 1986 (NFPA 491M). Original source yet to be consulted.*	*Mellor J.W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans, Green & Co., London, 1946-47.*
Hydrazine	*Distillation of anhydrous hydrazine (prepared by dehydrating hydrazine hydrate with solid sodium hydroxide) must be carried out under nitrogen to avoid the possibility of an explosion if air is*	*Bretherick's Handbook of Reactive Chemical Hazards. Original source yet to be consulted.*	*Day A.C. et al., Org. Synth., 1970, Vol. 50, p. 42.*

	present.		

Tool H supporting information

Databases of industrial accidents involving hazardous materials

The need to analyse the accidents and incidents that are due to industrial activity, in order to avert them in the future, has brought about the need for databases that document these. Databases of accidents and incidents have therefore been built up in many industrial organizations, and these databases, together with those administered by the authorities, can be valuable sources of information regarding the types of accidents that happen and their consequences.

The quality of data in these databases together with the amount of accidents reported has often been questioned. However, the value of the mere existence of data on these accidents and incidents is self-evident.

The European Union has had a compulsory industrial accident notification system since 1984 – the Major Accident Reporting System (MARS, which is being administered by JRC, the Joint Research Centre). Although this is a restricted database and the information contained in the database is not available to the general public, other more extensive databases are accessible for a fee.

The most important commercial accident data collection systems currently available in Europe are MHIDAS, which is run by AEA Technology in the United Kingdom, and FACTS, from TNO in the Netherlands. Other accident and incident databases are CHEMAX (JRC, Italy), ZEMA (Umweltbundesamt, Germany) and the corresponding French database (Service de l'Environnement Industriel, France). HAZInform (Ility Engineering, UK) is another relatively new worldwide database of hazards (not confined merely to process hazards).

The OECD has recently appointed an "*Ad hoc* group of experts on accidents involving hazardous substances", recommending voluntary accident notification to the OECD.

More recently, some larger companies have handed over their internal accident and incident databases. These have been combined with other previously unpublished collections and will soon provide more background data to the researcher.

Even your own company may have accident records that may be valuable sources of information when deciding on which process route alternative is inherently safer.

Potentially hazardous chemicals: their functional groups and reactions

An experienced chemist will certainly appreciate that a great deal of the inherent hazard of a chemical substance can be divulged from the functional groups of the substance. Thermal instability, extremely exothermic reactions and explosive qualities are among some of the facets of reactivity which can be asserted from investigation of the functional groups. Identification of some of the hazardous scenarios can thus be summarized as follows.

In particular, reactions in the presence of reducing agents are exothermic. Examples are:
- hydrogen, hydrides (e.g. sodiumborohydride), ammonia,
- alkali earth metals, organometallic compounds,
- silane.

The same is true for conversions in the presence of oxidizing agents like in:
- nitrations using concentrated nitric acid, nitrates, nitrous acids,
- chlorination using chlorine, concentrated perchloric acid, perchlorates, chlorates,
- oxidations with chromium (IV) oxide, chromates, potassium permanganate,
- oxidations with hydrogen peroxide, oxygen, ozone,
- sulphonation using sulphur trioxide, fuming sulphuric acid,
- conversions using alkyl nitrates.

Other exothermal reactions include:
- polymerizations,
- condensations,
- ring closures (aromatizations).

Typical values of heats of reaction of industrial reactions are:

Reaction	**Typical ΔH_r [kJ.mol^{-1}]**
Diazotization	–65
Sulphonation (SO_3)	–105
Nitration	–130
Epoxidation	–96
Hydrogenation (nitro-aromatic)	–560
Amination	–120
Neutralization (HCl)	–55
Neutralization (H_2SO_4)	–105
Heat of combustion (hydrocarbons)	–900
Diazo decomposition	–140
Nitro decomposition	–400

If a reaction mixture contains thermally unstable substances, it is possible that it will detonate. The following list of dangerously reactive chemical groups is indicative but not exhaustive.

Structure	Functional group name
–C≡C–	acetylinic compounds
–N_3	azides
–N=N–	azo- & diazeno- compounds, triazines, tetrazoles, high nitrogen containing compounds
–N^+≡N:	diazonium salts
–O–O–	peroxides, peracids, peroxyesters, ozonides
–O–ClO_x	(per-)chlorates, (hypo-)chlorites
–CNO	fulminates
>N–X	halogen azides, N-halogen compounds, N-haloimides
–NO_x	nitrates, nitrites, nitro- & nitroso- compounds
>C=N–OH	oximates

In addition, there are unsaturated (organic) substances and restrained cyclic structures that through polymerization reactions (triggered by heat or catalysts) may lead to a violent release of energy. Examples of these substances include:

Structure	Functional group name
O / \\ **>C – C<**	epoxides
NH / \\ **>C – C<**	aziridines
>C=C<	olefins, vinylic compounds
>C=N–	imines

Some classes of compounds possess the property of forming explosive peroxides when stored in a normal atmosphere for a longer period of time. These include:

Structure	Functional group name
–O–	ethers
O ‖ **–C–R**	aldehydes and ketones
>C=C<	olefins

Compounds or reaction systems that display autocatalytic behaviour must also be noted:
- acrylates,
- ammoniumbisulphate,
- cyanuric chloride,

- halo anilines,
- nitro compounds (especially nitro aromatics),
- sulpho compounds,
- thiophosphoric acids – ester.

If the decomposition products are not allowed to escape (or removed) from the reactor, a pressure rise may occur, even if the decomposition itself is endothermal.

Also, the physical state of a mixture or a compound may be of importance. Provided, for instance, that particles are small enough, the majority of solids will be able to cause a dust explosion. For a dust explosion, one needs "dust", which in this context means particles smaller than about 0.5 mm diameter. Unfortunately, bulk solids usually contain at least some fraction of fine material, either because of the way they were produced or because of the handling of the material.

Characterization by functional groups is further augmented in Tool L Supporting Information.

Incompatibilities

The notion of addressing incompatibility in the realm of chemical processing and synthesis may be confusing to some, as it is generally regarded that we want to have chemicals that react with each other. In designing and developing an inherently safer chemical process plant, the need to consider the consequences of incompatible substances inadvertently coming into contact is very important.

Incompatibilities may not only exist with the substances involved in the chemical process, but also with the materials that the plant and equipment are made of. These would not normally be specifically addressed at this stage, but any such incompatibilities identified at this stage should also be recorded here (see also *INSET* Stage IV).

Chemical compatibility charts may be of assistance at this stage. Recently, the Dow Chemical Company, together with the AIChE, have released their "CHEMPAT" software commercially. Designed to be customized to the specific needs of each chemical plant, this programme allows for easy assessment of the chemical compatibility and reactivity involved with a certain process by producing a compatibility or inter-reactivity chart, and includes the details of the consequences of any inadvertent mixing.

Important reference sources

Various literature dealing with the hazardous properties of chemicals has been published. Information on these hazardous properties also sometimes exists in the MSDSs of the substances. Some valuable reference sources include:

1. Urben P. (ed.), "Bretherick's Handbook of Reactive Chemical Hazards", 5th ed., October 1995, 2100 pp. (2 volumes).
   (This is also now available in cd-rom format as: "Bretherick's Reactive Chemicals Hazards Database")

2. "Manual of Hazardous Chemical Reactions", NFPA 491M, National Fire Protection Association, 1986.

3. Carson P.A. and Mumford C.J., "Hazardous Chemicals Handbook", Butterworth-Heinemann, 1994.

4. Sax and Lewis, "Dangerous Properties of Industrial Materials", Van Nostrand Reinhold, USA.

SUPPORT FOR TOOL I – ISHE PERFORMANCE INDICES

Tool I examples

Used during the chemical route assessment, the indices given in Tool I of the *INSET* Toolkit provide a set of indicators of the merits and shortcomings of the assessed alternatives. Example I.1-11.1 shows the calculated indices for some of the steps of alternative #2 to obtain the desired product "CNA".

Example I.1-11.1: CNA

One of the partners of the *INSIDE* Project considered starting the development of a compound given the name "CNA". The company found it useful to calculate the indices for the three steps in one of the identified route alternatives.

Project title: *CNA*

Date: *26/ 03/ 1997* **FEHI: Fire and Explosion Hazards Index (Tool I.1)** **Page:** *01/ 01*
Plant: ________ **Section:** ________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*___
Author: ________ **Proj. #:** ________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]	6	5	1.6			
B	Dominant material	50% H_2O_2	TEA	MeOH			
C	Temperature [°C]	100	110	77			
D	Atmospheric boiling point [°C]	100	89	65			
E	Item/inventory [Te]	5.3	3	10.5			
F	Fire and Explosion Hazard Factor (FEHF)	30	5	5			
G_a	Absolute FEHI $= E \times F$	159	15	52.5			
G_r	Relative FEHI $= E \times F / A$	26.5	3	32.8			
Refinement							
H	Heat of combustion correction (CF1)						
I	Reactivity/sensitivity correction (CF2)						
J	Liquids above b.p. correction (CF3)						
K_a	Corrected absolute FEHI $= G_a \times H \times I \times J$						

K_r	Corrected relative FEHI $= G_r \times H \times I \times J$						

Project title: *CNA*

Date: *26/ 03/ 1997* **ATHI: Acute Toxic Hazards Index (Tool I.2)** **Page:** *01/ 01*
Plant: ________ **Section:** ________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*______
Author: ________ **Proj. #:** ________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]	6	5	1.6			
B	Dominant material	NAO	$POCl_3$	MeOH			
C	Item/inventory [Te]	6	39	10.5			
D	Toxic Harm Factor (THF)	1	1	100			
E_a	Absolute ATHI $= C \times D$	6	39	1050			
E_r	Relative ATHI $= C \times D / A$	1	7.8	656			

Project title: *CNA*

Date: *26/ 03/ 1997* **HHI: Health Hazards Index (Tool I.3)** **Page:** *01/ 01*
Plant: ________ **Section:** ________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*____
Author: ________ **Proj. #:** ________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]	6	5	1.6			
B	Dominant material	NAO or H_2O_2	NAO or $POCl_3$	2-CNA or MeOH			
C	Health Harm Factor (HHF)	1 or 10	1 or 10	1 or 100			
D	Manual handling/exposure operations [number of manual operations per year]	41 or 0	71 or 0	94 or 0			
E	Equipment/sum of leak factors [Te/year]	20.4 or 5.4	8.4 or 9.9	14.7 or 12			
F_a	Absolute HHI $= C \times (0.6 \times D + E)$	45 or 54	51 or 99	71 or 1200			
F_r	Relative HHI $= C \times (0.6 \times D + E) / A$	7.5 or 9	10.2 or 19.8	44.4 or 750			
Refinement							
G	Leak shaping factor (CF1)						
H_a	Corrected HHI $= F_a \times G$						
H_r	Corrected HHI $= F_r \times G$						

Project title: *CNA*

Date: *26/ 03/ 1997* **AEII: Acute Environmental Incident Index (Tool I.4)** **Page:** *01/ 01*

Plant: ________________ **Section:** ________________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*______

Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]	6	5	1.6			
B	Dominant material	H_2O_2	$POCl_3$	MeOH			
C	Item/inventory [Te]	1.8	13	7			
D	Environmental Harm Factor (EHF)	10	1	100			
E_a	Absolute AEII $= C \times D$	18	13	700			
E_r	Relative AEII $= C \times D / A$	3	2.6	437			
Refinement							
F	Condition factor (CF1)						
G_a	Corrected absolute AEII $= E_a \times F$						
G_r	Corrected relative AEII $= E_r \times F$						

Project title: *CNA*

Date: *26/ 03/ 1997* **THI: Transport Hazards Index (Tool I.5)** **Page:** *01/ 01*

Plant: ________ **Section:** ________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*_____

Author: ________ **Proj. #:** ________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Daily production [Te/day]	6	5	1.6			
B	Dominant material	H_2O_2	$POCl_3$	MeOH			
C	Load/container size (inventory) [Te]	20	70	50			
D	Distance travelled per journey [km]	200	2000	2000			
E	Number of journeys per year (annual tonnage/load size)	2	3	7			
F	Transport Harm Factor (THF)	10	10	100			
G_a	Absolute THI = (C × D × E × F) / (1E7)	0.008	0.42	7			
G_r	Relative THI = (C × D × E × F) / (A × 1E7)	0.0013	0.084	4.4			

Project title: *CNA*

Date: *26/ 03/ 1997* **GEI: Gaseous/Atmospheric Emissions Index (Tool I.6)** **Page:** *01/ 01*
Plant: ________________ **Section:** ________________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*______
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]	50	50	50			
B	Dominant gaseous emission material	$O_2 + N_2$	HCl	MeOH			
C	Annual discharge rate [Te/year]	8	59	0.1			
D	Environmental Harm Factor (EHF)	0.1	1	1			
E_a	Absolute GEI $= C \times D$	0.8	59	0.1			
E_r	Relative GEI $= C \times D / A$	0.016	1.2	0.002			

Project title: *CNA*

Date: *26/ 03/ 1997* **AEI: Aqueous Emissions Index (Tool I.7)** **Page:** *01/ 01*
Plant: ________________ **Section:** ________________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*______
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]	50	50	50			
B	Dominant aqueous emission material	H_2O	salts	MeOH			
C	Annual discharge rate [Te/year]	107	74	375			
D	Environmental Harm Factor (EHF)	0.1	1	100			
E_a	Absolute AEI $= C \times D$	10.7	74	37500			
E_r	Relative AEI $= C \times D / A$	0.2	1.5	750			

Project title: *CNA*

Date: *26/ 03/ 1997* **SWI: Solid Wastes Index (Tool I.8)** **Page:** *01/ 01*
Plant: ________ **Section:** ________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*_____
Author: ________ **Proj. #:** ________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]	50	50	50			
B	Dominant solid waste material	–	–	C			
C	Annual discharge rate [Te/year]	0	0	5.5			
D	Environmental Harm Factor (EHF)	0	0	10			
E_a	Absolute SWI $= C \times D$	0	0	55			
E_r	Relative SWI $= C \times D / A$	0	0	1.1			

Project title: *CNA*

Date: *26/ 03/ 1997* **ECI: Energy Consumption Index (Tool I.9)** **Page:** *01/ 01*
Plant: ________________ **Section:** ________________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*______
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]	50	50	50			
B	Energy usage [GJ/year]	NA	NA	NA			
	Gas Fuel Oil Coal Electricity Other	NA	NA	NA			
C	Energy factor (EF) [Te CO_2/year]	NA	NA	NA			
	Gas B_{gas} × 0.067 = Fuel Oil $B_{f/oil}$ × 0.097 = Coal B_{coal} × 0.126 = Electricity B_{elec} × 0.214 = Other B_{other} × Total (Sum of above) =	NA	NA	NA			
D_a	Absolute ECI = C	NA	NA	NA			
D_r	Relative ECI = C / A	NA	NA	NA			

Project title: *CNA*

Date: *26/ 03/ 1997* **RHI: Reaction Hazards Index (Tool I.10)** **Page:** *01/ 01*
Plant: ________ **Section:** ________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*___
Author: ________ **Proj. #:** ________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]	50	50	50			
B	Dominant reaction scenario and materials	NA	NA	NA			
C	Reaction Risk Factor (RRF)	NA	NA	NA			
D	Reaction Harm Factor (RHF)	NA	NA	NA			
E	Reactor inventory [Te]	NA	NA	NA			
F_a	Absolute RHI = $C \times D \times E$	NA	NA	NA			
F_r	Relative RHI = $C \times D \times E / A$	NA	NA	NA			

Project title: *CNA*

Date: *26/ 03/ 1997* **PCI: Process Complexity Index (Tool I.11)** **Page:** *01/ 01*
Plant: ________________ **Section:** ________________ **Flowsheet #:** _*1 & 2*__ **Revision:** _*1*______
Author: ________________ **Proj. #:** ________________ **Ref. #:** ________

		Option A	Option B	Option C	Option D	Option E	Option F
A	Annual production [Te/year]	50	50	50			
B	Batch or continuous?	B	B	B			
C_a	Absolute PCI = total of values	38	44	31			
C_r	Relative PCI = C_a / A	0.76	0.88	0.62			

Tool I.6/I.7/I.8 supporting information

Environmental indices

Environmental index developed by ICI

ICI FCMO have developed a simple environmental index to assess the relative amount of waste generated per unit of product for comparing process options. The so-called "environmental loading factor" (ELF) is defined as:

ELF = SUM (mass discharge rate) for all waste streams/process product throughput.

Although this does not take any account of the degree of harm presented by any stream, it is simple to use and does not require any toxicity data.

Environmental index developed by HMIP

The HMIP in the United Kingdom have produced a consultative document "Environmental, economic and BPEO assessment principles for integrated pollution control" (HMSO, April 1994), which puts forward a detailed method for assessing process options in terms of their impact on the environment. However, the method is very detailed and too rigorous for basic process screening. It also needs good data – which may not be available – and is based on some simplistic assumptions. It may, therefore, not be that accurate despite its complexity. It does, however, include some means of relating harm to the "risk phrases" defined in EC Directive 84/449/EEC, and this may present a more practical way forward for our purposes.

The HMIP guide uses a log-based index of harm that is related to the concentration of the hazardous substance. This is then used to link the R-phrases to the index. The log basis used seems to have little scientific basis and distorts the index by reducing the apparent difference between the effects of hazards. For example:

for air (inhalation) toxicity:

- R26, very toxic Factor = 6
- R23, toxic Factor = 4
- R20, harmful Factor = 2
- No R-phrase Factor = 1
- Irritant/corrosive Factor = 2

This contrasts with the near 10-fold difference in concentration levels for LD_{50} between these groups (R26 = 0.5 mg/l, R23 = 2 mg/l, R20 = 20 mg/l).

Similar 10-fold differences in concentration levels can be found between the R-phrase definitions for ingestion (R28, R25, R22) and aquatic effects (R50, R51, R52).

SUPPORT FOR TOOL J – MULTI-ATTRIBUTE ISHE COMPARATIVE EVALUATION

Tool J examples

Two record sheets with their associated presentation charts are provided in Tool J of the *INSET* Toolkit. The first is for the qualitative scales, the second for the quantitative indices presentations. If the quantitative indices are to be used, the benchmark option must be entered as Option A. The use of Tool J requires that the corresponding sections of Tool I have been completed.

Example J.1: Presentation aid

A fictitious company intends to start developing a process to produce the fictitious chemical substance "Insetol". After several iterations to find the best process alternatives, four alternatives remain to be compared. Both the qualitative and the quantitative scales of Tool J have been used. The results of the comparisons are shown on the following pages.

Qualitative scales
- Chart 1 - Bar chart presentation of qualitative scales for the process options.
- Chart 2 - Spider diagram presentation of qualitative scales for the process options.

Quantitative scales
- Chart 3 - Presentation of the quantitative indices ratios (vs benchmark option A) for the process options.
- Chart 4 - Presentation of the quantitative indices ratios (vs average index for each aspect) for the process options.
- Chart 5 - Presentation of absolute indices values for all options.
- Chart 6 - Presentation of the quantitative indices ratios (vs suggested "norm") for the process options.

Project title: *INSETOL*

Date: *01 / 12 / 1996* **Inherent SHE All Options Summary Sheet (Tool J)** ☐ **Word picture** **Page:** ___ / ___

Process option: ______________ ☐ **Index range**

Author: _*JC*_____________ **Proj. #:** _*IT1*___________ **Ref. #:** ________

Index	Aspect	Index values/qualitative score for the different options						Comments
		Option A	Option B	Option C	Option D	Option E	Option F	
FEHI	Fire and explosion hazards	2	3	3	3			
ATHI	Acute toxic hazards	3	3	3	2			
HHI	Health hazards	2	3	3	3			
AEII	Acute environmental incidents	3	3	2	3			
THI	Transport hazards	3	3	3	3			
GEI	Gaseous emissions	3	2	3	3			
AEI	Aqueous emissions	2	3	3	4			
SWI	Solid wastes	1	2	1	2			
ECI	Energy consumption/ global warming	2	3	2	2			
RHI	Reaction hazards	2	2	3	3			
PCI	Process complexity	3	3	2	2			
TF	Technical feasibility	2	3	1	1			
EF CAPEX	Economic feasibility CAPEX	3	4	2	3			
EF OPEX	Economic feasibility OPEX	3	2	3	4			

Project title: *INSETOL*

Date: *01* / *12* / *1996* **Inherent SHE All Options Summary Sheet (Tool J)** ☐ **Word picture** **Page:** ___ / ___
Process option: ________________ ☐ **Index range**
Author: _*JC*_____________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

Index	Aspect	Index values/qualitative score for the different options						Comments
		Option A	Option B	Option C	Option D	Option E	Option F	
FEHI	Fire and explosion hazards	80	120	125	400			
ATHI	Acute toxic hazards	90	200	150	70			
HHI	Health hazards	90	110	250	200			
AEII	Acute environmental incidents	250	250	90	800			
THI	Transport hazards	0.2	0.25	0.28	0.35			
GEI	Gaseous emissions	250	50	220	450			
AEI	Aqueous emissions	80	180	250	520			
SWI	Solid wastes	9	20	9	25			
ECI	Energy consumption/ global warming	420	2000	350	200			
RHI	Reaction hazards	6	6	25	25			
PCI	Process complexity	32	28	15	18			
TF	Technical feasibility	10	100	1	1			
EF CAPEX	Economic feasibility CAPEX	100	1000	10	100			
EF OPEX	Economic feasibility OPEX	100	10	100	1000			

Project title: *INSETOL*

Date: *01*/ *12*/ *1996* **Inherent SHE All Options Summary Sheet (Tool J)** ☐ **Word picture** **Page:** ___ / ___

Process option: _______________ ☐ **Index range**

Author: _*JC*____________ **Proj. #:** _*IT1*___________ **Ref. #:** ________

Index	Aspect	Calculated ratios of "option value" / "benchmark value"						Comments
		Option A	Option B	Option C	Option D	Option E	Option F	
FEHI	Fire and explosion hazards	1	1.5	1.563	5			
ATHI	Acute toxic hazards	1	2.222	1.667	0.778			
HHI	Health hazards	1	1.222	2.778	2.222			
AEII	Acute environmental incidents	1	1	0.36	3.2			
THI	Transport hazards	1	1.25	1.4	1.75			
GEI	Gaseous emissions	1	0.2	0.88	1.8			
AEI	Aqueous emissions	1	2.25	3.125	6.5			
SWI	Solid wastes	1	2.222	1	2.778			
ECI	Energy consumption/ global warming	1	4.762	0.833	0.476			
RHI	Reaction hazards	1	1	4.167	4.167			
PCI	Process complexity	1	0.875	0.469	0.563			
TF	Technical feasibility	1	10	0.1	0.1			
EF CAPEX	Economic feasibility CAPEX	1	10	0.1	1			
EF OPEX	Economic feasibility OPEX	1	0.1	1	10			

Project title: *INSETOL*

Date: *01 / 12 / 1996* **Inherent SHE All Options Summary Sheet (Tool J)** ☐ **Word picture** **Page:** ___ / ___

Process option: ________________ ☐ **Index range**

Author: _*JC*_____________ **Proj. #:** _*IT1*____________ **Ref. #:** ________

Index	Aspect	Average	Calculated ratios of "option value" / "average value"						Comments
			Option A	Option B	Option C	Option D	Option E	Option F	
FEHI	Fire and explosion hazards	181.25	0.441	0.662	0.690	2.207			
ATHI	Acute toxic hazards	127.5	0.706	1.569	1.176	0.549			
HHI	Health hazards	162.5	0.554	0.677	1.538	1.231			
AEII	Acute environmental incidents	347.5	0.719	0.719	0.259	2.302			
THI	Transport hazards	0.27	0.741	0.926	1.037	1.296			
GEI	Gaseous emissions	242.5	1.031	0.206	0.907	1.856			
AEI	Aqueous emissions	257.5	0.311	0.699	0.971	2.019			
SWI	Solid wastes	15.75	0.571	1.270	0.571	1.587			
ECI	Energy consumption/ global warming	742.5	0.566	2.694	0.471	0.269			
RHI	Reaction hazards	15.5	0.387	0.387	1.613	1.613			
PCI	Process complexity	23.25	1.376	1.204	0.645	0.774			
TF	Technical feasibility	28	0.357	3.571	0.036	0.036			
EF CAPEX	Economic feasibility CAPEX	302.5	0.331	3.306	0.033	0.331			
EF OPEX	Economic feasibility OPEX	302.5	0.331	0.033	0.331	3.306			

Project title: *INSETOL*

Date: *01* / *12* / *1996* **Inherent SHE All Options Summary Sheet (Tool J)** ☐ **Word picture** **Page:** ___ / ___
Process option: ______________ ☐ **Index range**
Author: _*JC*____________ **Proj. #:** _*IT1*___________ **Ref. #:** ________

Index	Aspect	Norm	Calculated ratios of "option value" / "norm value"						Comments
			Option A	Option B	Option C	Option D	Option E	Option F	
FEHI	Fire and explosion hazards	2500	0.032	0.048	0.05	0.16			
ATHI	Acute toxic hazards	1000	0.09	0.2	0.15	0.07			
HHI	Health hazards	400	0.225	0.275	0.625	0.5			
AEII	Acute environmental incidents	5000	0.05	0.05	0.018	0.16			
THI	Transport hazards	0.5	0.4	0.5	0.56	0.7			
GEI	Gaseous emissions	1000	0.25	0.05	0.22	0.45			
AEI	Aqueous emissions	1000	0.08	0.18	0.25	0.52			
SWI	Solid wastes	1000	0.009	0.02	0.009	0.025			
ECI	Energy consumption/ global warming	10000	0.042	0.2	0.035	0.02			
RHI	Reaction hazards	1000	0.006	0.006	0.025	0.025			
PCI	Process complexity	70	0.457	0.4	0.214	0.257			
TF	Technical feasibility	100	0.1	1	0.01	0.01			
EF CAPEX	Economic feasibility CAPEX	100	1	10	0.1	1			
EF OPEX	Economic feasibility OPEX	100	1	0.1	1	10			

SUPPORT FOR TOOL K – RAPID ISHE SCREENING METHOD

Tool K examples

As an alternative to the more exhaustive treatment that is provided by Tool J, a rapid assessment method, Tool K, is supplied for completing Stage II of the *INSET* Toolkit. Together with the chemical screening, a process hazard classification ensures that every process alternative is assessed in a comprehensive, yet rapid, way. The basis of this tool is to allow the efficient documentation of the normal aspects that are used to evaluate the advantages and disadvantages of the different route alternatives.

Example K.1 shows how Tool K could be used to document and screen some of the route alternatives shown in the referenced article.

Example K.1: Rapid ISHE evaluation of a route for the production of
methyl methacrylate

Adopted from an article by D.W. Edwards and D. Lawrence (Loughborough University of Technology). (Edwards D.W. and Lawrence D., "Assessing the inherent safety of chemical process routes: Is there a relation between plant costs and inherent safety", Trans IChemE, Vol. 71, 1993, pp. 252-258.)

The problem

If Loughborough University of Technology had had access to the *INSET* Toolkit, a rapid screening of the ISHE performance of the alternatives mentioned in the article could have been made as shown on the last pages of this example.

Based on the information given in Table 8 of the referenced article, and together with other relevant information from MSDSs, the Chemistry Materials Hazards Classification has been completed here for a process alternative for methyl methacrylate.

In order to identify the alternatives, the abbreviations are used as given in Table 8 of the article. This table is provided in Tool G Examples. Using the information from Tool G concerning all the chemicals involved in the process, the chemicals are rated according to the basic version (**K**, **–**, **?**) given in Tool K.

Using the process block diagram (from Tool F) the Process Hazard Index Classification is completed using the scale defined. In this case, the focus is on the operations associated with the stages. By listing the main operations, and ranking them according to the index given, it becomes plainly evident where the weaker ISHE aspects of the route alternative lie. These aspects would be the focus of further challenging procedures using Tool B. The "comments" field is used for identifying specific problems.

Project title: *MMA*

Date: *03/ 09/ 1996* **Chemistry Materials Hazards Classification (Tool K)** **Page:** *01/ 01*

Author: _*H.K.*___________ **Proj. #:** _*MMA1*___________ **Ref. #:** _*A6 (TBA)*_

Chemical	Safety values				Health values				Environmental values			
	Explos. & fire	Stability	React.	Physical prop. *	Chronic	Acute (skin)	Acute (inhal.)	Acute (eyes)	Toxicity	Degrada bility	Bioaccu mulation	Physical prop.
t-Butyl alcohol	*K*	–	–	–	*?*	–	*K*	–	*K*	–	*K*	–
Air	–	–	–	–	–	–	–	–	–	–	–	–
Methacrolein	*K*	–	*K*	*K*	*?*	*K*	*K*	*K*	*K*	*?*	*?*	*?*
Water	–	–	*?*	–	–	–	–	–	–	–	–	–
Methacrylic acid	*K*	–	–	*K*	*?*	*K*	*K*	*K*	*?*	*?*	*?*	*?*
t-Butyl acetate	*K*	–	–	–	–	–	–	*K*	–	–	–	–
Methanol	*K*	–	*K*	–	–	*K*	*K*	*K*	*K*	–	–	–
MoBiSb	–	–	–	*K*	–	–	–	–	*K*	–	–	–
P-Mo	–	–	–	–	–	–	–	–	–	–	–	–
Carboxylic acid	–	–	–	–	–	–	–	–	–	–	–	–
Waste water												
Purged air												
Methyl methacrylate	*K*	–	–	–	*?*	*K*	*K*	*K*	–	–	–	–

** toxic fumes*

Project title: *MMA*

Date: *03/ 09/ 1996* **Process Hazard Index Classification (Tool K)** **Page:** *01/ 01*

Author: _*H.K.*___________ **Proj. #:** _*MMA1*___________ **Ref. #:** _*A6 (TBA)*_

Stage/unit operation	Index	Comments
TBA from the refinery	*2*	*Emits toxic fumes when heated*
Air	*1*	*-*
1st stage oxidation	*3*	*High temp. & moderate press.*
2nd stage oxidation	*3*	*High temp. & moderate press.*
Quencher	*2*	
Chemicals recovery	*2*	*Purged gas clean after absorber*
Absorber recovery - Solvent extraction unit	*3*	*(Butylacetate) a mixture of FLAMMABLE liquids*
Solvent stripping	*3*	
Solvent recovery	*3*	
Solvent storage tank	*3*	
Catalyst storage tank	*1*	
Esterification reactor	*2*	
Extraction with H_2O	*2*	
MAA-MeOH distillation	*3*	
Light end stripper	*3*	
Distillation column	*4*	*Bottoms product. * Portion is classified as hazardous waste*

SUPPORT FOR TOOL L – CHEMICAL REACTION REACTIVITY - STABILITY EVALUATION

Tool L supporting information

Chemical reaction hazards

1. Introduction

Many chemical reactions that are operated on the industrial scale involve the release of heat, that is, they are exothermic. In addition, even greater amounts of heat can be released when decomposition reactions are initiated through unsuitable operating conditions. The consequences of a violent exothermic runaway reaction can be as severe as those from the ignition and explosion of a fuel/air mixture.

It is important, therefore, that any exothermic reactions which could arise are identified and that possible chemical reaction hazards are considered [1]. This should be carried out at an early stage of reactor or process design, not only to ensure provision of an effective basis of safe operation, but also in order to design a reactor system or process such that the hazard is prevented from occurring, i.e. an inherently safe process. This minimizes the need for other expensive additional systems in order to protect against the consequence of the hazard.

The effect of scale-up is particularly important. A reaction which is apparently innocuous on the laboratory or even the semi-technical scale, can be disastrous on the manufacturing scale. Thus, the heat release from a highly exothermic process, for example the reduction of an aromatic nitro compound, can be controlled easily in laboratory glassware. If the same reaction is carried out in a large plant vessel with a much smaller surface area/vessel volume ratio, efficient cooling must be provided or a runaway reaction and violent decomposition may occur.

Similarly, a large quantity of gas produced by, for example, the sudden decomposition of a diazonium compound, can be vented easily on the laboratory scale, but the same decomposition on the large scale could pressurize and rupture a plant vessel.

In addition to the above, the consequences of possible process maloperation must be considered, for example overcharging or omission of one of the reactants, agitation failure, or poor temperature control.

Chemical reaction hazards principally arise from:

- rapid exothermic reactions which can raise the temperature to the decomposition temperature or cause violent boiling of the reactants,
- thermal instability of reactant mixtures and products,
- rapid gas evolution which can pressurize and possibly rupture the plant.

Thus, a knowledge of the heat associated with the desired reaction, ΔH_r, and information on the thermal stability, i.e. the temperature at which any decomposition reaction may occur on the plant scale and its magnitude, are essential to evaluate the hazards [2].

The critical information required can be seen in Figure 1, which shows the thermal timescale of a runaway scenario.

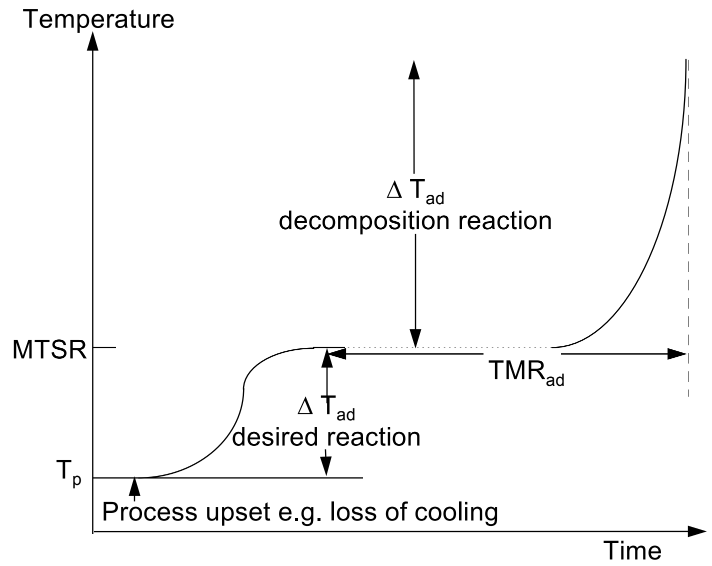


Figure 1 Schematic of a runaway scenario

The occurrence of an upset condition during the operation of an exothermic reaction will result in the temperature rising from the process temperature to the maximum temperature of the synthetic reaction, MTSR. This temperature equals the process temperature, T_p, plus the adiabatic temperature rise, ΔT_{ad}, resulting from the continuation of the desired reaction. The maximum adiabatic temperature rise which could occur can be calculated from the heat of the desired reaction and the specific heat, C_p, of the reaction mixture:

$$\Delta T_{ad} = \Delta H_r / C_p$$

The resulting temperature rise from a runaway may be sufficient in itself to cause an incident, particularly where the desired reaction has a high heat of reaction, for example polymerization reactions. In addition, the temperature reached, i.e. the MTSR, may be sufficient to initiate a secondary decomposition reaction. Such decomposition reactions are often highly energetic and an indication of their severity can again be obtained by calculating the resulting adiabatic temperature rise using, in this case, the heat of decomposition, ΔH_d.

In order to evaluate the potential hazard of a decomposition reaction it is also necessary to know whether it will be initiated at a particular temperature. Unfortunately, it is not possible to quote a specific temperature at which a particular reaction will runaway since the majority of chemical reactions follow an Arrhenius rate law, i.e. their rate is exponentially dependent on the temperature, and the temperature at which a runaway will occur is therefore critically dependent on the environment, i.e. size and heat loss. However, an indication of the probability of such a decomposition reaction being initiated can be obtained from the adiabatic time to maximum rate, TMR_{ad}. This can be estimated using:

$$TMR_{ad} = \frac{C_p \bullet R \bullet T_0^2}{q_0 \bullet E_a} [s] \quad 2$$

where: C_p = specific heat capacity [$J.kg^{-1}.K^{-1}$]
R = gas constant = 8,314 $J.mol^{-1}.K^{-1}$
T_0 = absolute initial temperature [K]
q_0 = heat output at T_0 [$W.kg^{-1}$]
E_a = activation energy [$J.mol^{-1}$].

The time to maximum rate gives an indication of how much time is available to introduce emergency measures once a process disturbance has occurred.

2. Thermal explosions

The occurrence of a runaway reaction or thermal explosion depends not only on the rate of heat generation from a chemical reaction, but also on the rate of heat loss from the system. As mentioned above, it is therefore not possible to determine and assign a stability temperature to a substance as one can with melting points or flash points. A material which is stable at some temperature in one situation may runaway from the same temperature if the system, in particular the rate of heat loss, changes.

The two extreme cases which can be considered in describing heat loss from a system are shown in Figure 2. In the first case, originally discussed by Semenov [3], the temperature is assumed to be uniform throughout the reactant mass. This situation occurs in gaseous and well-stirred liquid systems where the rate of heat loss is governed by heat transfer at the boundary.

In the second case, considered by Frank-Kamenetskii [4], the temperature distribution is non-uniform and heat loss is controlled by heat transfer through the bulk. This occurs in large unstirred liquid masses, powders and solids.

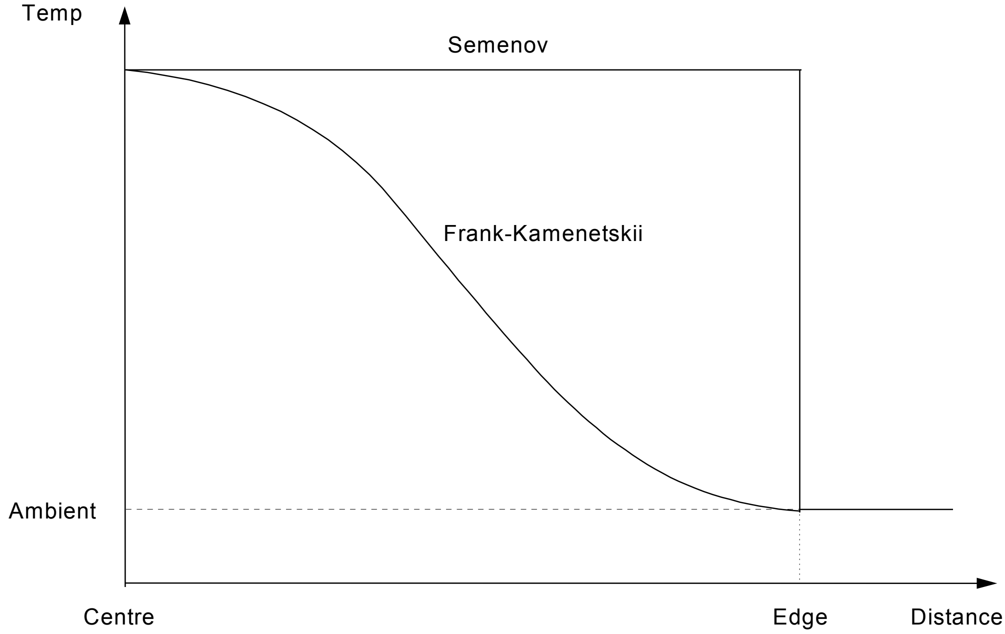


Figure 2 Semenov and Frank-Kamenetskii temperature profiles

Chemical reactions are often carried out in the liquid phase and the conditions pertaining to Semenov heat transfer conditions can be considered.

Semenov assumed a pseudo-zero-order exothermic reaction following an Arrhenius type rate law, that is the rate of reaction and therefore the rate of heat production increases exponentially with temperature. Thus, for an irreversible n^{th} order reaction $A \rightarrow R$ at constant volume V, the rate of heat production Q_r is given by:

$$Q_r = V(-\Delta H_r)\, k_0\, C_A \exp(-E_a/RT)$$

where: ΔH_r = heat of reaction
C_A = initial concentration (assumed to remain constant for a limited time)
k_0 = initial rate constant for the reaction with activation energy E_a.

The rate of heat loss Q_c is assumed to be governed by Newtonian cooling, that is, it is linearly dependent on the temperature difference, the heat transfer coefficient U, and area A:

$$Q_c = U A (T - T_a)$$

Three cases for difference ambient coolant temperatures can be discussed (Figure 3).

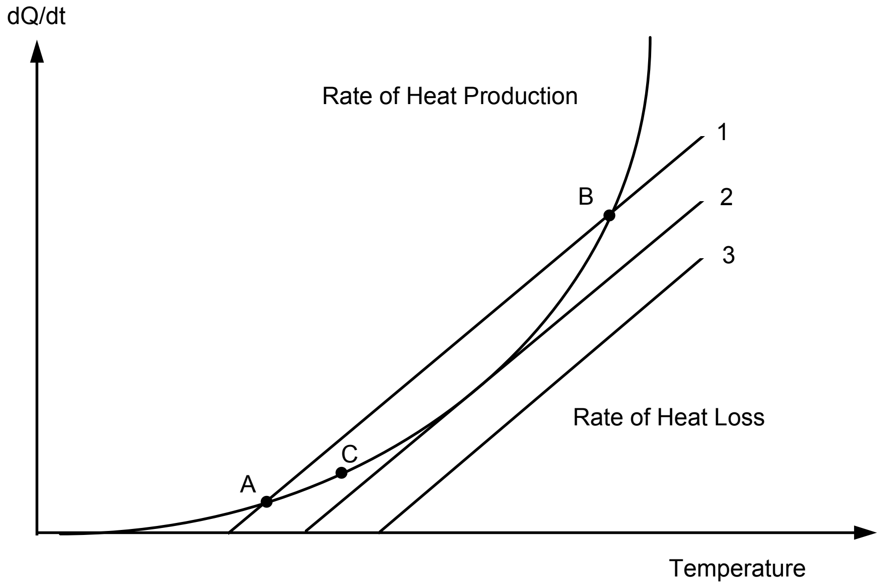


Figure 3 Heat balance for Semenov type systems

In the first case, the rate of heat loss (line 1) intersects the exponential heat production curve at two points, A and B, where the heat production rate is balanced by the heat removal capacity. The low temperature point, A, represents a stable situation which can be illustrated by considering an increase in temperature to point C. At this temperature, the rate of heat loss is greater than the rate of heat production and the temperature will return to point A. In contrast, point B is unstable as any slight increase in temperature will cause an increase in the rate of heat production not matched by the rate of heat loss and an accelerating runaway will occur.

Line 3 represents the situation where the rate of heat loss from the system is always less than the rate of heat production and a runaway reaction will always occur.

Line 2 describes the critical situation where the heat production is just equal to the heat removal.

In addition, since the rate of heat loss is dependent on the heat transfer coefficient and area, a decrease in either will lead to a decrease in the slope of the line and a reduction in the rate of heat loss from the system.

3. Characterization of exothermic primary reactions

As has been described above, the key parameter in evaluating the hazards of the primary or desired chemical reaction is its heat of reaction, ΔH_r. An initial estimate can be obtained from the literature or calculated from the heats of formation of the reactants and products according to Hess' law:

$$\Delta H_r = \sum \Delta H_{f_{Products}} - \sum \Delta H_{f_{Reactants}} \quad 3$$

The exothermic nature of many industrial reactions is illustrated by typical values for their heats of reaction as given in Table 1.

Table 1 Typical values of heats of reaction of industrial reactions

Reaction	Typical ΔH_r [kJ.mol^{-1}]
Diazotization	–65
Sulphonation (SO_3)	–105
Nitration	–130
Epoxidation	–96
Hydrogenation (nitro-aromatic)	–560
Amination	–120
Neutralization (HCl)	–55
Neutralization (H_2SO_4)	–105
Heat of combustion (hydrocarbons)	–900
Diazo decomposition	–140
Nitro decomposition	–400

The heat release of a specific reaction will often need to be measured, and the following calorimetric methods may be used to determine the heat of reaction:

- Differential thermal analysis DTA/DSC.
- Dewar calorimetry.
- Isothermal reaction calorimetry, i.e. heat flow or heat balance calorimetry.

Differential thermal analysis should only be used when the reaction components form a homogeneous mixture at room temperature or lower, and when the reaction begins at a higher temperature.

Dewar calorimetry is one of the most sensitive and absolute calorimetric methods, and is particularly suitable for batch processes, i.e. where all the reactant components are charged at the beginning of the reaction [5]. As no heat is lost from the Dewar, when it is operated in the adiabatic mode, the heat of reaction is directly proportional to the temperature rise measured.

Isothermal reaction calorimetry has the advantage that it uses a normal laboratory reactor and is particularly suitable for use with semi-batch processes. Calibrations must be carried out to measure either the heat flow between the reactor contents and the cooling/heating medium or the heat change occurring in the cooling/heating medium in heat balance calorimetry. The heat of reaction is then determined by integrating the heat release curve obtained.

3.1 Reaction kinetics

It is not necessary to have a complete description of the formal kinetics of a chemical reaction in order to evaluate its potential reaction hazards. However, it is important to determine whether, particularly for a semi-batch process, the reaction proceeds rapidly or whether reactant is accumulated during the dosing period. Similarly, sufficient data must be obtained to assess the effect of possible maloperations, for example:

- loss of agitation,
- temperature/pressure deviations,
- reactant charging errors – omissions/overcharging/wrong order,
- extended reaction times.

Such data can be obtained from reaction calorimetry experiments and needs to be interpreted and related to the particular plant situation.

3.2 Measurement of gas evolution

The rate of gas evolution during the normal process and under any envisaged maloperations is required to ensure adequate vent and/or scrubber sizing. The rate of gas evolution is not dependent on scale. Therefore, data obtained from small scale experiments can be directly related to the plant scale.

4. Characterization of exothermic decomposition reactions

4.1 Chemical composition

Certain chemical groups are known to reduce the stability and possibly confer explosive properties on a compound [6]. The compound types include:

Aromatic nitro	Azo	Hypochlorite
Aliphatic nitro	Azide	Chlorate
Nitrate ester	Peroxide	Perchlorate
Nitramine	Ozonide	Acetylenic.

However, not all organic compounds containing, for instance, nitro groups and nitrate esters, possess explosive properties. The possession of such properties is dependent on the oxygen balance. This is a measure of a compound's inherent "self-oxidation" ability and can be calculated, ignoring any atoms other than C, H and O, from the substance's empirical formula as follows:

$$C_aH_bO_c + (a + b/4 - c/2)\ O_2 \Rightarrow a\ CO_2 + b/2\ H_2O$$

The oxygen balance is then:

$$\text{Oxygen balance} = \frac{-1600\ (2a + b/2 - c)}{\text{Mol. Wt.}}$$

Compounds that have oxygen balances greater than –100 are likely to be detonating explosives, and those with balances between –100 and –150 may show detonation properties under severe confinement. Compounds with oxygen balances less than –200 are not likely to possess explosive properties though they may still be thermally unstable.

If the presence of one of the groups listed above or an oxygen balance of more positive than –200 suggests that a reactant or the reaction mixture may possess explosive properties, then in addition to the evaluation of its thermal stability, it should be tested for explosive properties.

4.2 Thermal stability

The thermal stability of a reactant or reaction mixture gives a measure of the maximum temperature at which a process can be operated. It can also be used to determine the effects of adding or omitting a solvent, varying the reactant ratios and consequently of possible process maloperations such as overcharging or omitting one of the reactants.

Some form of small-scale scanning calorimetry is generally used for the initial detection of any decomposition exotherm and gas generation. DSC or DTA using pressure-resistant sealed sample cells can be used, but these techniques may be limited by their small sample size (i.e. mg) and the difficulty of obtaining a representative sample.

Experimental determinations of thermal stability can be made by heating about 10 g of the mixture under test in a glass tube sealed with a pressure transducer and fitted with a re-entrant thermocouple pocket, so that the temperature at the centre of the sample can be recorded continuously. Materials of plant construction should be added to the sample which is then typically heated at 2 °C/min in an electric furnace.

The exotherm onset temperature is dependent on the sensitivity of the equipment, but on a 10–20 g scale, exothermicity can generally be detected at a self-heating rate of 2–10 °C/hr or approximately 3–10 W/l. This means that self-heating in a 5 m^3 vessel will occur at a temperature approximately 60–100 °C lower than that observed in the small-scale test provided that there is no induction period for the decomposition.

Depending on the results from the screening tests (i.e. exotherm size, proximity of decomposition onset temperature to process temperature), secondary testing may be required to more accurately determine:

- the minimum temperature above which the reactor will be unstable on the scale used and the time available to instigate safety measures,
- the consequences of the exotherm – heat of reaction, adiabatic temperature rise/pressure developed/venting requirements.

Such secondary testing usually involves some form of adiabatic calorimetry in order to minimize the heat loss from the sample during the test and, therefore, to detect the low rates of generation which may occur on the plant scale. These can be less than 1 W/l or 1–2 °C/hr for a large scale reactor.

In small-scale testing, the sample container often represents a substantial proportion of the system heat capacity and this will abate both the temperature rise and the total exotherm rise. This is indicated by the "phi" factor of the system which is given by:

$$\frac{\text{heat capacity of sample \& container}}{\text{heat capacity of sample}}$$

A sample of ca 10–20 g in a normal container will have a phi factor of about 1.5 compared to a phi factor of ca 1 on the plant scale. Thus, the magnitude of any exotherm seen in the laboratory test will be only half that which will actually occur during a runaway on the plant.

References

1. Barton J. and Rogers R.L., "IChemE Guide to chemical reaction hazards", IChemE, Rugby, UK, 1993.

2. Gibson N., Rogers R.L. and Wright T.K., "Chemical reaction hazards: An integrated approach", IChemE Symp. Series, No. 102, 1987, pp. 61-83.

3. Semenov Z., Phys. Chem., Vol. 48, 1928, p. 571.

4. Frank-Kamenetskii, "Diffusion and heat transfer in chemical kinetics", 2nd ed., Plenum Press, New York/London, 1969.

5. Rogers R.L., "The use of Dewar calorimetry in the assessment of chemical reaction hazards", IChemE Symp. Series, No. 114, 1989, pp. 47-107.

6. Bretherick, "Handbook of reactive chemical hazards", 3rd ed., Butterworths, London, 1985.

SUPPORT FOR TOOL M – PROCESS SHE ANALYSIS/PROCESS HAZARDS ANALYSIS AND RANKING

Tool M supporting information

There are numerous texts on the application of HAZOP and PHA. These give useful details on the application of the techniques, but may not provide an inherent SHE focus. A good example for further reference is:

> "Guidelines for Hazard Evaluation Procedures", Center for Chemical Process Safety, American Institute of Chemical Engineers, New York, USA.

SUPPORT FOR TOOL N – EQUIPMENT INVENTORY FUNCTIONAL ANALYSIS METHOD

Tool N examples

Example N.1: Distillation column with reboiler

Application of the IFA in regard to the reduction of inventory at the base of a distillation column with a reboiler and liquid being pumped to the next column is shown here.

Project title:

Date: ___ / ___ / ______ **Inventory Functional Analysis Record Sheet (Tool N)** **Page:** *01 / 01*

Plant: _*TRIPLE X*_______ **Item:** _*Lights distillation*_ **Material:** _C_4_____________

Author: ________________ **Proj. #:** _*C 2643*_________ **Ref. #:** ________ **Meeting #:** _*1*______

Function	Critical parameter	Datum	Specific/shared	Volume	Ideas to minimize
1. Stop vapour break-through into pump.	Head	Vessel outlet branch.	Specific.		1. Install vortex breaker. 2. Use pumps which can handle vapour/liquid mixtures.
2. Ensure stable operation of thermosyphon reboiler.	Head	Top tube-plate of reboiler.	Specific.		1. Can be controlled by weir and baffle within column to reduce volume. 2. Too high a head can result in very high velocities and erosion.
3. Ensure pump operates under design conditions.	Head	Above pump suction.	Could be shared.		1. Raise height of column base. 2. Use pumps with low NPSH. 3. Minimize inlet pressure drops.
4. Control of flow to next column.	Volume	Above 1, 2 or 3 above.	Specific.		1. More rapid control. 2. Use pumps which can tolerate vapour liquid flow and have no controller. (Need to evaluate possible instability.)
5. Response to failure of control valve (fails open).	Volume	Above 1, 2 and 3 above.	Shared with 4.		1. To be effective, need 5-10 mins hold-up. Rare event. 2. Improve reliability of control valve. 3. See 4 above. 4. Consider consequences of allowing failure to occur without action.
6. Response to failure of pump or control valve (fails closed).	Volume	Above normal level.	Specific.		1. Need vapour space between normal level and packing. 2. Vapour. Negligible inventory.

SUPPORT FOR TOOL O – EQUIPMENT SIMPLIFICATION GUIDE

Tool O examples

Example O.1: Bromine storage

This example shows how Tool O, the Equipment Simplification Guide, has been used on a system for storing and transferring bromine in a chemical plant.

The studied system consists of the following main equipments:
- a transportation container,
- a main storage vessel,
- two transfer pumps in parallel,
- a feed tank,
- a scrubber.

At the time of the study, a preliminary P&ID of the plant was available. The bromine is fed to the main storage tank by using pressurized nitrogen. The amount of bromine needed for one batch is then pumped to the feed tank, from which bromine is slowly added to the reactor. Gravity is used for the addition. A dedicated scrubber is available to neutralize any bromine fumes.

On the next page some of the results from the analysis are given. The example shows how the operation of the item in question (a transfer line) first has been challenged: is it necessary, are there better options, does the design fulfil all operational requirements, etc. Only then, the technical aspects of all the components that are part of the item (e.g. the pipe itself, flanges, valves, etc.) are studied. For many items no options were identified or the current design was found to be the best option, but for some items ideas on how to reduce leak points were presented.

Project title:

Date: *09/ 07/ 1997*
Plant: _*KFC*___________
Author: _*YM*____________

Equipment Simplification Assessment Record Sheet (Tool O)
Section: _*Bromine loading, storage and transfer (PID 25.6.97/JPJ)*_
Proj. #: _______________ **Ref. #:** ________

Page: ___ / ___

Guideword	Item	Function	Options	Comments
Operation	Transfer line 3002	Transfer of bromine from transport container to storage tank S9260	-	-
		- purging	-	- allow for nitrogen purging
Equipment	Line 3002	- Transfer of bromine	-	-
	- flanges	- PVDF-lined metal pipes can not be welded	- use of PVDF pipes	- less flanges needed
	- valve on container	- open/close	-	-
	- flexible hoses	- allow for flexibility between fixed line and transport container	-	- easily reached when the operator is on top of the transport container
	- flanges between fixed line and flexible hose	-	-	-
	- sight glass 3013	- observation of bromine flow	- use of transparent PVDF pipes	- less flanges needed
	- automated valve 9260	- open/close	-	-
	- bellow	- allows weighing of the storage tank	- flexible hose	- bellows have worked well in other applications
			- other methods to measure the content of storage tank	- weighing requires no extra inlets to the tank
	- manual valve 3014	- open/close	-	-

SUPPORT FOR TOOL P – HAZARDS RANGE ASSESSMENT FOR GASEOUS RELEASES

Tool P supporting information

Use of the process hazards range assessment record sheet

Material – list all materials involved in the process (see also Tool G).

Location/function – note the location the material is present in (i.e. process stage or section), and its basic function (i.e. raw material, reagent, intermediate, product, by-product, waste, etc.); see also Tool G. This may be useful information when seeking ideas on how to substitute or reduce the inventory of the material.

Inventory – estimate inventory of each material. This can be the total for the whole process, or you may wish to list the various inventories in different, isolatable sections of the process.

Leak rate – optional data if you wish to look at continuous rather than "inventory" releases, e.g. for a pipeline.

Hazard type – list the relevant flammable hazard types or toxic category which the material presents.

Hazard range, Affected area – read these off the tables for the relevant hazard and inventory/leak rate.

Comment/priority – use this column to record any comments on the scenario. It could also be used to note the hazards in order of severity with say 1 at the smallest hazard size, increasing to *n* at the largest hazard size. Alternatively you may wish to classify the hazards by range or affected area, e.g. <50 m, <100 m, <500 m, <1000 m, >1000 m.

Hazards range assessment for gaseous releases

1. Introduction

The hazard range tool is a series of simple nomographs which provide an order of magnitude indication of the hazard range and area affected for some common hazards arising from the release of flammable or toxic process materials. The data is based on relatively crude hazard models and has required many simplifying assumptions to be made, and so should be used with this in mind. Any critical aspects of the hazard or the design should be checked using specific models and calculations at an appropriate level of detail and accuracy.

The tool is intended to provide process chemists and engineers with an easy-to-look-up indication of the magnitude of hazards based on either the process inventory or the size of typical leak sites (expressed as a mass release rate). This should give an indication of aspects that must be considered when discussing plant siting and lay-out. The results also encourage the reduction in key inventories and the minimization of the size and number of key potential leak sites by allowing the user to quickly establish which areas of the plant/release scenarios are of most concern. In particular it shows how the magnitude of the hazard can be expected to increase/decrease as the inventory or release rate is changed.

Since there are numerous materials in use within processes, the data has been based on the flammability of a typical hydrocarbon (propane) and toxicity classifications have been based on the definitions use in EEC Directive 84/449/EEC.

There are "hazard range" charts and "area affected" charts for flammables and toxics – for both "instantaneous" releases of inventory and "continuous steady-state" release rates.

The output from the charts is the downwind hazard range [m] or the area affected by the hazard [m^2] for the release concerned. The hazard range/area is approximately that to the 1% fatality level for the harmful, toxic and very toxic categories, i.e. that concentration or level of harm that could lead to serious injury or fatality for some of the weaker or more vulnerable people. Given the complexity in estimating the effects of exposure to heat radiation, blast overpressure and toxic materials in particular, these estimates should be treated as indicative only.

2. Basis of data in the charts

Flammable hazards

The data for BLEVEs, pool, jet and flash fires, and VCEs has been taken from the paper "Rapid assessment of the consequences of LPG releases" by M. Considine and G.C. Grint (presented at Gastech 1984, session 3, paper 8).

The hazard range has been taken to the 1% fatality probability level (as specified in the above reference) for each hazard based on pressurized propane releases. The propane simulation results should be typical of many flammable hydrocarbons.

The hazard models behind these rapid assessment methods are relatively simple ones, such as the TNT equivalence model for explosions, empirical data for BLEVEs and jet fires, and the use of the DENZ and CRUNCH dispersion models for flash fires.

For comparison, releases of propane have been modelled using the current dispersion code DRIFT, version 2.22, to give the hazard range to the lower flammability limit (LFL) under typical weather and release conditions. These simulations assume the released material to be pure, undiluted propane in the gaseous state.

The VCE data has been cut off at 5 Te since it is generally assumed that smaller quantities are probably insufficient to cause an explosion unless some part of the cloud is confined or in a congested area, in which case a more appropriate model is required to take account of these factors.

The areas affected by the hazards have been based on:
- a circle with its centre at the release point for the pool fire, explosion and BLEVE,
- a triangle of width 0.25 × Length for the jet fire, and
- an ellipse for the flash fire and cloud drift to LFL based on the downwind and crosswind hazard ranges.

It should be noted that the flash fire model assumes a delayed ignition when the cloud edge is at the LFL. Earlier ignition would result in a smaller ignited cloud and reduced hazard ranges.

Toxic gas hazards

The data for toxic gas releases has been based on a Gaussian plume dispersion model within DRIFT, version 2.22, using low-pressure propane as the source. Propane was used because it has a similar (slightly heavier) density compared to air and so becomes neutrally buoyant very quickly. Since we are concerned about long range effects at low concentrations, the actual material used makes little difference to dispersion.

Simulations were carried out at D5 (typical onshore weather conditions with moderate wind) and F2 (relatively still air and low turbulence, giving longer hazard ranges) weather conditions. The F2 conditions gave greater hazard ranges, but still of the same order of magnitude as the D5 runs. The D5 data is presented in the charts.

The simulations assume all the material released is vapour. This assumption holds well for gases and vapours and some two-phase releases, but could be very conservative for liquids.

The categories for the toxic effects are based on the EEC Directive 84/449/EEC classifications of toxic materials (toxic by inhalation):
- Very toxic, R26 – LC 50 (rat) not more than 0.5 mg/litre/4 hour
- Toxic, R23 – LC 50 (rat) between 2.0 and 0.5 mg/litre/4 hour
- Harmful, R20 – LC 50 (rat) between 20 and 2 mg/litre/4 hour.

Interpreting these categories and concentrations and relating them to some common level of harm is not easy. As an approximation, use has been made of the ERPG/EEPG classification approach used in the Dow Chemical Company "Chemical Exposure Index", 1st edition, 1994. This defines the Emergency Response Planning Guidelines ERPG-3/EEPG-3 level as: the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects. This could be interpreted as the level around which some of the more vulnerable individuals could begin to experience life-threatening effects. This level has therefore been used to approximate to the 1% fatality level, and hence provide a common "harm level" for the flammable and toxic hazard charts.

The Dow Guide also suggests that the ERPG-3 can be derived by dividing the LC 50 concentration by 30. This rather crude approach has been used to estimate the concentrations for the cloud edge in the hazard simulation, by dividing the EEC LC 50 levels by 30:
- Harmful: 660 mg/m^3 to 66 mg/m^3
- Toxic: 66 mg/m^3 to 17 mg/m^3
- Very toxic: < 17 mg/m^3.

A final category has also been added to show when material reaches the ppm level. This is based a concentration of 1.7 mg/m^3 – one tenth that of the "very toxic" category, and representing approximately 1 ppm for propane.

The charts show the downwind hazard ranges to, and cloud area within these concentrations.

The areas of the clouds have been estimated by approximating the cloud to an ellipse using the length and maximum crosswind distance. For continuous releases the cloud length is the downwind distance, for instantaneous releases the ellipse has also been based on the downwind distance to take account of the area swept by the cloud.

SUPPORT FOR TOOL Q – SITING & PLANT LAYOUT ASSESSMENT

Tool Q supporting information

Advice on plant layout, siting and transportation

Further advice can be found in:

1. Scott D. and Crawley F., "Process plant design and operation", IChemE, 1992.

2. Mecklenburgh J.C. and Godwin G., "Process plant layout", IChemE, 1985.

3. CCPS, "Guidelines for chemical transportation risk analysis", Center for Chemical Process Safety of the American Institute of Chemical Engineers, 1995.

Transport containers

Where highly hazardous materials are being transported, various "improved" containers may be used to reduce the risk of spillage. In addition, consideration may be given to the size of container to be used.

Some examples of bulk transport vessels with increasing integrity are given below:

- Thin-walled tank.
- Thin-walled, fitted with steel crush barriers at sides, end, and over valves.
- Thick-walled (malleable mild steel) tank,
  - valves protected.
- Thick-walled,
  - valves in dome or fitted with internal seal.
- Thick-walled,
  - valves in end recess with gas-tight cover.
- Thick-walled,
  - valves in end recess with gas-tight cover,
  - steel crush barrier to sides and end.
- Thick-walled IBC carrier,
  - fitted inside strengthened frame,
  - valves in dome with internal seal.
- Low-centre-of-gravity dedicated trailer.

As additional measures are introduced, increasing the integrity, the cost also increases and the advice of an expert is essential.

SUPPORT FOR TOOL R – DESIGNING FOR OPERATION

Tool R supporting information

Examples of typical questions

1. Eliminate task

Can the task be eliminated by re-designing the process or plant, thereby avoiding the need to do the operation or using an automatic system?

Examples:
Replace expansion bellows with expansion loops to reduce inspection/maintenance.
Use welded pipework connections rather than gaskets.
Use of an in-line analyser, or automatic sampler, rather than manual sampling.
Providing a charging system to a reactor, so manual charging is not needed.
Using an installed wash jet system to clean vessels rather than manual washing.

2. Substitute task

Can the task or the process/plant be modified or replaced by a safer procedure that achieves the same objective?

Examples:
Use of a safer solvent for cleaning equipment.
Provide an access platform to reach high-level items.
Provide room for a "cherry picker" to be used to access high items rather than a ladder for access.

3. Reduce tasks

Can the number of tasks required be reduced by changing the equipment or design?

Examples:
Replace equipment with one that requires less frequent maintenance.
Design the process so sampling or batch transfers or charging operations are less frequent, say daily instead of per shift (this may need to be balanced against an increase in inventory).

4. Simplify task

Can the task be made simpler, so errors are less likely?

Examples:
Design tanks to take a full drum(s) or batch to simplify transfer operations.
If a task requires co-ordination between two people at different locations – can they see each other or keep in contact easily.

5. Make status clear

Does the task provide feedback to the operator so they know if it has worked or not?
Does the system give a clear indication of its status? (e.g. open or closed, on or off, pressurized or depressurized)
Are equipment, controls, etc. clearly labelled, and is the labelling system used logical and consistent with the plant and its layout?
Does the plant or equipment make clear where or how it may have failed – so the location and type of repair required is more obvious/easy to determine?

Examples:
Spectacle blinds are clearer than blanking plates.
Rising stem or ball valves with handles clearly show if they are open or shut.
Are there ways to check any pressure has been vented before opening for maintenance.

6. Allow for error detection & recovery

Are there opportunities for the operator to abort or recover if the task goes wrong?
And how will he know that things have gone wrong (timely detection/warning)?

Examples:
Arrange so the operator can see tank level as he fills the tank.
Provide tapping on-line so pressure can be checked before maintenance.

7. Make error "impossible"

Can the task or equipment be designed so that it can only be done "the right way"?
(making it practically impossible to do in the wrong order, fit things incorrectly, or fit the wrong thing.)
Equipment and controls labelling – must be clear, logical and consistent.

Examples:
Design pumps and non-return valves with different fittings at each end so they cannot be put in the wrong way around.
Rationalize materials of construction so different types of stainless steel, for example, cannot be mixed up.
Rationalize fittings and nuts and bolts so there is less chance of the wrong one being used – could the high-pressure or high-specification fittings be adopted throughout the plant to avoid installation of low-specification fitting on high-specification duty.

8. Improve working environment/make conditions easier

Is the equipment easy to access, and is there room to do the task safely?
Can the physical environment be made more suitable for carrying out the task? (lighting, noise, ventilation, temperature, etc.)

9. Segregate from hazards

Can the person be separated from the hazard by space or some form of protective barrier?
Can the task or equipment be designed so that operators are segregated from the hazards?
Can the task be performed by a remote machine/remote control?
Can the task be moved to a safer area away from other hazards?
Can the hazard be contained, so operator exposure is minimized?
(in sealed containment, partial containment/screen, or at reduced pressure/ventilated)
Can the equipment be designed so that it can be easily removed and transferred to a more suitable place to be worked on? Or is it better to work on it in-situ?

10. Minimize exposure

Can the task be made very simple so that it takes minimal time to complete?
(use of quick-release couplings, modular design)
Can the task or equipment be designed so that any complex operations/long duration operations can be carried out away from the hazards?
Can the item be taken away for maintenance and replaced by a spare in meantime, or continue to operate without item?

11. Simplify procedure

Does the procedure state the objectives of the task and the hazards involved?
Does the procedure state what to do if things go wrong or do not respond as they should?
Is the procedure clear and logically set out?
Is it clear which status the system needs to be in before the procedure can be started?
Does it state what tools, preparations, precautions and equipment are needed to perform the task and what problems/hazards may be encountered?