QUANTIFYING INHERENT SAFETY OF CHEMICAL PROCESS ROUTES

by

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ABSTRACT

Inherent safety is that which is intrinsic to a chemical plant. Chemical plants should be designed to be acceptably safe and it is better if this can be achieved through inherent safety, which can not be compromised, rather than engineered safety. The earlier that inherent safety is considered, the greater are the benefits. The choice of chemical route, that is the raw materials and the sequence of reactions that converts them to the desired products, is a key early design decision that influences the inherent safety of a plant. The inherent safety must be quantified in order to choose the optimum route from a number of alternatives.

A trial inherent safety index has been developed for ranking alternative chemical routes by inherent safety. The physical properties of the chemicals involved, and the conditions in the reaction steps are parameters in the index calculation procedure. The index has been tested on a number of routes to methyl methacrylate (MMA).

In order to verify and improve the index, a panel of experts was asked to rank the routes, and to make comments about the index and how it could be improved. This expert judgement exercise used three questionnaires and a group meeting to elicit the required information. Statistical methods were used to analyse the results from the questionnaires. The experts agreed closely among themselves on the rankings. The rankings from the trial index and the rankings from the experts matched closely.

A new index was produced based on the comments of the experts and further research. The new index is more structured than the trial index, and separation and storage steps are included in addition to reaction steps. The inherent safety of the routes to MMA has been assessed with the new index.

Developing a method for quantifying the inherent safety of chemical routes has proved to be a large and difficult task. Further research is needed to decide how the interactions between parameters affect the assessment of inherent safety. The ultimate goal is a computerised tool that could be used in the early stages of industrial process development.

KEYWORDS

Expert

Inherent

Intrinsic

Methyl methacrylate

Process

Quantify

Ranking

Routes

Safety

Scoring

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1. CHAPTER 1 - INTRODUCTION

The initial brief for this research was to produce an automated system to assist in the conceptual design of chemical plants. It would cover developing a design from an initial feasibility study through to process flowsheets. It was thought that this would be a three step process. The first step would simply calculate the added value of a product, that is, check if the product was worth more than the raw materials. The next stage would be a more detailed cost estimation, based on 'shortcut' estimates of raw materials consumption, utilities usage and capital requirements. The final stage would be a detailed conceptual design of the plant including flowsheet, mass and energy balances, and detailed costings. This system was to be built using artificial intelligence methods and tools to produce an 'expert' system for the conceptual design process.

In examining current literature on expert systems for chemical process and plant design, and other design methodologies, for example Douglas' hierarchical design method (1987), two points became evident. Firstly, that as designs were developed they should be continually checked for viability in order to sanction further development. This checking was nearly always done on an economic basis, making sure that the plant would be profitable. Secondly, very few of the systems and methods presented attempted to assess how safe the plant built from the proposed designs would be, or did not even mention safety at all. The only checks on safety were to use conventional hazard assessment techniques, when the design was sufficiently developed. No attempt was made to see how the level of safety changed through the course of the design, in order to exert pressure to improve it. Safety issues tended to be passed over in the early stages, in the belief that the Hazard and Operability studies (HAZOP) (Lees, 1980)would find all the hazards. In order that designs could be compared in a similar manner to economic comparisons, a measure of safety was needed. With this in place, the designs could be compared and contrasted for both economic viability and safeness. As well as making sure the proposed design was profitable, a continuing level of safeness could be assured.

Having considered these points, the basis for the research was changed. It was decided that trying to develop a suitable measure of safety was a large enough problem to tackle by itself, without trying to incorporate it into an automated design system. After further discussion, the broad problem of safety assessment was refined to quantification of inherent safety. Inherent safety (Kletz, 1991) is that which is intrinsic to something. For example, a bungalow is more inherently safe than a house according to Kletz. This is because the majority of accidents in the home are caused by stairs. Stairs can be made safer by adding on safety features, for example hand rails, child-gates or non-slip carpets. The inherently safer choice is to remove the stairs, that is to live in a bungalow. The

inherent safety philosophy is to remove hazards rather than try to control them or not to have them there by design.

Kletz (1991) suggests methods by which chemical process plants can be made inherently safer. Smaller inventories of hazardous materials, less extreme process conditions, or less hazardous chemicals should be used. All of these methods aim to remove a hazard wherever possible, rather than adding on 'engineered' safety. If a measure of safety that could be used in the very early stages of a design was available, then the inherent safeness of the design could be assessed before any additional safety measures were added. In this way a preliminary design could be assessed and then modified to give the best possible built-in safeness.

The stage of plant design when a measure of inherent safety could be used most effectively was carefully considered and it was decided that quantification of inherent safety would be of greatest benefit very early on in the design process. Then, a design would still be defined in very broad terms, allowing it to be easily changed to improve its inherent safety. However, early safety assessment is not generally practised because HAZOP has been such a great success. Methods for assessing safety existed for use during and after a piping and instrumentation diagram had been produced, for example fault tree analysis (Lees, 1980). So a method was needed for use before that stage. However, in order for the method to produce meaningful results, the stage must have sufficient information for the method to use. The point chosen to assess the inherent safety was when the choice of chemical route was being made, that is where the chemical reactions, reactants and products were being chosen. This was considered the earliest point at which an assessment could be made.

The aim of the research was fixed as: to develop a method for assessing the inherent safety of chemical process routes. The method would assess inherent safeness of a route. Alongside this assessment a preliminary economic estimate for the route could be calculated. Then both the economic and safety assessments could dictate whether a design is to be developed, or aid in the choice of which routes to develop into more detailed process designs, from a set of alternative routes.

Kletz claims that as inherently safer plants are smaller and safer, then they should cost less to build and run. A secondary aim of the research was to use the new method to investigate Kletz's claim.

Chapter 2 introduces the concept of inherent safety and inherently safer design, with examples of how inherently safer design is of benefit. It covers how the design develops through the design process, how the design can be made more inherently safe

by following the principles of inherently safer design. It also covers the arguments for assessing inherent safety at the route choice stage.

Chapter 3 reviews how inherent safety may be assessed. Present methods for assessing safety are examined to determine whether they could be adapted to assess inherent safety.

Chapter 4 introduces the work on developing an Inherent Safety Index (ISI). Individual parameters for assessing inherent safety are examined, along with how they could be quantified or 'scored' in relation to inherent safety. Possible methods for combining the individual scores into an 'index' are discussed. The first trial Inherent Safety Index is presented. The chapter concludes by describing test data, for processes producing methyl methacrylate (MMA), and presents the results of the first trial of the Inherent Safety Index.

Chapter 5 covers the topic of expert ranking. Having obtained results from the trial index, a panel of experts were consulted about the results, to see if they agreed. This was done with a series of questionnaires and a meeting of the panel of experts. The chapter covers the ideas behind expert ranking, the development of the questionnaires, the results from them, and the analysis and discussion of the results.'

Chapter 6 presents the development of a new ISI. Reasons are given for why a new index was needed, based on comments and suggestions made by the experts about the first trial index. Areas for development are discussed, along with possible ways in which to improve the new index. The chapter ends by describing the new index.

Chapter 7 presents example calculations of how to use the new index and the results from the new index which is tested using the MMA route data. Also presented is a regression analysis of the results of the trial index compared with preliminary economic estimates of the MMA routes. The chapter finishes with discussion about the new index.

Chapter 8 presents the conclusions from the work, along with recommendations for further research and development of the index.

The author recognises, and it must be stated at this point, that some parts of the methods developed in the research have an arbitrary basis. This work is only a small part of a much larger and more complex problem. It would not have been possible to explore all the fields that must provide a foundation for assessment of inherent safety. Rather a framework for inherent safety assessment has been produced. As the other fields which

require further work are developed, then the arbitrary elements within the framework presented here can be replaced. The methods suggested are a starting point for development and experimentation to produce more refined methods.

2. CHAPTER 2 - INHERENT SAFETY AND INHERENTLY SAFER DESIGN

2.1 Introduction

There is a great need to make chemical plants safer. History shows that chemical plants have the potential for large scale death and destruction when accidents happen. Public pressure and government legislation put pressure on and present challenges to designers to make plants safer. It is claimed that inherent safety costs nothing to add in and should be a realistic tool to make designs and plants safer.

Following the incidents at Flixborough (Lees, 1980) and later at Bhopal, papers were published suggesting methods by which these incidents could be prevented from happening again. Most advocated adding more trips, alarms, fire protection or other safety equipment. All but a few missed a simpler alternative - inherent safety.

In this chapter, the concepts of inherent safety (IS) and inherently safer design (ISD) are discussed. Where possible, real life examples are used to illustrate some of the ideas behind IS and ISD. The benefits and disadvantages of ISD are contrasted.

2.2 What is inherent safety?

For several decades, Inherent Safety has been promoted by Dr. T.A.Kletz. He advocates chemical plants that use less hazardous materials, in smaller quantities, at lower temperatures and pressures. This is said to be inherently or intrinsically safe. The term 'inherent' is used in preference to 'intrinsic' only because "intrinsically safe" has a technical meaning in relation to machinery. A plant that is made safer by adding control equipment is said to be extrinsically safe. Rogers and Hallam (1991) give an alternative definition of inherently safe: "An inherently safe process can be considered as one which by virtue of its design does not produce a hazard if a fault occurs." This has a slightly different emphasis than Kletz's definition. Kletz talks of firstly avoiding the hazard and if this is not possible, reducing the size of the hazard as much as possible. Rogers and Hallam talk of making a process inherently safer outside normal operation.

There are many everyday examples of inherent safety or lack of IS in the home. Kletz's example is stairs. Stairs are responsible for more accidents in the home than knives or electrical equipment. The extrinsic way of making stairs safer is to add hand-rails, put in landings, make steps shorter or make risers less steep. The inherently safer alternative is to live in a bungalow. The hazard, that is the stairs, is removed.

2.3 Process design stages

The process of designing a chemical plant moves from the first idea for a product through to the plant start up. It is possible to break this process down into distinct stages.

At each stage the level of detail in the design increases. The design process is not a once-through process, it is iterative. At various stages it may be necessary to review the design and return to an earlier stage. This could be due to the unviable economics of the proposed design, problems with materials of construction, or poor energy integration. The stages below are one example of the possible breakdown of the design process.

2.3.1 Product design

Coulson and Richardson (1985) identified the first stage of the design as more of a marketing task than an engineering task. A market niche is recognised and a product is designed for it. The product may be a new drug, a new type of plastic or a new soap powder. The level of detail is simply the specification for the product needed.

2.3.2 Research and development

Having chosen a product, the design process moves to the chemists. They will research and develop a suitable chemical to meet the specification of the product. In doing so, the raw materials needed and the methods for producing the chemical form the next level of the design. This is known as a chemical route. More than one chemical route could be possible for the product.

2.3.3 Preliminary design

If more than one route is possible, the 'best' is chosen on the basis of estimates of the economics of the process. The economic estimates show if the process will be economically viable. The chosen process may then be scaled up from the chemistry laboratory to a pilot plant for further exploration.

2.3.4 Flowsheet

The flowsheet incorporates the major process equipment, for example reactors, plant items for effecting separations, heat exchangers, etc. Process flowsheet design is usually done using automated flowsheeting software which calculates the sizes of the major process items and the flowrates of streams between items.

2.3.5 Piping and Instrumentation Diagram

The piping and instrumentation diagram (P&ID) is a further development of the flowsheet. In addition to the major plant items and major streams, piping, valves and pumps are included. Pneumatic and electrical lines are added to show the control equipment for the process.

2.3.6 Detailed design

The P&ID is progressively developed. Accurate sizes of the major and minor plant items are calculated, along with pipes. The physical plant layout including building and infrastructure are designed.

2.3.7 Equipment design

The larger plant items, for example reactors or distillation columns will be designed from the specifications of the detailed design.

Having identified the broad stages of a process design, it is now possible to examine ISD and see how the above design stages interact with the ideas behind inherently safer design.

2.4 Inherently safer design

Kletz has developed several key design strategies for making designs inherently safer. Many examples of these ideas are given in his book "Cheaper, safer plants" (1984). These strategies may be summarised by six keywords:

> Elimination
> Intensification
> Substitution
> Attenuation
> Simplification
> Limitation of effect

2.4.1 Elimination

Elimination of hazards is the ultimate aim of an inherently safer design. Elimination as a strategy has the greatest benefit when the chemical reaction path is being chosen, than at other stages in the design. At this stage, changes can be made to the choice of reactants and reactions before the design becomes too far advanced.

The process used at Bhopal, India, provides a very good example of how a hazardous intermediate could be eliminated (Kletz, 1988). The plant produced the insecticide Carbaryl via an intermediate chemical, methyl isocyanate (MIC). The MIC was kept in intermediate storage, of which 25 tonnes escaped causing at least 2000 deaths and many more injuries in 1984. The reaction route used in the plant was as follows:

$$CH_3NH_2 \quad + \quad COCl_2 \quad \rightarrow \quad CH_3OCN \quad + \quad 2HCl$$

methylamine + phosgene → methyl isocyanate + hydrogen chloride

$$CH_3OCN \quad + \quad \underset{OH}{\bigcirc\!\bigcirc} \quad \rightarrow \quad \underset{OCONHCH_3}{\bigcirc\!\bigcirc}$$

methyl isocyanate + α - naphthol → carbaryl
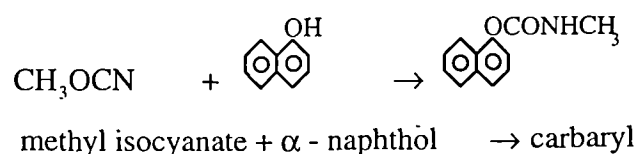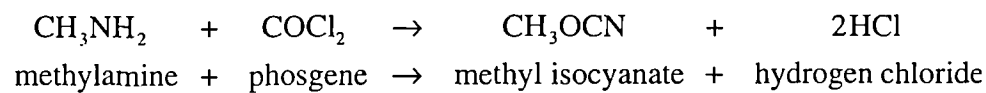
An alternative route to carbaryl exists which uses the same raw materials, but avoids methyl isocyanate.
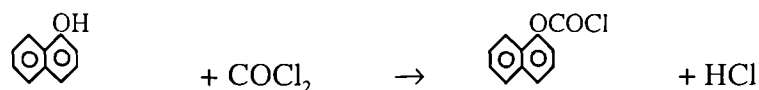
α - naphthol + phosgene → chloroformate + Hydrogen chloride
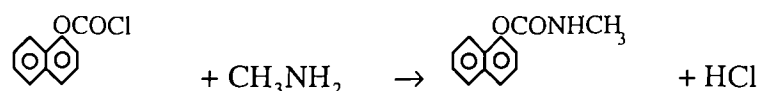
chloroformate + methylamine → carbaryl + Hydrogen chloride

This process is inherently safer than the one used at Bhopal because the MIC has been eliminated. However, both routes use phosgene, which is a very dangerous chemical in its own right, and therefore should still be considered as inherently unsafe.

2.4.2 Intensification

If it is not possible to eliminate a hazardous material from a process, then less of it should be used or stored. Often plants have large inventories of hazardous chemicals because reactions are slow or conversions are low, for example the per pass conversion of cyclohexane in the Flixborough plant was only 6%. Instead of using large inventories, reduce them by improving mixing or heat transfer, increasing reaction rates or use of catalysts.

A good example of how inherent safety is improved by inventory reduction is the manufacture of nitro-glycerine (Kletz, 1991). The reaction proceeds in the presence of concentrated sulphuric acid.

$$C_3H_5(OH)_3 \quad + \quad 3HNO_3 \quad \rightarrow \quad C_3H_5(NO_3)_3 \quad + \quad 3H_2O$$
glycerin + nitric acid → nitro - glycerine + water
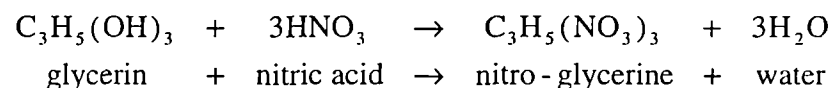
The reaction is very exothermic, and good mixing and cooling are essential to prevent an explosive runaway reaction. Until the 1950s, the reaction was carried out in one tonne batch reactors, with an operator watching the temperature as an indicator of a

possible runaway reaction. To stop him falling asleep and keep his attention on the task at hand, he was provided with a one legged stool to sit on.

In the redesign of the process, extrinsic safety equipment could have been added to control the process. However, a more inherently safer approach was chosen. The one tonne reactor was replaced with a continuous reactor similar in design to a gas ejector. The reaction was very fast, but good mixing was the rate limiting factor. In the gas injector, the reaction took place very quickly because of the good mixing. The residence time was reduced from 120 minutes to 2 minutes. The reactor inventory was reduced from 1000 kilograms to 1 kilogram.

Consideration of intensification has a large effect at the route stage, as it allows for the reduction in process inventories without the need for re-design of process equipment.

2.4.3 Substitution

In substitution, an alternative chemical is used in place of a hazardous chemical. It is also possible to replace a hazardous operation with a more inherently safe one, for example Higee distillation replaces conventional distillation columns (Kletz, 1991). An extreme form of substitution is to replace several reaction steps or a whole route to produce the required product. The ultimate form would be to completely change the required product.

Acrylonitrile can be produced by reacting acetylene with hydrogen cyanide (Puranik et al, 1990):

$$C_2H_2 \quad + \quad HCN \quad \rightarrow \quad CH_2 = CHCN$$
acetylene + hydrogen cyanide $\rightarrow$ acrylonitrile
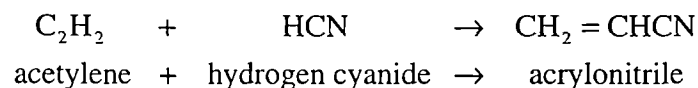
This uses hydrogen cyanide and acetylene, both very hazardous chemicals, as raw materials. However, there is an alternative route via propylene and ammonia:

$$2C_3H_6 \quad + \quad 2NH_3 \quad + \quad 3O_2 \quad \rightarrow \quad 2CH_2 = CHCN \quad + \quad 6H_2O$$
propylene + ammonia + oxygen $\rightarrow$ acrylonitrile + water
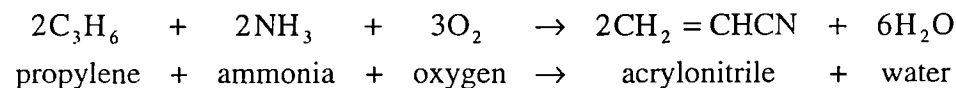
This is the main reaction, but even though the catalyst is highly selective, there is a side reaction that produces hydrogen cyanide:

$$C_3H_6 \quad + \quad 3NH_3 \quad + \quad 3O_2 \quad \rightarrow \quad 3HCN \quad + \quad 6H_2O$$
propylene + ammonia + oxygen → hydrogen cyanide + water
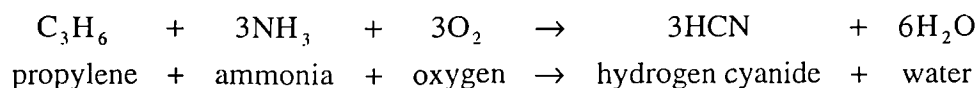
By changing the raw materials, the significance of the hydrogen cyanide in the process has been reduced from that of a major raw material to a small by-product. With the addition of a second reaction step the hydrogen cyanide is no longer a raw material or by-product and is only present as a small volume intermediate.

$$2C_2H_4 \quad + \quad 2HCN \quad + \quad O_2 \quad \rightarrow \quad 2CH_2=CHCN \quad + \quad 2H_2O$$
ethylene + hydrogen cyanide + oxygen → acrylonitrile + water
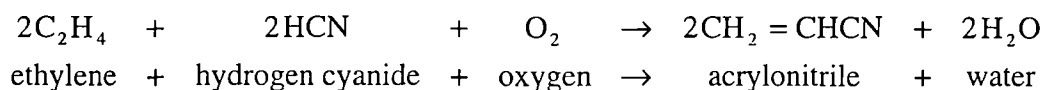
Substitution is applicable not only to the process chemicals, but also to service fluids. For example, heat exchangers could use water instead of potentially flammable cooling oils. Solvents used in separations can be substituted. For example, super-critical carbon dioxide, used in the food industries for decafeination of coffee or oil extraction, can replace hexane or ethanol which are more toxic and are flammable.

2.4.4 Attenuation

Hazards can be reduced by changing the conditions under which a reaction occurs. Chemicals can be made safer by storing them in less hazardous forms. Reactions that are operated away from temperatures where runaway reactions are possible are less hazardous. Operating away from flammable limits reduces the risk of fires or explosions. Storage of liquids in refrigerated conditions at atmospheric pressure should be preferred to pressurised storage.

Vinyl acetate can be produced by reacting ethylene or acetylene with acetic acid and oxygen (Puranik et al, 1990). This occurs in the vapour phase at 1 atmosphere and 100-200°C.

$$2CH_2=CH_2 \quad + \quad 2CH_3COOH \quad + \quad O_2 \quad \rightarrow \quad 2CH_2=CHCOOCH_3 \quad + \quad 2H_2O$$
ethylene + acetic acid + oxygen → vinyl acetate + water
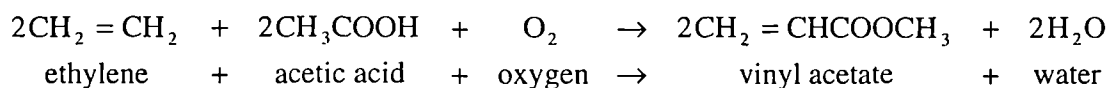
The per pass conversion of this reaction is only 10 to 15%. The problem with the reaction is that it requires the storage of large amounts of corrosive acetic acid as a raw material, and the unreacted acetic acid must also be recovered. An alternative reaction exists, using the same raw materials, but this reaction occurs in the liquid phase at 30 atmospheres and 100 - 150°C. The conversion is 95 to 98%.

$$2CH_2 = CH_2 \ + \ CH_3COOH \ + \ O_2 \ \rightarrow \ CH_2 = CHCOOCH_3 \ + \ H_2O \ + \ CH_3CHO$$

ethylene $\ +\ $ acetic acid $\ +\ $ oxygen $\rightarrow$ $\quad$ vinyl acetate $\quad +\ $ water $\ +\ $ acetaldehyde

$$2CH_3CHO \ + \ O_2 \ \rightarrow \ 2CH_3COOH$$

acetaldehyde $\ +\ $ oxygen $\ \rightarrow \ $ acetic acid
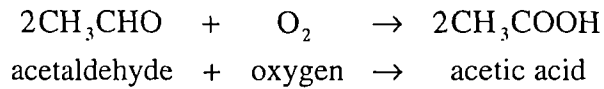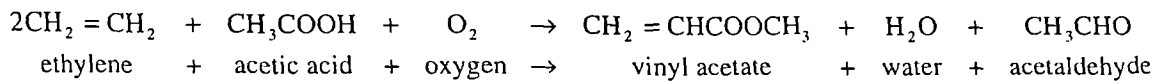
The acetic acid is recycled back to the first reaction. By changing the reaction conditions, from a gas phase to a liquid phase reaction, the acetic acid is now an intermediate, rather than a raw material, so it does not need to be stored, and the need for acid recovery is also removed.

It should be noted that attenuation may work against intensification. Lower temperatures and pressures may lead to a drop in conversion that consequently leads to an increase in inventory. Using materials diluted in solvents or inerts leads to an increase in overall inventory but not in the inventory of the hazardous material. However in its more dilute state, there may be improved reaction kinetics or better mixing, and the overall effects may be less hazardous.

2.4.5 Simplification

As chemical plants grow more complex, more trips, alarms and protective equipment are added to defend against identified hazards. Operation becomes more complicated, there is more equipment to maintain, there is more chance for human error and consequently greater chance for something to go wrong.

There is often a simpler way to reduce or remove hazards than adding protective equipment. By making the plant simpler by design, it becomes a more inherently safe plant. Kletz gives many examples of how simple design changes can lead to a safer plant without the need for additional equipment, and conversely, how a small hazard can become a large problem by the addition of too much extra equipment.

Kletz gives an example of what he calls a 'modification chain', where the consequences, in terms of complication of the design, of an initially small design change are nor foreseen.

He starts with a manhole cover that could leak flammable vapour.
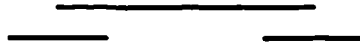
Figure 2.1-Manhole cover, stage 1

To this a 4 metre tall vent was added to protect passers by.
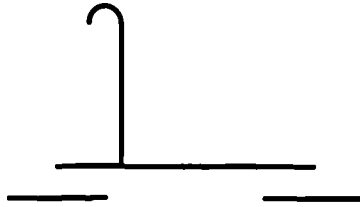
Figure 2.2 - Manhole cover, stage 2

In case of a fire, a flame arrestor was fitted.
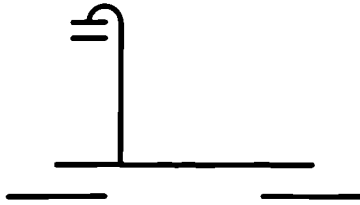
Figure 2.3 - Manhole cover, stage 3

To clean the flame arrestor, an access platform was added
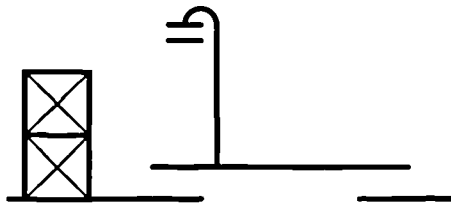
Figure 2.4 - Manhole cover, stage 4

And finally, hand rails were fitted to the access platform
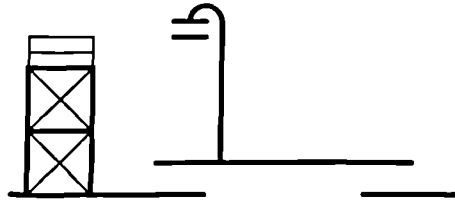
Figure 2.5 - Manhole cover, stage 5

Thus instead of stopping the leak by perhaps improving the seals on the manhole cover, the chain of modifications leads to an over complicated solution to the problem.

The simple solution to dealing with hazards in a design is to add on protection and control measures. Each add on measure may lead in turn to more add on measures and eventually escalate to create a very complicated method of control. A better and simpler solution may be reached by exploring methods which remove the hazard in the first place.

2.4.6 Limitation of effects

In addition to applying the above strategies to a design, méthods are applied to limit the effects of potential hazards. These methods are used when the size of a potential hazard has been reduced as much as practicable, but there is still potential for something to go wrong.

For example, if several chemicals are charged to a reactor in a certain order, there is the possibility of adding chemicals in an incorrect order, thus causing an unwanted reaction. If the chemicals are charged into more than one reactor, so that a chemical can only react with the correct chemicals, the possibility of unwanted reactions is removed.

Limiting the addition of energy, by lowering temperatures or pressures can reduce potential hazards. The incident at Seveso, Italy, in 1976 (Kletz, 1991) demonstrates the consequences of not limiting temperatures. 2,4,5-trichlorophenol was reacted at 158°C. It was known that a runaway reaction could occur at a temperature as low as 185°C. The reactor was normally heated by steam at 190°C, but due to reduced demand the steam temperature rose to 300°C. It is believed that this permitted inadvertent over-heating at the surface of the liquid in a partially filled reactor and a runaway reaction started. The relief from the reactor spread dioxin over the surrounding area rendering it uninhabitable. If steam below 185°C had been used, the runaway could not have occurred.

2.5 When to consider inherent safety?

Safety should influence design decisions from the moment the product is conceived, through until the plant is commissioned. In terms of the design stages discussed earlier, as the design progresses from stage to stage, the possibility for making the plant more inherently safe decreases. Therefore the benefits to be gained from inherently safer design decrease as the complexity of the design increases (Figure 2.6). Thus changes to a design need to be made early to be of most benefit. Inherently safer plants are so because hazards have been removed or avoided. It is easy to remove a potential hazard when the design for the plant is still only at a conceptual stage. Once the flowsheet has been fixed, the choices of chemicals, reactions and inventories have been made. From this point on, the safety measures will be largely extrinsic, that is additions of trips and relief systems etc.
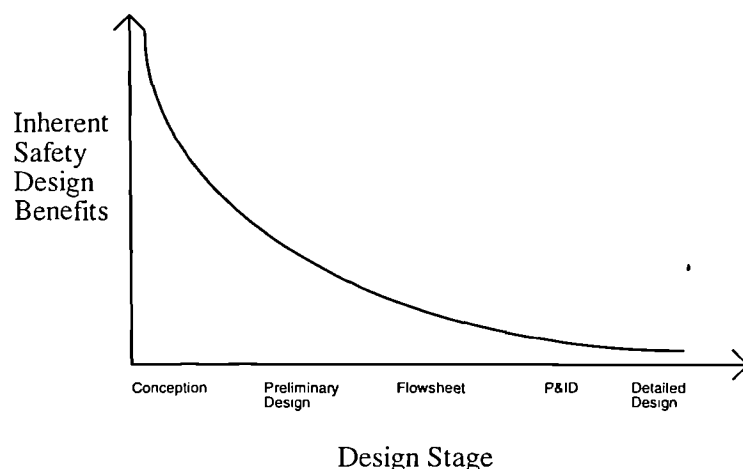
Figure 2.6 - Graph of relative benefit of inherently safe design versus design stage

Opportunities for changes later on in the design to improve inherent safety are less likely because the design will be too inflexible. Changes to one part of the design may unavoidably affect others and cause problems. Design changes at a late stage are also more costly and time consuming. Changes made earlier on in the design may only cost an hour or two in a flowsheet design package, but changes to a piece of equipment at the detailed stage could be measured in days, weeks, or even months and be very expensive.

2.6 Benefits of inherently safer design

2.6.1 Safer Plant

The conventional method for dealing with hazards is to add extra safety features, this is extrinsic safety. A hazard is controlled or contained, or the likelihood of an accident happening is reduced. The problem is that the hazard is still present. There

may still be a large inventory of a highly hazardous material present, which could escape and explode or poison humans, animals or plants.

If the above methods are applied to the design of the plant, potential hazards can be removed or reduced. The plant is made inherently safer. Either there is no longer a hazard to control, or if there is a hazard, it has been reduced to a level at which control is more successful.

Moreover the plant is safe under both normal conditions and in circumstances of deviation from normal. For example, changing a reactant improves safety under normal conditions, whereas removing the potential for a runaway reaction is dealing with a potential deviation.

In either case, the important point about inherently safer designs is that the 'as-built' chemical plants are safer.

2.6.2 Cheaper plant

There are several ways in which inherently safer design can make plants cheaper. The first is by intensification. In general, the cost of plant items decreases with size. Smaller inventories need smaller process vessels. Therefore, 'plants with smaller equipment should cost less to build.

Added-on extrinsic safety equipment adds cost to a plant. If a plant is inherently safer, the extra equipment is not needed. There is a hidden extra cost of safety equipment. Trips and alarms need to be tested and maintained, which costs money. These hidden costs can double the expected cost of safety equipment

Inherently safer plants present less of a problem for the public and local authorities. The choice of land increases, and thus the cost of land decreases. Inherently safer plants may attract lower insurance premiums. Plants that are simpler cost less to run, because they need fewer operators and less maintenance. Plants using less energy, because of simpler designs cost less to run.

2.7 Overall safety

When looking for ways to improve inherent safety, it is important to take a wider view than just looking at the design for the chosen process. Often by improving the inherent safety of the chosen design, a hazard is exported to another process, which may be at a different site or the responsibility of someone else. The hazard has not been removed or controlled, but passed on to someone else to deal with. For example, when Flixborough was rebuilt, the oxidation of cyclohexane was replaced with the

hydrogenation of phenol. But the production of phenol involves the oxidation of cumene to cumene hydroperoxide. This process is just as hazardous as the cyclohexane oxidation. The dangers inherent in the original Flixborough process were not removed, just exported to another place.

3. CHAPTER 3 - QUANTIFYING INHERENT SAFETY

3.1 Introduction

In chapter 2, the concepts of inherent safety and inherently safer design were introduced. This chapter reviews some of the ways in which inherent safety might be assessed. Some existing methods for assessing safety are examined to see if they can be adapted to assess inherent safety.

Safety can be described in both qualitative and quantitative terms. For example, a fault tree gives probabilities of events happening, this is a quantitative assessment of safety. Something can be described as more explosive, more toxic or more corrosive, but only in qualitative terms. But so far no methods have been proposed to say that something is safer in a quantitative manner, therefore allowing for the possibility of assessing how design changes improve the inherent safety.

3.2 Current methods for assessing safety

3.2.1 ICI 6-stage Hazard Study procedure

ICI has recognised the need for a thorough investigation of safety at an early stage in the design of a process and developed a 6 stage procedure to study safety at points throughout the development of a design and the consequent plant (Duxbury & Turney, 1989). Two safety studies were introduced prior to the conventional Hazard and Operability study of a piping line diagram, and three more studies afterwards.

Hazard Study 1 is carried out at the project exploration stage or the research and development stage. It looks at the properties of all the chemicals that are involved in the process. Any possible interactions between chemicals are investigated so that the chemistry of the process is fully understood.

Hazard Study 2 is carried out when the process flow diagram is available. Different sections of the plant are subjected to scrutiny to identify potential hazards. This is done by looking for 'top events', that is potential fires, explosions or large scale hazards. Fault tree analysis is carried out wherever possible, to estimate the probabilities of the 'top events', from 'base events', for example pump failures.

Hazard Study 3 is a conventional Hazard and Operability study carried out on a detailed Piping and Instrumentation diagram.

Hazard Study 4 is a review by the plant manager to ensure that all previous Hazard Studies are complete and have been implemented and recorded properly and that operating and emergency procedures are in place.

Hazard Study 5 covers more local hazards on the plant such as access and exits, machine guards and provision of safety equipment .

Hazard Study 6 is a final review of the plant during and after commissioning. This identifies unexpected changes to the plant from the original design intent and ensures that modifications carried out during commissioning are assessed for safety.

Between studies 1 and 2 there is the potential for an additional study. Study 1 concentrates on assessing the chemicals in a process. Study 2 then looks at the process flowsheet. Between these two studies the choice of chemical route is made. The additional study would look at the inherent safety of the potential routes, to help choose which route(s) should be developed into a flowsheet. This may be done alongside an economic assessment of the routes. Hazard Study 1 and this intermediate study could easily be used to assess several different potential routes to produce a chemical.

3.2.2 Dow and Mond indices

The Dow Chemical company developed a safety and loss prevention guide (Dow, 1980), for the assessment of potential hazards. The "Fire and Explosion Index" is used to calculate a value to express the potential hazard of a new chemical plant. The higher the value, the more unsafe the plant. The index is calculated using the Piping and Instrumentation Diagram, and a detailed plant equipment layout. The results are used as a guide to adding on safety equipment.

The ICI Mond division developed the Dow index into the 'Mond Fire, Explosion and Toxicity Index', (ICI, 1980). The main improvements included the consideration of toxicity, scores for good design and safety equipment, and the compilation of separate indices for fire, internal explosion and aerial explosions.

The calculation of the Mond index develops in stages, each more detailed than the previous one.

1. An assessment is made of each process unit using a method similar to the Dow index.

2. The individual indices for fire, explosion and toxicity are calculated, and compared with levels of acceptable risk.

3. The design is reviewed to see if the factors used to calculate the indices can be reduced by design changes.

4. Off-setting factors are applied for features of good design, for example fire protection or control equipment.

5. The off-setting factors modify the original indices to give the final hazard indices.

3.2.2.1 Calculating the Mond Index

The method for calculating the Mond index is as follows:

Division of a plant into units.

A unit is defined as a separate physical entity. It is separated from other units by walls, bunds or distance. A unit can be a reactor, separation unit, storage, pipework, or anything which can be divided from the rest of the plant.

Determination of the material factor.

The key material is the one which represents the greatest fire or explosion hazard. The material factor for the key material is calculated from the heat of combustion or decomposition. This can be modified to take into account mixtures or reactive combinations of chemicals. It does not have to be the material with the highest inventory in a unit. If a material is particularly reactive or flammable compared to another, but there is only a small amount, then the more abundant material is the key one. However, if the more abundant material presents only a low hazard or is inert, the less abundant, more hazardous material is taken as the key. If more than one material is considered hazardous, several assessments can be made on the unit and the worst taken.

Special material hazards.

These are hazards of the material which depend upon the circumstances of use and are not particular properties of the material. For example, the mixing and dispersion properties of the chemical, the viscosity of the material, whether it is prone to spontaneous heating or polymerisation, or whether it is explosive. It covers any properties which can be considered unusual and merit additional factors.

General process hazards.

This factor is dependent on the type of process in a unit, or operations associated with that unit, for example transportation of materials to and from the unit. Consideration is given to whether the process is batch-wise or continuous. If it is a batch process, could the use of the unit for a different reaction introduce additional hazards?

Factors are added for the manner in which a unit is filled or emptied, or how material is moved to and from the unit.

Special process hazards.

In a similar manner to special material hazards, these are factors which depend upon the operations in the unit. The factors consider extremes of operating conditions, that is very high or low temperatures and pressures. An assessment of the effects of corrosion can be included. If the unit is subjected to cyclic changes, for example pressure cycling in a batch, the potential for fatigue failure of the unit can be assessed. If a reaction is particularly difficult to control, for example one which is highly exothermic and subject to runaway, this can be penalised. There are several factors associated with particular fire and explosion hazards, for example dust explosions, operating within flammable limits, electrostatic hazards and ignition sources.

Quantity hazards.

A single factor is assigned for how much of the key material is in a unit.

Layout hazards.

The two key values for assessment are the height and the plan area of the unit, and the height at which material is present. Aspects of containment and drainage are considered including the 'domino effect', that is the collapse of structures onto adjacent units, or the spread of burning liquids, which can spread a fire through the plant. The height of the unit and the elevation with respect to adjacent units correlate with the potential for this.

Toxicity hazards.

The assessment of toxic hazards in the Mond Index relates to large releases following a fire or explosion. The material with the lowest Threshold Limit Value (TLV) is used for the factor. This may not be the key mat rial identified for fire and explosion factors.

Indices calculation.

Firstly, the Overall index, based on the Dow index, is calculated.

The Fire Potential index gives an indication of the duration of the fire. This is based on an assumption that only 10% of the quantity of material is burned in the fire.

The Internal Plant Explosion index is a measure of the hazard due to a unit catching fire or exploding.

The Aerial Explosion index is a measure of the effect of fire or explosion due to material which has escaped from the unit, for example a cloud of flammable material.

The Unit Toxicity index is a measure of the influence of toxicity on the control and supervision of the unit, when dealing with fires and explosions.

Finally, the Overall Risk Rating modifies the Overall index, using the above four indices (Fire Potential, Internal Plant Explosion, Aerial Explosion and Unit Toxicity).

For each of the above indices, factors are identified which either reduce the frequency of incidents or reduce the magnitude of incidents. These factors represent improvements to safety from good design, for example control systems or fire fighting equipment. The indices are then recalculated using modifiers for the safety improving measures. The new Overall index indicates the improvements in safety due to the design changes. However many of the factors are contributed to extrinsic safety factors, and thus improvements in safety from inherently safe factors are not accounted for.

3.2.3 Other Methods

There are many established methods for the identification and evaluation of hazards. The most commonly used identification method is the Hazard and Operability study (HAZOP). This uses detailed information about the plant, chemicals, operating procedures and equipment specifications. The plant is analysed piece by piece, applying various keywords representing deviations from normal operation, for example NOT, MORE, REVERSE, to each piece in turn and evaluating possible outcomes of the deviation. The output is a list of potential hazards and possible methods to mitigate their effects or actions to investigate their acceptability.

The HAZOP technique is a very thorough, formal method for identifying hazards. However, from the point of view of assessing inherent safety, the method requires too much information. A HAZOP is possible only when the design is at the equipment specification stage, when the opportunities to incorporate many inherently safer features are limited.

In a similar manner to using keywords, checklists (Wells, 1980) are used to question the reasons behind a design. They are intended to prompt lateral thinking about the design and possible alternatives. The problem with them is that they are either too general, for example: 'how can the process be changed to improve the safety?', or too specific, for example: ' can HIGEE be used instead of distillation?'.

There are many methods for the quantification of identified hazards. Such methods include Failure Mode and Effect Analysis , Fault Tree Analysis and the Epidemiological approach (Lees, 1980). The methods assess the likelihood of a hazard occurring. However; as with HAZOP, the information required, for example equipment failure rates, stems from a detailed design, therefore the methods are not very useful in inherent safety assessment.

3.3 Current methods for assessing inherent safety

3.3.1 Tyler et al

ICI Mond Division worked on a way to use the Dow and Mond indices for making inherent safety assessments at an earlier stage in the design of a process (Dransfield et al, 1981, Tyler, 1985). They first identified that not all of the indices were useful in assessing inherent safety. The ones that can be used are the Overall index, the Internal Plant Explosion Hazards index, and the Unit Toxicity index. A preliminary flowsheet, a plant layout and estimates of vessel sizes are needed. Each unit is analysed, the results being an assessment of each unit and an overall assessment of the inherent safety. This highlights the potentially highest hazards and makes selecting the safest units and processes easier.

The quantitative result from calculating the index is converted into broad bands describing the potential hazard. These range from light to very high. Thus the quantitative result, which could be used for comparison, is converted back into a qualitative result.

A more important drawback from the point of view of applying it very early is the information that is needed to make the assessment. This includes both the plant layout and the size of units, which suggests that the design is at a quite advanced stage, beyond the preliminary design stage, and probably past the flowsheet stage. This means that the design will be too inflexible to the changes necessary to improve inherent safety.

A criticism of both Mond and Dow indices is the time needed to complete a plant assessment. The claim by the authors of 30-60 minutes to assess a unit is quite reasonable, but assessing 6-10 units a day by a team of 4 people is still a lot of work for

an estimate of inherent safety, especially if several alternative processes are to be covered.

3.3.2 Mansfield Friendliness index

Mansfield (1992) proposed a very simple index to assess the inherent safety and 'environmental friendliness' of a process. It takes into account safety, health and environmental factors. It consists of five factors combined in the following equation to give an index for the plant:

$$(EHF + PHF) * AF * PSF * CSF \qquad (3.1)$$

where

EHF, Environmental Harm Factor, is a measure of the combined quantity of a discharge stream and its 'quality', that is the level of toxicity and persistence. This is assessed for all effluent streams.

PHF, People Harm Factor, is a similar measure to EHF, The 'quality' factor takes into consideration toxicity, fire and explosion risks and is combined with the quantity as an inventory/throughput ratio. This is assessed for each hazardous material in the process.

AF, Attenuation Factor, scales the temperature and pressure of the process.

PSF, Process Simplicity Factor, looks at the complexity of various processes present.

CSF, Control Simplicity Factor, is a log scale of the total number of reaction stages, additions of chemicals to the plant, heat boundaries where energy is added or removed, pressure boundaries, unit operations, transfer devices and recycle streams.

Few details were published, only the broad outline of the index.

4. CHAPTER 4 - A TRIAL INHERENT SAFETY INDEX

4.1 Introduction

Having reviewed the current methods for assessing safety and inherent safety, this chapter describes how a new index for assessing inherent safety was designed. It examines possible parameters that can contribute to the assessment of inherent safety and possible methods for combining them into an index. A trial Inherent Safety Index is described together with the method of using it. The index is tried out on some test data and the results presented. Finally, some of the shortcomings of the index and possible improvements are discussed.

4.2 Purpose of the index

An index was proposed to score how potentially safe or unsafe a chemical route is. Therefore it is an Inherent Safety Index (ISI). This index is designed to indicate a quantitative assessment of the inherent safety of a chemical route. It is not designed to be extremely accurate, hence it is defined as an index, giving an indication of the level of inherent safety. It is quantitative in order to remove the subjectiveness from the comparison of the routes.

The index actually gives a measure of inherent danger. The opposite of inherent danger is safety therefore lower values indicate a more inherently safe route. It is more logical to define a measure of inherent danger as it will always have a lower bound of zero. The safest chemical plant is an empty field. There is no upper bound of inherent danger, a plant can always be made more dangerous. Thus the score from the index will increase as the inherent danger increases.

The purpose of the index is threefold. Firstly, it scores chemical routes to allow them to be compared against each other by how inherently safe they are. Secondly, it is an additional method to compare chemical routes to a common product, rather than just looking at economic evaluations. Finally, it allows for the impact of changes to the chemical route to be assessed.

The index is intended to act as a guide. It does not lead to hard and fast recommendations on which route should be chosen. The aim is to narrow down the number of potential routes to examine, and allow more time for the chosen routes to be explored further. It should be simple to use and should not take a great deal of time to assess a route.

4.2.1 Ranking of routes and economic comparison

Conventionally new routes are assessed by their economics only. The capital costs of the new plant and the cost of production per tonne are readily estimated for

proposed designs. This allows the routes to be ranked by how cheap they are to build and run, but often this is the only criterion which is used to compare alternative routes.

Safety is often relegated to "other constraints", for example Hutton et al (1990). It is not that there is no wish to assess the safety of the routes, it is that there is no easy way to do a comparative assessment of safety. If there were such a method to rank routes by safety, this could be used in conjunction with the economic assessment. This is one aim of the proposed new index.

A further use for the index is to investigate the claim made by Kletz, that inherently safer plants are cheaper. If it is possible to rank the routes by how safe they are, they can be compared with an economic ranking to see if safer means cheaper.

4.2.2 Assessing design changes

A final use for the proposed new index is to see what impact a change made to a route has on the overall inherent safety of the route. For example, if a raw material is changed, or extra reactions are added with different intermediates, how is the improvement, or deterioration, of the safety in the route assessed? With the index, it is a simple matter to calculate the inherent safety score before and after the change, and see the impact on the overall safety.

4.3 The chemical route

The chemical route is defined as a series of reaction steps which convert raw materials to a required product(s) and waste(s), via intermediate chemicals. The physical properties of the chemicals and the reaction conditions needed to convert the chemicals from raw materials to product can be quantified and assessed. Once the chemical route is known, the inherent safety can be assessed.

The chemical route contains the minimum information with which to assess the inherent safety. Once this stage is passed, the flowsheet is defined, and thus the possibilities for affecting the inherent safety decrease. Thus the greatest benefits from assessing inherent safety can be made at this stage. From the point when the flowsheet is complete, the reactants, intermediates and inventories are fixed. After this point safety becomes more and more extrinsic. Therefore, changes should be made to enhance inherent safety prior to the flowsheet definition. If more information about the route is required, further design work may be needed. Therefore the chemical route is the most practical point to assess inherent safety, without the need for any design work.

4.4 Parameters influencing inherent safety

If a route is looked at in more detail, there are several key items to it. Firstly, there are the chemicals. These are either raw materials, intermediates, products or waste

materials. Each has a large number of physical properties by which they may be assessed. Secondly, there are the reaction conditions. Each reaction step will have a set of reaction conditions. Each step is assessed by these conditions. Finally, there are other aspects of the route, for example the number of reaction steps in it, which may be assessed.

A list of the possible parameters which could be used to assess inherent safety was compiled. Each of the following parameters is looked at individually for their benefits and disadvantages. However, the parameters can also interact with each other. A good example presented by Kletz is an interaction between reactor inventory and pressure. If a reactor has a small inventory and operates at a high pressure, then when a leak occurs the pressure will expel all the inventory, but this will only be a small amount. If a reactor has a large inventory and operates at a low pressure, when a leak occurs the pressure will only be enough to expel a small amount. However, if a reactor operates with an intermediate inventory and pressure, then when a leak occurs the loss will be greater. There may be combinations of two or more parameters, which make the combined safety assessment better or worse than the individual contributions. However, without first understanding how individual parameters may affect the inherent safety, it is not possible to say how interactions may further affect the inherent safety. Having decided how each parameter influences the inherent safety of a route, it is then possible to see how each parameter could be quantified.

4.4.1 Inventory

As the chemical route is made up of reaction steps, for the trial index the inventory is the amount of material present in the reactors. The inventory of a reactor will depend on the residence time of the reactor, which is related to the reaction rate and reaction conversion, and throughput. Inventory is an important parameter when assessing any potential route. One of the key methods to improve inherent safety is intensification, that is the reduction of inventories of hazardous materials. Large inventories of hazardous materials are inherently unsafe and their score should reflect this. The higher the inventory, the higher the score, starting from zero inventory giving zero score. The problem is in breaking up the range of inventory into sensible divisions.

4.4.2 Temperature

Firstly, this gives an indication of the thermal energy present in a reacting mixture. A high temperature indicates a high energy content. This energy could emerge in either a fire or an explosion.

Secondly, the temperature of the reaction may affect the phase of chemicals in it. For example, if the boiling point at atmospheric pressure of a liquid is below the reaction

temperature, that chemical may flash off if the pressure is released and could form a flammable cloud.

Finally, both high and low temperatures affect the properties of materials of construction. Low temperatures cause steels to become brittle, hence special grades are required. Similarly, high temperatures cause steels to weaken, therefore special high temperature steels are needed.

The temperature scale could be divided into two separate scales, both starting from zero. The score should increase to an upper limit as the temperature increases. Also an increasing score for sub-zero temperatures is needed, to cover the problem of low temperature materials of construction. The Dow and Mond indices both take the lower limit as -25° C.

4.4.3 Pressure

Pressure is also an indicator of the energy present in a vessel. This energy could cause materials to escape from its container at very high rates, leading to the release of large amounts of hazardous material in a very short time. The energy could be released in an explosive manner by transferring the energy to fragments of the container, forming missiles.

Low pressure also causes problems. Anything operating below atmospheric pressure and suffering a leak, will have an influx of air. This mixes with the vessel contents and could form an explosive mixture.

As with temperature, the pressure scale must be divided into two scales, starting at zero gauge pressure or atmospheric pressure. On one scale the score increases with increasing pressure up to an upper limit. The other smaller scale covers vacuums.

4.4.4 Conversion

The conversion is the fraction of the reactants which react. So the higher the fraction the better. A low conversion leads to two possible outcomes. Either the throughput needs to be increased to make the required amount of product, or there is a recycle around the reactor. In both cases the inventory of the reactor increases, which is less inherently safe.

Conversion may be treated in two ways. It could modify the value of the inventory. This would be done before the route is scored. The alternative is to score the value of conversion. A low value would get a high score. This assumes that the inventory is estimated with respect to a 100% conversion and the score for the inventory is penalised afterwards for a poor actual conversion.

4.4.5 Yield

Yield is defined as the product of the reaction conversion and the reaction selectivity to the product. The yield is the overall efficiency of the reaction to turn reactants into products. A high yield is good for inherent safety because more reactants are turned into the required product. A low conversion leads to the problems above. A low selectivity leads to the same problems but for a different reason. A low conversion means that there is a lot of unreacted material, whereas a low selectivity means that the reactants are turned into an undesired, possibly hazardous, product. As yield incorporates conversion, the same arguments can be put forward in respect of how it could be scored.

4.4.6 Toxicity

Toxicity is a measure of how physiologically harmful a chemical is. There are many different ways to measure how toxic a chemical is. The toxic effects of a chemical may be measured over both the short term and the long term. An example of a chemical which has short term, or acute, effects is chlorine, whereas a chemical which has long term, or chronic, effects is vinyl chloride, which is carcinogenic.

There are many different scales on which chemicals are classified for toxicity. They depend on two factors; the concentration of the chemical, expressed in parts per million (PPM) or mg/m^3 and the exposure time, in seconds through to hours. The combination of the two is called the dose. Some scales relate to levels of concentration, for example Threshold Limit Value, others relate to doses associated with specified lengths of time, for example Lethal Dose 50 (LD$_{50}$). The lower score limit is zero, whatever the units used. The scale of scoring depends upon the units used.

4.4.7 Flammability

Flammability is a measure of how easy it is for something to burn. There are several ways in which flammability can be expressed.

Firstly there is the flash-point. This is the lowest temperature at which the chemical is ignited by a naked flame. Many chemicals have flash-points which are below normal ambient conditions, for example petrol.

Secondly, there are the flammability limits. These are the lowest and highest concentrations of a material in air, at which it will burn when ignited. Not only are the two values important on their own, but so also is the flammable range, that is the difference between the upper and lower flammable limits. A chemical with a large range is more hazardous. Chemicals which have a very low lower limit will form explosive mixtures if only a small amount escapes from a vessel. Chemicals with a very high

upper limit will form explosive mixtures if only a little air enters a vessel. The combination of both the upper and lower limits and the range gives a good idea of how flammable a chemical is.

Finally there is the auto-ignition temperature. This is the temperature at which a material will spontaneously combust, without an ignition source.

There is no continuous measure for flammability. A material is either flammable or it isn't. There are criteria to decide whether a material is in a flammable state, depending upon its boiling and flash points and what temperature it is kept at. A score for flammability will be one score depending on whether the material is flammable or not.

4.4.8 Explosiveness

There are two types of chemical explosion. Firstly, there is detonation. This occurs with explosives such as T.N.T. The energy of the explosion is in the form of a supersonic blast wave. Large clouds of flammable mixtures can also detonate if the conditions are correct.

Secondly, there is deflagration. This occurs when large quantities of flammable materials burn in an explosive manner. The flame front moves at subsonic speeds and produces a slow blast wave. However, the blast wave is still large enough to produce considerable damage.

The most damaging explosions come from large clouds of flammable material, which escape and find an ignition source. Flixborough (Lees, 1980) is an example of the destruction which can result from a large flammable cloud.

The explosiveness of a material is estimated from its upper and lower explosive limits. This is how much or how little of a material must mix with air to form an explosive mixture. The range goes from 0 to 100 %. The limits could be scored on their own or combined in some manner, for example the explosive range might be used.

4.4.9 Corrosiveness

Chemicals which attack materials used in the plant may cause hazards. They require special containment to make them safer to handle. Such chemicals include strong acids, highly reactive gases, for example chlorine, and solvents which attack plastics. Some chemicals become more corrosive in different forms, for example, hydrogen chloride gas becomes much more corrosive when it dissolves in water. It is not only chemical corrosion which causes problems. Particularly abrasive materials can cause pitting and hence weaken pipes and process equipment.

The corrosive material may not only be a problem on its own, other parameters, for example toxicity, may make the material a big hazard. Corrosion could lead to loss of containment and this could release the hazardous materials.

Corrosiveness can be measured on a continuous scale. However as corrosion is usually quoted in mm/year, due to the slow rate at which it occurs, it may be simpler to assign a score for corrosion if it occurs or not.

4.4.10 Side reactions

Side reactions, in addition to the main reaction, cause problems in two ways. Firstly, reactants are used up but not turned into the required end product. This lowers the yield and leads to the problems associated with low yield described above. Secondly, side reactions produce unwanted chemicals. These may be more hazardous than either the reactants or required products. Side reactions are avoided or limited by changing reaction conditions to favour the product.

Side reactions can occur at the same time as the main reaction or they can occur when reaction conditions deviate from normal. Both present problems. Unwanted chemicals must be separated out and dealt with. Reactions which occur due to deviations may lead to more serious problems, for example runaway reactions.

There are two possibilities for how to treat side reactions. One is to score them simply by number, the more side reactions there are the higher the score. An alternative is to consider them on a mass basis, for example as a ratio of the amount of material formed as side products compared with the amount of product.

4.4.11 Waste and co-products

Waste and co-products differ from side reaction products, in that waste and co-products are unavoidable by-products of the main reaction. Even if they are not hazardous, they must be dealt with. Some may be usable in another process, but consideration must be given to chemicals which must be disposed of to ensure that it is done so in a safe manner.

These are treated in a similar manner to side reactions. It is probably better to consider a mass ratio of waste and co-products to desired product, to penalise processes which produce more waste than desired product.

4.4.12 Reaction rate

The reaction rate indicates how fast a reaction happens. The reaction rate has a large effect on the hold-up in a reactor. If the reaction is fast, then only a small amount

will need to stay in the reactor before it becomes the product. A slow reaction will mean that the chemicals must remain in the reactor for a long time before turning into product. This leads to a large inventory of material in the reactor. Changes to the reaction conditions to improve the reaction rate are preferred over large inventories. A fast reaction can also be a problem. A fast exothermic reaction generates heat at a rate which makes controlling the reaction difficult. Any temperature deviations may rapidly lead to a runaway reaction if the rate of cooling can not be increased. So there has to be a balance. Too slow reactions lead to large inventories. A too fast, exothermic reaction which is insufficiently cooled may lead to possible runaway reactions.

The scoring of the reaction rate in isolation will be difficult and will need to be considered along with other parameters such as the heat of reaction. It could be possible to have a score if the reaction rate could contribute to a potential runaway reaction.

4.4.13 Catalytic action

A catalyst improves the reaction rate. Some reactions may not be viable without a catalyst as they may happen too slowly. Catalysts are also used to limit reactions to reactors, that is so they cannot continue in pipes or other parts of a plant. Materials used as catalysts can also be a hazard, for example heavy metals. Certain reactions are catalysed by corrosion products, for example, rust may induce an unwanted reaction. The score could reflect the improvement in reaction rate or increase in yield over the uncatalysed reaction.

4.4.14 Heat of reaction

The heat of reaction indicates how much energy is given out, in the case of an exothermic reaction, or taken in, in the case of an endothermic reaction, by a reaction. Most reactions are exothermic. A high heat of reaction indicates a very energetic reaction. A high exothermic heat of reaction indicates that a runaway reaction is more likely. If adequate cooling is not maintained on an exothermic reaction, the reaction mixture heats up, which increases the reaction rate, then the situation may escalate to a runaway reaction which could lead to an overpressure. A high heat of reaction, combined with fast reaction kinetics, can give a problem with temperature control.

The score for heat of reaction should increase as the heat of reaction increases. It could be scored with reference to the value of the heat of reaction. Alternatively the score could be based on the type of reaction, for example condensation or oxidation reactions. This method recognises that different reactions produce different amounts of heat. There may also be a smaller scale to cover endothermic reactions, indicating the need for external heating which may cause a hazard.

4.4.15 Phase

The reaction phase affects the size of an incident, when a release of material occurs from a reactor or storage vessel. Reactions either take place in a liquid phase, or a gas or vapour phase. Kletz favours reactions in the gas or vapour phase. If a leak occurs from a gas phase reaction, the amount of material released is much less than from a reactor containing a liquid phase reaction, for the same reactor volume and hole size.

For storage vessels it is preferable to store liquefied gasses refrigerated and at atmospheric pressure rather than at ambient temperature and under pressure. Leaks from refrigerated storage are smaller as there is little pressure difference to expel material, and heat absorbed from the surroundings by the leaking chemical may aid in dispersing it.

It is possible to say that gas phase reactions are generally safer, because less is lost in a release than a liquid phase reaction. However, the reaction being in the gas phase may reduce the reactor inventory compared to the same reaction happening in the liquid phase. Therefore the benefits of a gas phase reaction over a liquid phase reaction show up in a reduction in reactor inventory, and thus a separate score based on the phase alone may not be necessary.

4.4.16 Phase change

A change of reaction phase can present problems. Evolution of large amounts of gas or vapour can lead to overpressure. The precipitation of solids can lead to blocked pipes or other process equipment. Both of these cases are more likely to be a problem when reactions deviate from normal.

This should be a score to penalise any reaction phase change such as evolution of gases or precipitation of solids, which would require special processing.

4.4.17 Viscosity

The viscosity of a material is an indication of its ease of mixing. A high viscosity gives problems due to insufficient mixing, for example, poor heat transfer from the chemicals to heat transfer surfaces or vice-versa. This can lead to hot spots in reactors, possibly giving rise to runaway reactions under certain conditions. Poor mixing limits the speed of reactions, leading to higher inventories.

The viscosity affects the mixing in a process and thus the reaction kinetics. It is difficult to say if a higher viscosity is more unsafe than a low one. Thus a score is needed to penalise a process which may suffer from viscosity related problems, for example chemicals which increase rapidly in viscosity when heated, for example sulphur.

4.4.18 Number of steps

The number of reaction steps in a route is a very simple measure of the complexity of the necessary plant. More steps implies more equipment, more intermediate chemicals and thus more chance for something to go wrong. Thus more steps gives a more unsafe process by virtue of having more step scores to combine. Therefore it may not be logical to assign an additional score to reflect a large number of steps.

4.4.19 Uniformity of steps

Reaction conditions across each step of a route are unlikely to be consistent. Temperatures and pressures will vary from step to step. To accommodate these changes, equipment will be added to increase or decrease temperature, for example heat exchangers, or to increase or decrease pressure, for example compressors or turbines. All of this additional equipment adds complexity and a need for control. If conditions are kept approximately constant then the complexity is reduced.

The degree of variability between the route steps could be a modifier to the final route score. When a process which has step conditions with large variations between them is penalised more than a uniform process.

4.5 Scoring of the parameters

The parameters fall into two categories. Firstly, there are the parameters which give a binary (yes or no) score depending upon whether the parameter does or does not indicate an inherent danger. These are chosen as flammability, corrosiveness, reaction rate, catalytic action, phase, phase change, and viscosity. Secondly, the rest of the parameters start from a point which can be scored as zero. The score can then increase as the value of the parameter increases. These are inventory, temperature, pressure, conversion, yield, toxicity, explosiveness, side reactions, waste and co-products, and heat of reaction.

Two possible methods are discussed below for how the parameters may be scored.

4.5.1 Matrix method

The first method, which has been called the Matrix method is presented by Humphrey (1987). He uses his method to estimate Beta Factors for common cause failures. The first task is to decide what are the contributing factors to the problem. In the case of inherent safety, to which this method has not been applied, these are the parameters presented earlier. In the example presented by Humphrey, the parameters which contribute to Beta factor estimation are first weighted in importance as follows:

Separation   8

Similarity   6

Complexity   6

Analysis   6

Procedures   10

Training   5

Control   6

Tests   4

Each parameter is then divided into a number of sub-divisions, in this case 5. Thus the matrix has 8 rows, one for each parameter, and 5 columns, 'a' to 'e'. The total for column 'a' should correspond to 0.3, the worst beta factor. The total for column 'e' should correspond to 0.001, the best beta factor. Using the relative weightings of the parameters and assuming a divisor for all the values of 50000, columns 'a' and 'e' are filled in. The intermediate values in the other columns are fitted using the equation

$$y = Ae^{Bx} \qquad (4.1)$$

although a linear fit or any other suitable equation could be used. For each column, a criteria is formulated for the parameter. For column 'a', the criteria represent the worst case for the parameter, for column 'e' the criteria represent the best case for the parameter. The final scoring matrix is as follows:

	a	b	c	d	e
Separation	2400	580	140	35	8
Similarity	1750	425	100	25	6
Complexity	1750	425	100	25	6
Analysis	1750	425	100	25	6
Procedures	3000	720	175	40	10
Training	1500	360	90	20	5
Control	1750	425	100	25	6
Tests	1200	290	70	15	4

To use the matrix, for each parameter, a criteria which bests fits the problem is chosen. The beta factor is calculated by adding together the score for each parameter, depending upon the criteria 'a' to 'e', and dividing the total by 50000.

4.5.2 Step scoring method

The second method is that of Taylor (1980). He presents a step scoring method for rapid capital cost estimation. His method differs from that of Humphrey in several ways. Firstly, the factors chosen do not all have the same number of subdivisions.

Secondly, all the factors are fitted to a common linear scoring scale, but are moved up or down the scale to adjust the relative weight of the scores. Finally, the scores for parameters can be placed either side of a zero score, so that factors can contribute a negative score, for example for a factor which improved the safety. Thus the score for a parameter could move from negative, indicating an improvement to the inherent safety, through to positive, indicating a deterioration in the inherent safety.

4.5.3 Reasons for rejection of Matrix and Step scoring methods

Both methods have some points which make them unsuitable as the only method for scoring the routes. The matrix method has two problems. Firstly, in order to fit all the parameters into one matrix, some parameters may need their contribution to the total score weighted more than others. However, at this stage in the development of the index it is not known if any parameters should be weighted more than others for their assessment of inherent safety. Secondly, the matrix method requires that the parameters must all be sub-divided into the same number of sub-divisions. This may lead to some parameters having too many or too few divisions for the range of the parameter. Therefore the divisions could be arbitrarily too small or too large. A small problem with the step scoring method is that the negative score part may not be used. Both methods also do not deal with parameters which only have a score if they do or do not meet a certain criterion.

The method devised to score the parameters in the index was to first choose the parameters to be scored. Next each parameter was assigned a scoring table. The steps are scored using the table for each parameter and finally the scores for each step are added together to score the route.

The parameters each have a scoring table. Leaving the parameters on a common scale could lead to some confusion. If two different parameters have the same score it could be interpreted as meaning they have the same effect on the inherent safety, for example temperature having the same effect as pressure. It may be possible at a later stage to equate different parameters to a common scale of inherent safety, but at this stage it is safer to treat the parameters separately. As each parameter has its own scoring table, it can have as may sub-divisions as required.

4.5.4 Parameters chosen for trial Inherent Safety Index

Although there were nineteen different parameters which had been identified, it was felt that this was too many for the first attempt at formulating an indicator of IS. So seven of these nineteen parameters were chosen to form the first trial index. The basis for choosing the parameters was that they should be known at the process route stage and that they have a large influence on the inherent safety of the route.

Having decided upon the parameters to use for the trial index, a set of scoring tables was compiled, one for each parameter.

4.5.5 Temperature

Temperature is an indicator of the heat energy content of a system. The higher the temperature, the higher the energy content. This energy may make a hazard more likely to occur, and also increase the magnitude of the hazard.

Temperature (°C)				Score
		T	< -25	10
-25	≤	T	< -10	3
-10	≤	T	< 10	1
10	≤	T	< 30	0
30	≤	T	< 100	1
100	≤	T	< 200	2
200	≤	T	< 300	3
300	≤	T	< 400	4
400	≤	T	< 500	5
500	≤	T	< 600	6
600	≤	T	< 700	7
700	≤	T	< 800	8
800	≤	T	< 900	9
900	≤	T		10

Table 4.1 - Temperature scoring table

For the positive temperatures, the temperature range was divided into ten equal steps for a score range of ten. The scores for negative temperatures account for material of construction problems at low temperatures.

4.5.6 Pressure

Pressure is an indicator of the energy present in a system. As with temperature, high pressures are more hazardous and increase the magnitude of the resultant effects.

Pressure (psi)	Score
0 - 90	1
91 - 140	2
141 - 250	3
251 - 420	4
421 - 700	5
701 - 1400	6
1401 - 3400	7
3401 - 4800	8
4801 - 6000	9
6001 - 8000	10
+1 point per 2500 psi	

Table 4.2 - Pressure scoring table

The pressure table is based on the pressure graph from the Mond index. The pressure of 8000 psi corresponds to a score of 150 from the graph in the Mond index. The score range has been reduced from 150 to 10 points.

4.5.7 Yield

The yield of a reaction indicates how much extra inventory or flow is needed to meet the required product rate. A low conversion and hence a low yield will often mean that a recycle stream is needed which increases the inventory of the reaction step. Therefore a low yield should be viewed as bad for inherent safety.

Yield (%)		Score
100		0
90	- 99	1
80	- 89	2
70	- 79	3
60	- 69	4
50	- 59	5
40	- 49	6
30	- 39	7
20	- 29	8
10	- 19	9
0	- 9	10

Table 4.3 - Yield scoring table

The range of the yield has simply been divided into ten steps.

4.5.8 Inventory

Chemicals are present in varying quantities around the chemical plant, in different size pieces of equipment. For a chemical route only the reactions are known about and therefore inventory estimation is limited to the reactor inventory.

The estimate used here for the inventory of a chemical is based on the annual throughput, an 8000 hour per year production rate, a nominal hold-up of one hour (unless known) and a 100% yield for the step. A 100% yield is used as the actual yield is used as a separate parameter. The production rate is calculated for each step from the stoichiometry of the reactions, working backwards through the steps from the product rate required to satisfy the plant capacity assuming a 100% yield.

Inventory (Tonnes)		Score
0.1	- 250	1
251	- 2500	2
2501	- 7000	3
7001	- 16000	4
16001	- 26000	5
26001	- 38000	6
38001	- 50000	7
50001	- 65000	8
65001	- 80000	9
80001	- 100000	10

Table 4.4 - Inventory scoring table

The table is based on the quantity factor charts from the Mond index. The continuous graph has been broken down into ranges, and the maximum score reduced from 1000 to 10.

Inventory contributes to the chemical score because the mass of a chemical could be the factor which makes it the most hazardous, compared with the other chemicals present in a step.

4.5.9 Toxicity

TLV (ppm)				Score
	TLV	<	0.001	8
0.001	≤ TLV	<	0.01	7
0.01	≤ TLV	<	0.1	6
0.1	≤ TLV	<	1.0	5
1.0	≤ TLV	<	10.0	4
10.0	≤ TLV	<	100.0	3
100.0	≤ TLV	<	1000.0	2
1000.0	≤ TLV	<	10000.0	1
1.0%	≤ TLV			0

Table 4.5 - Toxicity scoring table

This table is based on a table in the Mond index. TLV data may not be the ideal measure of toxicity in all situations, but the TLV data is readily available.

4.5.10 Flammability

There is a difficulty in giving a degree of flammability to a chemical. But an indication of whether a potentially flammable chemical is in a flammable state depending upon its physical properties can be given.

Flammability	Score
Non-combustible	0
FP > 60°C	1
37.7°C < FP < 60° C	2
FP < 37.7°C BP > 37.7°C	3
FP < 37.7°C BP < 37.7°C	4
FP = Flash point BP = Boiling point	

Table 4.6 - Flammability scoring table

This table is based on one from the Dow index which is used to determine the material factor for the chemical.

4.5.11 Explosiveness

The propensity of a chemical to explode is indicated by its ability for forming an explosive mixture with air. The easier it is to form an explosive mixture, the more likely is an explosion.

Explosiveness		
$S = (UEL - LEL)\%$		Score
0	$\leq S <$ 10	1
10	$\leq S <$ 20	2
20	$\leq S <$ 30	3
30	$\leq S <$ 40	4
40	$\leq S <$ 50	5
50	$\leq S <$ 60	6
60	$\leq S <$ 70	7
70	$\leq S <$ 80	8
80	$\leq S <$ 90	9
90	$\leq S <$ 100	10

Table 4.7 - Explosiveness scoring table

L.E.L and U.E.L are lower and upper explosive limits respectively. The combination of a low lower limit and a high upper limit represent the worst case. Therefore the difference between the two can be considered indicative of the explosion hazard, a large difference means a large risk. The maximum range has been divided into ten steps.

4.6 Index Structure

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

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

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

4.7 Details of the test routes

The index was tested on six routes to methyl methacrylate (MMA). There were two reasons for choosing MMA. Firstly there was access to a commercial report (Chem Systems, 1989) which detailed both the chemical and process aspects of the routes. In addition the report included cost estimates for the processes. These would be used to test whether the inherently safest routes are also the cheapest routes. Secondly, there was a good mix of potentially dangerous chemicals and processes among the routes.

Full details of the routes, including individual reaction step process conditions, the chemicals present, and the physical and chemical properties, are given in appendix A. A brief description of each route, including the main chemicals and reaction steps is given below for each route.

4.7.1 Acetone Cyanohydrin (ACH)

This is the conventional process for MMA manufacture. Hydrogen cyanide is produced by the Adrussow process. This is reacted with acetone to give acetone cyanohydrin (ACH). This is treated with sulphuric acid and heated to give methacrylamide. The final step is to react methacrylamide with methanol to produce MMA. The sulphuric acid is recovered from the ammonium bisulphate by-product.

4.7.2 Ethylene based via methyl propionate (C2/MP)

Ethylene (C2) is reacted with carbon monoxide in the presence of methanol to yield methyl propionate (MP). Methylal (dimethyl formal or modified fomaldehyde) is used to condense the methyl propionate to MMA.

4.7.3 Ethylene based via propionaldehyde (C2/PA)

Ethylene (C2) is reacted with carbon monoxide and hydrogen to yield propionaldehyde (PA). This is condensed with fomaldehyde to give methacrolein. The methacrolein is oxidised to methacrylic acid. Finally the methacrylic acid is reacted with methanol to give MMA.

4.7.4 Propylene based (C3)

Propylene (C3) is reacted with carbon monoxide in the presence of hydrogen fluoride to give isobutyryl fluoride. This is followed by hydrolysis to isobutyric acid. Hydrogen fluoride is recovered for recycle. The isobutyric acid is oxydehydrogenated to methacrylic acid. The methacrylic acid is reacted with methanol to yield MMA.

4.7.5 Isobutylene based (i-C4)

Isobutylene (i-C4) is oxidised first to methacrolein and then to methacrylic acid in two stages. The methacrylic acid is reacted with methanol to yield MMA.

4.7.6 Tertiary butyl alcohol based (TBA)

Tertiary butyl alcohol (TBA) is oxidised first to methacrolein and then to methacrylic acid in two stages. The methacrylic acid is reacted with methanol to yield MMA.

4.8 Scoring of the routes

Each route is broken up into reaction steps. For each step, starting from the last step, first the hourly throughput is calculated, from the stoichiometry and the required product flowrate.

For each step. the form of the reaction is

$$n_A \cdot A + n_B \cdot B + ... \Rightarrow n_C \cdot C + n_D \cdot D + ...$$
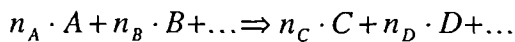
where

A = chemical species A

n_A = number of moles of species A

If chemical P is the main product of the reaction, whose flowrate is known and whose molecular mass is M_P, then

$$F_X = \frac{F_P \cdot n_X \cdot M_X}{n_P \cdot M_P} \tag{4.10}$$

where

F_X = flowrate of species X, t/hr

F_P = flowrate main product, t/hr

M_X = molecular mass of species X, g mol⁻¹

The inventory of the chemical species X in the reactor is·

$$I_X = F_X \cdot H \tag{4.11}$$

where

I_X = inventory of chemical X, tonnes

H = hold-up time, hours

If the hold-up in the reactor is not known, a hold-up of 1 hour has been assumed here.

4.8.1 Example

The reaction in step 4 of the ACH route is:
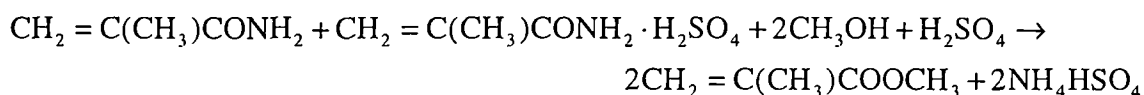
$$CH_2 = C(CH_3)CONH_2 + CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + 2CH_3OH + H_2SO_4 \rightarrow$$
$$2CH_2 = C(CH_3)COOCH_3 + 2NH_4HSO_4$$

Methacrylamide + Methacrylamide Sulphate + Methanol + Sulphuric Acid →
Methyl Methacrylate + Ammonium Bisulphate

A = Methacrylamide	$n_A = 1$	$M_A = 85$
B = Methacrylamide Sulphate	$n_B = 1$	$M_B = 183$
C = Methanol	$n_C = 2$	$M_C = 32$
D = Sulphuric Acid	$n_D = 1$	$M_D = 98$
E = Methyl Methacrylate	$n_E = 2$	$M_E = 100$
F = Ammonium Bisulphate	$n_F = 2$	$M_F = 115$

Table 4.8 - Molecular weights of chemicals used in example calculations

Species E is the main product, with flowrate $F_E = 6.25$ t/hr (based on 50000 t/year and 8000 h/year), then flowrates and inventories are, assuming a hold-up of 1 hour :

$F_A = (6.25 * 1 * 85) / (2 * 100) = 2.66$ t/hr, $I_A = 2.66$ t

$F_B = (6.25 * 1 * 183) / (2 * 100) = 5.72$ t/hr, $I_B = 5.72$ t

$F_C = (6.25 * 2 * 32) / (2 * 100) = 2.00$ t/hr, $I_C = 2.00$ t

$F_D = (6.25 * 1 * 98) / (2 * 100) = 3.06$ t/hr, $I_D = 3.06$ t

$F_F = (6.25 * 2 * 115) / (2 * 100) = 7.19$ t/hr $I_F = 7.19$ t

The inventory of the chemicals present is calculated as above for each step. Each chemical is then scored using the scoring tables for each parameter. The chemical with the highest score from all the steps is designated as the step chemical score.

Taking step 1 of the ACH route:

Methane + Ammonia + Oxygen → Hydrogen Cyanide + Water
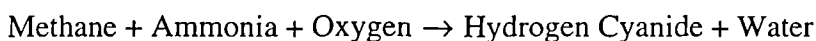
The scores for hydrogen cyanide are:

Inventory : 1.69 tonne scores 1 on the inventory table.

Toxicity : TLV = 10 ppm scores 3 on the toxicity table.

Explosiveness : U.E.L - L.E.L = 40 - 5.6 = 34.4 scores 4 on the explosiveness table.

Flammability : FP < 37.7°C, BP < 37.7°C scores 4 on the flammability table.

The step score for hydrogen cyanide = 1 + 3 + 4 + 4 = 12

This is larger than the scores for CH_4, NH_3, O_2 and H_2SO_4, so it is used as the chemical score.

Again for each step, the parameters for the process are scored.

Taking step 1 of the ACH route:

Methane + Ammonia + Oxygen → Hydrogen Cyanide + Water

Temperature : 1200°C scores 10 on the temperature table.

Pressure : 3.4 atm scores 1 on the pressure table.

Yield : 64% scores 4 on the yield table.

Process score for the step = 10 + 1 + 4 = 15

So the step score = Chemical score + Process score = 12 + 15 = 27

4.8.2 Scores for MMA routes

The table below shows the toxicity, flammability and explosiveness scores for each chemical. The inventory score is not listed because this depends upon the reaction step and some chemicals occur in different amounts in different steps.

CHEMICAL	SCORE FOR		
	TOXICITY	FLAMMABILITY	EXPLOSIVENESS
Acetone	2	3	2
Acetone Cyanohydrin	3	1	1
Ammonia	3	0	2
Ammonium Bisulphate	-	-	-
Carbon dioxide	1	0	-
Carbon Monoxide	3	4	7
Ethylene	1	4	4
Formaldehyde	5	4	7
HMPA	-	-	-
HMPASE	-	-	-
Hydrogen	1	4	8
Hydrogen Cyanide	4	4	4
Hydrogen Fluoride	4	-	1
Isobutylene	1	5	-
Isobutyric Acid	2	2	1
Isobutyryl Fluoride	-	-	-
Methacrolein	2	4	-
Methacrylamide	-	-	-
Methacrylic acid	-	1	-
Methane	1	4	2
Methanol	2	3	4
Methyl Methacrylate	3	3	2
Methyl Propionate	-	3	2
Methylal	2	3	2
Nitrogen	1	0	-
Oxygen	0	0	-
Propionaldehyde	-	3	2
Propylene	1	4	1
Sulphur dioxide	4	-	-
Sulphur trioxide	7	-	-
Sulphuric Acid	4	-	-
Tertiary Butyl Alcohol	3	3	1
Water	0	0	-

HMPA - 2-hydroxy-2-methyl propionamide

HMPASE - 2-hydroxy-2-methyl propionamide sulphate

Table 4.9 - Breakdown of chemical score for each chemical in MMA routes

The table below shows the breakdown of the process scores for each step.

| ROUTE | STEP NO. | SCORE FOR | | |
		TEMPERATURE	PRESSURE	YIELD
ACH	1	10	1	4
	2	1	1	1
	3	2	2	1
	4	2	2	0
	5	10	1	0
	6	5	1	1
C2/MP	1	2	7	2
	2	-	-	-
	3	4	-	2
C2/PA	1	2	3	1
	2	2	6	1
	3	4	-	5
	4	1	2	3
C3	1	1	7	1
	2	1	3	1
	3	4	1	3
	4	1	2	3
i-C4	1	4	-	6
	2	4	1	5
	3	1	1	3
TBA	1	4	1	2
	2	4	1	5
	3	1	1	3

Table 4.10 - Breakdown of process score for each step in MMA routes

The table below shows the chemical score, process score and total step score for each step, including which chemical had the highest score in each step and thus provides the chemical score.

ROUTE	STEP NO.	CHEMICAL WITH HIGHEST SCORE	CHEMICAL SCORE	PROCESS SCORE	STEP SCORE
ACH	1	HCN	13	15	28
	2	HCN	13	3	16
	3	ACH	6	5	11
	4	Methanol	10	4	14
	5	Methane	8	11	19
	6	Sulphur trioxide	8	7	15
C2/MP	1	CO	15	11	26
	2	Methanol	10	-	10
	3	Methanol	10	6	16
C2/PA	1	CO	15	6	21
	2	Formaldehyde	17	9	26
	3	Methacrolein	7	9	16
	4	Methanol	10	6	16
C3	1	CO	15	9	24
	2	Isobutyric acid	7	5	12
	3	Isobutyric acid	7	8	15
	4	Methanol	10	6	16
i-C4	1	Methacrolein	7	10	17
	2	Methacrolein	7	10	17
	3	Methanol	10	5	15
TBA	1	TBA	8	7	15
	2	Methacrolein	7	10 '	17
	3	Methanol	10	5	15

Table 4.11 - Breakdown of scores for each step in MMA routes

The graph below shows the scores from table 4.11. The graph actually shows inherent danger. A high score indicates a more inherently dangerous route.

Inherent Safety Index for MMA routes
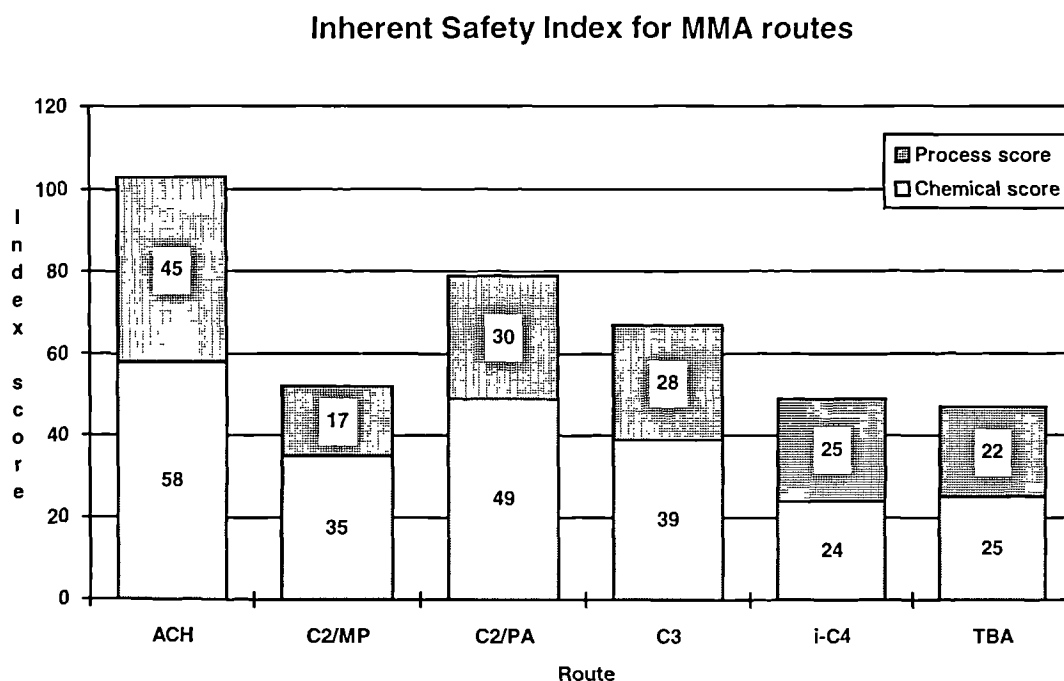
Figure 4.1 - Process score, chemical score and index for MMA routes

4.9 Discussion

Intuitively it would be expected that the ACH route should have a high index value because it uses HCN. Likewise the two ethylene-based routes (C2/PA and C2/MP) and the propylene-based route (C3) would be expected to do badly, because they involve carbon monoxide. It is logical that the C2/MP route has a lower index value than the other two, because it has one less processing step (3) than the other two (4). It would be expected that the two C4-based routes (i-C4 and TBA) have similar indices, because they are virtually the same process. They both involve an oxidation reaction, which contributes significantly to their score. The ACH process, which has the highest score, uses HCN, H_2SO_4 and SO_3 and has the most steps (6); it is not surprising that it has the highest index value, that is it is predicted that it is the most inherently unsafe process.

4.10 Relation of inherent safety to cost

One of the original aims of the research was to examine the assertion that the most inherently safe plants are also the cheapest. There are two key values in an economic estimation of a new process. These are the capital cost of the plant and the cost of production of the required product.

The capital cost is the money that must be spent to design, build and commission the plant. It is the cost of the vessels, pipes, pumps, buildings, etc., that is all the necessary hardware of the plant. This money also includes the cost of control and safety equipment.

The cost of production are all the costs associated with running the plant and producing the product. These include the cost of raw materials, power and other utilities, labour costs, and other financial costs, for example insurance.

These costs can be compared for each route with the ranking of their inherent safeness.

4.10.1 Explanation of cost data

Data has been used for plants in Western Europe in mid-1988, producing 50000 tonnes per year of MMA. The costs in German deutschmarks (DM) used to do a cost and safety comparison are presented in table 4.13

The capital costs, raw material costs, utilities costs and labour costs are actual costs for operating plants or, if no plant exists, are estimates made from design studies for the 6 plants, but the maintenance costs and overheads are estimated using generic factors. The various costs are as follows:

ISBL - Inside Battery Limits Capital Cost (Million DM) - This is the total capital cost of the main plant items, for example reaction vessels, distillation columns, heat exchangers, etc.

TFI - Total Fixed Investment (Million DM) - This is the sum of the ISBL and Outside Battery Limits Capital Cost (Offsites). Offsites include utilities, offices, laboratories and other buildings.

The costs below are DM per tonne of product (MMA).

Raw materials (DM/t) - This is the total cost of the raw materials required to produce a ton of the main product less any credits for saleable by-products that are made in addition to the main product.

Variable (DM/t) - These are any cost which directly depend on the production rate. They include raw materials costs, by-product credits and utilities costs.

Non-capital (DM/t) - These are costs which are not related to the capital costs. It includes the variable costs and the labour costs.

Direct cash (DM/t) - This is the non-capital costs plus maintenance costs (estimated as 4% of ISBL), direct overheads (75% of labour) and interest on the working capital.

Full cash (DM/t) - This is the direct cash plus general plant overheads (50% of labour and maintenance), insurance and property tax (1% of TFI). This is the total cost of production per tonne.

20% ROI - 20% Return on Investment (DM/t) - This is the full cash cost of production plus a 20% return on the total fixed investment.

No. of steps - This is not a cost but the number of reaction steps in the route.

Route	ISBL	TFI	Raw material	Variable	Non-capital	Direct cash	Full cash	20% ROI	No. of steps
ACH	166.4	244.7	813	1016	1125	1286	1433	2412	6
C2/PA	114.7	176.4	925	1054	1122	1231	1332	2038	4
C3	100.4	184.7	639	768	836	930	1026	1765	4
C2/MP	77.1	112.8	716	874	929	1005	1074	1525	3
i-C4	120.5	168.7	765	819	869	982	1078	1753	3
TBA	115.6	178.1	655	668	722	830	927	1640	3

Table 4.12 - cost estimates for MMA routes in DM per tonne of MMA

Route	Chemical score	Process score	Index score
ACH	58	45	103
C2/PA	49	30	79
C3	39	28	67
C2/MP	35	17	52
i-C4	24	25	49
TBA	25	22	47

Table 4.13 - scores for MMA routes from trial index

4.10.2 Regression analysis

Linear regression has been used to investigate whether there is any correlation between inherent safety, as measured by the trial index, and the costs, in table 4.12. Table 4.14 lists values of the R^2 statistic, expressed as a percentage, obtained when the above costs, as the dependent variables, are regressed against the independent variables: chemical and process scores and index values.

The R^2 statistic is defined as follows (Draper & Smith, 1981). Let:

SSM be the sum of squares of the deviations in the actual values of the dependent variable from their mean,

SSR be the sum of squares of the deviations of the predicted (from the regression line) values of the dependent variable from the mean of their actual values,

SSE be the sum of squares of the deviations of the actual values of the dependent variable from their predicted values.

Then:

$$SSM = SSR + SSE \tag{7.1}$$

This shows that some of the variation in the dependent variable about its mean can be ascribed to the regression line (SSR) and the rest to the actual values not lying on the line (SSE). There is a good correlation if SSR is a lot greater than SSE. This is equivalent to the ratio:

$$R^2 = \frac{SSR}{SSM} \tag{7.2}$$

being close to 1 (or 100%). A value of 100% for R^2 indicates a perfect correlation, while 0 tells us that there is no correlation; a value greater than 70% is normally taken to indicate a good correlation for this type of data.

COST	CHEMICAL SCORE	PROCESS SCORE	INDEX SCORE
ISBL	27.8	81.5	51.7
TFI	34.4	86.7	58.9
Raw Materials	34.3	20.5	31.1
Variable	68.6	34.8	58.7
Non-capital	76.7	44.2	68.6
Direct cash	78.8	56.4	76.3
Full cash	80.6	65.9	82.1
20% ROI	72.1	95.6	90.1
No. of steps	80.9	92.4	94.6

Table 4.14 - regression values (R^2) arising from cost versus safety analysis

Looking first at the correlations with the chemical score, it is surprising that the R^2 value for raw materials is not significant. It could be thought that more hazardous chemicals are more costly to produce and transport, and would therefore have a high correlation between cost and safety.

Apart from the raw materials, the chemical score is significantly correlated with the non-capital costs and the costs of production, that is direct cash, full cash and 20% ROI.

Looking next at the process scores, the ISBL and TFI correlate well. The process score reflects the need for plant items which can deal with high temperatures and pressures, and their size is partially related to the yield. Thus plant items will cost more as they have to be designed and built to deal with more extreme process conditions. The ISBL and TFI are directly related to the size and strength of plant items, as larger and stronger items cost more to build. Thus the good correlation between the process score and the capital costs agrees with practice. The process scores do not correlate significantly with the costs of production until a large proportion of capital related costs are added.

The index score is not correlated significantly to just the capital costs. Neither is the index score correlated significantly to the costs of production which include the variable costs. However, when the costs of production include more capital related costs, for example direct cash and full cash, the correlation is significant. The best cost

correlations to the scores and index are obtained for the 20% ROI cost of production, which has large contributions from both non-capital and capital-related costs.

However, the best correlations are between the scores and index and the number of process steps. This is consistent with the calculation of the index as a sum of step scores and agrees well with the idea that increasing complexity in a route decreases inherent safety.

5. CHAPTER 5 - EXPERT JUDGEMENT

5.1 Introduction

This chapter covers a part of the research that is important in its own right, having its own discussion and conclusions, but is also an important contribution to the work as a whole.

Having created an inherent safety index and used it on some test routes, the index and the results from testing it were given to a group of experts for their opinions and ideas about what had been done, and how it could be improved.

The chapter deals firstly with how experts should be consulted in a structured manner, that is the subject of expert judgement. Secondly, it explains why experts are needed to help in this exercise and what knowledge is required from them. Thirdly, it looks at the chosen method of eliciting the required information, that is a series of questionnaires and a meeting of the experts. It then presents the results from the questionnaires and an analysis of the results. Finally, it discusses what the exercise has shown and how the results can be used in developing the research.

Later in the chapter the phrase 'expert ranking' is used. Expert judgement covers the general topic of how information is elicited from experts and analysed. Expert ranking is the particular task that the experts have been set in this research, that of ranking of the MMA routes according to inherent safeness.

5.2 What is expert judgement?

Expert judgement is a method of obtaining knowledge from experts, which cannot readily be obtained from other sources. There are three types of information that are elicited from the experts. Firstly, there are the factual answers to specific questions, secondly, there is the reasoning behind their answers, and thirdly the form in which they give their answers, for example probabilities or rankings. All three types of information are important and are necessary for a satisfactory result.

There are several methods by which the judgement of experts may be elicited (Lees, 1994); each has its merits and disadvantages. These include the single interview, the group interview and the Delphi method.

The single interview method uses only one expert. It is good for obtaining detailed answers to questions and is useful for observing the expert's reasoning processes, but there is no interaction between experts discussing the problem and it is time consuming.

The group meeting method can resolve differences and lead to consensus answers as a result of discussion amongst the experts, but it may also suffer from group bias or disagreement.

In the Delphi method, a group of experts is used, but each works in isolation. This is free from group bias but the group interaction and discussion of ideas is lost.

There are a number of documented methods for eliciting rankings. The method of paired comparisons allows experts to rank a number of items in an easier manner than ranking them all at once. The expert is asked to give his or her preference between a pair of items. The results from choosing between the pairs of items are combined to give the ranking of all the items. Two methods are available; that of Saaty (Lees, 1994) and that of Hunns and Daniels (1980). Saaty's method gives a weight to each item ranked but these weights only indicate the order of items in a ranking, that is we cannot say for example that item A is three times more desirable than item B. Hunns' method gives a relative ranking of items on a linear scale.

Lees states that the choice and number of experts are important factors in the expert judgement exercise. The experts should come from a diverse background, but within the area of research, in order that there is no undue influence from any one individual. The number should be between 5 and 9, the lower bound is necessary for diversity and the upper bound is a manageable maximum number of experts.

5.3 Why use expert judgement?

One problem with the index is that it is not possible to say whether the ranking of the MMA routes is 'correct'. An expert can say that the ranking 'looks right', based on the information on the routes. For example he or she can see if the chemicals used are more toxic in one route compared with the other routes. However this process needs to be formalised to be of value, and to give an alternative ranking with which to compare the index.

Having tested the index on the MMA routes, several weak aspects have been recognised, which need further development. Expert judgement is being used firstly to provide additional rankings of the routes with which to compare the existing index-based ranking. Secondly, the exercise can provide information about the methods and procedures used to determine the rankings. Additional information about the features and hazards in each route will help to strengthen the index in these weak areas and to calibrate it to give sensible rankings. The methods used by the experts to compare

features and to formulate their rankings may also aid in defining a better structure for the index.

5.4 Method used for expert judgement

A panel of 8 experts was assembled. The experts came from academic and industrial backgrounds, with a strong interest in safety , including inherent safety. It was assumed that the experts were the type of people whose views and experience of inherent safety would be worthy of consideration. The panel consisted of:

Prof. F.P.Lees -	Loughborough University
M.Kneale -	Independent consultant
Prof. H.A.Duxbury -	Independent consultant/Loughborough University
Dr. T.A.Kletz -	Independent consultant/Loughborough University
C.C.Pinder -	BP Chemicals Ltd/Loughborough University
W.H.Orrell -	Independent consultant
M.L.Preston -	ICI Engineering
Dr. A.G.Rushton -	Loughborough University

In order to test the index, the panel of experts was asked to rank the MMA routes. The results were analysed in order to answer two questions.

Firstly, does a composite ranking, that is an average ranking across all the experts, agree with the index.

Secondly, are the individual rankings from the experts consistent with each other, that is, is there general agreement on the final composite ranking.

Accepting that the experts are indeed experts, then if their composite ranking agrees with the index, and there is consistency between their individual rankings, then the index is validated for the test case of MMA routes.

In order to elicit the experts' judgement and opinions on the inherent safeness of the routes a set of questionnaires was devised for the experts to complete and a panel meeting was planned to discuss the results. The experts were given the minimum information about our chemical routes which it is believed would be known at the beginning of a feasibility study.

The initial plan was to have three questionnaires. However, the process of analysing and devising the questionnaires was considered to be iterative. If the results of

the third questionnaire dictated that a fourth or fifth was needed, then more would be produced.

Questionnaires 1 and 2 were used to elicit rankings from the experts and to check that they were consistent in their rankings. Questionnaire 1 asked the experts to rank the routes for MMA by looking at the routes as a whole. In questionnaire 2, the individual steps in each route were examined. Then a composite ranking was built from the assessments of the individual steps. If there was any great difference between the rankings from the two questionnaires, then the rankings would be subject to further examination and further questionnaires would be devised.

Questionnaire 3 elicited opinions about the trial index, and suggestions for improving it or forming a new index.

The final part of the exercise was a meeting of all the experts on the panel. This was to discuss the results of the questionnaires, and perhaps to remedy any discrepancies in the results, or disagreements between the experts. It was also used to discuss ideas about a new index.

5.5 Questionnaires

It was suggested by Lees (1994a) that before the experts could rank the routes, they should have some criteria by which to compare them.

5.5.1 Criteria for ranking routes

In order to rank the routes, criteria are needed against which they can be ranked. Marshall (1987) and Lees both distinguish three main criteria. Marshall defines them as :

1. Major loss of life
2. Widespread injury
3. Widespread damage

Lees suggested :

1. Major hazard - A large toxic or flammable release and possible explosion, that affects the surrounding area and causes loss of life.

2. Medium scale event - A small explosion or implosion, which leads to loss of production and bad publicity. Loss of life is possible but due to 'bad luck'.

3. Unplanned event - This causes disruption to the local population, with alarms and evacuations. The event is newsworthy. It may not be dangerous in terms of loss of life, but leads to loss of production and claims for compensation.

Marshall suggests that loss of life is a good measure of the scale of an incident. However, there is the problem of whether to include deaths which occur some time after the initial incident, for example people dying from injuries several months afterwards. The recorded number of deaths depends on how an incident has been reported.

Another possible measure is number of injuries, but this also has problems associated with it. There is a wide scale of seriousness of injuries. They could be categorised, for example as major and minor injury, but the division may be difficult to place. There is also the problem of dealing with crippling injuries, for example those caused by toxic chemicals, again it is the time element which affects whether crippling injuries are reported in the incident reports.

A third measure which could be used is financial loss. Sums of money can be derived from:

1. Compensation for loss of life
2. Compensation for loss of income while injured
3. Compensation for damage to plant and equipment
4. Insurance payouts

A possible method for how the three types of measure could be combined is suggested by the author. The scale of hazard could be derived by combining the three types of measure for the scale of an incident. For example :

Loss of life   and   Injury and   Loss of money =   Major hazard

Injury   and   Loss of money   =   Medium hazard

Loss of money   =   Minor hazard

This gives three criteria for ranking routes. However they require a financial value to be put on injury and loss of life. This was deemed to be outside the scope of the project and ultimately these suggestions were rejected.

For simplicity, the three measures suggested earlier by Lees were used.

5.5.2 Route data

Prior to sending out the questionnaires, the experts were sent data on the MMA routes, including process conditions and chemical properties. This was to allow them to familiarise themselves with the routes. Details of the MMA routes are listed in appendix A.

Samples of the three questionnaires used are listed in appendix B.

5.5.3 Questionnaire 1

The experts were asked to rank the six routes with respect to the three criteria, using their 'gut feeling'. They were requested not to spend more than two hours completing the questionnaire. In this way the experts could give a ranking of the routes based on an overall impression of their safety, without paying undue attention to individual step details.

The introduction to the questionnaire states the ranking criteria. The first section is to rank the six MMA routes with respect to the criteria. There is also an additional criterion called 'overall' which was intended to elicit a ranking over all the three criteria. The experts were asked to assign a score of 1 for the safest route through to 6 for the least safe route. This gave a ranking which was compared with the ranking from the trial index.

In section two, the experts were asked to list the features of each route that were important in their assessment of inherent safety. They were asked to assign a measure of importance to each feature, with a score of 1 for high importance through to 5 for low importance. They could list as many features as they wanted. The results of this section were designed to elicit the features that experts look for when assessing inherent safety. This would help in highlighting extra parameters for the index or weighting the scoring of existing parameters.

In section three, the experts were asked to state the reasons behind their rankings with respect to each of the four criteria. This would show if the expert's assessment of inherent safety was influenced by the size of a potential hazard. For example, would the experts rank the routes differently if they were looking at the potential to cause large scale damage compared to looking at the potential to cause small scale 'nuisance' incidents.

In the final section the experts were asked : what data was incomplete or missing, what they would have done with the missing data if they had had it, and what they did to deal with its absence. This section tried to gain some idea of what data was absolutely

necessary, and what the experts did in assessing the inherent safety, given that data about some chemicals and route steps was missing.

Finally, the experts were asked if they had any general comments at this stage of the exercise.

5.5.4 Questionnaire 2

In the second questionnaire there was only one section. The data for the steps in the routes was presented, with the individual reaction steps in a random order. Some steps are common to more than one route and these were presented only once in this questionnaire. The experts were asked to score each step, assigning a score of 1 for the most inherently safe through to 5 for the least inherently safe. They were asked to look at the steps in isolation from the route of which they were a part. In later analysis the scores were added up for all the steps in each route, to give a 'composite' score for each route. These scores provided another ranking of the routes. This ranking was compared with the ranking from both the index and from questionnaire 1. The comparison with questionnaire 1 is part of the index validation procedure.

5.5.5 Questionnaire 3

The third questionnaire concentrated on eliciting comments and suggestions on both the trial index and its development. The questionnaire was divided into five sections. The first section presented the scoring tables of the present index and the scoring method for a route, with an example. The experts were asked to comment on both the method and the individual tables. For the scoring tables, the experts were asked to comment on the ranges of the parameters, the scores assigned to those ranges, and comment generally. If they thought that the tables were inappropriate, they were asked to suggest alternatives. A separate page was given for each of the seven parameters.

In the next section, the experts were asked for their opinion of which parameters were important in assessing inherent safety of reaction steps. One half of the section asks for a 'yes or no' indication of whether the expert considered the parameter essential for an inherent safety assessment. The second half asked the experts to give a score for how important they considered the parameter to be. This would show which parameters should be included in the development of the index. The experts were asked to suggest further parameters and provide a scoring table.

The experts were asked to list any interactions between parameters that they considered would affect an inherent safety assessment. This could help in deciding how to combining the various parameters or how to combine the scores for the parameters.

The next section was similar to the previous section except that the experts should consider parameters that they considered were important in assessing the inherent safeness of separation steps. The format of the table was the same, but it had more space for experts suggestions.

The final section presented to the experts a possible structure for developing the index. They are given a description of a proposed 'four factor' index . Details of this new index will be covered in the following chapters. The experts were asked to comment on and make suggestions about the proposals for the new index.

The questionnaire finishes with two questions. The first asked the experts about the circumstances in which they consider intermediate storage is needed. This would indicate if any additional route steps would be needed to estimate the hazards from intermediate storage. The second asked for what they consider is a practical measure of toxicity, to replace the use of TLV.

5.5.6 Panel meeting

The panel meeting was organised to follow questionnaire 3. The findings from the first two questionnaires were presented and discussed. The outcome from the third questionnaire was used to lead a discussion about how the new index should develop. The experts were asked about the structure discussed above, what parameters should definitely be included, how they should be included into the proposed structure and how they could be scored.

5.6 Methods for the analysis of the questionnaires

This section presents, analyses and discusses the results from the three questionnaires and the panel meeting.

5.6.1 Correlation and regression

Statisticians make a distinction between correlation and regression. Taking two sets of data from an experiment, X and Y, the Y variable is a random variable in both correlations and regressions. For a regression analysis of the data, X is described as a fixed variable. This means that the values for X are fixed prior to the experiment and the Y values come from the results. Therefore it is possible to define a relationship between X and Y which allows for the prediction of future values of Y if the experiment is repeated. Regression analysis shows how well the data fits the relationship.

In a correlation analysis, both X and Y are random variables, and thus a correlation analysis looks for a degree of correlation between the two data sets, but does not look for a relationship to fit the data to.

For analysing the rankings from both the experts and the trial index, a correlation analysis is needed to see how well they agree but not to define a relationship between them.

5.6.2 Tied data

Sometimes raw data is ranked but there are tied scores. The following method, which is described by example, can be used to rank the tied data (Howell, 1992).

Consider a set of data arranged in increasing order:

2, 3, 4, 5, 5, 7, 9, 12, 12, 12, 14, 16

The lowest value (2) is ranked 1. The next two values (3 and 4) are ranked 2 and 3. The two tied values (5) can occupy either position 4 or 5, so they are given the average rank of $(4 + 5)/2$ or 4.5. Values 7 and 9 are ranked 6 and 7. The next three tied values would occupy positions 8, 9 and 10 and so are all given position 9. Thus the values are ranked:

value: 2, 3, 4, 5, 5, 7, 9, 12, 12, 12, 14, 16
rank: 1, 2, 3, 4.5, 4.5, 6, 7, 9, 9, 9, 11, 12

5.6.3 Pearsons Product-Moment Correlation coefficient

There are several methods that can be used to analyse the rankings. Firstly, there is Pearson's Product-Moment Correlation Coefficient (Howell, 1992). The relation between two sets of data X and Y is measured by a correlation coefficient r. The coefficient ranges from 1 to -1. A high positive value shows a strong relation between X and Y, a high negative value shows a strong but inverse relation. A value of zero means no relation. r can be defined as follows.

Firstly define the sum of squares of the deviations of the values of X from the mean of X as

$$SS_X \equiv \sum_{i=1}^{N}\left(X_i - \overline{X}\right)^2 = \sum_{i=1}^{N} X_i^2 - \frac{\left(\sum_{i=1}^{N} X_i\right)^2}{N} \qquad (5.1)$$

and the sum of squares of the deviations of the values of Y from the mean of Y as

$$SS_Y \equiv \sum_{i=1}^{N}\left(Y_i - \bar{Y}\right)^2 = \sum_{i=1}^{N} Y_i^2 - \frac{\left(\sum_{i=1}^{N} Y_i\right)^2}{N} \tag{5.2}$$

and define the sum of products of the deviations of the values of X and Y from the means of X and Y respectively as

$$SP_{XY} \equiv \sum_{i=1}^{N}\left(X_i - \bar{X}\right)\left(Y_i - \bar{Y}\right) = \sum_{i=1}^{N} X_i Y_i - \frac{\left(\sum_{i=1}^{N} X_i\right)\left(\sum_{i=1}^{N} Y_i\right)}{N} \tag{5.3}$$

where

X_i = ith value of data set X

Y_i = ith value of data set Y

N = number of items

$$\bar{X} = \frac{\sum_{i=1}^{N} X_i}{N} \tag{5.4}$$

$$\bar{Y} = \frac{\sum_{i=1}^{N} Y_i}{N} \tag{5.5}$$

then define r as

$$r \equiv \frac{SP_{XY}}{\sqrt{SS_X SS_Y}} \tag{5.6}$$

Pearson's coefficient may be used on any raw data that might be related.

5.6.4 Spearman's correlation coefficient for ranked data

Spearman's coefficient (Howell,1992) is a development from Pearson's coefficient for use on ranked data.

It is known that the sum of the first N integers is N(N + 1)/2. Similarly, the sum of the squares of the first N integers is N(N + 1)(2N + 1)/6. If ΣX and ΣY are replaced by N(N + 1)/2 and ΣX^2 and ΣY^2 are replaced by N(N + 1)(2N + 1)/6 in the above Pearson's formulae, and D is defined as the difference between the X and Y ranks, then Spearman's coefficient, r_s , is defined as:

$$r_s = 1 - \frac{6 \sum_{i=1}^{N} D_i^2}{N(N^2 - 1)} \qquad (5.7)$$

where

$$D_i = X_i - Y_i \qquad (5.8)$$

However, if there are any tied data in the rankings, the formula is invalid because the set of N rankings no longer consists of the first N integers and so the replacements for the sums and sums of squares are incorrect. In this case Pearson's formula should be used to test the rankings.

5.6.5 Kendall's coefficient of concordance

Pearson's and Spearman's coefficients are both used to assess the relation between two sets of data (X and Y). To assess the relation between more sets of data, Kendall's coefficient of concordance (Gibbons, 1976) is used.

A rank is the position of an item in the ranking. Firstly, it is assumed that the data consists of k sets of n ranked items, for example k experts ranking n routes. The data is arranged in a table of k rows and n columns. In this case, each column corresponds to a route and each row corresponds to an expert. The intersection of row i with column j is expert i's rank for route j. Each row will have the first n integers appearing in it, assuming there are no equal ranks, thus the sum of the row elements will be:

$$1 + 2 + \cdots + n = \frac{n(n+1)}{2} \qquad (5.9)$$

The total of all the ranks in the table is kn(n + 1)/2, and the average total of the ranks in a column is k(n + 1)/2. This is the average total rank a route would have if the ranking was done randomly.

Let R_1, R_2, ... R_n be the actual totals for each column, that is the total rank for each route. The sums of squares of the difference between the actual total rank and the average total rank is:

$$S \equiv \sum_{j=1}^{n} \left[R_j - \frac{k(n+1)}{2} \right]^2 \qquad (5.10)$$

S is a measure of the agreement between the rankings from each expert, S is small for poor agreement and large for good agreement.

For a perfect match between all the experts, the column that had total rank 1 would be composed entirely of 1s, the column for total rank 2 would be composed entirely of 2 s, etc, that is all the experts agree on all the ranks. Thus the column sums are :

1k, 2k, 3k, ..., nk

The sums of squares of these column sums is:

$$\sum_{j=1}^{n}\left[jk - \frac{k(n+1)}{2}\right]^2 = k^2 \sum_{j=1}^{n}\left[j - \frac{(n+1)}{2}\right]^2$$

$$= \frac{k^2 n(n^2 - 1)}{12}$$

(5.11)

Kendall's coefficient of concordance, W, is the ratio of the sums of squares for actual agreement, S, to the sums of the squares for perfect agreement:

$$W \equiv \frac{12S}{k^2 n(n^2 - 1)}$$

$$= \frac{12\sum_{j=1}^{n}\left[R_j - k(n+1)/2\right]^2}{k^2 n(n^2 - 1)}$$

(5.12)

W has a value between 0, for no concordance, and 1, for perfect concordance. The expression can be rearranged for convenience to give:

$$W = \frac{12\sum_{j=1}^{n} R_j^2 - 3k^2 n(n+1)^2}{k^2 n(n^2 - 1)}$$

(5.13)

W can be used to define an average Spearman's coefficient by:

$$\bar{r}_s \equiv \frac{kW - 1}{k - 1}$$

(5.14)

This represents the average value obtained if r_s is calculated for all the possible pairs of rankings, that is comparing expert 1 to 2, 1 to 3, ... , 2 to 3, 2 to 4, etc.

5.7 Results

5.7.1 Questionnaire 1

The experts' replies to questionnaire 1 are listed in appendix C.

The experts were asked for a 'gut feeling' ranking of the six MMA routes. The rankings should be an overall impression of the relative inherent safety of the routes. The experts were also asked to tell us how they went about ranking the routes.

5.7.1.1 Section I - Ranking of routes

In section I the experts ranked the routes according to the three criteria and overall. These are the rankings with which the trial index were compared. Tables 5.1 to 5.4 below present the rankings from questionnaire 1 for all the experts in respect of criteria A, B, C and overall respectively. A '1' denotes the safest and a '6' represents the least safe route according to the expert. The last row lists the sum of the ranks over all the experts for each route. The columns (routes) of the tables have been ordered from safest to least safe based on the sum of the ranks. Tied rankings have been averaged as discussed earlier.

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	ACH	C3
1	1	2	3	4	5	6
2	1	2	3	4	6	5
3	1	2	4	6	5	3
4	1	2	4	3	6	5
5	1	2	5	4	3	6
6	1	2	3.5	5.5	3.5	5.5
7	1.5	6	1.5	3	4	5
8	1	2	3	5	4	6
SUM	8.5	20	27	34.5	36.5	41.5

Table 5.1 - Rankings for Criterion A from questionnaire 1

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	1	2	3	4	6	5
2	1	2	3	4	5	6
3	1.5	3	1.5	4	5	6
4	1	2	3	4	5	6
5	1	2	3	5	6	4
6	3.5	3.5	3.5	1	6	3.5
7	3	3	3	5	1	6
8	1	2	3	5	6	4
SUM	13	19.5	23	32	40	40.5

Table 5.2 - Rankings for Criterion B from questionnaire 1

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	ACH	C3
1	1	2	3	4	5	6
2	1	2	3	4	6	5
3	2	1	3	5	4	6
4	1	2	3	4	6	5
5	1	2	3	5	4	6
6	1.5	3.5	3.5	1.5	5	6
7	2	2	2	4.5	6	4.5
8	1	2	3	4	6	5
SUM	10.5	16.5	23.5	32	42	43.5

Table 5.3 - Rankings for Criterion C from questionnaire 1

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	ACH	C3
1	1	2	3	4	5	6
2	1	2	3	4	6	5
3	1	2	3	5.5	5.5	4
4	1	2	3	4	6	5
5	1	2	5	4	3	6
6	1	2.5	4	2.5	5	6
7	1.5	3	1.5	5	6	4
8	1	2	3	4.5	4.5	6
SUM	8.5	17.5	25.5	33.5	41	42

Table 5.4 - Rankings for Overall Criterion from questionnaire 1

For the four tables above, the Kendall's coefficient and the average Spearman's coefficient have been calculated for each criterion. In addition the Pearson's coefficient

has been calculated for each criterion, by comparing the totals for each route with the route scores from the trial index The results are tabulated below.

Criterion	W	$\bar{r}_s$	r
A	0.623	0.614	0.701
B	0.570	0.509	0.831
C	0.813	0.787	0.798
OVERALL	0.796	0.767	0.789

Table 5.5 - Correlation coefficients for each criteria from questionnaire 1

The values of W and $\bar{r}_s$ show that there is greater agreement among the experts for the C and overall criteria, than the other two. Apart from criterion B, the general level of agreement between the experts is good. The value of r shows that match between the scores from the trial index and the sums of the rankings for each route is best for criterion B. This presents a problem in that although the average ranking by the experts for criterion B is closest to the ranking from the trial index, the level of agreement between the experts for criterion B is the worst. The important point is that the two initial questions have been answered affirmatively.

Composite ranking of MMA routes and comparison with index.

For each criterion, the ranks for each route, according to all the experts, are added together. These are the column sums in the above tables. The route with the highest total is the one with lowest inherent safety and thus has a composite ranking of 6 for that criterion. The composite rankings derived from questionnaire one are given below.

RANK	EXPERT RANKINGS BY CRITERION				INDEX
	A	B	C	OVERALL	RANKING
1	TBA	TBA	TBA	TBA	TBA
2	i-C4	i-C4	i-C4	i-C4	i-C4
3	C2/MP	C2/MP	C2/MP	C2/MP	C2/MP
4	C2/PA	C2/PA	C2/PA	C2/PA	C3
5	ACH	C3	ACH	ACH	C2/PA
6	C3	ACH	C3	C3	ACH

r_s	0.829	0.943	0.829	0.829

Table 5.6 - Composite rankings for questionnaire 1

The values of the Spearman coefficient represent the closeness of the match between the experts' composite ranking and the trial index ranking. There is an interesting anomaly. The match for criterion B is better than for the other criteria, whereas the agreement between the experts, as measured by the average Spearman coefficient , is the worst for criterion B. This echoes the results in table 5.5 where the raw scores from the trial index are compared with the sums of the ranks for each route.

Given the complexity and lack of definition of the inherent safety assessment problem and the simplicity of the trial index, the match between the rankings of the experts and those for the trial index is very good. The difference in scores between the least safe two routes of the expert ranking is only one or two points. Therefore, the match would be closer if just one expert changed the positions of two routes. Again the two initial questions have been answered affirmatively.

An important result is that the rankings for the different criteria are almost identical. The small differences in individual experts' rankings between the different criteria average out across the panel. This suggests that either the inherent safety of the route and the scale of a potential hazard are not related or that the experts could not usefully distinguish between the routes using the criteria. This was discussed further in the panel meeting.

5.7.1.2 Section II - Key features of each route

In section II the experts identified important features of the individual routes and ranked them on a scale of 1 to 5. This helped decide what are the important features for assessing inherent safety.

Methods used for rankings

It was apparent that the experts used two distinct methods for ranking the routes. Most experts identified the key features of each route and scored them between 1 and 5. The scores were then added up and the total used to rank the routes. Some of the features that were scored included temperature, pressure, and toxicity. This method of scoring key features does at least compare favourably with the trial index, and shows that the method is not completely divorced from expert judgement.

Other experts based their final rankings on an overall impression of inherent safety in the route. They listed the features that they looked for, but did not assign any score to them only an overall score for the route. They may have mentally scored them, but this was not indicated in their answers.

One expert suggested that section two should have come before section one. The experts might have found the ranking easier, as required in section one, if they had first been asked to decide what factors affected the inherent safety, as required in section two.

There are several features of inherent safety which were picked out and which are common to all the routes.

1. All the experts looked for instances of flashing liquids or conditions which would cause liquids to flash off.

2. Experts readily identified highly flammable or potentially explosive chemicals as key chemicals in a route.

3. Partial oxidations were present in nearly every route. This was picked out as being significant, as was the presence of oxygen.

Particular features for each route, additional to the common features, are now itemised.

ACH

1. HCN, ACH, SO_2, SO_3 - toxic hazard. These were considered to be very important hazards by all.

2. Large number of steps. This is assumed to mean a large number of steps compared with the other routes. This was given low importance. It is possibly an indirect measure of the complexity of the route.

3. The presence of a strong acid was given low importance.

4. Several experts said pressure was of low importance. However, others said that high pressure combined with the toxicity of some of the chemicals gave a hazard of high importance. This indicates the need to consider combination or interaction of parameters.

5. Low yield. This may imply a high inventory or the need for recycles.

6. Gas phase reactions were described as good for inherent safety

C2/MP

1. Toxicity of CO was assigned high importance.

2. High pressures, again in conjunction with the potential for liquids to flash was given high importance.

C2/PA

1. Toxicity of CO and HCHO was given high importance.

2. Hydrogen and ethylene were highlighted as highly flammable.

C3

1. HF and CO were highlighted as highly toxic.

2. HF was highlighted as a heavy gas.

3. the Combination of HF and water presented a handling hazard or the need for 'exotic' materials of construction.

4. Propylene was highlighted as highly flammable.

5. Low yield.

i-C4

1. Isobutylene was highlighted as highly flammable.

2. Unstable intermediates.

3. Low yield was given high importance.

4. Low pressure was regarded as good.

TBA

No particular features were highlighted in addition to the general ones.

General comments

The comments ranged from quite specific, for example the toxicity of a particular chemical, to very broad, for example "fire hazard". The factor which was given the highest importance was toxicity, on its own or combined with high temperature and/or pressure. Only one expert treated temperature on its own. In general temperature was only used to identify whether flashing liquids may be present.

Keywords

The number of times key words were mentioned by the experts was recorded and the results are presented below.
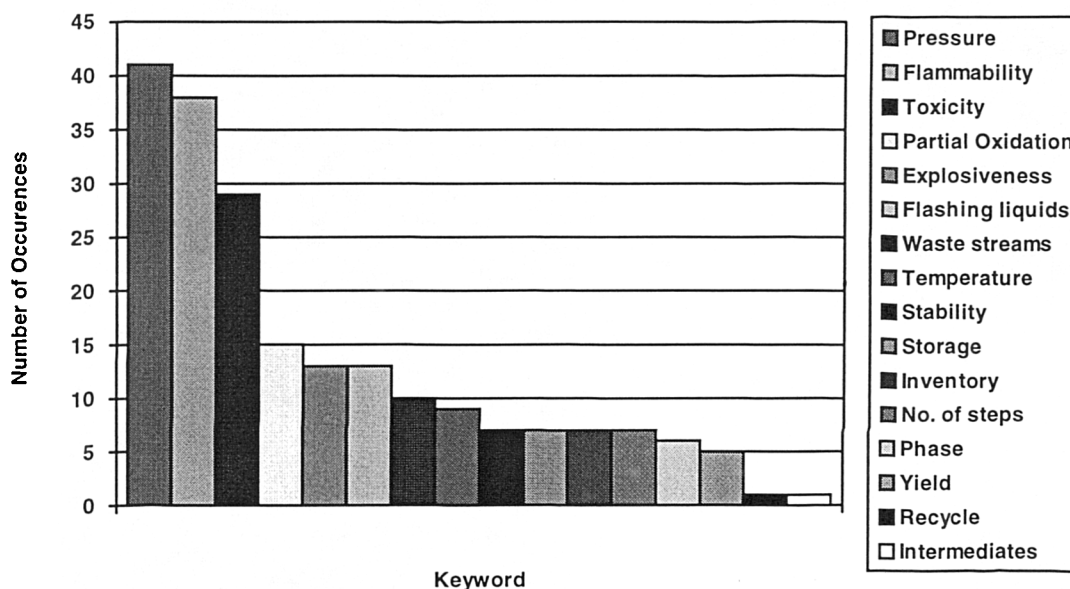
Figure 5.1 - Number of occurrences of keywords

The large number of times that both pressure and flammability was mentioned suggests that experts were concentrating on fire and explosion hazards. The same can be said for the number of times toxicity was mentioned. However, inventory was not mentioned very often, whereas inventory is considered very important for inherent safety. This is possibly because the only information given about inventory was the total annual output, which was the same for all the proposed routes. Therefore the few times that inventory was mentioned said that information about inventory was needed.

5.7.1.3 Section III - Reasons for ranking by criteria

In section III the experts gave reasons for their rankings with respect to the three criteria and overall inherent safety. This shows whether the scale of potential hazard has an effect on their assessment of inherent safety.

Only one expert gave the same ranking for all the four criteria .

Criterion A

Most of the experts looked for a large inventory of material which would flash off on release. Only two experts added anything about toxicity. The main threat is that of a large fire or explosion. The search for large flammable inventories agrees well with the given criterion.

Criterion B

Some experts included the reasons from criterion A before defining new ones.

Toxic release appears to be more important under this criterion than large amounts of flashing liquids. The comments suggest that the experts have looked for things which would cause small explosions or localised toxic releases. This is in contrast to very large releases which may affect people offsite. Once again the reasons given by the experts agree well with the criterion.

The number of steps was also mentioned more than once. This could imply that the number of steps increases the risk of an event happening. The larger number of steps could produce more small on-site events as opposed to a large event which may effect the whole site. For example, having more reaction steps leads to more connections between different parts of the process. This in turn leads to more places where leaks could occur, for example valves or flanges. Thus the chance of a small leak occurring and causing a localised hazard is increased.

Criterion C

Once again, reasons from A and B were included first. Half of the answers mentioned toxics or toxicity. This included toxics from possible fires, or substances which, although non-toxic, could be considered noxious, for example effluent waste streams.

The suggestion is that this criterion covers situations where anything, even if only slightly toxic, could penetrate beyond the site boundary.

Again, the reasons given by the experts match with the criterion well.

Overall

The 'overall' criterion was not defined in either questionnaires 1 or 2. This meant that the interpretation of it was left to the individual experts. The experts gave sensible definitions of their overall criteria. From their answers to section III, four chose to use their ranking with respect to criterion A, one chose to use the ranking with respect to criterion B, the remaining two used the same reasons for all four criteria, but did not say what they were.

It is possible to say from looking at the experts' tables of rankings from questionnaire one, that the methods that appear to have been used for the overall rankings are as follows.

One has the same rankings for all four criteria.

Two have the same rankings for the 'overall' criterion and the criterion that they chose to represent the overall criterion, for example the positions of routes in the overall criterion are the same for criterion B, because criterion B was chosen to represent the overall criterion.

The remainder of the experts have added up the three criteria scores, A+B+C, for each route and used the total to rank the routes in the overall criterion. This lead to some of the routes having equal rank in the overall criterion.

5.7.1.4 Section IV - Missing data

In section IV the experts described how they coped with incomplete route data. This shows if there are any parameters which have been missed and how missing data can be overcome.

1. 6 out of 8 experts listed the need for inventory or throughput. The only inventory data given was the total annual throughput. The throughputs of individual chemicals could have been calculated from the given data. However the two hour limit on completing the questionnaire prevented this. This confirms the comments made earlier about inventory.

2. Boiling points of mixtures. This could be used to see if a mixture would flash off.

3. Did O_2 mean air or pure oxygen? Pure oxygen would be more of a hazard than air, when performing partial oxidations and other reactions. This is a process detail which would probably be known.

4. Gas toxicity needed in addition to TLV. This problem would be dealt with in questionnaire 3 and in discussion with the panel.

5. Knowledge of relative risks of particular processes, for example oxidations, carbonylations, hydrolysis.

6. Layout. At the route choice stage, the plant layout could not be known.

7. Flammability data.

5.7.2 Questionnaire 2

The experts' replies to questionnaire 2 are listed in appendix D.

The experts had to rank the inherent safeness of the reaction steps in the routes, by giving each step a score on a scale from 1 (inherently safest) to 5 (least inherently safe).

5.7.2.1 Step ranking results

Firstly, the individual steps from questionnaire two were reformed into their respective routes. All the step scores were added up to give scores for each route. Then for each criterion, the scores for each route, from each expert, were added up. Tables 5.7 to 5.10 show the route scores from each expert and the totals for each route.

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	7	7	7	10	13	17
2	10	10	12	13	16	20
3	8	9	9	15	10	17
4	5	4	5	6	8	10
5	6	6	8	8	11	12
6	5	8	1	13	11	17
7	7	10	7	9	11	9
8	5	6	8	8	9	15
SUM	53	60	66	82	89	117

Table 5.7 - Data for Criterion A from questionnaire 2

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	7	7	7	10	13	17
2	10	10	12	13	16	20
3	7	7	8	12	17	27
4	8	7	6	9	9	18
5	5	7	9	10	13	16
6	5	8	10	13	11	16
7	7	8	6	9	11	13
8	5	6	8	8	9	15
SUM	57	60	66	84	99	142

Table 5.8 - Data for Criterion B from questionnaire 2

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	7	7	7	10	13	17
2	10	10	12	13	16	20
3	10	9	8	15	16	20
4	5	3	5	7	9	12
5	8	7	9	10	13	16
6	5	8	10	13	11	16
7	11	11	10	13	14	19
8	5	6	8	11	13	17
SUM	61	61	69	92	105	137

Table 5.9 - Data for Criterion C from questionnaire 2

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	7	7	7	10	13	17
2	10	10	12	13	16	20
3	8	8	8	14	14	21
4	6	5	5	7	9	13
5	7	7	9	9	12	15
6	5	8	10	13	11	16
7	8	10	8	10	12	14
8	5	6	8	9	10	16
SUM	56	61	67	85	97	132

Table 5.10 - Raw data for Overall Criterion (Rounded average of A, B & C) from questionnaire 2

The average route scores are significantly higher for some experts than others. This is because some experts are consistently scoring the steps one or two points higher than the others. Two experts may agree that one step is more dangerous than another, but one expert may score both steps one or two points higher than another expert. Thus the experts may agree on the order of how safe all the steps are, but they perceive the overall level of inherent safety differently or use the scoring scale differently.

For example, in the overall criterion table experts 3 and 4 have ranked the routes almost identically, but the average route scores are 9 and 13.5 respectively and the average score per step are 2.5 and 3.5 respectively. The second expert, number four, has on average scored all the steps one point higher than number three.

This is an interesting result in that it shows that the assessment of inherent safety can still be subjective, for example in interpreting the scoring scale, even when there is an agreement on the order of a particular set of chemical routes.

For each criterion, the scores are converted into rankings from 1 to 6, a 1 representing the lowest rank or the most inherently safe, through to a 6 for the highest rank or the least inherently safe. The routes are ordered from most inherently safe to least inherently safe based on the sums of the ranks over all the experts.

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	2	2	2	4	5	6
2	1.5	1.5	3	4	5	6
3	1	2.5	2.5	5	4	6
4	2.5	1	2.5	4	5	6
5	1.5	1.5	3.5	3.5	5	6
6	1	2	3	5	4	6
7	1.5	5	1.5	3.5	6	3.5
8	1	2	3.5	3.5	5	6
SUM	12	17.5	21.5	32.5	39	45.5

Table 5.11 - Rankings for Criterion A from questionnaire 2

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	2	2	2	4	5	6
2	1.5	1.5	3	4	5	6
3	1.5	1.5	3	4	5	6
4	3	2	1	4.5	4.5	6
5	1	2	3	4	5	6
6	1	2	3	5	4	6
7	2	3	1	4	5	6
8	1	2	3.5	3.5	5.	6
SUM	13	16	19.5	33	38.5	48

Table 5.12 - Rankings for Criterion B from questionnaire 2

EXPERT	ROUTE					
	i-C4	TBA	C2/MP	C2/PA	C3	ACH
1	2	2	2	4	5	6
2	1.5	1.5	3	4	5	6
3	2	3	1	4	5	6
4	1	2.5	2.5	4	5	6
5	1	2	3	4	5	6
6	2	1	3	5	4	6
7	2.5	2.5	1	4	5	6
8	2	1	3	4	5	6
SUM	14	15.5	18.5	33	39	48

Table 5.13 - Rankings for Criterion C from questionnaire 2

EXPERT	ROUTE					
	TBA	i-C4	C2/MP	C2/PA	C3	ACH
1	2	2	2	4	5	6
2	1.5	1.5	3	4	5	6
3	2	2	2	4.5	4.5	6
4	3	1.5	1.5	4	5	6
5	1.5	1.5	3.5	3.5	5	6
6	1	2	3	5	4	6
7	1.5	3.5	1.5	3.5	5	6
8	1	2	3	4	5	6
SUM	13.5	16	19.5	32.5	38.5	48

Table 5.14 - Rankings for Overall Criterion from questionnaire 2

For the four tables above, the Kendall's coefficient and the average Spearman's coefficient have been calculated, and are tabled below. In addition, the Pearson's coefficient found for each criterion by comparing the route sums with the trial index scores are tabulated.

Criterion	W	$\bar{r_s}$	r
A	0.764	0.730	0.903
B	0.643	0.592	0.933
C	0.883	0.866	0.928
OVERALL	0.854	0.834	0.932

Table 5.15 - Correlation coefficients for each criteria from questionnaire 2

The level of agreement between the experts for questionnaire 2 is higher for all the criteria than for questionnaire 1. As with questionnaire 1, criteria 'C' and 'Overall' show higher levels of agreement than the other two, with criterion B having a much lower level. The order of ranking of the four criteria, based on W and r_s, is the same for questionnaire 1 and questionnaire 2.

The Pearson's coefficients for the criteria show a very good agreement between the total of the experts' rankings and the trial index scores. The coefficient values are higher than for a similar comparison made with the results of questionnaire 1, showing that rankings derived from questionnaire 2 results match the trial index more closely than questionnaire 1. Therefore we have confirmed the affirmative answers to the two initial questions.

5.7.2.2 Composite ranking of MMA routes and comparison with index.

For each criterion, the scores for each route, from each expert, are added together. The route with the highest total is the one with lowest inherent safety. The composite rankings derived from questionnaire two are given below.

RANK	EXPERT RANKINGS BY CRITERION				INDEX RANKING
	A	B	C	OVERALL	
1	TBA	TBA	i-C4	TBA	TBA
2	i-C4	i-C4	TBA	i-C4	i-C4
3	C2/MP	C2/MP	C2/MP	C2/MP	C2/MP
4	C2/PA	C2/PA	C2/PA	C2/PA	C3
5	C3	C3	C3	C3	C2/PA
6	ACH	ACH	ACH	ACH	ACH

r_s	0.943	0.943	0.886	0.943

Table 5.16 - Composite rankings for questionnaire 2

The values of the Spearman coefficient represent the closeness of the match between the experts' ranking and the trial index ranking. The agreement is better than for questionnaire 1. As with questionnaire 1, the match between criterion C and the index is worse than that for the other criteria, but oddly the agreement between the experts, as measured by the Kendall's coefficient and the average Spearman coefficient, is the highest for criterion C.

5.7.2.3 Discussion

As with questionnaire one, the match between the derived expert rankings and the trial index is very good and is slightly better than for questionnaire 1. There is a difference in the order of the two least safest routes between the two questionnaires. However this may be due to the different method used to calculate the final ranking. In questionnaire 2, the summation of the individual step scores into route scores, followed by the summation over all the experts leads to larger scores than the summed expert route ranks of questionnaire 1. The method used for questionnaire 2 penalises routes with more steps. For example in the rankings derived from questionnaire 2, the ACH route has a much higher score than the other routes, because it has the highest number of steps.

5.7.2.4 Spread of step scores

As a further measure of the level of agreement between the experts, for each criterion, the spread of scores for each route step has b en plotted. In addition the mean score for the step is also plotted, this is the total score over all the experts divided by the number of experts. A large spread of scores for a step indicates a poor agreement, a

small spread a good agreement. However, if the mean score is near to either end of the spread, this indicates that most of the experts agree on one value in the spread. Therefore a large spread of scores with the mean near on end does not represent poor agreement. The three graphs below show the results for each criterion in questionnaire 2.
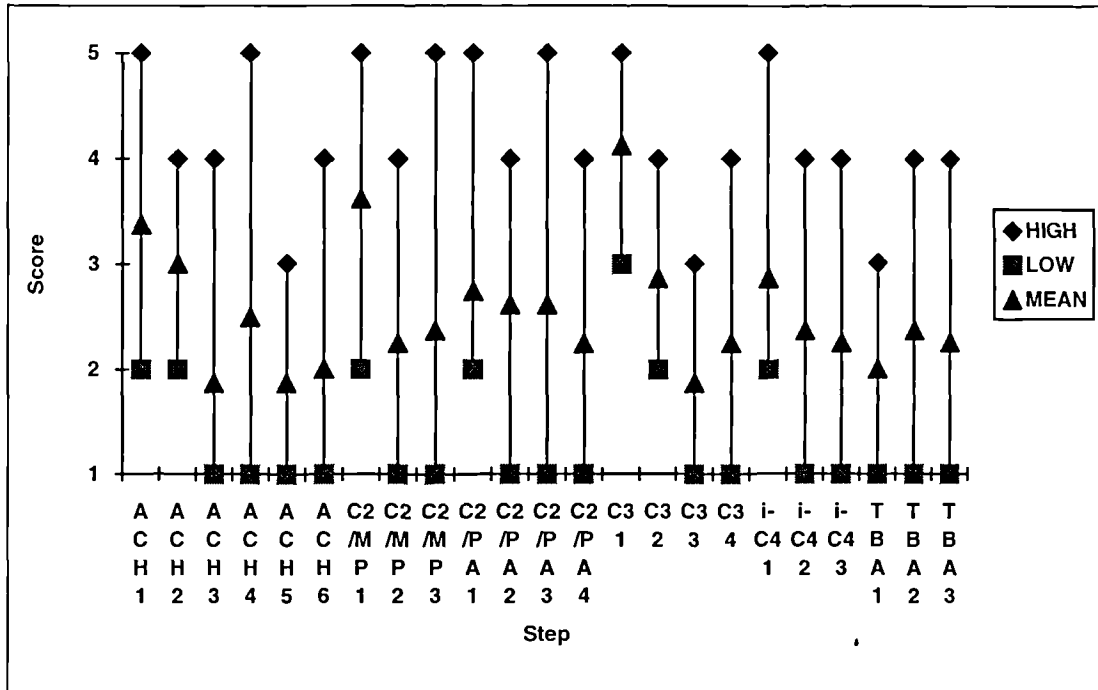
Figure 5.2 - Mean and spread of scores for each step of criterion A
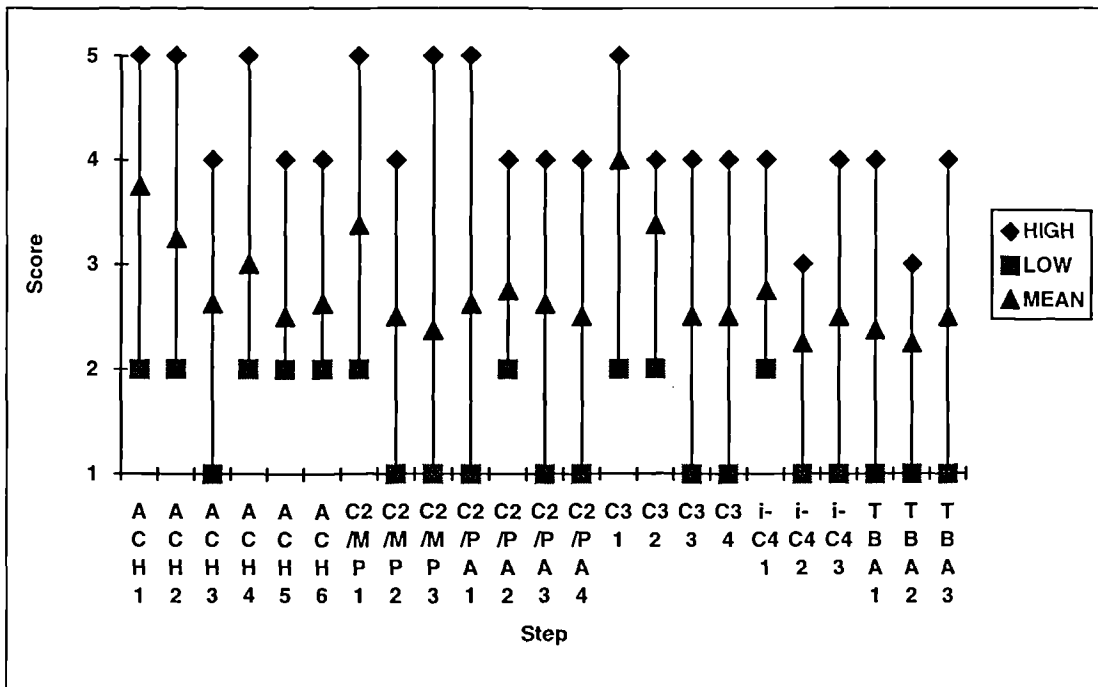
Figure 5.3 - Mean and spread of scores for each step of criterion B
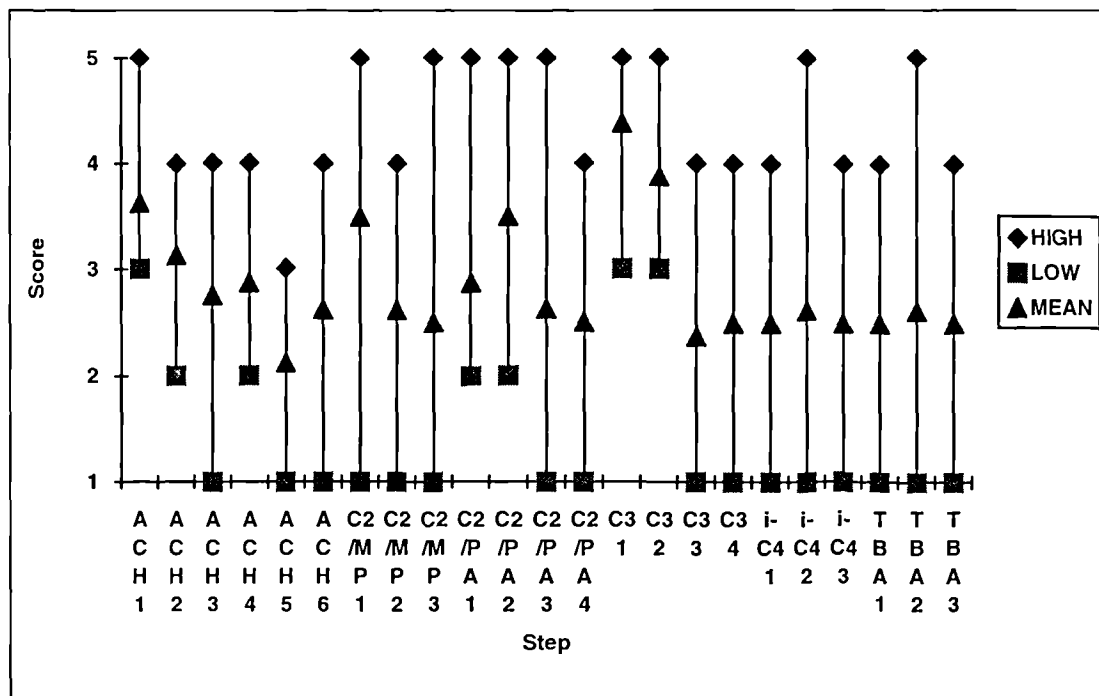
Figure 5.4 - Mean and spread of scores for each step of criterion C

As can be seen from the graphs, the least spread is two points, the most four points. Most of the steps have an average score between two and three points. The average score for most of the steps is between two and three points. This is where the effect from the number of steps takes effect. If the steps are all very similar, as they appear to be from these results, then the ranking will be biased by the number of steps in each route. However, because of this spread of scores amongst the panel, the overall match of the experts' ranking and the index is very good.

5.7.2.5 Comparisons of rankings between questionnaires 1 and 2 by expert

The reason for ranking the routes by two methods was to see if the experts were consistent. Given that the method by which they were asked to do the compare the routes were different, one being a 'gut feeling' ranking, the other being more calculated, a good match between the results would show that they rank consistently using different methods.

It would have been better if the experts had done the second questionnaire without help from the first. But on a few of the questionnaire 2 replies, the experts had worked out which step came from which route. Therefore some of the questionnaire 1 rankings may have influenced the second questionnaire. In future rankings, it would be better for the experts to rank the steps before the whole routes. This may give better results as the experts would be building up their rankings, from parameters to steps and from steps to routes, in a more logical manner.

In the tables below, the columns labelled Q1 are the rankings from questionnaire 1 and the columns labelled Q2 are the rankings from questionnaire 2.

Expert	1		2		3		4		5		6		7		8	
Route	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2
ACH	5	6	6	6	5	6	6	6	3	6	3.5	6	4	3.5	4	6
C2/MP	3	2	3	3	4	2.5	4	2.5	5	3	3.5	3	1	1.5	3	3.5
C2/PA	4	4	4	4	6	5	3	4	4	4	5.5	5	3	3.5	5	3.5
C3	6	5	5	5	3	4	5	5	6	5	5.5	4	5	6	6	5
i-C4	2	2	2	1.5	2	2.5	2	1	2	1	2	2	6	5	2	2
TBA	1	2	1	1.5	1	1	1	2.5	1	2	1	1	1	1.5	1	1

Table 5.17 - Comparison of rankings between questionnaires 1 and 2 for criterion A

Expert	1		2		3		4		5		6		7		8	
Route	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2
ACH	5	6	6	6	6	6	6	6	4	6	3.5	6	6	6	4	6
C2/MP	3	2	3	3	1.5	3	3	1	3	3	3.5	3	3	1	3	3.5
C2/PA	4	4	4	4	4	4	4	4.5	5	4	1	5	5	4	5	3.5
C3	6	5	5	5	5	5	5	4.5	6	5	6	4	1	5	6	5
i-C4	2	2	2	1.5	2	1.5	2	2	2	1	3.5	2	3	3	2	2
TBA	1	2	1	1.5	1.5	1.5	1	3	1	2	3.5	1	3	2	1	1

Table 5.18 - Comparison of rankings between questionnaires 1 and 2 for criterion B

Expert	1		2		3		4		5		6		7		8	
Route	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2
ACH	5	6	6	6	4	6	6	6	4	6	5	6	6	6	6	6
C2/MP	3	2	3	3	3	1	3	2.5	3	3	3.5	3	2	1	3	3
C2/PA	4	4	4	4	5	4	4	4	5	4	1.5	5	4.5	4	4	4
C3	6	5	5	5	6	5	5	5	6	5	6	4	4.5	5	5	5
i-C4	2	2	2	1.5	1	2	2	1	2	1	3.5	2	2	2.5	2	2
TBA	1	2	1	1.5	2	3	1	2.5	1	2	1.5	1	2	2.5	1	1

Table 5.19 - Comparison of rankings between questionnaires 1 and 2 for criterion C

Expert	1		2		3		4		5		6		7		8	
Route	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2	Q1	Q2
ACH	5	6	6	6	5	6	6	6	3	6	5	6	5	6	4.5	6
C2/MP	3	2	3	3	3	2	3	1.5	5	3	4	3	3	1.5	3	3
C2/PA	4	4	4	4	5	4.5	4	4	4	4	2	5	4	3.5	4.5	4
C3	6	5	5	5	4	4.5	5	5	6	5	6	4	6	5	6	5
i-C4	2	2	2	1.5	2	2	2	1.5	2	1	2	2	2	3.5	2	2
TBA	1	2	1	1.5	1	2	1	3	1	2	1	1	1	1.5	1	1

Table 5.20 - Comparison of rankings between questionnaires 1 and 2 for Overall criterion

The Pearson coefficient has been calculated for each expert, for each criterion. This gives a measure of the agreement between the questionnaire 1 and 2 rankings. The average value for each expert and each criterion is given.

CRITERION	EXPERT								AVG
	1	2	3	4	5	6	7	8	
A	0.880	0.986	0.841	0.812	0.618	0.736	0.926	0.783	0.823
B	0.880	0.986	0.868	0.754	0.829	-0.169	0.334	0.783	0.658
C	0.880	0.986	0.657	0.899	0.771	0.412	0.939	1.000	0.818
D	0.880	0.986	0.892	0.812	0.618	0.638	0.896	0.899	0.828
AVG	0.880	0.986	0.815	0.819	0.709	0.404	0.774	0.866	

Table 5.21 - Pearson coefficient for each expert for each criteria

The level of agreement for each expert is very good, apart from expert 6. The very low and negative values indicates that the rankings from that expert are not well correlated. The negative value also means that the average agreement for criterion B is lower than the others.

The above results show that the individual experts generally have a high level of agreement when ranking by two different methods. If this is combined with the high level of agreement between the results from questionnaires 1 and 2 and the trial index, then the results indicate that the trial index is validated, for the case of the MMA routes.

The order of the routes in questionnaire 2 is correlated with the number of steps. Routes TBA, i-C4 and C2/MP have 3 steps, routes C3 and C2/PA have 4 steps, and the ACH route has 6 steps. To see how much the number of steps affects the results, the total scores for each route, for each criterion from questionnaire 2 are divided by the number of steps. The routes are ordered from lowest average score, representing most inherently safe, to highest average score, representing the least inherently safe.

RANK	CRITERION				ORIGINAL INDEX	MODIFIED INDEX
	A	B	C	OVERALL		
1	TBA	TBA	TBA	TBA	TBA	TBA
2	i-C4	i-C4	i-C4	i-C4	i-C4	i-C4
3	C2/PA	C2/PA	ACH	C2/PA	C2/MP	C3
4	C2/MP	C2/MP	C2/PA	ACH	C3	ACH
5	ACH	ACH	C2/MP	C2/MP	C2/PA	C2/MP
6	C3	C3	C3	C3	ACH	C2/PA

r_s - original	0.714	0.714	0.486	0.543
r_s - modified	0.429	0.429	0.6	0.486

Table 5.22 - Rankings from questionnaire 2 modified for number of route steps

In the table above, the column headed 'Modified index' is the ranking obtained from the trial index, with the total step scores divided by the number of steps, giving the average step score.

'r_s - original' are the correlation coefficients obtained by comparing the trial index ranking with the questionnaire 2 rankings, modified by the number of steps.

'r_s - modified' are the correlation coefficients obtained by comparing the ranking from the trial index, modified by the number of steps, with the rankings from questionnaire 2, modified by the number of steps.

Comparing the Spearman coefficients for 'r_s - original' and r_s from table 5.16, removing the influence of the number of steps has reduced the level of correlation between the questionnaire 2 rankings and the trial index ranking. Removing the influence of the number of steps from the trial index ranking, reduces the level of correlation even further. This implies that the number of steps has a strong influence on the ranking of the routes in the methodology of questionnaire 2 but this does not affect the conformity result found from questionnaire 1. The number of steps is an indicator of the complexity of the routes, and more complex routes are more inherently unsafe. By removing the influence of the number of steps, the correlation is greatly reduced. This means that the experts could be assessing individual steps in a different manner than the index. In order to test this the individual step scores from the trial index are compared with the individual step scores from each expert.

	EXPERT							
CRITERION	1	2	3	4	5	6	7	8
A	0.311	0.256	0.212	0.567	0.478	0.411	0.565	0.172
B	-0.286	0.098	0.212	0.567	0.478	0.203	0.591	0.010
C	-0.187	0.184	0.212	0.547	0.478	0.203	0.591	0.021

Table 5.23 - Pearson's coefficient from comparing trial index step scores with individual experts step scores

The very low scores for some of the experts confirm the above deduction that the experts are assessing steps in a different manner than the trial index. However, this should be expected. The trial index may have a more structured method in calculating a step score than the experts use. The experts may score a step on an overall impression of how inherently safe the step is, whereas the index scores the step in more detail. The results from questionnaire 3 may show how the experts are assessing individual route steps and may serve to improve a new index.

Taking the above findings into consideration, it is clear that the number of steps in a route is an influential factor in deciding how inherently safe the route is. However it is important to refine the methods by which the steps are scored so that any measure of route inherent safety is not arbitrarily related to the number of steps but that the number of steps is accounted for in a defined manner.

5.7.3 Questionnaire 3

The experts replies to questionnaire 3 are listed in appendix E.

In the first part of the questionnaire, criticism of the trial index was requested about both the method used and the individual parameters. Suggestions for alternative parameters to use in place of unsuitable ones were requested. The second part aimed to find out what parameters are important in assessing the inherent safety of reaction steps and their relative order of importance. Similarly, important parameters for assessing separation steps were asked for. The final part asked for opinions on the proposed new index. It was intended that through discussion this would be developed into something more useful than the trial index.

5.7.3.1 Current index comments

There were only a few comments on the method of the old index. These were:

'Why not use the Dow index?' This has been discussed in the introductory chapters.

'How do you decide if the relationships are additive or multiplicative?' This question was answered in the panel meeting, which is discussed later.

'Why is only the highest chemical score used?' This reflects the method used in both the Dow and Mond indices, which use the chemical which presents the worst hazard in the step.

5.7.3.2 Comments on specific parameters

Inventory

The general consensus is that the table of scores should focus on the range 0 to 250 tonnes, because anything above 250 tonnes is probably oil storage. However, the other more realistic suggestion is to have the inventory itself as a multiplicative factor and not an additive score. This coincided with the ideas for the new index which are introduced later.

Flammability

There is agreement on checking if the chemicals in question are stored or used above their flash point or boiling point. Also the degree of flash, that is how much material would flash off in a release, could be calculated.

Explosiveness

Several suggestions were made for this table. The simplest was to ignore it, as most explosive ranges are similar. The second was to have a simple yes or no answer to the question 'is the material flammable/explosive through the range in which it is used?'. Finally, it was shown that the L.E.L. and the range is more important than just the range. In an example, given by one expert, ammonia turns out to be less safe than ethane or pentane using the explosive range, whereas ethane and pentane have lower L.E.L's and are therefore more hazardous.

Ammonia: explosive range = 27 - 16 = 11
Ethane: explosive range = 12.5 - 3 = 9.5
Pentane: explosive range = 7.8 - 1.4 = 6.4

Ammonia, having the highest L.E.L, requires a richer mixture in air before it will ignite. Therefore it will ignite after ethane or pentane, and is therefore safer.

Toxicity

It is agreed that TLVs are not the best measure for short term toxic hazards. Short Term Toxic Limits (STTL) or probits are suggested. The other suggestion is to use Lethal dosage, in particular LD_{50}.

Pressure

Comments varied on this table. One suggestion is to bias the scores towards lower pressures. Another expert suggests that it scores a well known process, the ACH route, too high and thus the scores should be biased towards higher pressure. Another suggestion is to consider it combined with volume to give a measure of energy, or perhaps combined with temperature. It is also considered important to estimate how it affects leak rates.

Temperature

The importance of the effect of low and high temperatures on materials is recognised. However, the relation between temperature and flashing liquids seems more important than absolute temperature. A combination of both, using temperature to calculate the degree of flash, and also penalising very high temperatures and sub-zero temperatures for material problems, seems sensible.

Yield

It is agreed that scoring yield on its own is irrelevant. It will be used in calculating the inventories.

5.7.3.3 Relative importance of parameters for ranking reaction steps

The experts were asked to indicate the importance they attached to the various parameters used to assess process routes. In the table below a 5 means the parameter is very important and a 1 means unimportant. The parameters have been ordered according to their total score. The column labelled 'Essential' gives the number of experts who consider the parameter essential for assessing inherent safety. The total score for each parameter represents its relative importance. There were no results from expert number 4.

Parameter	EXPERT								Total	Essential
	1	2	3	4	5	6	7	8		
Inventory (*)	5	5	5		5	5	5	5	35	7
Toxicity (*)	5	5	5		5	5	4	5	34	7
Chemical Stability	5	5	2		5	5	3	5	30	7
Temperature (*)	3	2	5		5	5	3	5	28	7
Pressure (*)	3	3	5		3	5	3	3	25	7
Flammability (*)	4	5	5		-	5	4	2	25	7
Explosiveness (*)	5	5	5		-	-	4	3	22	7
Flash point	3	2	2		-	5	4	2	17	4
Side Reactions	2	-	-		5	5	-	5	17	3
Waste streams	2	3	2		4	4	-	-	15	3
Reaction phase	2	-	-		4	4	2	-	12	3
Yield (*)	1	1	3		-	-	-	5	10	3
Recycles	3	-	-		-	3	-	-	6	0
Mitigation	5	-	-		-	-	-	-	5	0
Temperature relative to atmospheric boiling point	-	-	-		-	-	-	5	5	1
Mat. Corrosion	4	-	-		-	-	-	-	4	0
Complexity	4	-	-		-	-	-	-	4	0
Human factors	3	-	-		-	-	-	-•	3	0

Table 5.24 - Scores for importance of parameters for measuring inherent safety

The parameters in the table marked with an asterix were the parameters that were in the trial index. Apart from yield, the table confirms that the choice of the seven parameters for the trial index was a good choice in that it agrees with the expert view.

Importance of each parameter for separation steps

The experts were asked to fill out a similar table for the importance of parameters in separation steps. The parameters were given identical scores in both tables for reaction steps and separation steps. Thus the table is identical to the one for reaction steps and is not repeated here. It is only possible to conclude from the tables of results that the experts consider that there is no difference between reaction steps and separation steps when considering inherent safety. Some experts clearly stated that they did not consider there to be any difference.

5.7.3.4 Analysis

The table above indicates what the panel consider are the important parameters for assessing inherent safety. This is an aid for choosing which parameters should be included in the new index. However, just because a parameter is low in importance , this does not mean it should be excluded. It could be included in the index, but its

contribution to the index be weighted lower than other parameters. As the table compiles the results from individual experts, a parameter suggested by only one expert may be a parameter suggested by the rest of the experts but worded differently. For example, 'temperature relative to atmospheric boiling point' may have been considered as just 'temperature' by the other experts. The table was open to discussion in the panel meeting, and some of these low importance parameters were pushed up or down the table.

From the comments about separation steps, most of the parameters and methods proposed for assessing reaction steps can be used for separation steps. A different method will be needed for assessing the inventory of a separation step, depending on the type of separation process. Parameters which are reaction specific, for example reaction rate or heat of reaction, will not be used.

5.7.3.5 New index structure

Development of the new index was proceeding in parallel with the expert ranking work. One of these developments was a new four part structure for the index, the details of this are covered in the following chapter. The proposed structure for the new index, as presented to the experts, was :

$$\text{Inventory} * \text{Hazard Coefficient} * \text{Probability of Release} * \text{Effects Multiplier} \quad (5.15)$$

where the '*' means 'combined with' and does not necessarily imply multiplication.

The proposed new index structure met with many favourable comments. There was one particular comment that the effects multiplier may be too subjective. This is discussed further in the next chapter. A suggestion for the final index value was to take the 4th root, that is :

$$\sqrt[4]{\text{Inventory} * \text{Hazard Coefficient} * \text{Prob. of Release} * \text{Effects Multiplier}} \quad (5.16)$$

One expert said that 'multiplication is said to create dimensionality, whereas addition destroys it'. Combining parameters by multiplication retains the units of the combined parameter. In order to add terms they must have the same units or be first rendered dimensionless.

The suggestion in equation 5.16 above makes the score proportional to both inventory and probability of release, which was considered good by the experts.

5.7.4 Expert Panel meeting discussion

Five out of the eight experts attended the panel meeting. There were two main parts to the proceedings. In the first part the results and analysis of questionnaires 1 and 2 and the comparisons between the two questionnaires, were presented. The experts commented on the findings. In the second part, the results from questionnaire 3 were used to lead a discussion on developing the index. One of the aims was to try to get the experts to fit the parameters they had ranked to the proposed four factor structure.

Throughout the meeting, a portable tape recorder was used to record the proceedings. Below are the experts' comments and suggestions which came out of the meeting. A white board was used, with columns marked on it to represent the four factors in the proposed new index. A scale down the side of each column indicated the relative importance of the parameters in the factor. The parameters were written on 'post-it notes' and placed on the white board, the higher up the board, the greater the importance.
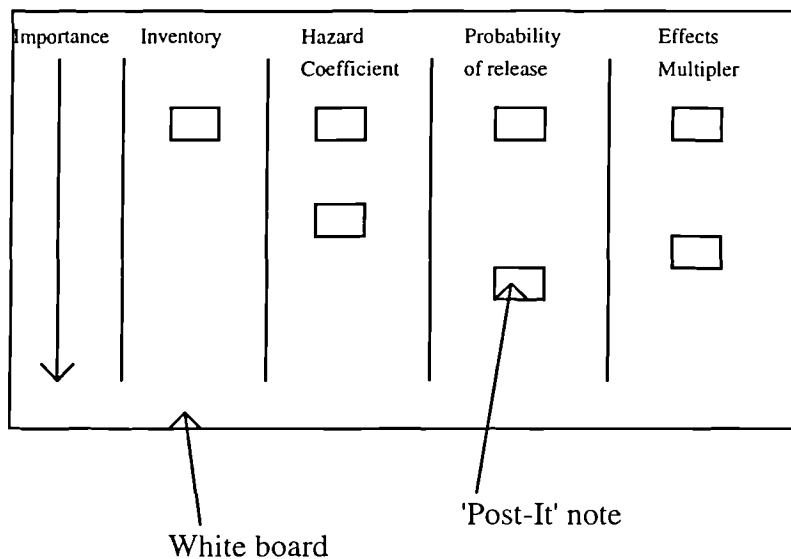
Figure 5.5 - Diagram of white board used in panel meeting

5.7.4.1 Questionnaire 1

The experts were presented with the data collated from the first questionnaires. The rankings of the results, in both tabular and graphical form, were shown along with a comparison with the results from the trial index and figure 5.1 showing the number of occurrences of keywords.

The first point raised related to the terminology of 'Expert' throughout the exercise. It was agreed that the panel had relevant expertise or experience within the safety field, and that their opinions would carry weight. However they were not to be considered experts in performing an inherent safety assessment of chemical routes. The ranking exercise would be considered more valuable if the experts were more practised in inherent safety assessment of chemical routes. More practice would help in the development of rules for doing the rankings.

Some problems were highlighted in completing questionnaire 1. Firstly, there was not enough time to fill in the questionnaire. More time was needed either to do more calculations or to devise rules to do the rankings. The assessments may have been more quantitative if more time was available.

With respect to the initial premise about using the agreement between experts to validate the index, it was accepted that agreement between the experts' ranking and the index would validate the index. However, disagreement between the experts, as opposed to disagreement with the index, may only indicate that the experts could not satisfactorily perform the ranking, given the reasons above.

The analysis of the questionnaires shows that the experts nearly all identified the same features when doing the ranking. But the experts considered this as not very extraordinary. It would have been more surprising if the experts came up with different reasons. Even though the experts identified the same features they may have weighted their assessment of each feature differently, but still arrived at the same ranking.

The experts were asked to comment on why the rankings for each criterion used in the questionnaires were the same. Two answers arose. Firstly, the experts had difficulty distinguishing between the different criteria. Secondly, the experts made distinctions between the criteria, but the inherent dangers in the routes could give the same spread of effects for each criterion.

Another criterion of long term toxic emissions was suggested. This would differentiate between short term and long term toxic hazards, which may have produced a different ranking.

5.7.4.2 Questionnaire 2 and comparison between questionnaires 1 and 2

The experts were presented with the rankings from the second questionnaire, in both graphical and tabular form, along with comparisons with the trial index and the rankings from questionnaire 1.

An important issue arising from questionnaire 2 was the validity of simply adding together the step scores. This gave equal weight to each step in the routes. Some of the panel suggested that this is not necessarily valid. They suggested that a two step route is not necessarily twice as bad as a one step route. One expert suggested that from a practical point of view, more steps means more pipe work, and as pipes account for 30% of leaks, more steps can be considered more unsafe. However if the steps are all of similar inherent danger, then the number of steps is a dominating factor in the safety assessment.

A similar point was raised about the comparison between questionnaires 1 and 2. This assumed that the experts applied equal weighting to the steps in questionnaire 1. Some experts might not have done this.

As more time was allowed to do questionnaire 2 than questionnaire 1, the experts questioned the validity of the comparison between the rankings of the two questionnaires. As the results from the two questionnaires are quite similar, the results would suggest that the comparison is valid.

There was some general discussion about the overall problem of assessing inherent safety at an early stage. The experts suggested that if there were only a few rules that could be devised, and the problems to be assessed were obvious, then an algorithmic approach to solving the problem was possible, but whatever the approach to the problem, it was better than avoiding it. One expert stated that simply adding scores for disparate hazards was not a justifiable solution.

A particular comment was made with respect to the ACH route. Two experts had 'down -graded' their assessment of the hazards in the light of past experience of working on plants making ACH.

5.7.4.3 Questionnaire 3

Table 5.24 (Score for importance of parameters for measuring inherent safety) was presented to the experts as a starting point for the discussion. Figure 5.5 was prepared on a white board and the aim of the layout explained to the experts.

The meeting moved on to discuss the structure of the new index and its parameters. The following questions were raised regarding how to devise the new index : 'How were different parameters distinguished?', 'Should parameters have linear relationships between them and their score?', 'Where does a parameter influence the overall assessment?', 'How do you scale the assessment of a parameter?', 'How do parameters interact?'

The panel were asked to start discussing the individual parameters in relation to the table of importance. They were asked where each parameter should fit into the four parameter model that was suggested. However they thought it would be better to decide first on how the parameters were to be treated and scored before trying to fit them to the model.

Low temperature was considered to be more of a problem than high temperature, giving problems with steels that become brittle at low temperatures.

Controllability was put forward as an additional parameter. If the reaction kinetics were against you, for example the presence of a highly exothermic reaction, then active control would be needed.

Corrosion was considered to be similar to the low temperature embrittlement problem. Corrosive materials could be designed for in a similar way as for low temperature processes. But if corrosive materials got into part of the plant not designed for it, or part of the plant were replaced with incorrect materials, then problems could arise. Two subsets of corrosion were suggested as 'susceptibility to air' and 'susceptibility to water'. These two were considered common enough to affect most processes.

However, no suggestions on how to score the suggested new parameters were forthcoming.

There was general disagreement that hazards would be proportional to inventory. A mixture of small inventories of several chemicals was considered more hazardous than the same total inventory of one chemical.

Several different toxicity measures were mentioned including Lethal Load (LL_{50}), Lethal Dose (LD_{50}), Maximum Exposure Limit (MEL), Short Term Exposure Limit (STEL) and Lethal Concentration (LC_{50}). The LC_{50} could be used with a fixed time for exposure of 10 or 30 minutes or a time in which somebody could physically do something to save themselves. However, a suitable measure of toxicity must have the relevant data available for all of the chemicals in the route to be of any use. The difference between short term and long term toxic hazards also needs to be considered.

As a general method to deal with some of the parameters, a series of 'Landmark values' was suggested. These would be quantitative values based on qualitative issues. For example, looking at the reaction temperature relative to chemical boiling points or flash points, to see if chemicals would flash on release.

A suggestion for dealing with inventory was to look at the chemical at ambient conditions and then modify any score for the chemical from the actual process conditions.

The problems of constructing a suitable index were highlighted. These included: deciding on 'suitable scenarios or dimensions of inherent safety', deciding landmark values relative to the chosen scenario for turning "breakpoint measures" into quantitative values, and inventing rules to do the hazard study with.

It was suggested that this type of index would fit in well between ICI's Hazards Studies 1 and 2.

5.8 Discussion and conclusions

The expert judgement/expert ranking exercise had two main aims. Firstly to obtain a ranking of the MMA routes from the experts, with which to compare the ranking from the trial inherent safety index. Secondly to elicit ideas and information from the experts on how to develop the index.

For the first aim, the two questionnaires have given rankings which are very close to that of the trial index. A very important point was raised at the meeting of the experts with regard to how the rankings from questionnaire 2 are derived. A simple assumption was made when devising questionnaire two. When the scores for the individual steps are added together to give a route score, this assumes that the steps all contribute the same weight to the route score. This is also true in the trial index. At the moment the index is a linear combination of the step scores. Some of the experts do not think this is necessarily true, as can be seen from the transcription of the meeting. Suggestions that two steps may be three times as bad as one step, were put forward. A linear relationship

between number of steps and score for the route is not always valid. It was suggested that there should be an extra score depending upon the number of steps to bias routes having large numbers of step. However, if the steps were all weighted equally, then the number of steps must be the dominating factor in comparing routes. This goes some way towards explaining the good match between our index and the questionnaire 2 rankings. But the match between the index and questionnaire 1 is also close. This implies that the experts, when completing questionnaire 1, must have been doing something similar to adding steps together to get their route rankings. In the absence of a better or simpler alternative to combining the steps, it is assumed that the steps have equal weighting and the step scores are added together.

For the second aim, the third questionnaire has provided some useful results. There was good support for the proposed index structure. There was some doubt about actually implementing some of the four parts; they may still be too subjective to be useful.

What has become clear from comments about the trial index has been coined the 'apples and pears' problem. Most of the experts agree that there are problems combining factors, or scores for factors, that are not related, for example adding scores for temperature and pressure together.

There is an additional problem in deciding which of the 'landmark values' for different parameters have the same score. For example, should a pressure of 10 bar and a temperature of 300°C both have a score of 25? The interaction of parameters is a large problem which will be considered further in developing the new index. Overall, the expert judgement exercise has produced results consistent with the first index. It has also produced many suggestions for improving the trial index.

6. CHAPTER 6 - AN IMPROVED INHERENT SAFETY INDEX

6.1 Introduction

This chapter covers the development of an improved inherent safety index. Firstly, it deals with the problems and weak areas in the trial index. Secondly, it examines the new 'four factor' index introduced in chapter 5 in more detail. It presents the idea behind the overall structure of the index, with suggestions and ideas for the individual factors. Finally, it presents the index in its present state.

6.2 Problems with the trial index

Following critical examination of the trial index, and taking into consideration the comments that the experts made both in the questionnaires and at the meeting, problems have been identified with the trial index. The weak areas of the index were identified and work done to improve them. This was aided by the suggestions made by the experts in the questionnaires and at the meeting. This section discusses some of the issues arising from the examination of the trial index.

6.2.1 Poor inventory estimation and scoring

It has been established that inventory is one of the most important factors affecting inherent safety. Therefore, reliable, estimation of inventory is important. At an early stage it is not possible to estimate it accurately. However, this in not crucial as the index is only used as a guide to choosing the inherently safest route. If the larger plant items have inventories of several tonnes, trying to calculate the inventory to the nearest kilogram is unnecessary, when what is needed is an *estimate*.

The treatment of inventory in the trial index suffers from two main problems. The first relates to the scoring table. The table is based on the graphs used by the Mond index. The trial index uses the scores for inventory divided into a scale of one to ten. The problem lies in the division of the inventory scale for the ten divisions. The inventory range for a score of one goes from 0.1 tonnes to 250 tonnes. In the scoring of the MMA routes, all the inventories for the steps came in this range. The experts recognised the problem with this table. The higher scores have inventory ranges which are almost all related to large scale storage vessels, for example refinery crude oil storage tanks.

The suggestion which came from the expert ranking exercise was to increase the scores for the range 0 - 250 tonnes. Anything above 250 tonnes was likely to be a storage vessel. For reaction vessels, 250 tonnes was to be considered the upper limit for scoring purposes. Therefore, 250 tonnes should score 10, in a revised scoring table.

The second problem is with the assumption made about reactor hold-up times. In the absence of reaction hold-up time data, a hold-up of one hour was assumed. However, based on a study of data for various reactions, reaction times vary from a few seconds to a few hours. The assumption of one hour hold-up times can lead to a reactor inventory estimate being incorrect by several orders of magnitude. Therefore, a better method to estimate the hold-up time.

Both the Dow and Mond indices treat inventory as a distinct score. This line of approach was followed in the trial index. The experts suggested that inventory should not be treated as a separate parameter. It is better to use inventory in combination with other parameters, so that the size of hazard relates directly to the inventory. This would directly relate step score to the inventory in the step. The greater the inventory of a hazardous chemical the more inherently dangerous is the step. In the new index the inventory should be used explicitly, in combination with other parameters, to give a direct measure of a hazard.

6.2.2 Simplistic division of parameter ranges and scores

A major criticism made by the experts, was that some of the parameter scoring tables were arbitrary. The experts suggested that some of the tables be modified to move the scores more or less towards the ends of the parameter ranges. For example the temperature table should be biased towards temperatures above 600° C. In order to improve these tables, a more accurate way is needed to relate the score to the value of the parameter, to reflect the influence on inherent safeness due to that parameter.

6.2.3 Methods for weighting parameters and combining parameter scores

All the scores for the parameters in the index contribute equally to a step score. 5 out of the 7 parameters in the trial index are scored out of 10. However, it was suggested in the questionnaires that the scores for parameters which exert more of an influence on inherent safety should be weighted more than less important ones. For example, obviously the score for the toxicity of a chemical should have more weight than the score for its viscosity. What was needed was some way of finding common levels of inherent safety across different parameters. One of the aims of the questionnaires, was to find out if certain parameters are more important than others. The scores for the parameters were weighted accordingly based on the perceived levels of safety and this is reflected in the new scores for the parameters.

How this weighting is applied depends upon how the parameters are scored and how the scores are combined. It could, for example, be a multiplicative factor applied to the sum of the scores from a group of parameters. An alternative is to change the range of scores for some parameters to bias the scores for the parameter higher or lower than other parameters.

An initial aim was to keep the index structure simple. Therefore the scores for the various parameters were added. Although this means that the index is simple to use, the experts agreed that simply adding together scores for disparate parameters and hazards was not appropriate. A better method was needed in which parameters of a dissimilar nature could be scored and combined together more appropriately.

Instead of giving an arbitrary score to a parameter, the parameter could be used to calculate a physical quantity. These quantities can then be compared across routes or combined together across steps. For example, it may be possible to calculate a potential blast radius for a mass of chemical, based on an equivalent mass of TNT. The total equivalent mass of TNT could be calculated for all the chemicals present and this converted into the total blast area. Alternatively, the blast area could be calculated for individual chemicals and the largest area taken. The latter method would mean that the worst chemical is used for the step score. Whichever method was used, the parameters would have a common unit of comparison, or a common quantity with which they can be combined, and not just an arbitrary score.

6.2.4 The method of combining step scores

An important point raised at the expert panel meeting, was how the scores for steps should be combined together to give a route score. The method used in the trial index is to simply add them together. It was agreed that the number of steps was a broad indicator of the complexity of the route. Therefore, if the steps all have an equal score, the number of steps is the deciding factor for which route is the inherently safest. However it was the view that there might be occasions where the score for a route with ten steps should be more than twice the score for a five step route. A factor could be included to weight the sum of the step scores, biasing routes with a large number of steps higher than routes with only a few steps. This would then be an additional measure to reflect the higher complexity of the route.

6.3 Development of the improved index

The trial index has a very simple structure consisting of adding scores looked up in tables. In order to improve the index, and to allow for its possible future expansion, it was felt that the index should have a more deterministic structure.

The new index should reflect the areas for development discussed earlier. It should be related to inventory. It should combine related parameters, either scoring them directly or by relating them to a common physical quantity. It should allow for future inclusion of additional parameters. A four factor structure was devised for the improved index.

6.3.1 Four factor structure

A four factor structure is proposed to assess the inherent safety of a route reaction or separation step with respect to the toxic or fire and explosion hazards posed by a chemical:

Inventory * Hazard Assessment * Probability of release * Effects modifier (6.17)

The '*' means 'combined with in some way' and not necessarily multiplication. These combining functions will depend upon how the factors are structured. For example, if they are all scores then addition is most appropriate, whereas if inventory is in tonnes and hazard assessment is in hazard per tonne then multiplication is more appropriate.

6.3.1.1 Inventory

This is a more rigorous estimation of the inventory of a chemical in the route step in tonnes or kilograms. In addition to the reaction steps, the inventory in storage vessels and separation steps are estimated.

6.3.1.2 Hazard assessment

This includes fire and explosion, and toxic effects. It is a quantitative assessment of how much damage could be caused for each of the three hazards, on a unit inventory basis. Combining this with the inventory would give a result which is related to both inventory and the degree of the particular hazards. It could be, for example, a T.N.T. equivalent or the Mortality index for the hazard.

6.3.1.3 Probability of release

This is derived from parameters such as propensity for runaway reaction, corrosiveness, extremes of pressure or temperature. These parameters are assessed to give a measure of the likelihood of a hazardous incident in the step. A high value would indicate that a hazardous event is more likely to happen.

6.3.1.4 Effects modifier

This quantifies how much the hazard could be amplified or attenuated by process conditions or other circumstances, for example materials used under conditions which could lead to flashing in the event of a leak, or toxic materials which are persistent, such as dioxins.

6.3.2 Inventory estimation

Inventory is recognised as a key factor influencing inherent safety. Inventory can be assessed by estimating it. However, it is not possible to do detailed estimates of the inventory because necessary data is not available, being limited to the expected yearly

output of the process, the reaction stoichiometry, and conversions and selectivity of the reactions. From this an estimate of the inventory of any major containers, that is reaction vessels, storage vessels and separation vessels must be generated. There are other sources of inventories, for example pumps, pipes and heat exchangers. However it is not possible to estimate how many pumps or heat exchangers are needed, nor their size, nor how much pipe work is needed to build the plant at the route stage. This information will only become available as the design reaches a P&ID diagram or even more detailed design. Therefore, only the major inventories in the route are estimated.

This is not to say that the minor inventories are inherently safe. The combined inventory of all the minor plant items could be quite substantial. But individual items may only have inventories of a few kilograms, compared to a reactor which may be several tonnes. It is not realistic to calculate an inventory of a few kilograms, when larger estimates may only be accurate to 500 kg.

6.3.2.1 Calculation of feed and product rates

In order to calculate the feed and product rates for each step, the yearly output expected from the plant is required along with the assumed average operating hours per year. Douglas (1987) gives the average operating hours as:

Continuous - 8150 hours/year
Batch - 7500 hours/year

From these two values the hourly production rate of the main product is calculated. To calculate the feed and product rates for the route steps, the stochiometric factors for the chemical reactions in each step, the molecular weights of all the chemicals present, and the reaction step yields are required. The calculations chain backwards through the steps, starting with the step where the main product is formed. The feed and by-products for that step are calculated. If a feed chemical is produced in a previous step, that feed rate forms the product rate in the previous step and the calculations are repeated until all feed and product rates have been calculated.

Some assumptions about recycles must be made. The information about the reaction yield, defined as the product of the conversion and the selectivity, coming from the laboratory, relates to a single pass through a reactor. This yield may be too low for economic operation of a plant. Therefore, recycles are used to increase the overall conversion of the reaction. The required overall reaction conversion is not known at the route stage. Therefore, the size of the recycle is not known.

For simplicity it is assumed that economic optimisation would tend to minimise raw material consumption which implies that there is a recycle around the reactor which gives an overall conversion of 100 %.

This assumption is made because the details for calculating recycles would only be known at the process design stage. This method represents the simplest way in which the inventory can be calculated with sufficient accuracy and is consistent with the desire for simplicity in the index. As simplicity in the overall index is important, the above can be justified because it is the best possible result that can be obtained from the data available.

Given the above assumptions, and referring to figure 6.1 below, where flows are in mass/hour, the flow **into a reaction step** is found from a mass balance:

mass of reactants in (F) = mass of products out (P) (6.18)

The flow **into the reactor**, this being the sum of feed and recycle streams, is calculated from:

mass of reactants in (F+R)= required mass of desired product out (P) / yield of reaction (X) (6.19)
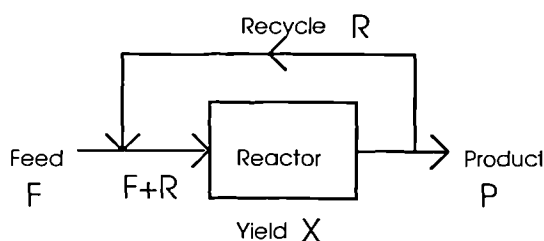
Figure 6.1 - example recycle

There will generally be more than one raw material and more than one product. A certain amount of the desired product is needed, as either the main product or as feed to the next step.

Example

The reaction in step 4 of the ACH route is:

$$CH_2 = C(CH_3)CONH_2 + CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + 2CH_3OH + H_2SO_4 \rightarrow$$
$$2CH_2 = C(CH_3)COOCH_3 + 2NH_4HSO_4$$
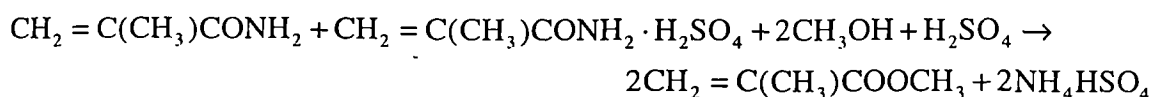
Methacrylamide (MMAm) + Methacrylamide Sulphate + Methanol + Sulphuric Acid →
Methyl Methacrylate (MMA) + Ammonium Bisulphate
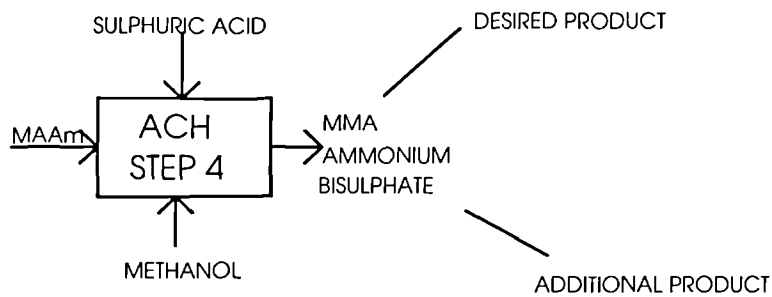
Figure 6.2 - example reaction step

A = Methacrylamide	$n_A = 1$	$M_A = 85$
B = Methacrylamide Sulphate	$n_B = 1$	$M_B = 183$
C = Methanol	$n_C = 2$	$M_C = 32$
D = Sulphuric Acid	$n_D = 1$	$M_D = 98$
E = Methyl Methacrylate	$n_E = 2$	$M_E = 100$
F = Ammonium Bisulphate	$n_F = 2$	$M_F = 115$

Table 6.1 - Molecular weights of chemicals used in example calculations

Species E is the main product, with flowrate F_E = 6.13 t/hr (based on 50000 t/year and 8150 h/year), step yield = 100%. The other flowrates are :

$F_A = 6.13 * 1 * 85 /(2 * 100) = 2.60$

$F_B = 6.13 * 1 * 183 / (2 * 100) = 5.58$

$F_C = 6.13 * 2 * 32 / (2 * 100) = 1.96$

$F_D = 6.13 * 1 * 98 / (2 * 100) = 3.00$

$F_F = 6.13 * 2 * 115 / (2 * 100) = 7.05$

where

F_x = flowrate of species x, t/hr

In this example the flowrates into the reaction step and into the reactor are the same, since the yield is 100%.

6.3.2.2 Storage

Storage is split into two categories, intermediate storage, and raw material and product storage.

Intermediate storage

Intermediate storage is placed between reaction and separation steps. It is used to help control the process (for example to act as a buffer where reactions are producing and using chemicals at different rates), to help in start-up or shut-down of the process, or simply for the convenience of the operators.

At the route choice stage of the development process, it is not possible to say where intermediate storage will be placed or how much will be needed. Decisions about intermediate storage are made at the detailed design stage, when the process flowsheet is available. In any case provision for intermediate storage goes counter to the principle of inherently safer design. Therefore, for the purpose of the index, intermediate storage is left out of the inventory estimation. If the user of the index wishes to include intermediate storage at this stage, they can use the method for raw material and product storage.

Raw material and product storage

It is important to contrast the need for raw material and product storage, which is required for logistic reasons, that is that materials cannot continually be transferred to and from a site as needed, with intermediate storage, which can be avoided.

The user of the index must decide whether a chemical is to be stored. Certain chemicals, for example hydrogen cyanide, are not stored or transported because they are extremely hazardous. In this case they would be produced on site or supplied as a by-product from another plant on site. For the case of a small production plant, this will count as additional steps in the route to be assessed. For the case of the chemical being a by-product, the inclusion of a whole separate process in the assessment would mean that the potential route would have an index equivalent to two separate routes. In this case the analysis would be done for the other plant and does not affect the new plant. Therefore it would be more sensible to say that the chemical in question is not stored and thus does not contribute a step to the index.

The conditions under which the chemicals are stored will have an effect on how much is released by a vessel leak. The worst case is pressurised storage at a temperature above the atmospheric boiling point of the chemical. A better option is liquefied storage of gases at low temperatures. However, the manner in which the chemical is stored will be decided at the detailed design stage. Therefore the worst case must be assumed and so for the purpose of assessing the potential hazard of a storage step it is assumed that *all* the contents of the vessel escape.

To calculate the potential number of deaths, the inventory of the storage vessel must be known. This will depend upon the usage or production rate, on either an hourly or daily basis, and for how long it will be stored. Once again, this decision will be taken at a more detailed design stage. However, for purposes of the new index, it is assumed that the chemicals are stored for 14 days.

After calculating all the flow rates for the reaction steps, calculate any storage inventories for raw materials and products as :

Storage inventory (kg) = 14 days * daily flow rate (kg/day)   (6.20)

This inventory is then used in the four factor calculations.

6.3.2.3 Reactor sizing

The calculated mass flow into the reaction step is used to calculate the inventory. The size of the reactor is determined by the flow rate of the material entering it and the residence time. If the residence time is not known it can be calculated using the following equation :

$$\theta = \frac{V}{F/\rho} = \frac{V}{F_A/C_A} = \frac{V}{v} = \frac{1}{S}$$ (6.21)

where

θ = reactor residence time, s

F, F_A = flowrates, total and of reactant A, kg/s

V = reactor volume, m^3

ρ = average chemical density, kg/m^3

C_A = concentration of A in feed kg/m^3

v = volumetric feed rate, m^3/s

S = space velocity, 1/s

To calculate the inventory on a mass flow basis :

$$Q = F * \theta$$ (6.22)

where

Q = inventory, kg

Example

Continuing the previous example:

Total flowrate into reactor = 2.6 + 5.58 + 1.96 + 3.00 = 13.14 t/hr

Step residence time, θ = 1 - 2 hours

Therefore required inventory for step 4 reactor is :

$$13.14 * \theta = \quad 13.14 \text{ t, for } \theta = 1$$
$$26.28 \text{ t, for } \theta = 2$$

6.3.2.4 Separation inventory estimation

In the trial index only the reactor inventory is estimated. For the new index in addition to storage inventory, it was decided to estimate the inventory of separation steps. Even if a route only has one reaction step, it is necessary to separate the products, and unreacted feed materials from each other. This could mean several separation steps, all with potentially hazardous inventories. The separation steps will have a throughput similar to that of the reaction steps, and therefore if the separation steps have similar or larger residence times, they will have similar or larger inventories. However, the separation steps will need detailed process design to determine the type of separation step required. Therefore, for the new index, some easily identifiable separation types are examined.

It was decided to estimate the inventories of distillation columns most rigorously because they represents a large proportion of separation operations. Furthermore, distillation involves an input of heat to make liquids flash, and is therefore hazardous. It was chosen as an operation which can be classed as inherently unsafe.

There are other separation processes, for example liquid-liquid separation, other vapour-liquid separations, or solids separation, for example filtration. More detailed inventory estimation for these types of separation is a future refinement of the index.

6.3.2.5 Estimation procedure

For each reaction step, first look at the yield for the step. If the yield is greater than 95%, then assume that the reactants remaining are in insignificant amounts compared to the reaction products. Therefore no separation step are required for separating products and reactants. Separation steps may still be needed if the reaction step has more than one product.

This assumes that the required purity of the product streams will be no greater than 95%, and therefore several separation steps would be needed to remove the small amounts of unwanted reactants. This is a design decision which cannot be reasonably based on the amount of information present from the routes, unless the user of the index decides otherwise.

Looking at each chemical in turn, either reactants or products, decide how the chemical may be separated. If the chemical can be separated by a simple vapour/liquid separator, for example a flash drum, let the inventory of the separation for that chemical be 5 minutes times the total mass flow of all the chemicals to be separated.

If the chemical may be separated by liquid/liquid separation or any special technique, for example aezotropic distillation, let the inventory of the separation be 15 minutes times the total mass flow of all the chemicals to be separated.

The values of 5 and 15 minutes are based on estimates from Coulson and Richardson (1985) for distillation processes.

If two chemicals may be separated by binary distillation, then use the method detailed below to calculate the inventory for the separation of the two chemicals.

As a chemical is removed from the chemicals to be separated, reduce the total mass flow to the next separation by the mass flow of the chemical last removed.

Abdon Zomosa (1983) has devised a method for the rapid sizing of columns for cost estimation. It calculates the major dimensions and flows through the column, and with the addition of a few extra steps, it is used to give an estimate of the inventory in a column, both liquid and vapour. Below is a description of the steps in Zomosa's method adapted for inventory estimation. He uses a series of nomographs to aid in the quick calculation of various equations.

Step 1 - Minimum reflux ratio

$$R_m = \left(\frac{L}{D}\right)_m = \frac{X_D\left[1 + (\alpha - 1)X_F\right] - \alpha X_F}{X_F(\alpha - 1)(1 - X_F)} \tag{6.23}$$

where

R_m = minimum reflux
α = relative volatility at top of column

X = mole fraction of more volatile component

subscript D = distillate stream

subscript F = feed stream

L = reflux rate (lb/h)

D = distillate rate (lb/h)

Assume that $X_D = 1$, that is pure distillate. This gives:

$$R_m = \left(\frac{L}{D}\right)_m = \frac{1}{X_F(\alpha - 1)} \qquad (6.24)$$

Step 2 - Optimum reflux ratio

The optimum reflux ratio occurs between $1.1 - 1.5 * R_m$. Zomosa suggests an average is 1.3 or 1.4 R_m.

$$R = 1.3 \text{ or } 1.4 * R_m \qquad (6.25)$$

where

R = reflux ratio

A value of 1.4 is used for future examples.

Step 3 - Number of trays

The number of trays at total reflux is based on the Smoker equation (1942).

Knowing X_D, X_W and α, use nomograph 1 from appendix F to give S_m.

where

S_m = number of trays at minimum reflux.

X_W = mole fraction of more volatile component in bottoms stream

Step 4 - Trays at given reflux ratio

The number of theoretical trays is based on R, R_m and S_m, and is calculated from Gilliland (1940) or Erbar-Maddox (1961) correlations, or using nomograph 2 in appendix F.

where

S = number of theoretical trays at given reflux ratio

Step 5 - Overall tray efficiency

Overall tray efficiency is given as 60 - 70%.

Step 6 - Actual number of trays

$$S_A = S / E \qquad (6.26)$$

where

S_A = actual number of trays
E = tray efficiency

Step 7 - Column vapour velocity

This is based on the Brown-Souders method (1934)

$$G = C\left[\delta_V\left(\delta_L - \delta_V\right)\right]^{0.5} \qquad (6.27)$$

where

G = allowable vapour velocity (lb/h.ft^2)
C = coefficient derived from tray spacing and liquid surface tension = 600 (ft/h)
$\delta_{L,V}$ = Liquid and Vapour density (lb/ft^3)

Step 8 - Column diameter

$$d = \left[D(R+1)/0.785G\right]^{0.5}$$ (6.28)

where

d = column diameter (feet)

Step 9 - Column vapour inventory

Coulson and Richardson (1985) give the plate spacing as 0.15m to 1m. Take 0.5m as an average value then:

$$H = SP * S_A$$ (6.29)

where

H = height of column (m)
SP = plate spacing (m)
S_A = number of plates

By simple geometry and assuming a cylindrical column:

$$I_V = H * \pi * (d/2)^2 * \delta_V$$ (6.30)

where

I_V = vapour inventory (kg)

Step 10 - Column liquid inventory

Coulson and Richardson give the plate weir height as 40 - 90 mm, take 50mm as typical. They also give the proportion of a plate which is for the down comer as 12%.

$$I_L = S_A * \pi * (d/2)^2 * H_W * A_D * \delta L$$ (6.31)

where

I_L = liquid inventory (kg)
H_W = weir height (m)
A_D = fraction of plate remaining after loss of downcomer area = (plate area - down comer area)/plate area = 0.88

The above assumes that the trays and other internals have negligible volume.

Step 11 - reflux drum and reboiler

There is also an additional inventory in the reflux drum and the reboiler. Coulson and Richardson state that the reflux drum should have between 5 and 15 minutes hold-up to allow for process fluctuations. Therefore, taking a typical hold-up time of 10 minutes, the additional inventory in the reflux drum is:

$$I_{RD} = L'/6 \qquad (6.32)$$

where

I_{RD} = reflux drum inventory (kg)

L' = reflux rate (kg/h)

For the reboiler, it is assumed that there must be sufficient inventory in the reboiler to supply the distillate and reflux vapour flow, again assuming 10 minutes hold-up time as for the reflux drum. The inventory of the reboiler is:

$$I_{RB} = (L'+D')/6 \qquad (6.33)$$

where

I_{RB} = reboiler inventory (kg)

D' = distillate rate (kg/h)

Step 12 - Total inventory

The total inventory for the column is:

$$I_{TOTAL} = I_L + L_V + L_{RD} + L_{RB} \qquad (6.34)$$

where

I_{TOTAL} = Total column inventory (kg)

The inventory of each component in the column:

$$I_x = FRAC_x * I_{TOTAL}$$

where

I_x = Inventory of component x in column (kg)

$FRAC_x$ = mass fraction of component x in feed stream (%)

This assumes the average composition of the contents of the column is equal to the feed stream.

6.3.2.6 Example

An example is given in Zomosa's paper.

Feed - 20% benzene / 80% toluene, 20000 lb/hr.
Product - 99% Benzene tops, 99% toluene bottoms (all are mass percentages)
The column operates at atmospheric pressure.

Step 1 - Minimum reflux ratio

Let A=benzene, B=toluene
A mixture of 99% benzene and 1% toluene boils at 82.2°C.
The vapour pressures of benzene and toluene at 82.2°C are:
P_A=811 mm Hg
P_B=314 mm Hg

Therefore relative volatility = 2.6
Taking a basis of 100lb of feed
Benzene in feed = 20/78 = 0.26 lb-mol
Toluene in feed = 80/92 = 0.87 lb-mol
Total feed = 0.26 + 0.87 = 1.13 lb-mol
X_F = 0.26/1.13 = **0.23**
From nomograph 1 - R_m = **3.0**

Step 2 - Optimum reflux ratio
Using eqn 6.9 - Optimum reflux ratio R = 1.4 * R_m
R = 4.2

Step 3 - Number of trays
Number of theoretical steps at total reflux

X_D=0.99, X_W=0.01, Relative volatility = 2.6
Gives S_m = **10** from nomograph 2

Step 4 - Trays at given reflux ratio

R/R+1 = 4.2/5.2 = 0.80

$R_m/R_m+1 = 3/4 = 0.75$

$S_m/S = 0.58$ from nomograph 3

$S = 10/0.58 = 17.2$

Steps 5&6 - Actual number of trays

Given efficiency = 60%

Using eqn. 6.10 - $S_A = 17.2/0.6 = 28.8$, say 29

Step 7 - Column vapour velocity

Liquid density = 50 lb/ft^3

Vapour density = 0.17 lb/ft^3

Liquid -vapour = 49.83 lb/ft^3

Eqn. 6.11 gives **G = 1700** lb/h.ft^2

Step 8 - Column diameter

The column diameter is found using nomograph 4

d= 48 in. = 1.2 m

Step 9 - Column vapour inventory

Number of plates = 29

0.5m gap between plates

Height = 0.5*29 = 14.5m

Vapour inventory = 14.5 * 0.6 * 0.6 * 3.1415 * 2.72 = 44.6 kg

Step 10 - Column liquid inventory

Liquid inventory = 28 * 0.6 * 0.6 * 3.1415 * 0.05 *0.88 * 800 = **1114.7 kg**

Step 11

Distillate rate = 1787 kg/h (from mass balance)

Reflux rate = R * D = 4.2 * 1787 = 7547.4 kg/h

Reflux drum inventory = 1787/6 = **297.8 kg**

Reboiler inventory = (1787 + 7547.4)/6 = **1555.7 kg**

6.3.3 Hazard assessment

There are three types of major hazards to be considered: fire, explosion and toxic release. They must be assessed separately, because the physical effects of each are different. Then there is the problem of combining the individual assessments in some manner, to give an overall hazard assessment.

The ideal solution would be a common measure for all three hazards. In addition, to fit in well with the four factor structure, a measure of hazard per unit inventory is preferable. This would then scale the assessment of the hazards with the inventory. The next sections cover some of the possible methods for assessing the three types of major hazard.

6.3.3.1 Marshall

Marshall (1987) gives an introduction to the problems of quantifying hazards and safety. His arguments focus on what constitutes a major hazard; for example, is it loss of life and, if so, is it one death or one hundred deaths? He gives three levels of potential hazard:

Major loss of life

There are problems in assessing loss of life, such as whether to include deaths which occur after the initial incident, for example dying from injuries several months afterwards. The total number of attributed deaths depends on how an incident has been reported.

Widespread injury

Injuries also have problems associated with them. Injuries may be categorised into major and minor injuries, thus having two levels of assessment Toxics can have long lasting effects, for example asbestosis, and thus depend upon the time span for

reporting the incident. He also asks how a crippling injury or the effects of radiation are classified.

Widespread damage

This is measured in monetary terms, that is by loss of property or insurance claims.

His conclusion is to use potential loss of life as the primary measure of the size of hazard, as this is a measure which is easily and clearly recognised.

6.3.3.2 Probit method

A probit equation (Lees, 1980) relates the intensity of a hazard, for example heat radiation, to the degree of damage which results from it. The result from a probit equation, called simply the probit, is the 'percentage of the vulnerable source which sustains injury or damage'. The general equation for a probit is:

$$Y = k_1 + k_2 \ln V \tag{6.35}$$

where
Y = probit value
V = measure of the intensity of the hazard
k_1, k_2 = constants relating to type of hazard

The constants are obtained by fitting data relating the intensity of the hazard and the degree of damage or injury.

For fires the variable used in the probit equation is

$$V = \text{Radiation intensity (W/m}^2) * \text{Time (s)} \tag{6.36}$$

Marshall gives an extensive list of equations to calculate the intensity of various types of fire. Therefore, it is relatively easy to calculate the probit value for a potential fire.

For explosions the probit variable is

$$V = \text{Peak Overpressure (N/m}^2) \tag{6.37}$$

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But this is calculated from a scaled distance which is related to the mass of explosive and the distance from the explosion, and thus the pressure is related to distance. It would be necessary first to calculate the distance at which an injury or death occurred, next to calculate the scaled distance, and from this calculate the overpressure. Finally the probit is calculated. The probit is related to distance from the explosion and thus a distance would need to chosen at which to assess the hazard which adds to the complexity.

For toxic releases, the probit variable is

$$V = \text{Concentration (ppm)} * \text{Length of time of release(s)} \qquad (6.38)$$

It is very difficult to model a toxic release. Data about the release, the prevailing weather conditions, the local geography and local population are all needed. Thus, any method used would be too advanced to be used in a simple probit calculation. The other problem is that constants for the probit equations are only available for chlorine and ammonia.

Even if the probit is easy to calculate, the result is a proportion of the vulnerable source, that is people or property, which is damaged or injured. The information about process location, local population or number of employees is not known at the route stage. Therefore the absolute number of people affected cannot be calculated. If the vulnerable source is assumed constant for all the routes, the individual problems with calculating the three probits still limit its use at the route stage.

6.3.3.3 Poblete et al

The work of Poblete, Lees and Simpson (1984) describes a short cut method for calculating the number of injuries from a given radius of a hazard. The equation derived is:

$$N_i = \pi \, r_{50}^2 \, d_p \qquad (6.39)$$

where

N_i = number of people injured

r_{50} = radius at which the probability of injury is 0.5 (m)

d_p = population density (people/m^2)

However, some of the calculations require the use of probits. The calculation of the radii, r_{50}, for hazards suffer from the problems with probits discussed above, in terms of information needed and the calculations that need to be done. The authors accept that

their method does not fit well with physical models for toxic releases. Thus it is not suitable for the simple estimates that the index requires.

6.3.3.4 Simmons et al

Simmons et al (1974) define theoretical estimates of the number of fatalities involved in crashing 90 tonne rail cars full of chlorine. This is limited in its use, as it can not be applied to other types of hazards or even other toxic materials.

6.3.3.5 Wilson approach

Wilson (1980) proposes to compare hazards using a 'damage zone'. This compares how much material is needed to damage a 1 sq km area. This may be by fire, explosion or toxic hazard. Marshall disputes its validity, because it compares directly disparate hazards. He also criticises the simple criteria used to assess each type of hazard. Wilson also tries to compare directly, the effects of both short term and long term hazards.

6.3.3.6 Mortality index

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

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

For explosives:

$$M_I = P_D \times Q^{-1/3} \tag{6.40}$$

where

M_I = mortality index, fatalities per tonne of explosive

P_D = population density in thousands per sq. km.

Q = mass of explosive, tonnes

For vapour cloud explosions and fireballs:

$$M_I = 3P_D \times Q^{-1/3} \tag{6.41}$$

where

Q = mass of flammable material, tonnes

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

Chlorine M_I = 0.5

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

Ammonia M_I = 0.02-0.052

Methyl isocyanate M_I = 12.5

The number of potential fatalities is calculated by multiplying the mortality index for the hazard by the mass of the hazardous material:

$$F = M_I * Q \qquad (6.42)$$

where

F = number of fatalities

This makes the number of *fatalities proportional to* $Q^{2 \, 3}$ *for explosions.*

The empirical equations derived by Marshall for fire and explosion are consistent with theoretical analysis of the effects of the hazard. If a fire or explosion produces a hemispherical area of effect, then:

$$r^3 \propto Q \qquad (6.43)$$

where

r = radius of effect (m)

Q = mass of fire or explosive hazard (tonnes)

The number of fatalities will depend on the circular area covered by the hemisphere. The area is proportional to the square of the radius:

$$F \propto r^2 \qquad (6.44)$$

where

F = number of fatalities (people)

Thus, combining the two equations:

$$F \propto Q^{2/3} \qquad (6.45)$$

This is the result obtained by Marshall from analysis of the data.

6.3.3.7 Radius of effect

The scale of hazards could be compared by a radius of effect. For the mass of hazardous material, a fire, explosion and toxic radius could be calculated. For fire, the radius is where the intensity of the fire would cause fatal burns to people. For explosion, the radius is where the overpressure would cause rupture of internal organs or worse. For toxics, the true radius is where the concentration in the hemisphere is equal to a lethal dose or TLV.

The problem with toxics is that a hemispherical release can not be assumed in a manner similar to a fire or explosion. The weather and other factors have a large influence in the shape of a toxic cloud when released. For fire and explosion, the radius of effect requires extensive calculations and assumptions, based on the shape of the fireball or explosion, or incident angles of radiation. This is avoided to keep the index simple to use.

6.3.4 Relating hazards to the Mortality Index

The problem with assessing the hazards is that it is difficult to compare the three types of hazard on a common scale. The effects of fires and explosions could be estimated from the mass of hazardous material using some of the methods above, and these can then give a comparable scale of hazard. But there is the problem with working out the scale of hazard for a toxic release.

A solution is to use the mortality index. Although it is based on historical data, some of it from military sources, it does give a simple figure for a hazard, that is the number of possible deaths. This puts all hazards on a comparable scale.

There is still a problem in using the mortality index for assessing toxic hazards. An alternative method is needed to deal with toxics because the mortality index only exists for four chemicals. If it was possible to find a relation between the mortality index and an alternative measure of toxicity, for example TLV or lethal doses, then this relation could be used to give the mortality index for other chemicals.

6.3.4.1 Toxicity

As an alternative to the mortality index, Marshall (1981) has suggested considering the number of lethal doses for quantifying toxic hazards. His idea is to

categorise chemicals by how much is required to produce 10^7 or 10^8 lethal doses, based on the LD_{50} value of the chemical. This represents a threshold value above which an inventory is considered a major hazard.

The LD_{50} value may be used in a slightly different way. The mass of a toxic material in a reactor or storage vessel is converted into a number of lethal doses. Assuming one lethal dose can kill one person, then toxic hazards can be compared. Furthermore toxic hazards can be directly compared with fire and explosion hazards, because both are then measured by the number of deaths.

The LD_{50} value is a dose, expressed in milligrams per kilogram of body weight, which will kill 50% of an exposed population. It is quoted for various animals, including rats and mice, and for varying methods of application, for example oral dosage or skin application.

An assumption is now made which must be viewed in light of what the index is aiming to achieve. The assumption is that the doses used on the test animals scale up to give the same effects on humans. This assumption must be treated with caution. Some chemicals cause different effects in humans than in test animals. The benefit in making this assumption, is that masses of hazardous chemicals can be converted to numbers of doses that would have a certain effect on a human.

The number of possible human lethal doses is:

$$PLD = \frac{Q}{M_H \cdot LD_{50}} \qquad\qquad (6.46)$$

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

A scaling function or factor may be necessary, as an example shows:

The number of lethal doses from 1 tonne of formaldehyde, $LD_{50} = 800$ mg/kg :

PLD = 1,000,000,000 / (70 * 800) = 17857.1

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

Comparing the mortality index of the chemicals that Marshall has calculated, with the LD_{50} values in the graph below (Methyl isocyanate has been left out as the mortality index is calculated from only one incident, where there was a very high population density near to the plant), it is possible to derive a relationship.
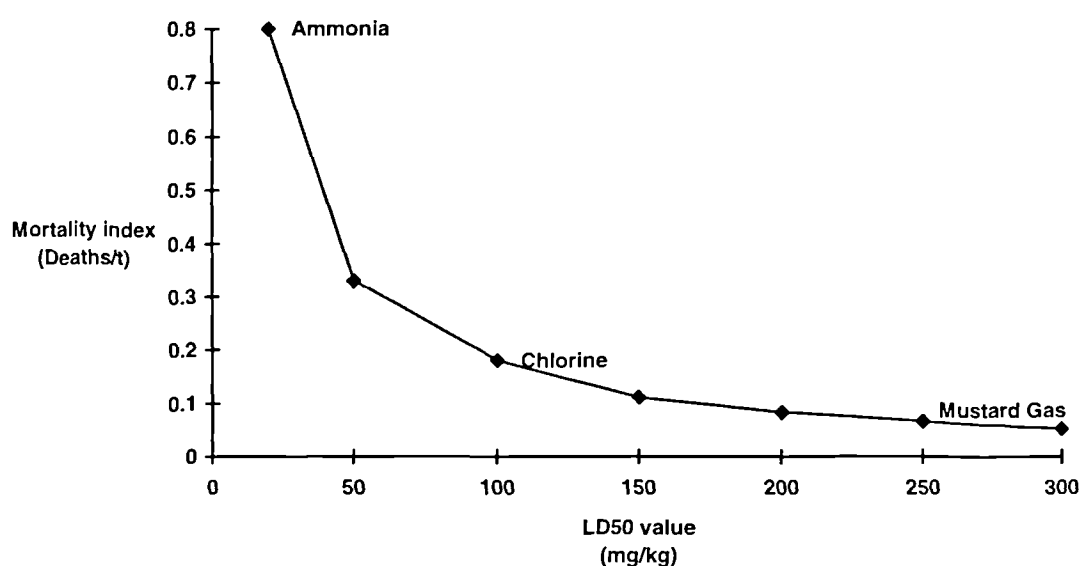
Figure 6.3 - graph of LD50 versus mortality index

If a straight line is fitted through the data points, it would intercept the x-axis between 200 and 400 mg/kg. This would imply that any chemical with an LD_{50} value greater than 400 has a mortality index of zero. This cannot be so, because the chemical would kill someone if given in sufficient quantity. The graph, and the problem suggest an inverse relationship between LD_{50} and mortality index. As the value of the LD_{50} decreases, representing increasing toxicity, the value of the mortality index should increase. A linear relationship would have intercepts on both axes, representing limits of LD_{50} and mortality index.

A better model is to assume that the curve becomes asymptotic to both axes. As the toxicity decreases, and the LD_{50} value increases, the mortality index should approach zero, when a chemical becomes nontoxic. Moving in the opposite direction there is a

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limit on LD_{50} which is that of the most toxic substance available and the curve will be asymptotic to this value. Practically this would be zero as the LD_{50} of very toxic materials approach zero. Therefore, based on the above assumptions, a possible relationship between LD_{50} and mortality index is:

$$LD_{50} * \text{Mortality Index} = \text{Constant} \qquad (6.47)$$

Using the information from the graph above, a suitable constant can be estimated.

Chemical	LD_{50} (mg/kg)	Mortality index (deaths/t)	LD_{50} * Mortality index
Ammonia	300	0.052	15.6
Chlorine	100	0.18	18.0
Mustard gas	20	0.8	16.0

Table 6.2 - Sample data for toxicity relationship

The average value of LD_{50} * mortality index is 16.5. Therefore the relationship :

$$LD_{50} * \text{Mortality Index} = 16.5 \qquad (6.48)$$

can be used to give an estimate of the mortality index for a chemical, knowing its LD_{50} value.

There is another small problem with some chemicals. Some are classed as simple asphyxiants. They do not do any chemical damage to the body but simply deprive it of oxygen. In order for harm to come to someone, they would have to be placed in an atmosphere consisting of a high proportion of the asphyxiant. This is not a problem if a large amount of an asphyxiant escapes into the atmosphere, but is more likely to kill people in enclosed spaces, for example during maintenance of vessels. Therefore, it is not possible to calculate the mortality index or the number of deaths that could occur from asphyxiants, but there may not be as many compared to an explosion or toxic release.

6.3.4.2 Fires

To calculate the mortality index for a fire, the mass of flammable material that will contribute to the hazard is needed. The total inventory of the reactor or vessel can be used, but to be more accurate, the mass of flammable vapour produced should be used. This assumes that the vessel is under conditions where a proportion of any liquid in it will flash off when a leak or failure occurs. If the vessel is full of vapour then all of it will escape. King (1990) gives an equation for calculating the amount of flammable

vapour that will be produced immediately from a liquid at a temperature above its atmospheric boiling point:

$$Q_V = \frac{2Q_L C_P (T_1 - T_2)}{H_V}$$ (6.49)

where

    Q_V = mass of flammable vapour released (kg)

    Q_L = mass of liquid (kg)

    C_P = specific heat at $(T_1 + T_2)/2$ of liquid (kJ/kg.°C)

    T_1 = liquid temperature (°C)

    T_2 = atmospheric boiling point of liquid (°C)

    H_V = heat of vaporisation of liquid at T_2 (kJ/kg)

The quantity of vapour released is arbitrarily doubled to allow for entrainment of liquid spray. The maximum mass of vapour is equal to the mass of liquid. For liquefied flammable gasses with boiling points below ambient temperature:

$$Q_V = Q_L$$ (6.50)

6.3.4.3 Explosions

For explosions involving flammable liquids or materials other than recognised explosives, a measure of the explosive capability is needed for the mortality index calculation. The quantity of flammable material available to explode, Q_V, is first calculated as for fires.

King gives a further equation to calculate the TNT equivalent of the mass of flammable vapour:

$$Q_E = \frac{Q_V H_C f}{H_{TNT}}$$ (6.51)

where

    Q_E = equivalent mass of TNT (tonnes)

    H_C = heat of combustion of vapour (kJ/kg)

    f = explosive yield factor

    H_{TNT} = heat of combustion of TNT = 4652 (kJ/kg)

The explosive yield factor is based on studies of vapour cloud explosions, and is taken as 0.05. This allows for vapour which burns before the main explosion and other vapour which escapes from the cloud.

6.3.5 Combined fire and explosion

In the new index, fire and explosion are treated as one hazard and not considered as separate hazards. The reason for this is as follows. Explosions are considered to be internal explosions, that is explosions which occur inside reaction vessels or other plant items. This may be caused by a runaway reaction or a thermal decomposition of a chemical. It could also be a rapid overpressure of the vessel, which is too great for any pressure relief equipment. The important factor is that it leads to a rupture of the vessel or plant item. This event may be violent enough to cause injury or death. This is often due to fragments of the plant item forming missiles which hit people. However, the injuries and damage caused by this type of explosion will be localised in effect, perhaps only within tens of metres of the plant item. The more important result is that the plant item is now releasing its contents.

When a release occurs a flammable vapour cloud will form. If this cloud explodes, the effects will, in general, be much greater than those of an internal explosion. Large vapour cloud explosions can destroy much of a chemical plant, and possibly have effects outside the plant boundary. It is this difference in the magnitude of effect between internal explosions and vapour cloud explosions which lead to the index only considering vapour cloud explosions.

When calculating the size of the possible vapour cloud, the amount which flashes off is only dependent on the process conditions and the physical properties of the chemicals. There is no additional allowance for material which evaporates due to additional heat from fires in the ruptured plant item, because the amount of heat generated is difficult to estimate.

6.3.6 Probability of release

The first two factors of the proposed structure estimate a measure of the effect of a possible hazardous event, in terms of a number of possible deaths. The third factor, probability of release, is derived from parameters which influence the likelihood of a release occurring.

In both this factor and the effects modifier factor, scores are assigned to the various parameters in each factor. As discussed earlier in this work, most of the scores for the trial index and the developing index are based arbitrarily. The scores are not the

final scores for the index. They are scores which are intended to be modified as the index is used and developed. Thus it is not intended to imply that because two parameters have the same score for particular values, that they represent an equal level of inherent safety. The relative scores between parameters is based on the relative importance of the parameters as judged by the experts in the expert judgement exercise.

6.3.6.1 Temperature

The initial idea about temperature as a parameter, which lead to the scoring table in the trial index, was that temperature indicated the heat energy content of a system, and thus the higher the temperature the greater is the likelihood of a hazardous event occurring.

Liquids at higher temperatures are more likely to be hazardous by being turned into vapour or a flashing liquid, or by exceeding the temperature where a runaway reaction may occur. Both high and low temperatures may necessitate using-non-standard materials of construction in the plant giving scope for error. If plant items are replaced with ones which are not designed for the temperature range, problems can occur. The temperature of a reaction in one step may also affect the steps around it. Therefore, the temperature of the reaction step should have a score assigned to it, which reflects the need for special materials of construction and the scope for error that this introduces.

Both Dow and Mond indices have a method for assessing the flammability of a material. This gives a relative assessment of how flammable a material is. However, it does not mean that the material is in a hazardous state, that is the material may not be at a temperature above its flash point. It is more important to compare the process temperature with the materials flammable properties. For example:

Process temp. > Auto ignition temperature
      worse than
Process temp. > Boiling point
      worse than
Process temp. > Flash Point
      worse than
Process temp. < Flash point

To some extent, a material which will flash has been dealt with in the hazard assessment parts. However, if the material is above its auto ignition temperature, a score should be assigned to reflect this possible danger.

6.3.6.2 Pressure

The basis for the pressure scoring table in the trial index is similar to that for temperature, that is, high pressure implies high potential energy content. Even if vessels are designed to deal with these pressures, a high pressure can make a release more likely.

Both the Dow and Mond indices state that design standards change for pressure vessels above 3000 psi. The scoring table in the trial index was based on the charts from the Mond index, which increased more steeply after 3000 psi. The Dow index has a score that increases up until 3000 psi. It then has a constant score for 3000 - 10000 psi, and another highest score for anything over 10000 psi. The pressure scoring table has been amended to account for these changes in design standards. The range up to 3000 psi is based on the graph from the Mond index. For example:

Pressure PSI			Score
0	-	75	1
75	-	100	2
100	-	150	3
150	-	200	4
200	-	300	5
300	-	400	6
400	-	600	7
600	-	850	8
850	-	1500	9
1500	-	3000	10
3000	-	10000	15
10000	+		20

Table 6.3 - example scoring table for pressure

High pressure is also detrimental when leaks occur. It makes the leak rate higher, and in the case of pressurised storage of liquefied gases, can lead to rapid formation of explosive clouds. Lees (1980) gives a graph to show how pressure difference affects mass flow through an orifice, for gases, vapours and liquids. The calculations of actual flowrates from ruptured vessels are very extensive. The pressure difference, contents of the vessel, shape and size of the orifice all effect how to calculate the flowrate and type of flow. Because the calculations are complicated, in the interest of simplicity estimation of leak rates is not included in the index.

6.3.6.3 Exothermic and endothermic reactions

Both the Dow and Mond indices have a factor for the type of reaction occurring, but they do not give any values, in terms of joules per gram, for the exotherm of the

reaction. King (1990) states values of the heat of reaction for various types of reaction. There are some inconsistencies between the two sources. Some types of reaction are grouped differently in the Dow and Mond indices than by King. However, the groups due to King are more useful, as he assigns ranges of exotherm values to each group. The groups are:

$\Delta H_R \leq$ -3000 kJ/kg - extremely exothermic, for example: direct oxidation of hydrocarbons, chlorination reactions, ethylene polymerisation

-1200 $\geq \Delta H_R >$ -3000 kJ/kg - strongly exothermic, for example: nitration, propylene, styrene, butadiene polymerisation

-600 $\geq \Delta H_R >$ -1200 kJ/kg - moderately exothermic

-200 $\geq \Delta H_R >$ -600 kJ/kg - mildly exothermic, for example: condensation and polymerisation reaction of molecules 60-200 M.W.

200 $\geq \Delta H_R >$ -200 kJ/kg - thermally neutral, for example: aqueous reactions forming precipitates, esterification between organic acids and alcohols

$\Delta H_R >$ 200 kJ/kg - endothermic, for example: cracking and dehydrogenation of hydrocarbons, metal oxide reduction

Example scores are shown below:

Heat of reaction / Extent of exotherm	Score
$\Delta HR \leq$ -3000 kJ/kg - Extremely exothermic	20
-1200 $\geq \Delta HR >$ -3000 kJ/kg - Strongly exothermic	15
-600 $\geq \Delta HR >$ -1200 kJ/kg - Moderately exothermic	10
-200 $\geq \Delta HR >$ -600 kJ/kg - Mildly exothermic	5
200 $\geq \Delta HR >$ -200 kJ/kg - Thermally neutral	0
$\Delta HR >$ 200 kJ/kg - Endothermic	5

Table 6.4 - example scoring table for heat of reaction

6.3.6.4 Chemical and reaction stability

Any instability in the reaction which is inherent, as opposed to caused by variations in the process conditions, increases the chance of a hazard occurring.

There are certain classes of chemicals which are considered to be unstable. An obvious example is explosives. To a lesser extent, any chemical which is self oxidising

presents a hazard, for example peroxides. Any chemical in a route, which presents a hazard by itself, should be highlighted and scored according to the degree of potential instability. Unfortunately, there is no measure of chemical stability. However, as the experts considered chemical stability to be a very important parameter, a maximum score of, for example, 20 can be assigned to unstable chemicals.

In a similar manner, potentially unstable reactions can be identified. A good example is partial oxidation reactions. These have the potential to become a full oxidation and therefore cause a release.

A similar problem was brought out in the expert panel discussion. A measure of controllability of the reaction was proposed as a parameter. It was intended to highlight difficult to control reactions, or reactions which could easily runaway. Reactions operating close to the conditions at which runaway could occur were classed as potentially hazardous. King classes a reaction which can have a 300°C temperature rise as a hazard.

In addition to highlighting unstable chemicals, any reactions which are classed as unstable, or operate close to a point at which they can become unstable, should be quantified according to the degree of potential instability. This is an area which would benefit from more extensive research, that is beyond the scope of this present work. For the present, the scoring is left up to the user of the index, again with a maximum score of, for example, 20.

6.3.6.5 Corrosiveness

Corrosion can lead to weakness, and eventually holes, in plant items, which in turn lead to leaks and releases of material. Corrosion is not a problem if the plant items are constructed from suitable materials. However, if unsuitable materials are used for a section of the plant, or plant items are replaced with ones made of unsuitable material, corrosion problems will arise. Certain chemicals are highly corrosive, for example strong acids, oxidising agents, or halogens. If any highly corrosive chemicals are present, highlight these and assign a score up to a maximum of , for example, 5.

At the panel meeting it was pointed out that hydrogen chloride (HCl), when dry, will not attack mild steel. However, if a small amount of water is present, mild steel is rapidly attacked by HCl. Similar corrosion problems can occur when water forms an electric pathway between metals of different electric potential. It was suggested that there should be a parameter which indicated the 'susceptibility to water'. The same was suggested for air, that is any situation where air enhanced the effects of corrosive materials should be penalised. Therefore, situations where air or water can increase or

start corrosion, should be recognised and assigned a score up to a maximum of, for example, 5.

6.3.6.6 Probability of release from storage

Compared to reaction steps, storage steps are low risk (Lees, 1980). There is no heat input or output, or heat generation. Generally storage conditions are less severe than reaction conditions. Therefore the probability of a release from storage is much less than that from the process. However, the inventory of storage steps is considerably greater than process steps. The large amounts of chemicals in storage can not be ignored because they are relatively unlikely to be released. There is always public concern over large storage vessels in chemical plants. Although storage vessels themselves are low risks compared to process steps, they are at risk from process related hazards, because of their proximity to the process.

It is possible to estimate the probability of a release from storage from a more detailed design of a process. However at the route stage there is insufficient information to estimate a likelihood of release. Therefore, in order that the large number of possible deaths from storage steps is not reduced by a very small probability of release factor, it is assumed that the probability of release factor is one for storage steps. This reflects the large scale hazard that storage inventories represent.

The probability release factor is defined as:

$$F_{POR} = \frac{\text{Sum of probability of release scores for the step}}{\text{Maximum possible probability of release score for step}} \quad (6.52)$$

If all the parameters contribute their maximum score, the factor has a value of 1. Theoretically this implies that a release will occur, but practically it indicates that the step is very hazardous and is very likely to cause a release.

The maximum possible score is 105. For storage steps, let $F_{POR} = 1$ assuming that all the contents is released.

6.3.7 Effects modifier

In the fourth factor, the parameters modify the assessment of the inherent safety. They reflect physical or chemical properties, which may influence how a chemical acts after release or how a process behaves after malfunction. The same point raised earlier in the probability of release factor about the basis for parameter scores applies to the effects modifier.

6.3.7.1 Flammability limits

In the first index the measure of flammability was found by taking the difference between upper and lower flammable limits. This was based on the assumption that a large flammable range is undesirable. The experts suggested using the lower limit, because this indicates flammable materials from the viewpoint of chemical releases.

A different suggestion was also raised in the questionnaires. Most flammable chemicals have very similar flammable ranges. Instead of scoring the size of the range, score the step if the reaction occurs within the flammable range of any chemical in the step.

6.3.7.2 Vapour density

The buoyancy of a gas effects its dispersion characteristics and the formation of explosive or toxic clouds. Some gases, for example hydrogen, are very buoyant and therefore disperse quickly. Others, for example carbon dioxide or hydrogen fluoride, are very dense gases and tend to stay at ground level, forming pockets of gas which are slow to disperse.

Dispersion of gases and vapours is good for inherent safety. The density of air can be taken as a breakpoint for scoring. For example:

Gas or vapour density << density of air - good, gas disperses - score -10

Gas or vapour density $\approx$ density of air - score 5

Gas or vapour density > >density of air - bad , poor dispersion - score 20

6.3.7.3 Chemical odour and colour

Some chemicals have distinct odours or colours. This is a benefit if any escapes from a vessel. The effects of large releases are decreased if the chemical can be detected and thus the chance of taking evasive action is increased. This does not necessarily apply to all toxic chemicals. If the chemical is highly toxic, the sniff which identifies it may be enough to kill. But for some of the less toxic chemicals, which require a large dose, any indication of its presence can be helpful. It must be assumed that the majority of chemicals are clear or odourless. Therefore chemicals with colour or odour should be scored as a benefit to the step. For example:

Clear or odourless gases - no score.

Strong odours or colour in gas - score -5

6.3.7.4 Mixing and viscosity

This is related indirectly to the heat of reaction and reactor control. Poor mixing can cause hot spots in reactors or poor heat transfer in heat exchangers. Then a runaway

reaction might develop. High viscosity would imply a poor mixing or dispersion hazard. Sulphur is a good example of the problems that can occur with viscosity. At 135 -140°C the viscosity of sulphur is 8cp, but at only 170°C it increases to 4500cp.

Immiscible liquids, if not mixed adequately or if mixing is stopped, can form layers. If mixing is then applied, an instantaneous reaction can occur which produces more heat than is normally removed by a cooling circuit and this can lead to an overpressure of the reactor.

It is not logical to score the viscosity of chemicals in a scoring table. It is difficult to assess the inherent danger of one chemical being twice as viscous as another. However, in the case of sulphur, if a chemical goes from a consistency of warm cooking oil to that of thick treacle, problems can occur. It is better to penalise steps where mixing problems, or chemicals with viscosity problems, occur. For example score 5 for a chemical which gives mixing problems.

6.3.7.5 Waste and by-products

This parameter is included because more waste and by-products imply greater inventory and complexity, although in other contexts environmental aspects are clearly important. It is important to reduce the inventory and complexity of plants. If a process is making waste material or by-products in equal or greater proportions to the required product, this must be more inherently unsafe than a process which makes a small amount of waste in proportion to required product, for the same product flowrate. The former process will have larger reactors and larger separation steps. The ratio of the amount of waste and by-products produced per tonne of product can indicate the efficiency of the process. For example the higher the ratio, the higher the score.

The effects multiplier factor is defined as:

$$F_{EM} = 1 + \frac{\text{Sum of effects modifier scores for the step}}{\text{Maximum possible effects modifier score for step}} \qquad (6.53)$$

The maximum score for the factor is 2. The score may be less than one, indicating that certain parameters are beneficial to the inherent safety. The maximum score is 55. For storage and separation steps, let $F_{EM} = 1$

6.3.8 Parameter combination

In the first index, it was decided not to consider the combination of parameters, as the structure was too simple. In developing the new index, there is some combination of parameters. There is interaction between inventory (the first factor) and measures of

flammability and explosiveness, and toxicity, for the second factor. These parameters are combined to give a common measure of number of potential deaths for a hazard.

However, with the other parameters in the index, there is still the problem that they are scored individually and then the scores are combined. However, unlike the scoring of parameters for the trial index, the scores for parameters in the new index are based on the order of importance from the expert ranking.

6.3.9 3 or 4 factor index?

For calculating the number of deaths from a toxic release, the index uses four factors - Inventory, Hazard coefficient, Probability of release and Effects modifier. For calculating the number of deaths from fire and explosion, it could be viewed as using only three factors. The probability of release factor, effects modifier factor and inventory factor are as described. However, the hazard coefficient factor includes the inventory in calculating the mortality index. Therefore the first two factors, inventory and hazard coefficient, could be combined into one factor. This would make the number of deaths proportional to inventory$^{2/3}$ instead of proportional to inventory . More accurately, the result for a step is proportional to the (TNT equivalent, of the flash fraction, of the step inventory)$^{2/3}$. The inventory is calculated in the first factor, but instead of being multiplied by the second factor, is used in the second factor.

6.4 New index

The following is a stage by stage breakdown of how to calculate the new index for a chemical route.

Stage 1 - breakdown of route into steps

Break down the route into reaction steps. This will be one for each potential reactor, but if two or more reactions could occur in the same reactor by a change in the reaction conditions, then treat them as separate reaction steps.

Stage 2 - flowrate calculation

Working backwards through the steps, from the last step, calculate the flowrates of all chemicals present, including feed and product streams using the method described in the section "Calculation of feed and product rates". Use equation 6.18 for flows between steps and equation 6.19 for flows into reactors.

Stage 3 - which materials are stored?

For each reaction step, decide which raw materials are stored or piped in. If a chemical is supplied from a purpose built plant, include the additional reaction steps in the route. If the chemical is a by-product from a separate process, do not add extra steps.

Stage 4 - storage inventory calculation

For each chemical which is stored, use the method described in the section "Storage" to calculate the inventory of the storage vessel.

Stage 5 - number of possible deaths

For each stored chemical, calculate the Fire and Explosion deaths and Toxicity deaths, using the methods detailed below in section 6.4.1 assuming loss of the total inventory. Let these totals be NOD_{FE} and NOD_{TOX} respectively.

Stage 6 - reactor inventory calculation

For each reaction step, calculate the reactor inventory using the method described in the section "Reactor sizing". Calculate the mass fraction of each reactant and product in the reactor from the reaction yield.

Stage 7 - number of possible deaths

For each chemical, in each reaction step, calculate the Fire and Explosion deaths and Toxicity deaths using the method described below in section 6.4.1. Let the highest totals from all the chemicals in a step be NOD_{FE} and NOD_{TOX} respectively for that step.

Stage 8 - probability of release calculation

For each reaction step, calculate the probability of release scores, and effects modifiers scores using the method described below in sections 6.4.2 and 6.4.3.

Stage 9 - necessary separations

For each reaction step, decide what type of separations are necessary or are to be sized.

Stage 10 - separation inventory calculation

For each separation step, calculate the inventory using the methods described in the section "Separation inventory estimation". Calculate the mass fraction of each of the chemicals in the stream which are to be separated using the reaction yield.

Stage 11 - number of deaths

For each chemical, in each separation step, calculate the Fire and Explosion deaths and Toxicity deaths using the method described below in section 6.4.1. Sum the Fire and Explosion deaths and Toxicity deaths for all the chemicals. Let these totals be NOD_{FE} and NOD_{TOX} respectively.

Stage 12 - probability of release factor

For reaction steps let the Probability of Release factor for a reaction step, F_{POR}, be:

$$F_{POR} = \frac{\text{Sum of probability of release scores for the step}}{\text{Maximum possible probability of release score for step}} \quad (6.54)$$

Maximum score = 105

For storage steps, let $F_{POR} = 1$

Stage 13 - effects multiplier factor

For reaction steps let the Effects Multiplier factor for a reaction step, F_{EM}, be:

$$F_{EM} = 1 + \frac{\text{Sum of effects modifier scores for the step}}{\text{Maximum possible effects modifier score for step}} \quad (6.55)$$

Maximum score = 55

For storage and separation steps, let $F_{EM} = 1$

Stage 14 - fire and explosion deaths for each step

Let the modified number of Fire and Explosion deaths for a step, $MNOD_{FE}$, be:

$$MNOD_{FE} = NOD_{FE} * F_{POR} * F_{EM} \quad (6.56)$$

Stage 15 - toxicity deaths for each step

Let the modified number of Toxicity deaths for a step, $MNOD_{TOX}$, be:

$$MNOD_{TOX} = NOD_{TOX} * F_{POR} * F_{EM} \quad (6.57)$$

Stage 16 - route totals

Let the total potential number of Fire and Explosion deaths for the route be:

$$\sum_{\text{ALL STEPS}} MNOD_{FE} \quad (6.58)$$

Let the total potential number of Toxicity deaths for the route be:

$$\sum_{\text{ALL STEPS}} MNOD_{TOX} \quad (6.59)$$

These two values are the index values for the route.

6.4.1 Method for calculating possible number of deaths for a route step

	FIRE & EXPLOSION		TOXICITY
STEP		STEP	
1	INVENTORY	1	INVENTORY
2	DEGREE OF FLASH	2	DEGREE OF FLASH
3	CONVERT TO TNT	3	LD_{50} DOSES
4	MORTALITY INDEX	4	POSSIBLE DEATHS
5	POSSIBLE DEATHS		
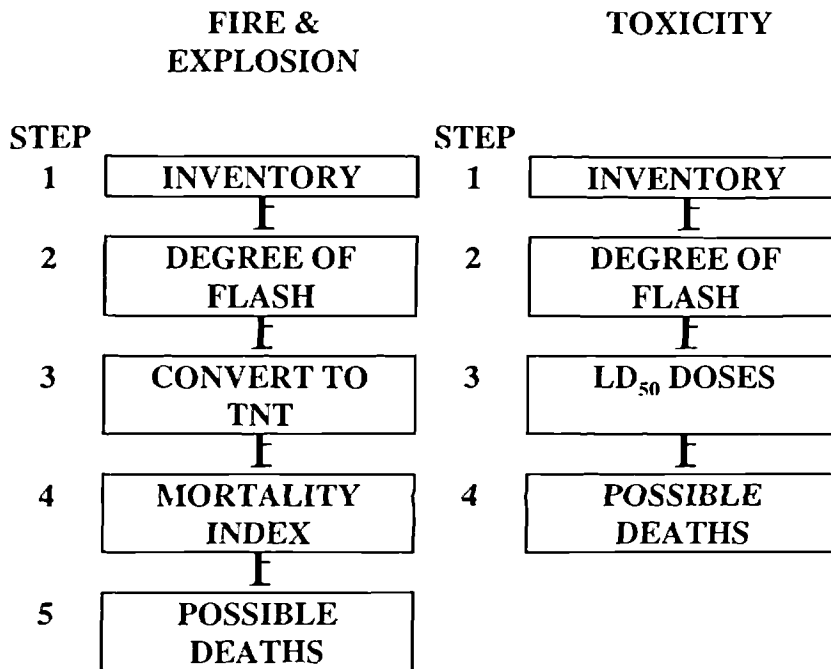
6.4.1.1 Fire and Explosion - number of possible deaths

6.4.1.1.1 Step 1 - Inventory

Use the inventory calculated in stage 4 for a storage step, stage 6 for a reaction step, and stage 10 for a separation step.

6.4.1.1.2 Step 2 - Degree of flash

Calculate how much of the chemical will flash off if a release occurs using:

$$Q_v = \frac{2Q_c \cdot C_p \cdot (T_1 - T_2)}{H_v}$$

(6.60)

where

Q_V = mass of flash vapour, kg

Q_c = mass of chemical in reactor, storage or separation, kg

C_p = specific heat capacity, kJ/kg.°C

T_1 = liquid temperature, °C

T_2 = atmospheric boiling point, °C

H_v = heat of vaporisation at T_2, kJ/kg

6.4.1.1.3 Step 3 - Convert to TNT

For each chemical in the reactor, convert its flashing inventory to an equivalent mass of TNT using:

$$Q_e = \frac{Q_V \cdot H_C \cdot f}{H_{TNT}}$$

$\hspace{10cm}$ (6.61)

where

Q_e = equivalent mass of TNT, kg

Q_V = mass of flashing vapour, kg

H_C = heat of combustion of chemical, kJ/kg

f = explosive yield factor = 0.05 (5%)

H_{TNT} = heat of combustion of TNT, 4652 kJ/kg

6.4.1.1.4 Step 4 - Mortality index

Calculate the mortality index for the equivalent mass of explosive using:

$$M_I = P_D \times Q_e^{-0.333}$$

$\hspace{10cm}$ (6.62)

where

M_I = mortality index, fatalities per tonne

P_D = population density in thousands per sq. km

Q_e = equivalent mass of explosive, tonnes

Take P_D = 0.85 (based on average population density around chemical plants) (Marshall, 1987), or the actual value if known for the location.

6.4.1.1.5 Step 5 -Number of possible deaths

Calculate the number of possible deaths from the mortality index using

$$NOD_{FE} = Q_e \times M_I$$

$\hspace{10cm}$ (6.63)

where

NOD = number of deaths

M_I = Mortality index, fatalities per tonne

Q_e = equivalent mass of explosive, tonnes

6.4.1.2 Toxicity - number of possible deaths

6.4.1.2.1 Step 1 - Inventory

Use the inventory calculated in stage 4 for a storage step, stage 6 for a reaction step, and stage 10 for a separation step.

6.4.1.2.2 Step 2 - Degree of flash

Calculate how much of the chemical will flash off if a release occurs using:

$$Q_V = \frac{Q_c \cdot C_p \cdot (T_1 - T_2)}{H_v} \qquad (6.64)$$

where

Q_V = mass of flash vapour, kg

Q_c = mass of chemical in reactor, kg

C_p = specific heat capacity, kJ/kg.°C

T_1 = liquid temperature, °C

T_2 = atmospheric boiling point, °C

H_v = heat of vaporisation at T_2, kJ/kg

6.4.1.2.3 Step 3 - Mortality index

Calculate the mortality index from the chemicals LD50 value using :

$$LD_{50} * M_I = 16.5 \qquad (6.65)$$

where

LD_{50} = Lethal dose, mg/kg

M_I = mortality index, fatalities per tonne

6.4.1.2.4 Step 4 - Number of possible deaths

Calculate the number of possible deaths from mortality index using

$$NOD_{TOX} = Q_V \times M_I \qquad (6.66)$$

where

NOD = number of deaths

6.4.2 Method for calculating probability of release score for a reaction step

PROBABILITY OF RELEASE

```
┌─────────────────────┐
│      HIGH/LOW        │
│   TEMPERATURE        │
└─────────────────────┘
          +
┌─────────────────────┐
│      CORROSION       │
└─────────────────────┘
          +
┌─────────────────────┐
│     DEGREE OF        │
│     EXOTHERM         │
└─────────────────────┘
          +
┌─────────────────────┐
│      CHEMICAL        │
│     STABILITY        │
└─────────────────────┘
          +
┌─────────────────────┐
│   PROCESS TEMP.      │
│      > AUTO          │
│  IGNITION TEMP       │
└─────────────────────┘
          +
┌─────────────────────┐
│      PRESSURE        │
└─────────────────────┘
```
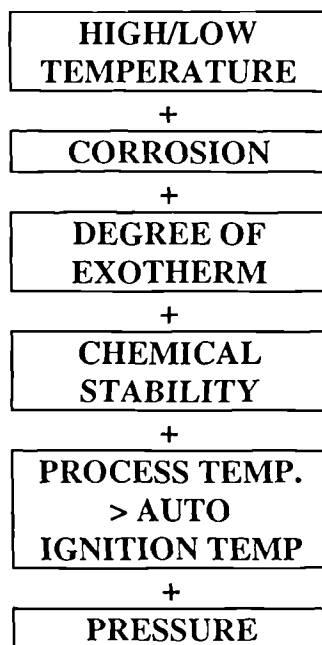
6.4.2.1 High/Low temperature

Use the table below to score the temperature.

Temperature range (°C)				Score
	T	<	-25	5
-25	≤ T	<	600	0
600	≤ T	<	700	4
700	≤ T	<	800	8
800	≤ T	<	900	12
900	≤ T	<	1000	16
1000	≤ T			20

Table 6.5 - Temperature scoring table

6.4.2.2 Corrosion

Are any of the chemicals present corrosive?

Score 5 points for yes

Do any chemicals present become highly corrosive upon ingress of either air or water?

Score 5 points for yes

6.4.2.3 Degree of exotherm

For the reaction step assign a score based on the step heat of reaction.

Heat of reaction / Extent of exotherm	Score
<= -3000 kJ/kg - Extremely exothermic - direct oxidation of hydrocarbons, chlorination reactions, ethylene polymerisation	20
<= -1200 > -3000 kJ/kg - Strongly exothermic - nitration, propylene, styrene, butadiene polymerisation	15
<= -600 > -1200 kJ/kg - Moderately exothermic	10
<= -200 > -600 kJ/kg - Mildly exothermic - condensation and polymerisation reaction of molecules 60-200 M.W.	5
<= 200 > -200 kJ/kg - Thermally neutral - aqueous reactions forming precipitates, esterification between organic acids and alcohols	0
>200 kJ/kg - Endothermic - cracking and dehydrogenation of hydrocarbons, metal oxide reduction	5

Table 6.6 - degree of exotherm scoring table

6.4.2.4 Unstable chemicals or reaction

Are there any highly unstable chemicals present in the reaction or is the reaction difficult to control?

Score 20 points for yes

6.4.2.5 Auto ignition

Is the process temperature above the Auto ignition temperature of any chemicals in the step?

Score 20 points for yes

6.4.2.6 Pressure

Use the table below to score the pressure.

Pressure PSI			Score
0	-	75	1
75	-	100	2
100	-	150	3
150	-	200	4
200	-	300	5
300	-	400	6
400	-	600	7
600	-	850	8
850	-	1500	9
1500	-	3000	10
3000	-	10000	15
10000	+		20

Table 6.7 - pressure scoring table

6.4.3 Method for calculating effects modifier score for a reaction step

EFFECTS MULTIPLIERS

FLAMMABLE LIMITS

+

VAPOUR DENSITY

+

WASTE/BY PRODUCTS

+

ODOUR/COLOUR

+

MIXING/VISCOSITY

6.4.3.1 Flammable limits

Does the reaction occur within the flammable limits of any chemicals present?

Score 20 points for yes

6.4.3.2 Vapour density

Are there any gases or vapours whose density is greater than air?

Gas or vapour density << density of air - score -10

Gas or vapour density ≈ density of air - score 5

Gas or vapour density > >density of air score 20

6.4.3.3 Waste and by-products

Is the mass of waste products 5 or more times greater than the mass of product?

Score 10 points for yes

Is the mass of waste products between 1 and 5 times greater than the mass of product?

Score 5 points for yes

6.4.3.4 Odour and colour

Are any highly toxic chemicals strongly odoured and/or coloured?

Score -10 points for yes

6.4.3.5 Mixing and viscosity

Are there any problems which can arise due to poor mixing of chemicals or the viscosity of any chemicals?

Score 5 points for yes

7. CHAPTER 7 - RESULTS AND DISCUSSION

7.1 Introduction

In this chapter the methods and formulas developed in the previous chapter are used on the data for the MMA routes. A sample calculation is shown for some steps in the ACH route.

The results for all the steps have been calculated and are presented in tabulated form later in the chapter along with comparisons of the results with that from the first index and the expert ranking results.

7.2 Example index calculation for an MMA route

The following section presents some example calculations using the new index. Appendix A gives the details of the routes and chemicals used in the examples. For these examples, the proposed plant capacity is 50000 tonnes per annum.

The ACH route is used for the example calculations.

Example storage step calculation

Step 2 of the ACH route is used:

$$(CH_3)_2 CO + HCN \rightarrow (CH_3)_2 COHCN$$
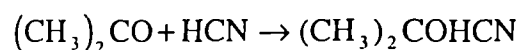
Acetone + Hydrogen Cyanide $\rightarrow$ Acetone Cyanohydrin

Stored raw material = Acetone (HCN is not stored due to its very toxic nature)
Stage 2 calculations gives usage of acetone = 3.63 t/hr
Stage 4 calculations give total inventory = 3.63 * 24 * 14 = 1219.68 t

Stage 5:
For fire and explosions :
Acetone : H_C = 30810 kJ/kg - this gives Q_e = 403.89 t, MI = 0.115 deaths/t,
N.O.D = 46.4, round up to 47
For toxics :
Acetone : LD_{50} = 5800 mg/kg - this gives MI = 0.0028 deaths/t and N.O.D = 3.42

Example reaction step calculation

Step 4 of the ACH route is used:
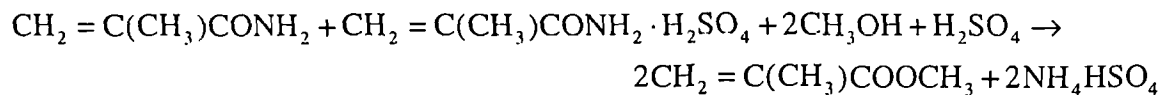
$$CH_2 = C(CH_3)CONH_2 + CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + 2CH_3OH + H_2SO_4 \rightarrow$$
$$2CH_2 = C(CH_3)COOCH_3 + 2NH_4HSO_4$$

Methacrylamide + Methacrylamide Sulphate + Methanol + Sulphuric Acid → Methyl Methacrylate + Ammonium Bisulphate

The calculations for stage 2 are the same as for the example in chapter 6. These give:

Throughput of step = 13.44 t/hr

Reaction residence time = 2 hrs.

Reaction yield = 100%

Therefore stage 6 calculations give reactor inventory $Q_C = 2 * 13.44 = 26.88$ t

Reaction temperature $T_1 = 130°C$

Therefore out of the chemicals present, methanol (BP = 64.6°C) and MMA (BP = 100.1°C) would flash off if there was a loss of containment.

There is no data for methacrylamide or methacrylamide sulphate, ammonium bisulphate is a solid and will not flash off, and sulphuric acid will not flash off.

Methanol : $C_p = 2.53$ kJ/kg.°C, $H_V = 1129$ kJ/kg, $T_2 = 64.6$ °C - This gives $Q_V = 7.88$ t for fire and explosions, and 3.94 t for toxics.

MMA : $C_p = 1.9$ kJ/kg.°C, $H_V = 360$ kJ/kg, $T_2 = 100.1$ °C - This gives $Q_V = 8.48$ t for fire and explosions, and 4.24 t for toxics.

Stage 7

For fire and explosions :

For Methanol : $H_C = 22662$ kJ/kg - This gives $Q_e = 1.9$ t, MI = 0.68 deaths/t and NOD = 1.3

For MMA : $H_C = 47721$ kJ/kg - This gives $Q_e = 4.35$ t, MI = 0.52 deaths/t and NOD = 2.27

MMA has highest NOD value for fire and explosions.

For toxics :

For Methanol : $LD_{50} = 5628$ mg/kg - This gives MI = 0.003 deaths/t and NOD = 0.012

For MMA : $LD_{50} = 7872$ mg/kg - This gives MI = 0.0021 deaths/t and NOD = 0.01

Methanol has highest NOD value for toxics.

Stage 8

For Probability of release scores:

Temperature = 130°C - score 0

Corrosiveness - sulphuric acid present - score 5, no additional score for ingress of air or water

Exotherm - esterification - score 0

Chemical stability - no highly unstable chemicals or reaction - score 0

Autoignition temp. - no chemicals above Auto ignition temp. - score 0

Pressure = 103 psi - score 2

Total score = 7

Stage 12

$F_{POR} = 7/105 = 0.067$

For effects modifier scores:

Flammable limits - no oxygen present - score 0

Vapour density - no heavy gas - score 0

Waste streams - mass ratio of ammonium bisulphate to MMÅ = 1.15 - score 5

Odour - no highly toxic chemicals - score 0

Mixing - no potential problems - score 0

Total score = 5

From stage 13, $F_{EM} = 1 + (5/55) = 1.09$

From stage 14, $MNOD_{FE} = 2.27 * 0.21 * 1.09 = 0.52$,

From stage 15, $MNOD_{TOX} = 0.012 * 0.21 * 1.09 = 0.0027$,

Example separation step calculation, ACH step 1

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$
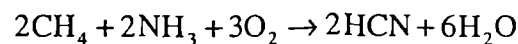
Methane + Ammonia + Oxygen → Hydrogen Cyanide + Water

Yield of step = 64%

From stage 10, flowrate of output stream :

HCN = 1.08 t/hr

H_2O = 2.16 t/hr

O_2 = 1.08 t/hr

NH_3 = 0.38 t/hr

CH_4 = 0.36 t/hr

Methane and oxygen are removed in a vapour/liquid separation - 5 minutes hold-up.

Inventory of separation :

HCN = 0.09 t

H_2O = 0.18 t

O_2 = 0.09 t

NH_3 = 0.032 t

CH_4 = 0.03 t

Oxygen and water present no fire or toxic hazard.

For fire and explosions :

HCN : H_C = 41034 kJ/kg - this gives Q_e = 0.04 t, MI = 0.227 deaths/t, NOD = 0.05

NH_3 : H_C = - no data

CH_4 : H_C = 55527 kJ/kg - this gives Q_e = 0.018 t, MI = 3.24 deaths/t, NOD = 0.058

For toxics :

HCN : LD_5 = 1.43 mg/kg - this gives MI = 11.5 deaths/t and NOD = 1.04

NH_3 : LD_5 = 350 mg/kg - this gives MI = 0.047 deaths/t and NOD = 0.0015

CH_4 : LD_{50} = Asphyxiant NOD not calculable

Composition of stream for next separation :

HCN = 1.08 t/hr

H_2O = 2.16 t/hr

NH_3 = 0.38 t/hr

Next separation - liquid/liquid extraction of ammonia - 15 minutes hold-up

Inventory of separation :

HCN = 0.27 t

H_2O = 0.54 t

NH_3 = 0.095 t

Water presents no fire or toxic hazard.

For fire and explosions :

HCN : MI = 0.95 deaths/t - this gives NOD = 0.62

NH_3 : NOD not calculable

For toxics :

HCN : LD_{50} = 1.43 mg/kg - this gives MI = 11.5 deaths/t and NOD = 3.1

NH_3 : LD_{50} = 350 mg/kg - this gives MI = 0.047 deaths/t and NOD = 0.0045

Composition of stream for next separation :

HCN = 0.27 t

H_2O = 0.54 t

Binary distillation :

Using method from chapter 6 :

Column inventory = 522.3 kg of which 174 kg is HCN

For fire and explosions :

HCN : MI = 1.099 deaths/t - this gives NOD = 0.5

For toxics :

HCN : LD_{50} = 1.43 mg/kg - this gives MI = 11.5 deaths/t and NOD = 2.0

7.3 Results from new index

The table below is a breakdown of the number of possible deaths from both fire
and explosions (F&E), and toxic releases (TOXIC), for all the steps in all the routes. It is
broken down further into reaction, separation and storage steps.

TOTAL NUMBER OF POSSIBLE DEATHS (F&E) AND LETHAL DOSES (TOXIC)							
		REACTION STEPS		SEPARATION STEPS		STORAGE STEPS	
ROUTE	STEP	F&E	TOXIC	F&E	TOXIC	F&E	TOXIC
ACH	1	1	1	2	7	30	17
	2	1	3	1	3	47	4
	3	1	2	N/S	N/S	-	8
	4	1	1	N/S	N/S	26	2
	5	1	1	-	-	19	-
	6	1	-	-	-	-	-
TOTAL		6	8	3	10	122	31
C2/PA	1	1	-	1	-	40	-
	2	1	1	1	1	22	13
	3	1	1	1	1	-	-
	4	1	1	2	1	26	3
TOTAL		4	3	5	3	88	16
C2/MP	1	1	1	3	1	65	3
	2	1	1	1	1	53	7
	3	1	1	2	1	N/S	N/S
TOTAL		3	3	6	3	118	10
C3	1	1	-	1	-	51	-
	2	1	1	1	1	N/S	N/S
	3	1	1	2	1	-	-
	4	1	1	2	1	26	3
TOTAL		4	3	6	3	77	3
TBA	1	1	1	N/S	N/S	11	11
	2	1	1	1	1	-	-
	3	1	1	2	1	26	3
TOTAL		3	3	3	2	37	14
i-C4	1	1	1	1	1	59	-
	2	1	1	1	1	-	-
	3	1	1	2	1	25	3
TOTAL		3	3	4	3	84	3

Table 7.1 - Results from new index for MMA routes

In the above table, for reaction steps, a '-' means that data was not available to calculate the number of deaths. For storage steps, N/S means there was no raw material storage for the step and a '-' means no data was available. For separation steps, N/S means no separation was necessary and a '-' means no data was available.

	PROCESS			STORAGE			TOTAL		
	F&E	TOXIC	TOTAL	F&E	TOXIC	TOTAL	F&E	TOXIC	TOTAL
ACH	9	18	27	122	31	153	131	49	180
C2/PA	9	6	15	88	16	104	97	24	121
C2/MP	9	6	15	118	10	128	127	16	143
C3	10	6	16	77	3	80	87	9	96
TBA	6	5	11	37	14	51	43	19	62
i-C4	7	6	13	84	3	87	91	9	100

Table 7.2 - Totals for each MMA route from the new index

The most obvious result from the table above is the large difference in scores between storage steps, and the process steps, that is the reaction and separation steps. This is to be expected. The storage steps have inventories of several hundreds or thousands of tonnes of material compared with, at most, one or two tonnes for the majority of the process steps. This large difference in the number of possible deaths confirms an important point made in chapter 6. Most of the reactions and separations involve high temperatures and pressures and large amounts of energy, either produced from reactions or added to reactions and separations. This is more likely to lead to a problem. However, the greatest damage, in terms of possible deaths, comes from the storage of large amounts of hazardous material.

This result is very important. It reinforces Kletz's suggestion of minimising the storage of chemicals on chemical plants

Most of the reaction step and separation step results have been rounded up to the nearest death. However, this does not give an accurate picture of the results. Some of the inventories of the reaction steps are only 10 or 20 kg. This gives the number of deaths as less than 0.1.

Although some reactions only have inventories of the order of tens of kilograms, the subsequent separation steps have inventories in the hundreds of kilograms. In addition, for one reaction step there may be three or four separation steps, each having several hundred kilograms of inventory. Therefore the reactor inventory may not be the dominant inventory in a route step.

The rankings from the new index are presented in table 7.3:

	PROCESS	STORAGE	TOTAL	TRIAL INDEX	Q1 RANKING (overall criterion)	Q2 RANKING (overall criterion)
SAFEST	TBA	TBA	TBA	TBA	TBA	TBA
	i-C4	C3	C3	i-C4	i-C4	i-C4
	C2/MP	i-C4	i-C4	C2/MP	C2/MP	C2/MP
	C2/PA	C2/PA	C2/PA	C3	C2/PA	C2/PA
	C3	C2/MP	C2/MP	C2/PA	ACH	C3
UNSAFEST	ACH	ACH	ACH	ACH	C3	ACH

Table 7.3 - comparison of rankings from the new and trial indices, and expert ranking questionnaires

The total ranking is the sum of the deaths for fire and explosions and toxics. The column headed 'PROCESS' is the sum of the reaction and separation deaths for a step.

	SPEARMAN COEFFICIENT r_s		
NEW INDEX RANKING	TRIAL INDEX RANKING	Q1 RANKING (overall criterion)	Q2 RANKING (overall criterion)
PROCESS	0.943	0.943	1.00
STORAGE	0.714	0.371	0.60
TOTAL	0.714	0.371	0.60

Table 7.4 - Spearman coefficients for comparisons of the new index rankings with the trial index and expert ranking questionnaires

When comparing the rankings of the new index with the trial index and the rankings from the questionnaires, it is important to remember that both the trial index and the experts only considered the information about the process areas of the routes. There was no information about any storage given to the experts or scored in the trial index. Therefore, the fact that the correlation between the ranking of the process scores are better than for the storage and total scores is not very surprising.

The rankings and correlation coefficients for the storage scores and the total scores are identical, this shows that the storage scores dominate the index.

The perfect correlation between the process scores for the new index and ranking from questionnaire two highlights again the influence of the number of steps in a route. Almost all the process steps score the same. Therefore the number of steps is the factor which influences the rankings the most.

In compiling the data to present to the experts, it was not possible to gain access to data held by individual companies. Original patents on the process routes may be available, but these are often difficult to decipher, containing a lot of information which is difficult to extract from the jargon of patents. But there are many other readily available sources of data, including guides to properties of hazardous chemicals and chemical engineering encyclopaedias. However, not even these have details of all the routes or chemical properties. Therefore, it was not possible to present all the necessary data to the experts, or to use it in testing the index.

In the first questionnaire, the experts were asked what missing data they needed to complete the questionnaire. This was partially to find out what additional information could be added to the index. The other aim was to devise a method by which missing data could be taken into account when calculating the index. However, if the index was being used in an industrial situation, more of the data would be available to the user. Therefore, the problem of incomplete data only affected the research and the results of testing the index.

8. CHAPTER 8 - CONCLUSIONS AND FURTHER WORK

8.1 Conclusions

8.1.1 Dealing with a large problem

There are many factors influencing the inherent safety of an object as complicated as a chemical plant. Quantifying and estimating the inherent safety of such a complicated object is very difficult even with all the data that describes it available. It is even more difficult to estimate the inherent safety from only the data known about a chemical route. There are also many different measures that could be used to quantify inherent safety. It is impossible to perfectly identify the hazards, predict the probabilities and model the effects of such a complicated system.

The aim of the research was to distil the essence of inherent safety into something that is simple to use, that is the index. This work is a first attempt at quantifying inherent safety, and although it is finished, it is by no means the end of the work to devise a usable index. It must be recognised that some of the work is arbitrary. Some of the values assigned to the scoring parameters have been done so arbitrarily, but this is because the problem being examined is so large and benchmark values do not exist. The scores are a starting point for further exploration and refinement.

What the research does show is that it is possible to attempt to quantify inherent safety, and the results from the expert ranking show that a reasonable attempt has been made for the MMA routes. There are many aspects of inherent safety which are not easy to quantify, and it may not even be possible to quantify some of them. However, there are areas where quantification is possible and this has been attempted in the research presented.

8.1.2 Balance between simplicity and accuracy

A primary aim in producing the index was to keep it simple, because it is to be used at an early stage in the design process with limited information. It is meant to give an estimate of the inherent safety of routes, and therefore the methods used to calculate the estimates should not be complicated. Because of the simplicity of the index the results it gives should be viewed as a guide.

As the design develops, more information becomes available and more accurate estimates of existing data, for example inventories, are made. If the index is used to estimate the inherent safety at a later stage in the design it may produce different results, perhaps suggesting to look at a different route. As more and more information becomes available, and the level of accuracy of calculations increases, then the ease of use of such an index will decrease because of the number of calculations necessary.

A balance must be struck between the accuracy of the estimates and the simplicity of the calculations. If a method for calculating inventory increases the accuracy to three decimal places from one decimal place but takes three times as long, is the extra effort justified? An example of this is comparing the methods for calculating the reaction inventory with distillation column inventory. Reaction inventory comes from one calculation, whereas to calculate the column inventory takes 12 steps of either calculations or using graphs. However, in many steps where there is a reaction and separation by distillation the column inventory is much more than the reaction inventory and the difference in accuracy and simplicity can be justified.

The main point is to remember that the index is to be used as a guide to inherent safety, and the results from it are not hard and fast recommendations.

8.1.3 Expert judgement

The expert judgement exercise was a success because although the experts had not done anything like it before, the results showed that their thinking and rankings were consistent. Their task may have been made easy for the MMA routes, as most of the routes had particular unsafe features for example obviously hazardous chemicals. The statistical analysis of the results showed good agreement between the rankings from the questionnaires and the trial index, and between the experts. Their comments showed that the work done on the trial index and the proposed development of the new index was reasonable.

8.1.4 Cost versus inherent safety

A secondary aim of the research was to see if the inherent safety of plants was related to their cost. In particular, were inherently safer plants cheaper to build and run. The regression analysis of the results from the trial index and the cost estimates showed that the inherent safety of the routes using the trial index correlated well with the estimated capital costs and costs of production. The capital costs correlate best with process related scores and the non-capital costs and costs of production correlate best with the chemical related scores.

However, it would be wrong to say that inherently safer plants are cheaper, only based on the results from six different routes. More routes would have to be tested to better verify the statement.

8.1.5 Index sophistication

The first index only gave a broad indication of which plant is potentially the safest based on the reaction steps of the routes. The second index moved on to look at

separation and storage steps in addition to the reaction steps. However the amount of calculations increased to determine the new index scores.

If any further sophistication is required to the index, then more design work will need to be done on each route to provide further data. Hence, a balance point must be found between output of results from the index versus the amount of time spent on calculating the results.

8.2 Recommendations for further work

8.2.1 Testing of more routes

In order to refine the index further, and to gain a greater understanding of the interaction of the parameters involved, it is recommended that the index be tried on more test data. This could be done in conjunction with more expert ranking. If several more sets of test data were ranked by experts, then the index could be fine tuned.

8.2.2 Statistical analysis of incidents

A statistical analysis of a large number of incidents is needed to determine the number of incidents which occurred in storage steps and the number which occurred in reaction steps. From this a weighting could be devised for the probability of release from storage versus process steps.

8.2.3 Expert judgement

One of the comments from the expert ranking was that the experts were not practised at expert ranking. They were not sure what they should be looking for to measure inherent safety, or what calculations to do to quantify it. As a separate line of research, in addition to ranking more sets of routes, a defined and structured method for expert ranking of routes could be developed.

The results from the expert ranking could be used as a starting point. Individual interviews could be used to question the experts more rigorously. They should be asked what information they require to assess inherent safety, what features they would look for and what calculations they would use to analyse the information. The process would be similar to the elicitation process used to obtain rules for an expert system.

8.2.4 Inventory estimation

The inventory estimation has concentrated on the reactions, storage and on distillations. Firstly, reactor inventory estimation needs improvement. Secondly, other methods could be developed to improve on the current estimating methods. In addition, more plant items could be analysed to develop quick ways to estimate their inventory. A

possible route is to see if a residence time, similar to a reactor residence time, could be calculated from suitable parameters for each plant item. For separation steps a generic method for calculating inventory is needed, without needing to know the specifics of the separation method.

8.2.5 Improved measure of toxicity

As discussed previously, the mortality index for toxics does not cover many chemicals. There are many different measures of toxicity, and more appear all the time. An investigation is needed to find out which measures of toxicity are best suited for assessing inherent safety. Some are directed towards occupational health and long term exposure, but other measures of dose may be more useful. However, both aspects could be incorporated into the index.

An alternative is to look at historical records of toxic releases of all chemicals, and try to convert a measure of toxicity into a mortality index.

8.2.6 Collaboration with industry

The ultimate test of the index would be to use it in industrial process development. This would then add some 'real world' factors to the index, the factors that professional process designers look for when assessing inherent safety. If designers look at inherent safety, positive feed back from them would help develop the index into a usable tool.

To a lesser extent, more process routes, complete with all the necessary process parameters and chemical data would aid in the refining of the index.

8.2.7 Development into software

An area for development, as opposed to research, is to convert the index in to computer software. It could be developed as an expert system, to deal with the qualitative nature of inherent safety. Ideally it should be able to access databases on chemical properties and hazardous properties. Also it could interface with existing design programs so that the routes chosen for development could be transferred straight into the next stage of design.

9. CHAPTER 9 - REFERENCES AND BIBLIOGRAPHY

9.1 References

Brown, G, and Souders, M Jr, 1934, *Industrial and Engineering Chemistry*, 26, p26

Chem Systems International Ltd., 1989, *'Methyl Methacrylate - An Analysis of Processes, Strategies and Markets'*, Chem Systems International Ltd., London

Coulson, J M, and Richardson, J F, 1985, *'Chemical Engineering Vol.6'*, Pergamon Press, Oxford

Douglas, J M, 1987 *'Conceptual Design of Chemical Processes'*, McGraw-Hill, New York

Dransfield, P B, Lowe, D R T, Tyler, B J, 1981, 'The problems involved in designing reliability into a process in its early research or development stages', *IChemE Symposium Series No. 66*, 67 - 83

Draper, N R, and Smith, H, 1981, *'Applied Regression Analysis'*, John Wiley and Sons, 17-33

Duxbury, H A, and Turney, R D, 1989, 'Techniques for the analysis and assessment of hazards in the process industries', *Seminar of Safety and Hazards Evaluation, New Mexico Technical Research Centre for Energetic Materials*

Erbar, J H, and Maddox, R N, 1961, *Petroleum Refining*, 40, 5, p183

Gibbons, J D, 1976, *'Nonparametric Methods of Quantitative Analysis'*, Holt, Rinehart and Winston, New York

Gilliland, E R, 1940, *Industrial and Engineering Chemistry*, 32, p1220

Green, A E, and Bourne, A J, 1972, *'Reliability Technology'*,

Howell, D C, 1992, *'Statistical Methods for Psychology'*, Duxbury Press, California

Humphreys, R A, 1987, 'Assigning a Numerical Value to the Beta Factor Common Cause Evaluation', *Reliability '87*, 2c/5/1 - 2c/5/8

Hunns, D M, and Daniels, B K, 1980, 'The Method of Paired Comparisons', National Centre for Systems Reliability, *6th Adv. in Reliability Technology Symposium*, Bradford

Hutton, D, Ponton, J W , Waters, A , 1990, 'AI Applications in Process Design, Operation and Safety', *The Knowledge Engineering Review 5:2*, 69-95

Imperial Chemical Industries Limited - Mond Division, 1980, *'Technical Manual for Mond Fire, Explosion and Toxicity Index'*, Imperial Chemical Industries Limited, Winnington

King, R, 1990, *'Safety in the Process Industries'*, Butterworth-Heinemann, London

Kletz, T A, 1984, *'Cheaper, Safer plants or Wealth and Safety at Work'*, IChemE, Rugby

Kletz, T A. 1988, *'Learning from accidents in industry'*, Butterworths, London

Kletz, T A, 1991, *'Plant Design for Safety: A User-Friendly Approach'*, Hemisphere Publishing Corporation, New York

Lees, F P, 1980, *'Loss Prevention in the Process Industries vols. 1&2'*, Butterworths, London

Lees, F P, 1994, 'Safety and Loss Prevention', draft of second edition

Lees, F P, 1994a, Private communication

Mansfield, D, 1992, 'Overall Plant Friendliness Index', *HSE/SRD Internal Report*

Marshall, V C, 1977, 'How lethal are explosions and toxic escapes?', *The Chemical Engineer*, 573-577

Marshall, V C, 1981 , 'Quantification as a means of control of toxic hazards', *IChemE Symposium Series No 71*, 69-85

Marshall, V C, 1987, *'Major Chemical Hazards'*, Ellis Horwood Limited, Chichester

Perry, R H, and Green, D, 1987, *'Perry's Chemical Engineering Handbook, 6th ed.'*, McGraw-Hill International Editions, New York

Poblete, B R, Lees, F P, Simpson, G B, 1984, 'The assessment of major hazards: Estimation of injury and damage around a hazard source using an impact model based on inverse square law and probit relations', *Journal of Hazardous Materials*, 9, 355-371

Puranik, S A, Hathi, K K, Sengupa, R, 1990, 'Prevention of hazards through technological alternatives', *IChemE Symposium Series No 120*, 581-587

Rogers, R L, and Hallam, S, 1991, 'A chemical approach to inherent safety', *Hazards XI, IChemE Symposium Series No 124*, 235-241

Simmons, J A, Erdmann, R C, Naft, B N, 1974, 'Risk of catastrophic spills of toxic chemicals', *Report No. UCLA-Eng-7425*

Smoker, E H, 1942, *Industrial and Engineering Chemistry*, 40, p510

Taylor, J H, 1980, 'The Process Step Scoring Method for Making Quick Capital Estimates', *Cost Engineering*, 4, 207-211

The Dow Chemical Company, 1980, '*Fire and Explosion Index Hazard Classification Guide, 5th edn*', The Dow Chemical Company, Midland

Tyler, B J, 1985, 'Using the Mond index to measure inherent hazards', *Plant/Operations Progress*, vol 4, no. 3, 172 - 175,

Wells, G L, 1980, '*Safety in Process Plant Design*', George Godwin Limited, London

Wilson, D C, 1980, 'Flixborough versus Seveso - Comparing the Hazards', *IChemE Symposium Series No 58*, 193-208

Zomosa, A, 1983, 'Quick design of distillation columns for binary mixtures', *Chemical Engineering*, 95-98

9.2 Bibliography

Bosch, W W, 1992, 'Identify, Screen and Rank Toxic Chemicals', *Chemical Engineering Progress*, 9, 33-39

Bretherick, L, 1990, 'Chemicals, Reactions, Hazards', *IChemE Symposium Series No 120*, 247-254

Bretherick, L, 1990, 'Bretherick's Handbook of Reactive Chemical Hazards 4th ed.', Butterworths

Englund, S M, 1991, 'Design and Operate Plants for Inherent Safety - Part 1, Chemical Engineering Progress, 87, 3, 85-91

Englund, S M, 1991, 'Design and Operate Plants for Inherent Safety - Part 2, Chemical Engineering Progress, 87, 5, 79-86

Gillett, J, 1985, 'Rapid Ranking of Process Hazards', Process Engineering, 66, 2, 19-22

Gressel, M G, and Gideon, J A, 1991, 'An Overview of Process Hazard Evaluation Techniques', American Industrial Hygiene Association Journal, 52, 4, 158-163

Gygax, R, 1988, 'Chemical Reaction Engineering for Safety', Chemical Engineering Science, 43, 8, 1759-1771

Husmann, C A W A, and van de Putte, T, 1982, 'Process Safety Analysis: Identification of Inherent Process Hazards', IChemE Symposium Series No 71, 285-290

Kirk, E, and Othmer, F D, 1981, 'Kirk-Othmer Encyclopaedia of Chemical Engineering', Wiley, New York

Kletz, T A, 1987, 'Optimisation and Safety', IChemE Symposium Series No 100, 153-162

Kletz, T A, 1989, 'Plants Should be Friendly', IChemE Symposium Series No 120, 423-435

Kletz, T A, 1989, 'Friendly Plants', Chemical Engineering Progress, 85, 7, 18-26

Kletz, T A, 1990, 'Inherently Safer Plants - An Update', American Institute of Chemical Engineers, 24th Annual Loss Prevention Symposium, California

Kletz, T A, 1990, 'The need for Friendly Plants', Journal of Occupational Accidents, 13, 3-13

Kletz, T A, 1991, 'Inherently Safer Plants - Recent Progress', IChemE Symposium Series No 124, 225-233

Kletz, T A, 1991, 'Process Safety - An Engineering Achievement', *Journal of Process Mechanical Engineering*, 205, E1, 11-15

Lenga, R E, 1988, *'The Sigma Aldrich Library of Chemical Safety Data 2nd ed. vols 1&2'*, Sigma-Aldrich Corporation

Mansfield, D, and Cassidy, K, 1993, 'Inherently Safer Approaches to Plant Design', *IChemE Symposium Series No 134*, 285-299

Ozog, H, and Bendixen, L M, 1987, 'Hazard Identification and Quantification', *Chemical Engineering Progress*, 4, 55-64

Poblete, B R, Lees, F P, Simpson, G B, 1986, 'The assessment of major hazards: Generalisation of the impact model for the estimation of injury and damage around a hazard source', *Journal of Hazardous Materials*, 13, 187-196

Sax, N I, and Lewis snr., R J, 1988, *'Dangerous Properties of Industrial Materials 7th ed. vols 1-3'*, Van Nostrand Reinhold

Turney, R D, 1990, 'Designing Plants for 1990 and Beyond: Procedures for the Control of Safety, Health and Environmental Hazards in the Design of Chemical Plants', *Trans IChemE*, 68B, 12-16

Tyler, B J, Thomas, A R, Doran, P, Greig, T R, 1993, 'A Toxicity Hazard Index', *IChemE Symposium Series No 134*, 351-366

Ullman, F, 1988, *'Encyclopaedia of Industrial Chemistry'*, VCH, Weinheim

Vilchez, J-A, and Casal, J, 1991, 'Hazard Index for Runaway Reactions', *Journal of Loss Prevention in the Process Industries*, 4, 125-127

Walas, S M, 1985, 'Chemical Reaction Data', *Chemical Engineering*, Oct, 79-83

10. APPENDIX A - MMA ROUTE DETAILS

<div align="center">

Acetone Cyanohydrin based route (ACH)

</div>

Step 1

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$
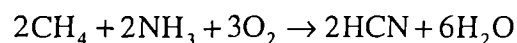
Methane + Ammonia + Oxygen → Hydrogen Cyanide + Water

Gas Phase

Pressure: 3.4 Atm

Temperature: 1200° C

Yield: 64%

Step 2

$$(CH_3)_2 CO + HCN \rightarrow (CH_3)_2 COHCN$$
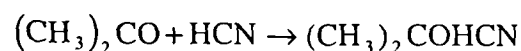
Acetone + Hydrogen Cyanide → Acetone Cyanohydrin

Liquid Phase

Pressure : Atmospheric

Temperature : 29-38° C

Yield : 91%

Step 3
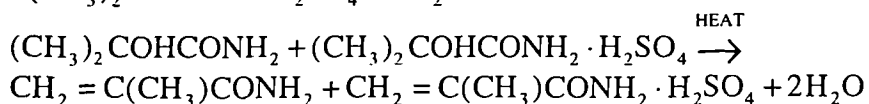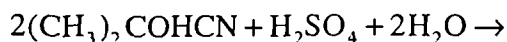
$$2(CH_3)_2 COHCN + H_2SO_4 + 2H_2O \rightarrow$$
$$(CH_3)_2 COHCONH_2 + (CH_3)_2 COHCONH_2 \cdot H_2SO_4 \xrightarrow{\text{HEAT}}$$
$$CH_2 = C(CH_3)CONH_2 + CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + 2H_2O$$

Acetone Cyanohydrin + Sulphuric Acid + Water →

2-Hydroxyl-2-Methyl Propionamide + 2-Hydroxyl-2-Methyl Propionamide Sulphate→

Methacrylamide + Methacrylamide Sulphate + Water

Liquid Phase

Pressure : 7 Atm

Temperature : 130-150 ° C

Yield : 98%

Step 4

$$CH_2 = C(CH_3)CONH_2 + CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + 2CH_3OH + H_2SO_4 \rightarrow$$
$$2CH_2 = C(CH_3)COOCH_3 + 2NH_4HSO_4$$

Methacrylamide + Methacrylamide Sulphate + Methanol + Sulphuric Acid →

Methyl Methacrylate + Ammonium Bisulphate

Liquid Phase

Pressure : 7 Atm

Temperature : 110-130 °C

Yield : 100%

Step 5
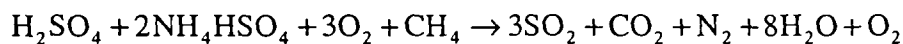
$$H_2SO_4 + 2NH_4HSO_4 + 3O_2 + CH_4 \rightarrow 3SO_2 + CO_2 + N_2 + 8H_2O + O_2$$

Sulphuric acid + Ammonium bisulphate + Oxygen + Methane →

Sulphur dioxide + Carbon dioxide + Nitrogen + Water + Oxygen

Gas phase

Pressure : Atmospheric

Temperature : 980-1200 °C

Yield : 100%

Step 6

$$2SO_2 + O_2 \rightarrow 2SO_3$$
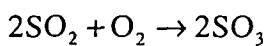
Sulphur dioxide + Oxygen → Sulphur trioxide

Gas phase

Pressure : Atmospheric

Temperature : 405-440° C

Yield : 99.7%

Acetone Cyanohydrin route (ACH)
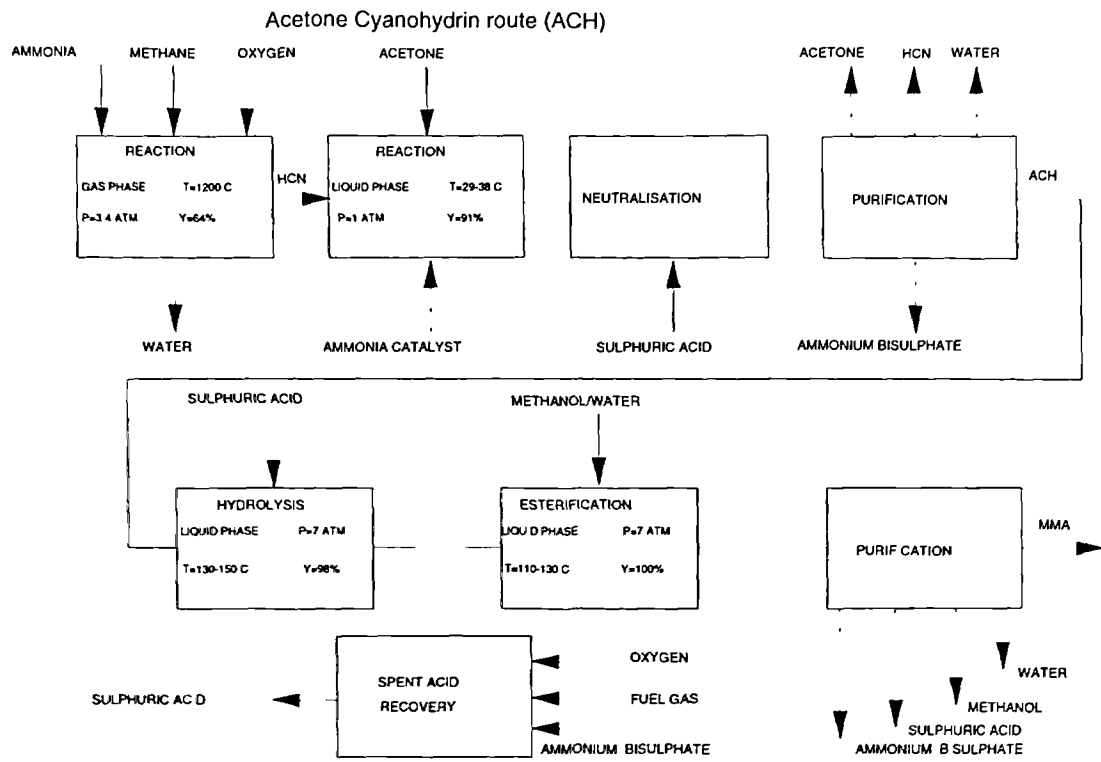
Figure A.1 - ACH route diagram

Ethylene via Propionaldehyde based route (C2/PA)

Step 1

$$CH_2 = CH_2 + CO + H_2 \rightarrow CH_3CH_2CHO$$
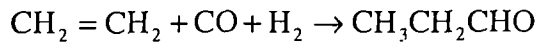
Ethylene + Carbon Monoxide + Hydrogen $\rightarrow$ Propionaldehyde

Gas Phase

Pressure : 15 Atm

Temperature : 30 °C

Yield : 90.7%

Step 2

$$CH_3CH_2CHO + CH_2O \rightarrow CH_2 = C(CH_3)CHO + H_2O$$
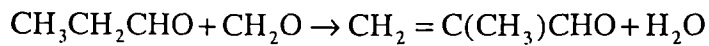
Propinaldehyde + Formaldehyde $\rightarrow$ Methacrolein + Water

Liquid Phase

Pressure : 49 Atm

Temperature : 160-185 °C

Yield : 98.2%

Step 3

$$2CH_2 = C(CH_3)CHO + O_2 \rightarrow 2CH_2 = C(CH_3)COOH$$
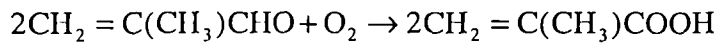
Methacrolein + Oxygen $\rightarrow$ Methacrylic Acid

Gas Phase

Pressure : 350 Atm

Temperature :

Yield : 57.75%

Step 4
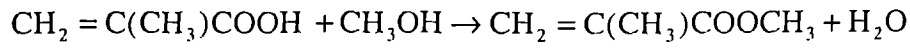
$$CH_2 = C(CH_3)COOH + CH_3OH \rightarrow CH_2 = C(CH_3)COOCH_3 + H_2O$$

Methacrylic Acid + Methanol → Methyl Methacrylate + Water

Liquid Phase

Pressure : 6.8-7.5 Atm

Temperature : 70-100 °C

Yield : 75%
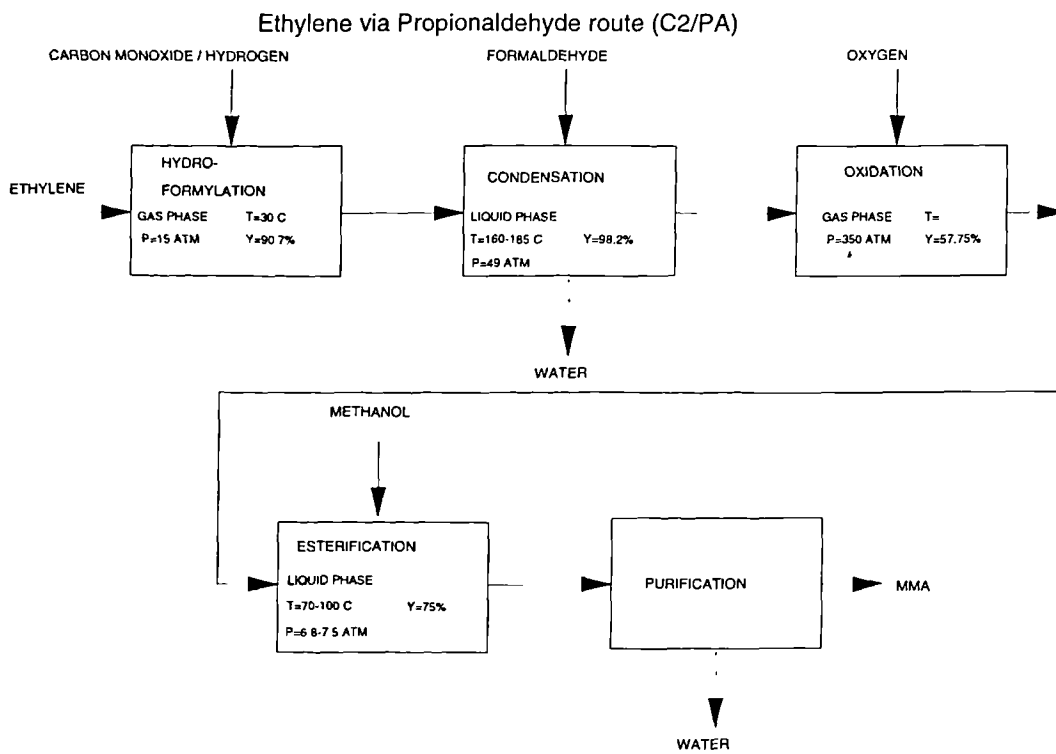
Figure A.2 - C2/PA route diagram

Ethylene via Methyl Propionate based route (C2/MP)

Step 1

$$CH_2 = CH_2 + CO + CH_3OH \rightarrow CH_3CH_2COOCH_3$$
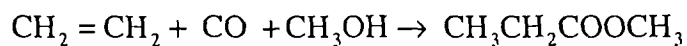
Ethylene + Carbon Monoxide + Methanol → Methyl Propionate

Liquid Phase

Pressure : 100 Atm

Temperature : 100 °C

Yield : 89%

Step 2

$$6CH_3OH + O_2 \rightarrow 2CH_3OCH_2OCH_3 + 4H_2O$$
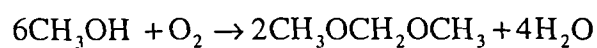
Vapour Phase

Methanol + Oxygen → Methylal + Water

Pressure :

Temperature :

Yield :

Step 3

$$CH_3CH_2COOCH_3 + CH_3OCH_2OCH_3 \rightarrow CH_2 = C(CH_3)COOCH_3 + 2CH_3OH$$
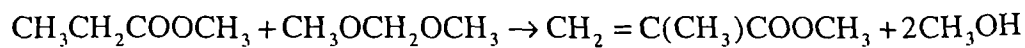
Methyl Propionate + Methylal → Methyl Methacrylate + Methanol

Liquid Phase

Pressure :

Temperature : 350 °C

Yield : 87.4%

Ethylene via Methyl Propionate (C2/MP)
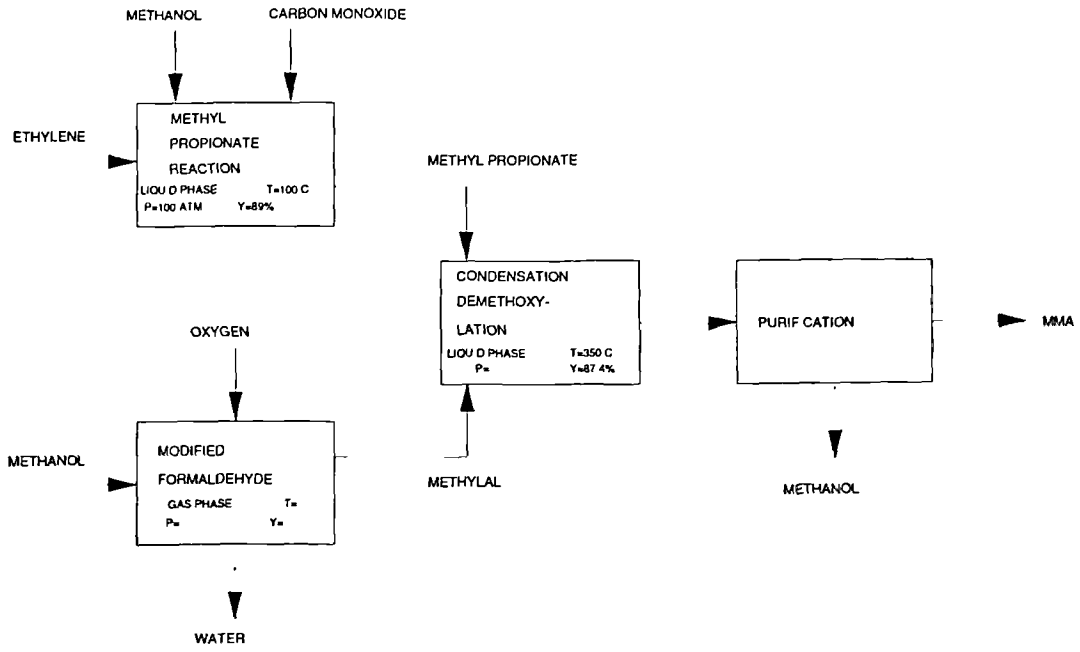
Figure A.3 - C2/MP route diagram

Propylene based route (C3)

Step 1

$$CH_3CHCH_2 + CO + HF \rightarrow (CH_3)_2CHCOF$$
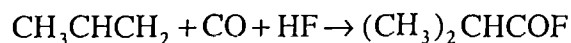
Propylene + Carbon Monoxide + Hydrogen Fluoride → Isobutyrl Fluoride

Liquid Phase

Pressure : 90-100 Atm

Temperature : 70 °C

Yield : 94.5%

Step 2

$$(CH_3)_2CHCOF + H_2O \rightarrow (CH_3)_2CHCOOH + HF$$
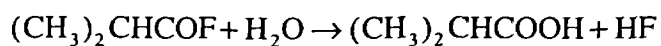
Isobutyrl Fluoride + Water → Isobutyric Acid + Hydrogen Fluoride

Liquid Phase

Pressure : 10 Atm

Temperature : 40-90 °C

Yield : 96.2%

Step 3

$$2(CH_3)_2CHCOOH + O_2 \rightarrow 2CH_2 = C(CH_3)COOH + 2H_2O$$
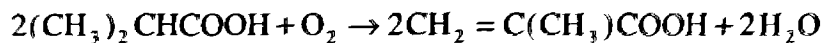
Isobutyric Acid + Oxygen → Methacylic Acid + Water

Vapour Phase

Pressure : 2.5-3 Atm

Temperature : 320-354 °C

Yield : 70.5%

Step 4
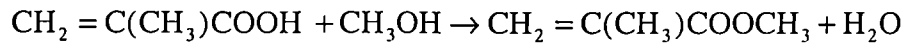
$$CH_2 = C(CH_3)COOH + CH_3OH \rightarrow CH_2 = C(CH_3)COOCH_3 + H_2O$$

Methacrylic Acid + Methanol → Methyl Methacrylate + Water

Liquid Phase

Pressure : 6.8-7.5 Atm

Temperature : 70-100 °C

Yield : 75%
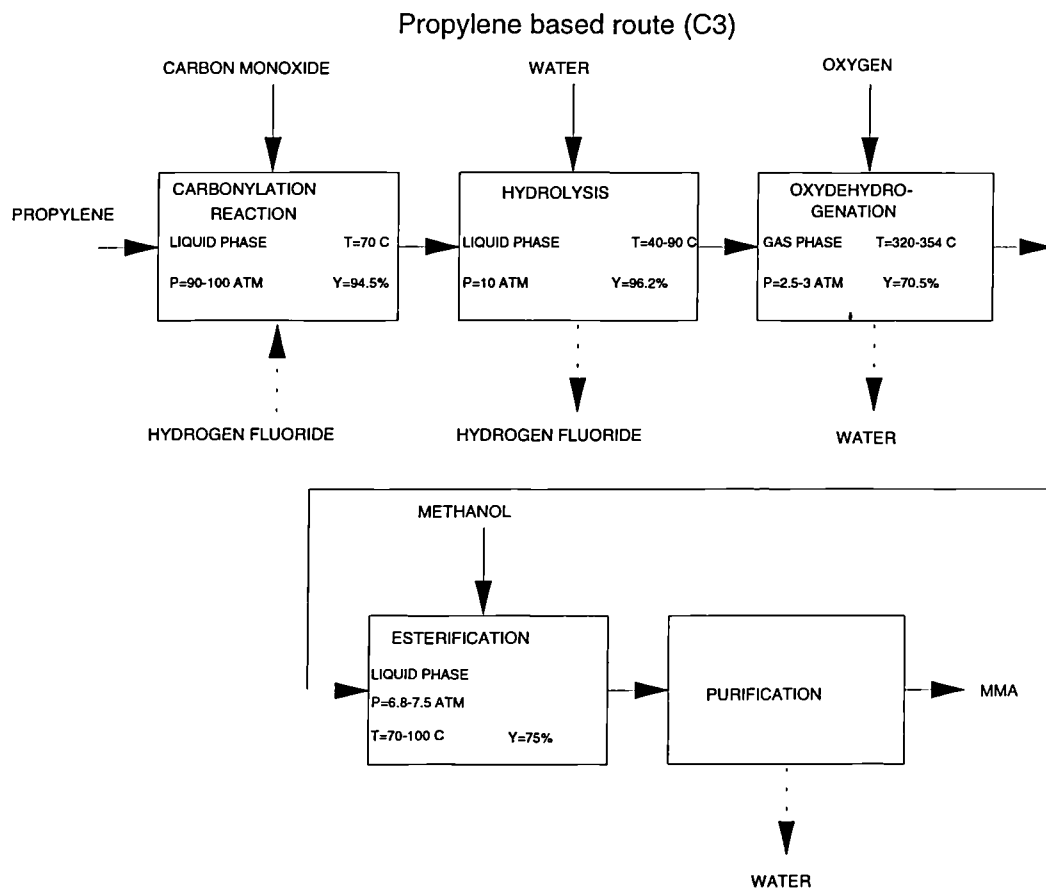
Figure A.4 - C3 route diagram

Tertiary Butyl Alcohol based Route (TBA)

Step 1

$$CH_3)_3COH + O_2 \rightarrow CH_2CCH_3CHO + 2H_2O$$

Tertiary Butyl Alcohol + Oxygen → Methacrolein + Water

Vapour phase

Pressure : 4.8 Atm

Temperature : 350 °C

Yield : 83%

Step 2
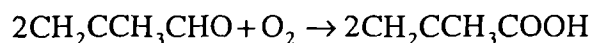
$$2CH_2CCH_3CHO + O_2 \rightarrow 2CH_2CCH_3COOH$$

Methacrolein + Oxygen → Methacrylic Acid

Vapour Phase

Pressure : 3.7 Atm

Temperature : 350 °C

Yield : 57.75%

Step 3

$$CH_2 = C(CH_3)COOH + CH_3OH \rightarrow CH_2 = C(CH_3)COOCH_3 + H_2O$$
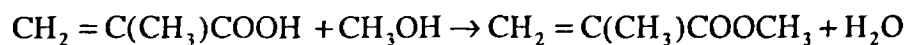
Methacrylic Acid + Methanol → Methyl Methacrylate + Water

Liquid Phase

Pressure : 6.8-7.5 Atm

Temperature : 70-100 °C

Yield : 75%

Tertiary Butyl Alcohol based (TBA)
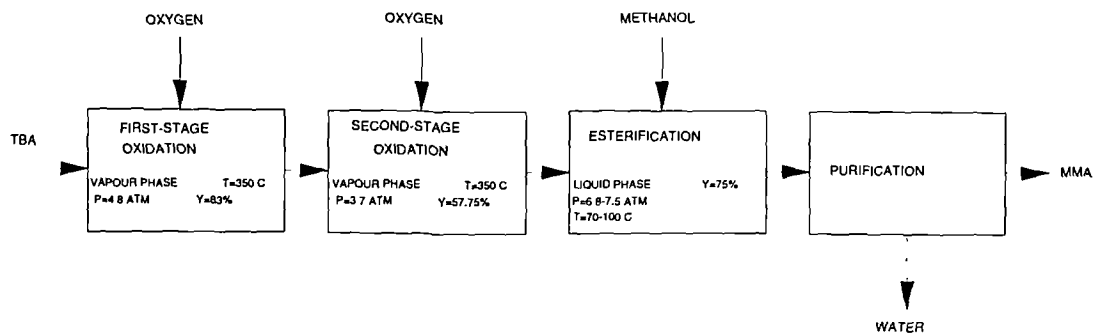
Figure A.5 - TBA route diagram

Isobutylene based Route (i-C4)

Step 1

$$(CH_3)_2CCH_2 + O_2 \rightarrow CH_2CCH_3CHO + H_2O$$
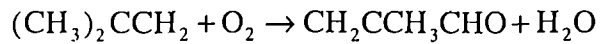
Isobutylene + Oxygen → Methacrolein + Water

Vapour Phase

Pressure :

Temperature : 395 °C

Yield : 41.8%

Step 2
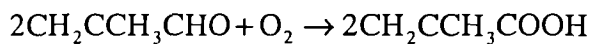
$$2CH_2CCH_3CHO + O_2 \rightarrow 2CH_2CCH_3COOH$$

.

Methacrolein + Oxygen → Methacrylic Acid

Vapour Phase

Pressure : 3.7 Atm

Temperature : 350 °C

Yield : 57.75%

Step 3

$$CH_2 = C(CH_3)COOH + CH_3OH \rightarrow CH_2 = C(CH_3)COOCH_3 + H_2O$$
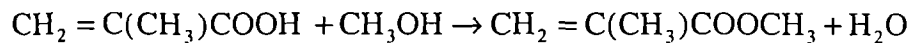
Methacrylic Acid + Methanol → Methyl Methacrylate + Water

Liquid Phase

Pressure : 6.8-7.5 Atm

Temperature : 70-100 °C

Yield : 75%

Isobutylene based route (i-C4)
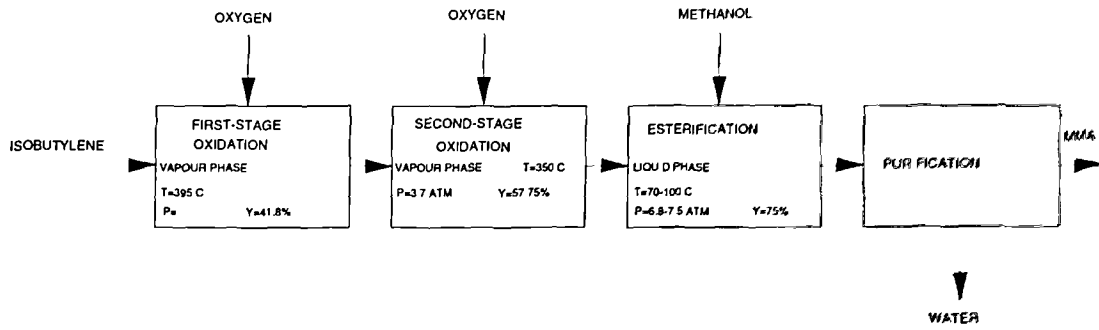
Figure A.6 - i-C4 route diagram

| CHEMICAL	M.W. (g)	BOILING POINT (°C)	FLASH POINT (°C)	L.E.L. (%)	U.E.L. (%)	T.L.V. (ppm)
Acetone	58	56.5	-17.7	2.6	12.8	750
Acetone Cyanohydrin	85	82.0	63.8	2.2	12	10
Ammonia	17	-33.0		15	28	25
Ammonium Bisulphate	115					
Carbon dioxide	44					5000
Carbon Monoxide	28	-191.5	-89.4	12.5	74.2	50
Ethylene	28	-104.0	-70.5	2.7	36.0	asphyx
Formaldehyde	30	-19.4	56.0	7.0	73.0	1
HMPA	103					
HMPASE	201					
Hydrogen	2	-252.8	-106.7	4.1	74.2	asphyx
Hydrogen Cyanide	27	-3.5	-17.7	5.6	40	10
Hydrogen Fluoride	20	-7.0				3
Isobutylene	56	-6.9	-10.0	1.8	9.6	asphyx
Isobutyric Acid	88	153.0	55.6	2.0	9.2	300
Isobutyrl Fluoride	90					
Methacrolein	70	69.0	-15.0			210
Methacrylamide	85					
Methacrylic acid	86	162.6	76.0			
Methane	16	-161.0	-119.6	5	15	asphyx
Methanol	32	64.6	12.2	6.0	36.5	200
Methyl Methacrylate	100	100.0	10.0	2.1	12.5	100
Methyl Propionate	88	79.0	6.0	2.5	13	
Methylal	76	41.0	-17	1.6	17.6	1000
Nitrogen	28	-195.8				asphyx
Oxygen	32	-183.0				
Propionaldehyde	58	46.0	-26.0	2.9	17	
Propylene	42	-47.7	-107.8	2.4	10.1	asphyx
Sulphur dioxide	64	-10.0				2
Sulphur trioxide	80	44.7				.001
Sulphuric Acid	98	143.3				1mg/m³
Tertiary Butyl Alcohol	74	83.0	10.0	2.4	8.0	100
Water	18	100.0				

HMPA - 2-hydroxy-2-methyl propionamide
HMPASE - 2-hydroxy-2-methyl propionamide sulphate
M.W. - Molecular weight
L.E.L. - Lower Explosive Limit
U.E.L. - Upper Explosive Limit
T.L.V. - Threshold Limit Value
asphyx - asphyxiant
☐ Data not available
☐ Not applicable

Table A.1 - MMA route chemical and physical properties

CHEMICAL	LD$_{50}$ (mg/kg)	Autoignition (°C)	Heat of Vap. (kJ/kg)	Heat of Comb. (kJ/kg)	Specific Heat (kj/kg.°C)
Acetone	5800	538	501.7	30810	2.6
Acetone Cyanohydrin	17.8	963	514.9		
Ammonia	350	511	1370.0		2.2
Ammonium Bisulphate					
Carbon dioxide		609	348		
Carbon Monoxide		925	215.8	10105	1.04
Ethylene	Asphyx	490	483.6	50393	2.4
Formaldehyde	800	430	776.7	18867	1.18
HMPA					
HMPASE					
Hydrogen	Asphyx	385	449	141853	9.85
Hydrogen Cyanide	1.43	538	933.3	41034	2.63
Hydrogen Fluoride			374.7		2.53
Isobutylene	Asphyx	465	394.8	44768	2.33
Isobutyric Acid	280	503	467.0		1.88
Isobutyrl Fluoride					
Methacrolein	116	280	414.3	32843	
Methacrylamide	459				
Methacrylic acid	2000	400	486.0	48139	2.2
Methane	Asphyx	811	513.4	55125	2.34
Methanol	5628	470	1129	22662	2.53
Methyl Methacrylate	7872	435	360.0	47721	1.9
Methyl Propionate	5000	469	366.5		1.92
Methylal	5708		376.5		2.18
Nitrogen	Asphyx				
Oxygen					
Propionaldehyde	1410	207	487.9		2.19
Propylene	Asphyx	860	438.3	48952	
Sulphur dioxide			311.5		0 62
Sulphur trioxide			584.3		3.22
Sulphuric Acid	2140				
Tertiary Butyl Alcohol	2460		535.4	35581	3.04
Water					

HMPA - 2-hydroxy-2-methyl propionamide
HMPASE - 2-hydroxy-2-methyl propionamide sulphate
Asphyx - asphyxiant

Table A.2 - MMA route chemical and physical properties

11. APPENDIX B - SAMPLE QUESTIONNAIRES

These are samples of the questionnaires sent out to the experts for the expert judgement exercise.

INHERENT SAFETY ASSESSMENT OF ROUTES TO METHYL METHACRYLATE

EXPERT RANKING QUESTIONNAIRE 1

In this first questionnaire, we would like you to spend no more than two hours. Try to do the rankings using your 'gut feeling'.

Section I - Please rank the six methyl methacrylate (MMA) routes with respect to the three stated criteria and also for overall inherent safety.

Section II - Please identify important features of the individual routes.

Section III - Please give reasons for your rankings with respect to the three criteria and overall inherent safety.

Section IV - Please describe how you dealt with incomplete data about the routes.

SECTION I

Rank the six (MMA) in order of their inherent safeness, with respect to the following criteria:

A - Major hazard
A large toxic or flammable release and/or explosion, affecting the surrounding area, with loss of life.

B - Medium scale event
For example, a small explosion or implosion, leading to loss of production and bad publicity. Any loss of life is due to 'bad luck'.

C - Unplanned event
This causes disruption to local population, for example these might be alarms and evacuations, and the event makes the news. The event may not be dangerous but it leads to loss of production and claims for compensation.

Please assign a score of 1 to the route you consider inherently safest through 6 for the route you consider least inherently safe.

ROUTE	A	B	C	OVERALL
ACH				
C2/MP				
C2/PA				
C3				
i-C4				
TBA				

Routes based on:
ACH - Acetone Cyanohydrin
C2/MP - Ethylene via Methyl Propionate
C2/PA - Ethylene via Propionaldehyde

C3 - Propylene
i-C4 - Isobutylene
TBA - Tertiary Butyl Alcohol

SECTION II

What are the important features that influence the inherent safety of each route and how important do you consider they are on a scale of 1 (high importance) to 5 (low importance)? You may list any number of features.

ACH

C2/MP

C2/PA

C3

i-C4

TBA

SECTION III

What are the main reasons for your rankings with respect to:

Criterion A:

Criterion B:

Criterion C:

Overall:

SECTION IV

Was there any data that you needed but did not have?

What would you have done with this data if you had had it?

How did you deal with not having this data?

Do you have any general comments at this stage?

Please attach further sheets if you need more space.

INHERENT SAFETY ASSESSMENT OF ROUTES TO METHYL METHACRYLATE

EXPERT RANKING QUESTIONNAIRE 2

In this second questionnaire we would like you to look more closely at the individual reaction steps.

Please rank the reaction steps with respect to the following criteria:

A - Major hazard
A large toxic or flammable release and/or explosion, affecting the surrounding area, with loss of life.

B - Medium scale event
For example, a small explosion or implosion, leading to loss of production and bad publicity. Any loss of life is due to 'bad luck'.

C - Unplanned event
This causes disruption to local population, for example these might be alarms and evacuations, and the event makes the news. The event may not be dangerous but it leads to loss of production and claims for compensation.

Please assign a score of 1 to the step you consider most inherently safe through to 5 for the step you consider least inherently safe. More than one step may have the same score.

Please attach additional sheets if you wish to give reasons for your ranking or comments.

Key for Phase

L - Liquid phase
V - Vapour phase
G - Gas phase

Throughput is the total chemical feed to the step.

PROCESS STEP	PHASE	TEMPERATURE °C	PRESSURE Atm	YIELD %	THROUGHPUT Tonne/hr	CRITERION A	B	C
$CH_2 = C(CH_3)CONH_2 + CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + 2CH_3OH + H_2SO_4 \rightarrow$ $2CH_2 = C(CH_3)COOCH_3 + 2NH_4HSO_4$ Methacrylamide + Methacrylamide Sulphate + Methanol + Sulphuric Acid → Methyl Methacrylate + Ammonium Bisulphate	L	110-130	7	100	13.19			
$2CH_2CCH_3CHO + O_2 \rightarrow 2CH_2CCH_3COOH$ Methacrolein + Oxygen → Methacrylic Acid	V	350	3.7	57.75	12.17			
$CH_2 = C\ CH_3)COOH + CH_3OH \rightarrow CH_2 = C(CH_3)COOCH_3 + H_2O$ Methacrylic Acid + Methanol → Methyl Methacrylate + Water	L	70-100	6.8-7.5	75	9.64			
$(CH_3)_2 CCH_2 + O_2 \rightarrow CH_2CCH_3CHO + H_2O$ Isobutylene + Oxygen → Methacrolein + Water	V	395	-	41.8	29.76			
$CH_2 = CH_2 + CO + CH_3OH \rightarrow CH_3CH_2COOCH_3$ Ethylene + Carbon Monoxide + Methanol → Methyl Propionate	L	100	100	89	6.92			
$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$ Methane + Ammonia + Oxygen → Hydrogen Cyanide + Water	G	1200	3.4	64	8.71			
$2CH_2 = C(CH_3)CHO + O_2 \rightarrow 2CH_2 = C(CH_3)COOH$ Methacrolein + Oxygen → Methacrylic Acid	G	-	350	57.75	12.17			
$CH_3CHCH_2 + CO + HF \rightarrow (CH_3)_2CHCOF$ Propylene + Carbon Monoxide + Hydrogen Fluoride → Isobutyrl Fluoride	L	70	90-100	94.5	11.57			
$6CH_3OH + O_2 \rightarrow 2CH_3OCH_2OCH_3 + 4H_2O$ Methanol + Oxygen → Methylal + Water	V	-	-	-	7.85			
$CH_2 = CH_2 + CO + H_2 \rightarrow CH_3CH_2CHO$ Ethylene + Carbon Monoxide + Hydrogen → Propionaldehyde	G	30	15	90.7	9.20			

PROCESS STEP	PHASE	TEMPERATURE °C	PRESSURE Atm	YIELD %	THROUGHPUT Tonne/hr	CRITERION A	B	C
$2(CH_3)_2CHCOOH + O_2 \rightarrow 2CH_2 = C(CH_3)COOH + 2H_2O$ Isobutyric Acid + Oxygen → Methacrylic Acid + Water	V	320-354	2.5-3	70.5	12.06			
$H_2SO_4 + 2NH_4HSO_4 + 3O_2 + CH_4 \rightarrow 3SO_2 + CO_2 + N_2 + 8H_2O + O_2$ Sulphuric acid + Ammonium bisulphate + Oxygen + Methane → Sulphur dioxide + Carbon dioxide + Nitrogen + Water + Oxygen	G	980-1200	ATM	100	13.51			
$(CH_3)_2 CO + HCN \rightarrow (CH_3)_2 COHCN$ Acetone + Hydrogen Cyanide → Acetone Cyanohydrin	L	29-38	ATM	91	5.84			
$CH_3CH_2CHO + CH_2O \rightarrow CH_2 = C(CH_3)CHO + H_2O$ Propionaldehyde + Formaldehyde → Methacrolein + Water	L	160-185	49	98.2	12.66			
$(CH_3)_2 CHCOF + H_2O \rightarrow (CH_3)_2 CHCOOH + HF$ Isobutyrl Fluoride + Water → Isobutyric Acid + Hydrogen Fluoride	L	40-90	10	96.2	13.01			
$CH_3CH_2COOCH_3 + CH_3OCH_2OCH_3 \rightarrow CH_2 = C(CH_3)COOCH_3 + 2CH_3OH$ Methyl Propionate + Methylal → Methyl Methacrylate + Methanol	L	350	-	87.4	11.50			
$(CH_3)_3COH + O_2 \rightarrow CH_2CCH_3CHO + 2H_2O$ Tertiary Butyl Alcohol + Oxygen → Methacrolein + Water	V	350	4.8	83	18.06			
$2(CH_3)_2COHCN + H_2SO_4 + 2H_2O \rightarrow$ $(CH_3)_2 COHCONH_2 + (CH_3)_2 COHCONH_2 \cdot H_2SO_4 \rightarrow$ $CH_2 = C(CH_3)CONH_2 + CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + 2H_2O$ Acetone Cyanohydrin + Sulphuric Acid + Water → 2-Hydroxyl-2-Methyl Propionamide + 2-Hydroxyl-2-Methyl Propionamide Sulphate → Methacrylamide + Methacrylamide Sulphate + Water	L	130-150	7	98	9.51			
$2SO_2 + O_2 \rightarrow 2SO_3$ Sulphur dioxide + Oxygen → Sulphur trioxide	G	405-440	ATM	99.7	7.36			

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INHERENT SAFETY ASSESSMENT OF ROUTES TO METHYL METHACRYLATE

EXPERT RANKING QUESTIONNAIRE 3

Introduction

The purpose of this third questionnaire is to aid us in the development of a new index. The questionnaire is divided into several sections:

Current index comments - we would like you to comment on and constructively criticise our present index.

Ranking parameters - please complete the table to help us decide how important various safety parameters are.

Separation steps - please complete the table in a similar manner to the previous table to help us decide what are the important parameters in assessing separation stages.

Structure for new index - your comments and suggestions are requested for the development of our new index.

Other questions - some questions for you to answer on general topics.

Current Index Comments

Currently our index is calculated by scoring parameters that describe each of the reaction steps in the route and then summing these scores.

Method

The route is divided into reaction steps.

For each step a score is calculated for each chemical involved. This is the sum of the scores for: inventory (based on the hourly production rate for 8000 hours per year , 100% conversion and a nominal holdup of 1 hour), flammability, explosiveness and toxicity. The highest score over all the chemicals in the step becomes the **Chemical score.** The chemical and physical parameter scores are found from the tables, which are listed on pages 3 - 6.

The scores for pressure, temperature and yield are summed to give the **Process score** for the step. The tables for these parameters are listed on pages 7 - 9.

The **step score** is the sum of the Chemical score and the Process score.

The final **route score** is the sum of all the scores for all the steps in the route.

Example

The scoring for the first step of the ACH route is as follows:

Chemical score - the highest is for HCN:

Inventory (1) + Flammability (4) + Toxicity (4) + Explosiveness (4) = 13

Process score:

Temperature (10) + Pressure (1) Yield (2) = 13

Total step score = Chemical score + Process score = 13 + 13 =26

The same procedure yields the scores for steps 2 to 6, which are: 15, 13, 15, 20, 19.

The total score for the route, that is the index value is given by:

Index for ACH route = 26 + 15 + 13 + 15 + 20 + 19 = 108

We would like you to comment on and positively criticise the scoring tables and the method used for calculating the current index. If you think a table of scores is inappropriate or that the ranges in the tables are incorrect, please suggest alternatives.

Comments on method.

Comments on range of parameter   Comments on scores for parameter

Inventory (Tonnes)		Score
0.1	- 250	1
251	- 2500	2
2501	- 7000	3
7001	- 16000	4
16001	- 26000	5
26001	- 38000	6
38001	- 50000	7
50001	- 65000	8
65001	- 80000	9
80001	- 100000	10

General comments on this parameter

Comments on range of parameter   Comments on scores for parameter

Flammability	Score
Non-combustible	0
FP > 140°F	1
100°F < FP < 140° F	2
FP < 100°F BP > 100°F	3
FP < 100°F BP < 100°F	4
FP = Flash point BP = Boiling point	

General comments on this parameter

Comments on range of parameter   Comments on scores for parameter

Toxicity (ppm)				Score
		TLV	< 0.001	8
0.001	≤	TLV	< 0.01	7
0.01	≤	TLV	< 0.1	6
0.1	≤	TLV	< 1.0	5
1.0	≤	TLV	< 10.0	4
10.0	≤	TLV	< 100.0	3
100.0	≤	TLV	< 1000.0	2
1000.0	≤	TLV	< 10000.0	1
1.0%	≤	TLV		

General comments on this parameter

Comments on range of parameter   Comments on scores for parameter

Explosiveness			
S = (UEL - LEL)%			Score
0	≤ S <	10	1
10	≤ S <	20	2
20	≤ S <	30	3
30	≤ S <	40	4
40	≤ S <	50	5
50	≤ S <	60	6
60	≤ S <	70	7
70	≤ S <	80	8
80	≤ S <	90	9
90	≤ S <	100	10

General comments on this parameter

Comments on range of parameter Comments on scores for parameter

Temperature (°C)				Score
		T	< -25	10
-25	≤	T	< -10	3
-10	≤	T	< 10	1
10	≤	T	< 30	0
30	≤	T	< 100	1
100	≤	T	< 200	2
200	≤	T	< 300	3
300	≤	T	< 400	4
400	≤	T	< 500	5
500	≤	T	< 600	6
600	≤	T	< 700	7
700	≤	T	< 800	8
800	≤	T	< 900	9
900	≤	T	<	10

General comments on this parameter

Comments on range of parameter   Comments on scores for parameter

Pressure (psi)	Score
0 - 90	1
91 - 140	2
141 - 250	3
251 - 420	4
421 - 700	5
701 - 1400	6
1401 - 3400	7
3401 - 4800	8
4801 - 6000	9
6001 - 8000	10
+1 point per 2500 psi	

General comments on this parameter

Comments on range of parameter   Comments on scores for parameter

Yield (%)	Score
100	0
90 - 99	1
80 - 89	2
70 - 79	3
60 - 69	4
50 - 59	5
40 - 49	6
30 - 39	7
20 - 29	8
10 - 19	9
0 - 9	10

General comments on this parameter

Ranking Parameters

In making an assessment of the inherent safety of a reaction step, how important do you consider the following parameters.

In the left-hand column, record whether you consider that the parameter is essential in making an assessment of inherent safety, that is would the assessment be invalid without the piece of information.

In the right-hand columns, tick one box to indicate the importance of the parameter in assessing inherent safety. Column 1 is very important, through to column 5, unimportant.

Essential		Importance of Parameter				
Yes or No	Parameter	1	2	3	4	5
	Inventory					
	Temperature					
	Pressure					
	Yield					
	Toxicity					
	Flammability					
	Reaction Phase					
	Waste streams					
	Explosiveness					
	Flash point					
	Chemical stability					
	Recycles					
	Side reactions					

Please add any further parameters in the space provided that you may consider, and your rating of them.

Do you consider that there are any important interactions between these parameters that make assessments of safety better or worse?

Separation Steps

In the development of a new index, we are assessing not only reaction steps but also separation steps. Using the table below, list the parameters that you consider are needed to assess the inherent safety of a separation step, and indicate their importance using the same scale as for the above table.

Essential		Importance of Parameter				
Yes or No	Parameter	1	2	3	4	5
	Inventory					
	Temperature					
	Pressure					

General comments.

Structure of new index

In our new index, we are using a four factor approach to assess the steps:

Inventory * Hazard Assessment * Probability of release * Effects multiplier

The '*' means 'combined with in some way' as opposed to a multiplication.

Inventory is a more rigorous estimation of the contents of a reaction or separation step.

Hazard assessment includes explosion, fire and toxic effects. It is a quantitative assessment of how much damage could be caused for each of the three hazards per unit inventory. It could be for example a T.N.T. equivalent or the Mortality index for the hazard.

Probability of release is derived from parameters such as propensity for runaway, corrosiveness, extremes of pressure or temperature, etc.

Effects multipliers quantifies how much the hazard could be amplified or attenuated by process conditions or other circumstances, for example materials used under conditions which could lead to flashing in the event of a leak, or toxic materials which have are persistent, like dioxins.

Inventory and hazard assessment are likely to be combined to give a qualitative assessment of the hazards for comparison between routes. Probability and effects multipliers will give an additional measure to the index to indicate if a route is more likely to have things go wrong with it.

Your comments and suggestions about this new approach would be much appreciated.

Other questions

In what circumstances do you consider that intermediate storage is needed in a plant?

What do you consider is the most practicable measure of toxicity, that can be used to assess the inherent safety of chemical routes?

12. APPENDIX C - QUESTIONNAIRE 1 RESULTS

These are the answers copied as accurately as possible from the completed questionnaire 1s.

INHERENT SAFETY ASSESSMENT OF ROUTES TO METHYL METHACRYLATE

EXPERT RANKING QUESTIONNAIRE 1

In this first questionnaire, we would like you to spend no more than two hours. Try to do the rankings using your 'gut feeling'.

Section I - Please rank the six methyl methacrylate (MMA) routes with respect to the three stated criteria and also for overall inherent safety.

Section II - Please identify important features of the individual routes.

Section III - Please give reasons for your rankings with respect to the three criteria and overall inherent safety.

Section IV - Please describe how you dealt with incomplete data about the routes.

12.1 Section I

Rank the six (MMA) in order of their inherent safeness, with respect to the following criteria:

A - Major hazard
A large toxic or flammable release and/or explosion, affecting the surrounding area, with loss of life.

B - Medium scale event
For example, a small explosion or implosion, leading to loss of production and bad publicity. Any loss of life is due to 'bad luck'.

C - Unplanned event
This causes disruption to local population, for example these might be alarms and evacuations, and the event makes the news. The event may not be dangerous but it leads to loss of production and claims for compensation.

Please assign a score of 1 to the route you consider inherently safest through 6 for the route you consider least inherently safe.

12.1.1 Criterion A

ROUTE	EXPERT							
	1	2	3	4	5	6	7	8
ACH	5	6	5	6	3	5	4	4
C2/MP	3	3	4	4	5	5	1	3
C2/PA	4	4	6	3	4	6	3	5
C3	6	5	3	5	6	6	5	6
i-C4	2	2	2	2	2	4	6	2
TBA	1	1	1	1	1	3	1	1

Table C.1 - Scores for criterion A

12.1.2 Criterion B

ROUTE	EXPERT							
	1	2	3	4	5	6	7	8
ACH	5	6	6	6	4	4	6	4
C2/MP	3	3	1	3	3	4	2	3
C2/PA	4	4	4	4	5	3	5	5
C3	6	5	5	5	6	5	1	6
i-C4	2	2	2	2	2	4	2	2
TBA	1	1	1	1	1	4	2	1

Table C.2 - Scores for criterion B

12.1.3 Criterion C

ROUTE	EXPERT							
	1	2	3	4	5	6	7	8
ACH	5	6	4	6	4	4	6	6
C2/MP	3	3	3	3	3	3	1	3
C2/PA	4	4	5	4	5	2	4	4
C3	6	5	6	5	6	5	4	5
i-C4	2	2	1	2	2	3	1	2
TBA	1	1	2	1	1	2	1	1

Table C.3 - Scores for criterion C

12.1.4 Criterion Overall

ROUTE	EXPERT							
	1	2	3	4	5	6	7	8
ACH	5	6	5=	6	3	13	6	4=
C2/MP	3	3	3	3	5	12	1	3
C2/PA	4	4	5=	4	4	11	5	4=
C3	6	5	4	5	6	16	4	6
i-C4	2	2	2	2	2	11	3	2
TBA	1	1	1	1	1	9	1	1

Table C.4 - Scores for Overall criterion

Routes based on:
ACH - Acetone Cyanohydrin
C2/MP - Ethylene via Methyl Propionate
C2/PA - Ethylene via Propionaldehyde

C3 - Propylene
i-C4 - Isobutylene
TBA - Tertiary Butyl Alcohol

12.2 Section II

What are the important features that influence the inherent safety of each route and how important do you consider they are on a scale of 1 (high importance) to 5 (low importance)? You may list any number of features.

Expert 1

ACH

1 No. of toxic and flammables involved and severity (NH_3, HCN, CH_4 etc)
2 Number of process stages and recycle complexity
4 Pressures involved $1 < P < 7$ (higher=worse)
5 Volume of waste streams esp. water

C2/MP

1 No. of toxics and flammables (CO, C_2H_4)
2 No. of process stages
4 Pressures $5(?) < P < 100$
5 Waste streams

C2/PA

1 No. of toxics and flammables (CO, H_2, C_2H_2)
2 No. of process stages
3 Pressures $7 < P < 350$
5 Waste H_2O

C3

1 No. toxics and flammables (HF, CO, Prop)
2 No. of stages
4 Pressures $2.5 < P < 100$
5 Waste H_2O

i-C4

1 No. toxics and flammables (Isobutylene, MMA)
2 No. of process stages
4 Pressure $3.7 < P < 8+$?
5 Waste streams

TBA

1 No. of toxics and flammables
2 Stages
4 Pressure $4.0 < P < 7.5$

Expert 2

ACH

HCN 1
Oxidation 3
High pressure oxygen 3
Med pressure CO 4
Many stages 4
Strong acid 5

C2/MP

Oxidation 3
High pressure oxygen 3
Med pressure CO 4

C2/PA

Oxidation 3
High pressure oxygen 3
High pressure CO 3
Flashing liquid (C_2H_4) 3

C3

Oxidation 3
High pressure oxygen 3
Med pressure CO 4
HF (high pressure) 1
Flashing liquid (C_3H_6) 3

i-C4

Oxidation 3
Med pressure oxygen 4
Flashing liquid (C_4H_8) 4

TBA

Oxidation 3
Med pressure oxygen 4

Expert 3

ACH

Liquid phase high pressure 2
Low yield 2
Toxic gas release 1

C2/MP

Liquid phase high pressure 1
Low yield 2

C2/PA

Liquid phase high temp. 1

C3

HF toxicity 1
High pressure 2
Low yield 1

i-C4

Liquid phase pressure 1
Unstable intermediates 2
Low yield 1

TBA

Liquid phase pressure 2

Expert 4

ACH

Stored ammonia 2   Step 1 (O_2/CH_4 and HCN)   1
    methane 4   Step 2 (ACH)   2
    O_2 5   Step 3 (High P and ACH)   1
    acetone 4   Step 4 (Methanol)   3
    H_2SO_4 4   Step 5 (SO_2 and O_2/CH_4)   2
      Step 6 (SO_2 and SO_3) 3

C2/MP

Stored ethylene 1   Step 1 (High P and flammable) 2
    CO 2   Step 2 (Partial oxidation [PO]) 2
    methanol 4   Step 3 (Methanol)   3
    O_2 5

C2/PA

Stored ethylene 1   Step 1 (High P flammable)   2
    CO 2   Step 2 (High P toxic and flammable) 1
    H_2 3   Step 3 [PO] 2
    formaldehyde 2 ? Step 4 (Methanol) 3
    O_2 5
    methanol 4

C3

Stored propylene 1   Step 1 (CO and HF + high pressure) 1
    CO 2   Step 2 (HF) 2
    O_2 5   Step 3 [PO] 2
    methanol   Step 4 (Methanol) 2

-C4

Stored isobutylene 1 Step 1 [PO] 2
    oxygen 5   Step 2 [PO] 2
    methanol 4   Step 3 (Methanol) 3

TBA

Stored TBA 4   Step 1 [PO] 2
    O_2 5   Step 2 [PO] 2
    methanol 4   Step 3 (Methanol) 3

Expert 5

ACH

A 3
Flashing inventory in stages 3,4 of flammables
B 4
Reaction in stage 1, high temperatures, O_2; HCN (Toxic); sulphuric acid
Large no. of stages
C 4
Numerous liquid effluents; HCN; sulphuric acid

C2/MP

A 5
Flashing inventory in stage 1 of methyl propionate (flammable)
B 3
Reaction in stage 2, O_2; ethylene (flammable); CO (toxic)
C 3
Little effluent or toxics

C2/PA

A 4
Flashing inventories in stages 2,4 of flammable
B 5
Reaction in stage 3, O_2; ethylene, hydrogen (flammable); CO (toxic)
C 5
Little effluent or toxic

C3

A 6
Flashing inventory in stage 1 of isobutyrl fluoride (assumed flammable) + HF (nasty toxic)
B 6
Reaction in stage 3, O_2; propylene (flammable); HF, CO (toxic)
C 6
HF

i-C4

A 2
Flashing inventory in stage 3 of MM (flammable)
Storage of isobutylene (Flammable)(Bpt < atmospheric temp)
B 2
Reaction in stages 1,2 O_2; isobutylene (flammable)
C 1

Little effluent or toxics

TBA

A 1
Flashing inventory in stage 3 of MM (flammable)
B 1
Reaction in stages 1, 2, O_2
C 1
Little effluents or toxics

Expert 6

ACH

Toxicity	1	Flammability	2	
Pressure	5	Quantity		?
Temperature	1	Chemical stability	5	

C2/MP

Toxicity	2	Flammability	1	
Pressure	2	Quantity		?
Temperature	5	Chemical stability	3	

C2/PA

Toxicity	2	Flammability	1	
Pressure	1	Quantity		?
Temperature	2	Chemical stability	3	

C3

Toxicity	1	Flammability	1	
Pressure	1	Quantity		?
Temperature	3	Chemical stability	1	

i-C4

Toxicity	4	Flammability	1	
Pressure	?	Quantity		?
Temperature	1	Chemical stability	2	

TBA

Toxicity	3	Flammability	3	
Pressure	4	Quantity		?
Temperature	1	Chemical stability	2	

Expert 7

ACH

Step   1 Explosion risk / Toxicity   3 1
          2 Fire hazard
          3 Pressure (low risk)
          4   "
          5 Explosion risk
          6   "

C2/MP

Step   1 Explosion risk + possible large inventory 2 1
          2 Explosion hazard
          3 Fire risk

C2/PA

Step   1 Explosion risk : ACH step 1   2 2
          2 Fire risk, High T, P
          3 Gas explosion
          4 Fire risk - not as high as step 2

C3

Step   1 No oxidant - fire risk   1 2 LPG
          2 Not serious. HF + H_2O require exotic materials to contain
          3 Explosion risk
          4 No oxidant - fire risk

i-C4

Step   1 Explosion risk **t** 2 1 LPG
          2   "
          3 Fire risk

TBA

Step   1 Explosion risk
          2   "
          3 Fire risk

Expert 8

ACH

Good - low pressure (1) - especially for liquid
        - gas phase step 1 (2)

- not much above bpt in step 2 (1) - (little flashing)

Bad   - highly toxic HCN, ACH (1)
       - oxygen present (4)
       - many present steps (2)

C2/MP

Bad   - very high pressures (1)
       - toxic CO (1)
       - flammables (2)
       - liquids will flash (1)
       - explosion risk in the equipment (2) (step 2)

C2/PA

Bad   - highly toxic HCHO (1)
       - liquid in step 2 will flash (1)
       - highish pressures (3)
       - hydrogen present (2)
       - flammables
       - oxygen present (4)

C3

Bad   -high pressures (1)
       - will flash on release (1)
       - flammables (3)
       - very toxic HF (1)
       - heavy gas (HF) (1)
       - O_2 in step 3 (4)

i-C4

Bad   - flammables in process (2)
       - poor yield (4)

Good   - low pressure (1)

TBA

Bad   - flammables (3)
       - oxygen in process (4)

Good   - low pressure (1)

12.3 Section III

What are the main reasons for your rankings with respect to:

Expert 1

Criterion A:

Not ranked, as this will be more dependent on initiation event and e.g. inventories, scope for loss of containment which relate as much to integrity of design, Hazards studies etc.

Criterion B:

Use of factors in section 2
i.e. Number and nature of toxics and flammables
Number of stages (measure of complexity ?)
Pressures (Medium (3 -10) atm better than high (15+))
Effluents esp. waste water

Criterion C:

Most likely same criteria but reversed (?)

Overall:

Gut feel and above easily established
TBA + i-C4 'best'
C3 + ACH 'worst'
Hence C2/PA + C2/MP in middle with C2/PA slightly the worse because of H_2 and higher pressures.

Expert 2

Criterion A:

Same reasons for all criteria.

To get overall rankings I reversed the marks in section II
(1 → 5
2 → 4
3 → 3
4 → 2
5 → 1)

and then added them up.

Criterion B:

Criterion C:

Overall:

Expert 3

Criterion A:

> Liquid phase high pressure
> <u>Presumably</u> high inventory

Criterion B:

> Toxic release

Criterion C:

> Toxic release
> Hydrogen fluoride (on which I am not knowledgeable!)

Overall:

> High inventories above flash point
> Toxicity

Expert 4

Criterion A:

> Storage of flammable which is gas at ambient conditions but not over buoyant.
> Large inventory of volatile or gaseous toxic.
> (Large inventory of condensed phase explosive - not used).
> (Fire or explosion - airborne toxic combustion products or ultra-toxic dispersion - not used)
> Physical or chemical explosion - transport of toxic over long range.

Criterion B:

> process conditions - chemical explosion
> > or - physical explosion
> > or - loss of containment flammable - short range.
> > or - loss of containment toxic - short range
> > > e.g. not normally gaseous

Criterion C:

> Toxics or toxic combustion products in fire conditions

Overall:

> Due to relative case of control of off-site risks and their dependence on storage choices, I went along with the category B ranking.

Expert 5

Criterion A:

Main factor used is potential for a large vapour cloud from an inventory of supersaturated liquid, particularly at high pressure.

Criterion B:

As A
Pressure of flammables, toxics
Reactions involving oxygen
Large no. of stages

Criterion C:

As B but particular emphasis the dispersion of flammables, toxics across factory fence.
Release of noxious liquid effluents
High profile in-works emergency

Overall:

Not clear what this really means - I have chosen to base thinking here on major hazard criteria.

Expert 6

Criterion A:

The reasoning behind all of the criteria are similar and based on

Pressure
Toxicity
Quantities
Chemical and physical characteristics
Past experience of incidents

Criterion B:

Criterion C:

Overall:

Expert 7

Criterion A:

Two of the processes appear to require the storage of LPG (Propylene based route, Isobutylene based route). With these there could be a risk of fore in the plant. Vapour phase reactions with explosion hazards can be handled with good control systems and relief systems.

Criterion B:

All these processes have the possibility of explosions. These will happen, but will be contained by the systems referred to in Criterion A above. In general the fewer the steps the better.

Criterion C:

Again in general the fewer the steps the less overall pipework etc. Piping is a prime contribution to this level of event.

Overall:

1 LPG's are bad news.
2 Explosion, fire can be handled.
3 Toxic risks are handled by good design and adequate training.

Expert 8

Criterion A:

Bad - high pressure, especially if linked with a liquid which will flash on release, and even more so if it is toxic.
    - the possibility of explosion within the plant equipment.
    - gas toxicity, especially if it is a heavy gas.

Criterion B:

Same as for criterion 'A'

Criterion C:

Toxicity more important, otherwise as for 'A' and 'B'.

Overall:

As for criteria 'A' and 'B'

12.4 Section IV

Expert 1

Was there any data that you needed but did not have?

More detailed flowsheets showing especially

recycles
'service' materials and reagents
approximate sizes of main plant items
approximate sizes of storage inventories
Materials of construction and resistance to attack

What would you have done with this data if you had had it?

Use risk-size-pT ($m^3.bar.k$) as measure for flammables and toxics

How did you deal with not having this data?

Had to assume no extra hazards from other materials
Effect of plant size(s) same for all processes

Do you have any general comments at this stage?

Interested that intuitive answers not necessarily same as Gut feel and parameter method

Expert 2

Was there any data that you needed but did not have?

1. Boiling point of mixtures
2. Does O_2 mean air or pure oxygen?
3. Are reactions liable to runaway?
4. Inventories in process and storage

What would you have done with this data if you had had it?

1. Would tell me if leaks would flash.
2. Pure O_2 more hazardous - explosions in p/o more likely
3. Obvious
4. Possibly the most important single factor.

How did you deal with not having this data?

1. Guessed
2. Assumed air is used.
3. Ignored.
4. Ignored

Do you have any general comments at this stage?

In view of uncertainties I doubt the value of this exercise.

Expert 3

Was there any data that you needed but did not have?

Inventories of reactants and other obvious gaps.

What would you have done with this data if you had had it?

Used it for the ranking.

How did you deal with not having this data?

Guessed - reluctantly.
(In real life I would not guess!)

Do you have any general comments at this stage?

1. I don't like the idea of doing the ranking without data!
2. I don't have confidence in the judgement of people who don't know the processes.

Expert 4

Was there any data that you needed but did not have?

1 (Relative flowrates)
2 Combustion energy
3 (Process temperature vs. flash point)
4 (Ambient temperature vs. flash point)
5 Ambient vapour buoyancy
6 Ambient vapour pressure vs. TLV
7 Chemicals ordered by boiling point (+ process step temperatures marked)
8 Side reactions (e.g. complete oxidations)
9 Distinction between stored and transient chemicals + scale of recycle
10 Fuel gas requirements
11 Some account of toxic effects (e.g. exposure time to realise certain death)
12 Difficulty of separation

What would you have done with this data if you had had it?

1 Scale of transient chemical risks
2 Scale of fire/explosion consequences
3 Scale of short range fire/explosion risk + internal explosion risk
4 Scale of long range fire/explosion risk + storage fire/explosion risk
5 Scale of range of fire/explosion/toxic risk
6 Scale of short range toxic/flammable risk
7 State of material on loss of containment
8 Scale of risk of unwanted by-products or exotherms
9 Scale of storage risks
10 'Hidden' flammable risk

11 Scale of opportunity for self-rescue. Relative effects of acute vs. chronic exposure.

12 Scale of loss of containment risks in separation processes and recycles

How did you deal with not having this data?

1 Ignored

2 Guessed (qualitatively)

3/4 Tried to bear in mind when relevant (given 2 hr time constraint)

5 Guessed (qualitatively)

6 Used general knowledge - very unsure of this

7 as 3/4

8 Assumed complete oxidation could occur. This was a serious shortcoming.

9 Assumed all possible recycles made and intermediate storage minimised Assumed all   incoming material stored.

10 Ignored

11 Used general knowledge (very dubious)

12 Ignored. Another serious shortcoming.

Do you have any general comments at this stage?

Expert 5

Was there any data that you needed but did not have?

Inventories of liquid phase processes. To some extent, I have inferred reactor inventories from reaction yields (lower yield probably means higher inventory)

Toxicity of isobutyrl fluoride, methyl propionate (in general, there is need for gas toxicity as well as TLV data)

What would you have done with this data if you had had it?

Self explanatory - see section II, III

How did you deal with not having this data?

Do you have any general comments at this stage?

Need for knowledge of relative risk of particular processes e.g oxidation, carbonylation, hydrolysis

Expert 6

Was there any data that you needed but did not have?

Quantities of materials

What would you have done with this data if you had had it?

Estimated potential scale of problem

How did you deal with not having this data?

Guessed that significant quantities would be processed

Do you have any general comments at this stage?

1. Section 1 should have followed section 2 - you use the outcome of section 2 to arrive at the answers to section 1

2. Changing the scale and meaning is confusing (1 - 6 vs. 1 - 5)

3. The boiling points for acetone and methanol are wrong.

Expert 7

Was there any data that you needed but did not have?

Inventories of raw materials
Layout
Distance to works boundary, general public   .

What would you have done with this data if you had had it?

Modified the answers given

How did you deal with not having this data?

Assumed inventories of LPG's in two cases

Do you have any general comments at this stage?

ICI have a good safety record in running the ACH route for 60 years (1 death).
Yet for various reasons this has come out as the least inherent safe route on my
ranking. The chances of killing the general public are minuscule

Expert 8

Was there any data that you needed but did not have?

Flammability data needed for all compounds

What would you have done with this data if you had had it?

In absence of data, I assumed flammability

How did you deal with not having this data?

See previous paragraph

Do you have any general comments at this stage?

The combination of high pressure (likely to cause a leak) with liquid which will flash on release (therefore causing large release + large vapour cloud) seems more important than the factors of pressure and liquid alone; the combination should be weighted.

13. APPENDIX D - QUESTIONNAIRE 2 RESULTS

These are the answers from the completed questionnaire 2s with the steps re-arranged into the correct sequence in the six routes.

13.1 Criterion A

ROUTE	STEP	1	2	3	4	5	6	7	8
ACH	1	4	3	4	3	2	4	2	5
ACH	2	4	4	4	2	2	4	2	2
ACH	3	2	4	1	2	2	1	1	2
ACH	4	3	4	5	1	2	2	1	2
ACH	5	2	3	2	1	2	2	1	2
ACH	6	2	2	1	1	2	4	2	2
C2/MP	1	3	5	2	2	4	5	4	4
C2/MP	2	2	2	3	2	2	4	2	1
C2/MP	3	2	5	4	1	2	1	1	3
C2/PA	1	3	2	4	2	2	5	2	2
C2/PA	2	3	4	3	1	2	4	2	2
C2/PA	3	2	3	5	2	2	2	4	1
C2/PA	4	2	4	3	1	2	2	1	3
C3	1	5	5	3	3	4	5	5	3
C3	2	4	4	2	2	3	3	3	2
C3	3	2	3	2	2	2	1	2	1
C3	4	2	4	3	1	2	2	1	3
i-C4	1	3	3	2	2	2	4	5	2
i-C4	2	2	3	4	1	2	2	4	1
i-C4	3	2	4	3	1	2	2	1	3
TBA	1	3	3	1	3	2	1	2	1
TBA	2	2	3	4	1	2	2	4	1
TBA	3	2	4	3	1	2	2	1	3

Column header: EXPERT (spanning columns 1-8)

Table D.1 - Scores for criterion A

13.2 Criterion B

ROUTE	STEP	EXPERT							
		1	2	3	4	5	6	7	8
ACH	1	4	3	6	4	3	4	2	5
ACH	2	4	4	5	3	2	4	2	2
ACH	3	2	4	4	3	3	1	2	2
ACH	4	3	4	5	4	2	2	2	2
ACH	5	2	3	4	2	3	2	2	2
ACH	6	2	2	4	2	3	3	3	2
C2/MP	1	3	5	2	2	4	5	2	4
C2/MP	2	2	2	3	3	3	4	2	1
C2/MP	3	2	5	3	1	2	1	2	3
C2/PA	1	3	2	1	3	3	5	2	2
C2/PA	2	3	4	3	2	2	4	2	2
C2/PA	3	2	3	4	3	3	2	3	1
C2/PA	4	2	4	4	1	2	2	2	3
C3	1	5	5	5	3	4	5	2	3
C3	2	4	4	4	2	4	3	4	2
C3	3	2	3	4	3	3	1	3	1
C3	4	2	4	4	1	2	2	2	3
i-C4	1	3	3	2	3	2	4	3	2
i-C4	2	2	3	1	3	3	2	3	1
i-C4	3	2	4	4	1	2	2	2	3
TBA	1	3	3	2	4	3	1	2	1
TBA	2	2	3	1	3	3	2	3	1
TBA	3	2	4	4	1	2	2	2	3

Table D.2 - Scores for criterion B

13.3 Criterion C

		EXPERT							
ROUTE	**STEP**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
ACH	1	4	3	4	3	3	4	3	5
ACH	2	4	4	4	2	2	4	3	2
ACH	3	2	4	3	2	3	1	3	4
ACH	4	3	4	4	3	2	2	3	2
ACH	5	2	3	1	1	3	2	3	2
ACH	6	2	2	4	1	3	3	4	2
C2/MP	1	3	5	2	1	4	5	4	4
C2/MP	2	2	2	3	2	3	4	4	1
C2/MP	3	2	5	3	2	2	1	2	3
C2/PA	1	3	2	3	2	3	5	3	2
C2/PA	2	3	4	4	3	2	4	3	5
C2/PA	3	2	3	5	1	3	2	4	1
C2/PA	4	2	4	3	1	2	2	3	3
C3	1	5	5	5	3	4	5	3	5
C3	2	4	4	5	3	4	3	4	4
C3	3	2	3	3	2	3	1	4	1
C3	4	2	4	3	1	2	2	3	3
i-C4	1	3	3	1	1	2	4	4	2
i-C4	2	2	3	5	1	3	2	4	1
i-C4	3	2	4	3	1	2	2	3	3
TBA	1	3	3	2	3	3	1	4	1
TBA	2	2	3	5	1	3	2	4	1
TBA	3	2	4	3	1	2	2	3	3

Table D.3 - Scores for criterion C

14. APPENDIX E - QUESTIONNAIRE 3 RESULTS

These are the answers copied as accurately as possible from the completed questionnaire 3s.

INHERENT SAFETY ASSESSMENT OF ROUTES TO METHYL METHACRYLATE

EXPERT RANKING QUESTIONNAIRE 3

INTRODUCTION

The purpose of this third questionnaire is to aid us in the development of a new index. The questionnaire is divided into several sections:

Current index comments - we would like you to comment on and constructively criticise our present index.

Ranking parameters - please complete the table to help us decide how important various safety parameters are.

Separation steps - please complete the table in a similar manner to the previous table to help us decide what are the important parameters in assessing separation stages.

Structure for new index - your comments and suggestions are requested for the development of our new index.

Other questions - some questions for you to answer on general topics.

14.1 Current Index Comments

Currently our index is calculated by scoring parameters that describe each of the reaction steps in the route and then summing these scores.

Method

The route is divided into reaction steps.

For each step a score is calculated for each chemical involved. This is the sum of the scores for: inventory (based on the hourly production rate for 8000 hours per year , 100% conversion and a nominal holdup of 1 hour), flammability, explosiveness and toxicity. The highest score over all the chemicals in the step becomes the **Chemical score**.

The scores for pressure, temperature and yield are summed to give the **Process score** for the step.

The **step score** is the sum of the Chemical score and the Process score.

The final **route score** is the sum of all the scores for all the steps in the route.
Example

The scoring for the first step of the ACH route is as follows:

Chemical score - the highest is for HCN:

Inventory (1) + Flammability (4) + Toxicity (4) + Explosiveness (4) = 13

Process score:

Temperature (10) + Pressure (1) Yield (2) = 13

Total step score = Chemical score + Process score = 13 + 13 =26

The same procedure yields the scores for steps 2 to 6, which are: 15, 13, 15, 20, 19.

The total score for the route, that is the index value is given by:

Index for ACH route = 26 + 15 + 13 + 15 + 20 + 19 = 108

We would like you to comment on and positively criticise the scoring tables and the method used for calculating the current index. If you think a table of scores is inappropriate or that the ranges in the tables are incorrect, please suggest alternatives.

Comments on method.

Expert 1

Why only one (highest) chemical score, whereas P + T + V are summed?
Perhaps should add $\ln P + 1/T_{abs}$ (or something?)

Expert 2
No comment
Expert 3
No comment
Expert 4
No reply
Expert 5

I will comment on the individual tables in the current index but I have grave doubts about it. In particular, two

1 If you use an index of this type, why not the Dow index?

2 How do you decide if the relationship is additive or multiplicative? I have had a student do an MSc in which he produced a more structured version of the Dow index, i.e rather like a fault tree.

Expert 6

In principle, I can see the value of a scoring system but I have difficulty in rationalising a consistent scoring system. How much "inventory" is equal to what flammability/toxicity/explosiveness and is it logical to add them together?

We should discuss the relative weighting of each parameter.

Expert 7

No comment

Expert 8

No comment

Inventory (Tonnes)	Score
0.1 - 250	1
251 - 2500	2
2501 - 7000	3
7001 - 16000	4
16001 - 26000	5
26001 - 38000	6
38001 - 50000	7
50001 - 65000	8
65001 - 80000	9
80001 - 100000	10

14.2 Inventory

General comments on this parameter

Expert 1

Strange intervals. HSE assume Risk $\propto$ (Inventory)^2 . Is this basis?

e.g I = 26k   score =5

$\quad$ I = 4 * 26 k   score = 10   i.e Risk $\propto \sqrt{Inventory}$?

For toxics anything > 2500 te alarming! (i.e. score 2?). Should penalise rate.

Expert 2

What is the logic underlying the sizes of the step?

According to page 1, last paragraph, inventory is based on hourly production rate, assuming 100% conversion and 1 hour hold-up. It should be based on the actual inventory. The production rate is irrelevant. The actual inventory depends on the conversion per pass, the efficiency (i.e. are unwanted by-products formed?), equipment design and buffer storage. The old and new methods for nitroglycerine production had the same hourly production rate but the old method had 1000 times more inventory.

Expert 3

For toxic substances the low range 0.1 - 250 is too low.

Expert 4

No reply

Expert 5

Range 0.1 - 250 covers many cases of interest. Subdivide it. Inventories of 50 - 100000 te sound like oil storage rather than most other material.

For explosive and possibly flammable clouds, for a given effect

$$\frac{\text{Distance}}{\text{Mass}^{1/3}} \propto \text{Constant}$$

So a 1/3 power may have a role to play.

Expert 6

What counts as inventory? Feedtanks, reactors, intermediate storage, final storage?

Again, I have difficulty justifying the breakdown of quantities but at the moment cannot suggest a more logical split.

Expert 7

Range should cover

0.1 - 1.0   Maybe score for 0.1 te should be 0.1
1.0 - 10.0
10.0 - 50.0
50 - 500

e.g Propylene tanker disasters in Spain, 20 te = many deaths

Almost the most important parameter.

What you don't have can't leak!

Expert 8

As I read your definition on page 1, 1000 te/yr gives an 'Inventory' of 1000/8000 te/hr * 1 hr = 0.125 te. So 100000 te inventory corresponds to 8 * 10^8 te/yr! Do you mean that?

I would expect that the risk is proportional to the number of streams in parallel. hence for higher tonnages (say > 10000te/yr), score might be proportional to tonnage. Furthermore I would think the parameter should then be a multiplier, not an additive factor.

Flammability	Score
Non-combustible	0
FP > 140°F	1
100°F < FP < 140° F	2
FP < 100°F BP > 100°F	3
FP < 100°F BP < 100°F	4
FP = Flash point BP = Boiling point	

14.3 Flammability

General comments on this parameter

Expert 1

Too sophisticated for me esp. °F rather than °C

Flash point not always the issue (can depend on dispersion characteristics and flammable limits (LFL, UFL))

Expert 2

Why not use °C?

Expert 3

OK

Expert 4

No reply

Expert 5

For a flammable, what matters is how much participates. That in turn depends on the phenomenon e.g flash fire (vapour cloud fire), vapour cloud explosion.

The important thing is how much flashes off. would concentrate on boiling point. 100°F is rather high.
    -40°C -10°C +10°C ?

Expert 6

How were the temperatures chosen? Could we not align them with figures in legislation e.g. 21°C (Petroleum act), 32°C (Highly flammable), 55°C (HSE Guidance Booklets) for flashpoint? This would avoid yet more arbitrary divisions and classifications.

Expert 7

Chemical plants usually store reactants at ambient T and react at elevated T. Crucial question is

Is material above its flash point at room temperature?

If at flash point = LEL

°F now abandoned!

Expert 8

There is a recognised definition of "highly flammable liquid" based on F.P. of 32°C (See e.g. F.P.Lees book, P506).

Should this be the lowest FP limit?

Also, should be in °C.

Toxicity (ppm)				Score
	TLV	<	0.001	8
0.001	≤ TLV	<	0.01	7
0.01	≤ TLV	<	0.1	6
0.1	≤ TLV	<	1.0	5
1.0	≤ TLV	<	10.0	4
10.0	≤ TLV	<	100.0	3
100.0	≤ TLV	<	1000.0	2
1000.0	≤ TLV	<	10000.0	1
1.0%	≤ TLV			

14.4 Toxicity

General comments on this parameter

Expert 1

Again TLV (based on health = long term)
Look at probits (constant) = dosage-time?

Expert 2

In the UK TLVs have now been replaced by Maximum Exposure limits and Occupational Exposure Standards (see COSHH Regulation)

TLV' (and their successors) do not always measure the risk to life. Some are based on discomfort, for example, lachrymatory substances such as tear gases. LD_{50} would be a better measure of toxicity.

Expert 3

I'd prefer the range to be biased to the lower TLVs e.g

TLV < 0.0001 8
     < 0.001   7
     < 0.01   6
     < 0.1   5
     < 1   4
     < 10   3
     < 100   2
     < 1000   1

Expert 4

No reply

Expert 5

See comments on p13 on toxicity. TLV is a valid parameter for long-term exposure. A TLV of 1 ppm is pretty strict. TLVs below that not likely to be quite explosive to obtain.

Expert 6

EH40 from the HSE no longer use TLVs and use instead maximum exposure limits (MELs) and occupational exposure standards (OESs). I think these should be used in the UK. There should be a weighting depending upon whether there is an MEL or not and perhaps taking account toxic dose levels.

Expert 7

1 TLV now OEL

2 TLV poor index of hazard - replace with Short Term Toxic Limit.

e.g HCN 10 ppm is not very toxic but 300 ppm for 1 min = death.

Expert 8

I suspect the scales for low TLV's should be greater.

Explosiveness		
S = (UEL - LEL)%		Score
0 ≤ S < 10		1
10 ≤ S < 20		2
20 ≤ S < 30		3
30 ≤ S < 40		4
40 ≤ S < 50		5
50 ≤ S < 60		6
60 ≤ S < 70		7
70 ≤ S < 80		8
80 ≤ S < 90		9
90 ≤ S < 100		10

14.5 Explosiveness

General comments on this parameter

Expert 1

Again not sure of physical basis. Something about energy ?

Expert 2

The value of LEL is more important than the value of S as a low LEL is more easily reached than a high one.

Ammonia has an LEL of 16% and is therefore much more difficult to ignite than light hydrocarbons which have a much lower LEL but a lower value of S.

Ammonia: S = 27 - 16 = 11
Ethane: S = 12.5 - 3 = 9.5
Pentane: S = 7.8 - 1.4 = 6.4

Expert 3

OK

Expert 4

No reply

Expert 5

Most flammability limits ranges are fairly similar, except hydrogen. I am doubtful whether this is worth including.

Expert 6

Does this actually provide much variation for a lot of chemicals? Looking at some of the figures I suspect not.

Why not use autoignition temperatures along the lines of area classification guidance?

Expert 7

This might better be presented as YES/NO to question - Is material flammable/explosive through range in which it is used?

Expert 8

None

Temperature (°C)				Score
		T <	-25	10
-25	≤	T <	-10	3
-10	≤	T <	10	1
10	≤	T <	30	0
30	≤	T <	100	1
100	≤	T <	200	2
200	≤	T <	300	3
300	≤	T <	400	4
400	≤	T <	500	5
500	≤	T <	600	6
600	≤	T <	700	7
700	≤	T <	800	8
800	≤	T <	900	9
900	≤	T <		10

14.6 Temperature

General comments on this parameter

Expert 1

Don't understand why low temperatures penalised (H_2O/NaCl mixtures go to -25!)

Should exponential ? $R \propto e^{kT}$

Expert 2

Temperature is not dangerous in itself, only in relation to flash point and boiling point, which you have already taken into account on page 4. Are you double-counting?

Expert 3

OK

Expert 4

No reply

Expert 5

Yes, this recognises problems in both low and high temperature ranges.

Low temperature have potential to cause low temperature brittle fractures i.e probability of release.

Likewise high temperatures increase probability of release.

But consequences are very different. At high temperatures there will be a massive flashoff. At low temperature relatively slow vaporisation.

But it will depend upon inventory.

Expert 6

What is the justification for the ranges and the scoring?

Expert 7

Two effects

1 Enhances risk in handling flammables
2 Strength of plant

Score doesn't really reflect 2 as superior materials can be selected to combat high temperatures.

OK as a crude start.

Expert 8

Ranges 10 - 30 to 500 - 600 suggested as scoring 0
Ranges 600 - 700 to 900 + scored as 1 to 4

For high temperatures the relationship of temperature to the atmospheric bpts seems more important by far absolute temp, since it determines how much liquid will flash on release.

Pressure (psi)	Score
0 - 90	1
91 - 140	2
141 - 250	3
251 - 420	4
421 - 700	5
701 - 1400	6
1401 - 3400	7
3401 - 4800	8
4801 - 6000	9
6001 - 8000	10
+1 point per 2500 psi	

14.7 Pressure

General comments on this parameter

Expert 1

Looks okay

Could look at energy pV. (cf Trevors LP IP HP)

Expert 2

What is the logic underlying the sizes of the steps? They should be based on the effect of pressure on leak rate. See, for example, Lees, Figure 15.2 on page 416.

Expert 3

Prefer it biased lower e.g.

0 - 50 psi	2
51 - 100	3
101 - 150	4
151 - 200	5
201 - 500	6
501 - 1000	7
1001 - 4000	8
4001 - 6000	9
6001 - 8000	10

Expert 4

No reply   -

Expert 5

I can think to the propensity to flash off. What matters is whether fluid is a saturated liquid under pressure. And pressure has to be considered in conjunction with temperature.

Expert 6

Basis for figure?

Expert 7

About right.

Expert 8

Should be in bars?

This would give the high pressure polyethylene process (1500 bar) a score of 16 on pressure alone - seems high in light of experience? - especially if we are considering safety to public as well as employees.

Yield (%)	Score
100	0
90 - 99	1
80 - 89	2
70 - 79	3
60 - 69	4
50 - 59	5
40 - 49	6
30 - 39	7
20 - 29	8
10 - 19	9
0 - 9	10

14.8 Yield

General comments on this parameter

Expert 1

Not relevant - capture an inventories recycle rates. Again don't understand basis. Most bioprocess have very low yields.

Expert 2

As stated above, yield is irrelevant; inventory is the property that matters. Of course, yield effects inventory, but so do other things and we should measure the final inventory.

Expert 3

OK

Expert 4

No reply

Expert 5

Presumably point about yield is that low yield can lead to large recycles, large separation section. Is this not dealt with already by inventory parameter.

Expert 6

Does it necessarily follow that the bigger the yield the lower the score?

Expert 7

Need to discuss this - not quite sure of relevance. Surely rate would be better (
to look at chances of a runaway reaction)

Expert 8
OK

14.9 Ranking Parameters for reaction and separation steps

In making an assessment of the inherent safety of a reaction step, how important do you consider the following parameters.

In the left-hand column, record whether you consider that the parameter is essential in making an assessment of inherent safety, that is would the assessment be invalid without the piece of information.

In the right-hand columns, tick one box to indicate the importance of the parameter in assessing inherent safety. Column 1 is very important, through to column 5, unimportant.

| Parameter | EXPERT | | | | | | | | Total | Essential |
	1	2	3	4	5	6	7	8		
Inventory	5	5	5		5	5	5	5	35	7
Toxicity	5	5	5		5	5	4	5	34	7
Chem. Stability	5	5	2		5	5	3	5 ·	30	7
Temperature	3	2	5		5	5	3	5	28	7
Pressure	3	3	5		3	5	3	3	25	7
Flammability	4	5	5		-	5	4	2	25	7
Explosiveness	5	5	5		-	-	4	3	22	7
Flash point	3	2	1		-	5	4	2	17	4
Side Reactions	2	-	-		5	5	-	5	17	3
Waste streams	2	3	2		4	4	-	-	15	3
Reaction phase	2	-	-		4	4	2	-	12	3
Yield	1	1	3		-	-	-	5	10	3
Recycles	3	-	-		-	3	-	-	6	0
Mitigation	5	-	-		-	-	-	-	5	0
Temp. relative to atm. B.P	-	-	-		-	-	-	5	5	1
Mat. Corrosion	4	-	-		-	-	-	-	4	0
Complexity	4	-	-		-	-	-	-	4	0
Human factors	3	-	-		-	-	-	-	3	0

Table E.1 - scores for importance of parameters

Do you consider that there are any important interactions between these parameters that make assessments of safety better or worse?

Expert 1

Pressure temperature inventory - source term esp. for toxic release

Expert 2

Beware of double counting, e.g. temperature and flashpoint, explosiveness, flammability and chemical stability.

Expert 3

Of course - too complex for simple answer.

Expert 4

No reply

Expert 5

Explosiveness, chemical stability are similar - no sorry I see by explosiveness you mean flammable/explosive range.

Inventory/temperature/pressure interact.

Expert 6

No comment

Expert 7

No comment

Expert 8

Re: inventory - see previous comments - should be a multiplier.

A combination of temp >> bpt, and high flammability or toxicity is particularly bad.

It is clearly possible to generate table, based on proportion flashing.

14.10 General comments

Expert 3

It may be possible to distinguish between reaction steps and separation steps - however in my experience the same factors apply.

Where do dust explosions during drying and mechanical accidents e.g centrifugation apply?

Expert 8

I do not see why separation steps are any different to reaction steps.

14.11 Structure of new index

In our new index, we are using a four factor approach to assess the steps:

Inventory * Hazard Assessment * Probability of release * Effects multiplier

The '*' means 'combined with in some way' as opposed to a multiplication.

Inventory is a more rigorous estimation of the contents of a reaction or separation step.

Hazard assessment includes explosion, fire and toxic effects. It is a quantitative assessment of how much damage could be caused for each of the three hazards per unit inventory. It could be for example a T.N.T. equivalent or the Mortality index for the hazard.

Probability of release is derived from parameters such as propensity for runaway, corrosiveness, extremes of pressure or temperature, etc.

Effects multipliers quantifies how much the hazard could be amplified or attenuated by process conditions or other circumstances, for example materials used under conditions which could lead to flashing in the event of a leak, or toxic materials which have are persistent, like dioxins.

Inventory and hazard assessment are likely to be combined to give a qualitative assessment of the hazards for comparison between routes. Probability and effects multipliers will give an additional measure to the index to indicate if a route is more likely to have things go wrong with it.

Your comments and suggestions about this new approach would be much appreciated.

Expert 1

I' wish I'd read this first. Seems simpler yet more realish.

Could $_4\sqrt{I*HC*PR*EM}$ * better than + as it creates rather than destroys dimensionality.

Expert 2

The new approach seems to meet many of the comments I have made.

Expert 3

Unless the mathematics of the asterix and formula can be very transparently explained the method will not be credible.

The effects multiplier sounds too subjective. Rules for it will need to be published

Expert 4

No reply

Expert 5

I am much happier with this, which I can relate to in logic tree/fault tree.

Expert 6

No comment

Expert 7

Dominant hazardous material, Material factor, Specific material hazards, Type of process, process conditions, quantities, plant layout, toxicity.

Expert 8

Much, much, better approach, I think.

$\propto$ Inventory for larger tonnage
$\propto$ Probability of release

14.12 Other questions

In what circumstances do you consider that intermediate storage is needed in a plant?

Expert 1

Quality control
Operability/reliability upstream/downstream
Comfort!
Economics (Seasonal variation in energy and raw mats. cost)

Expert 2

Intermediate storage is justified when intermediate is not hazardous and the cost of storing is (fixed plus working capital) is justified by the saving in output.

Expert 3

Many

e.g when lengthy testing is needed.
when multi product routes exist
etc.
etc.

Expert 4

No reply

Expert 5

Intermediate storage is used to allow plant to keep running in face of unreliability of 1. upstream and /or 2. downstream sections. The need for it depends on how acceptable it is to have an interruption of the product flow.

Expert 6

Startup + upset

Expert 7

Only when the consequences of <u>not</u> having it give rise to other hazards. e.g difficult start up regions. Even then one should attack the difficult start up e.g with computer based control.   .

Expert 8

Batch processes, particularly if blending required.

What do you consider is the most practicable measure of toxicity, that can be used to assess the inherent safety of chemical routes?

Expert 1

Some derivation from probit/dist. is $f(c_s t)$ regrettably

Perhaps [Time] should be a parameter?

Expert 2

LD_{50} is probably the best available measure of toxicity. In theory LD_{10} might be better but data is rarely available.

Expert 3

Death hazard to off-site personnel

Death hazard to on-site personnel

Expert 4

No reply

Expert 5

There are two distinct measures of toxicity

1. Occupational hygiene - long term exposure of workers - TLV

2. Lethal effects - Toxic load

Toxic load $L = f(C,t)$

where C concentration
t exposure time

It could be

$$L = Ct$$

But it is not necessarily so

It can be expressed as

LL_{50}, LCt_{50} etc

Expert 6

LD_{50} for animal
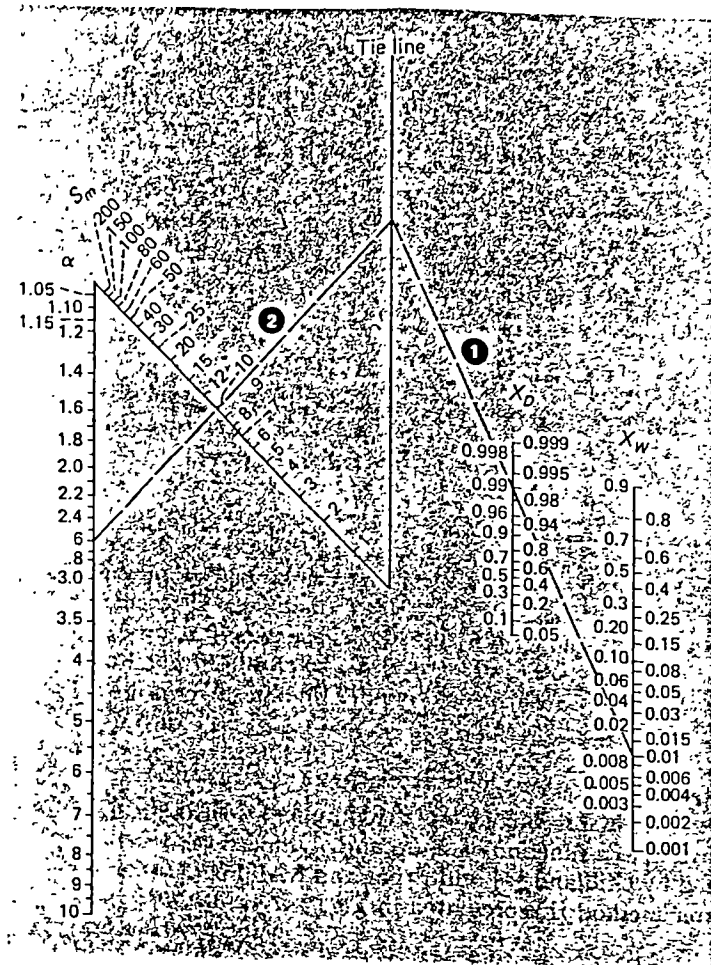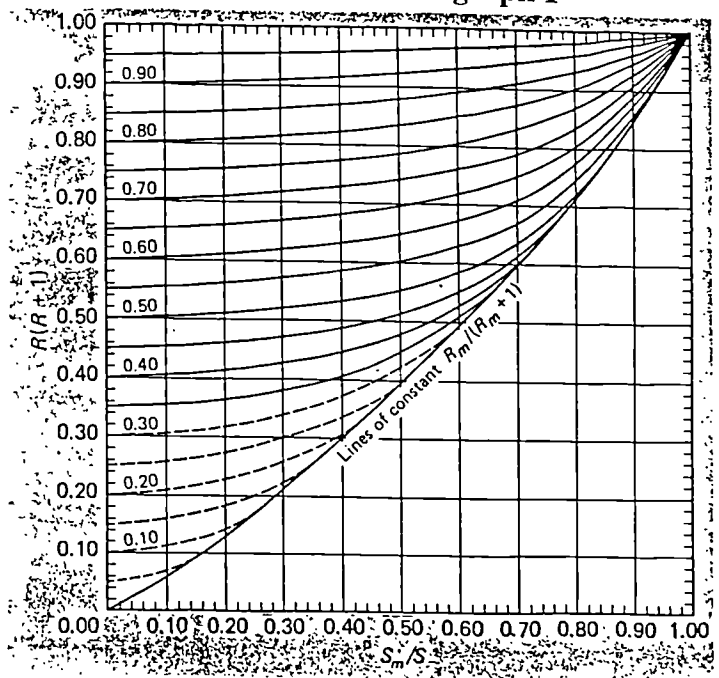
Expert 7

See p 6 STTL

Expert 8

No comment

Figure 15.1 - Nomograph 1

Figure 15.2 - Nomograph 2