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SVILUPPO DI METODI QUANTITATIVI PER L'ANALISI DELLA SOSTENIBILITÁ DI PROCESSO
-
DEVELOPMENT OF QUANTITATIVE METHODS FOR SUSTAINABILITY ASSESSMENT IN PROCESS INDUSTRY

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0.1 – General introduction

Since several years the society is showing an increasing concern about the development of sustainable and safe production processes. The growing competitiveness of the market caused an important acceleration in R&D activities, introducing new opportunities for the implementation of sustainable criteria in the design of industrial production processes. Therefore, the constraints and the priorities in the goals of the research and design activities were forced to change from the traditional ones, in particular in the chemical sector. In fact, till the 90s the key factors in process design concerned the overcoming of technological constraints and the sole economic optimization of the industrial operations. Instead, in the last decade the focus of design improvement shifted to the problem of coping with external constraints as environmental impact and process safety. Nowadays, the increasing aversion to technological risks of the society requires the development of inherently safer and environmental friendly processes, beside assuring the economic competitiveness of the industrial activity. The perspective of sustainability allows encompassing all these aspects at once. In fact, the impacts of a production process can be classified, according to sustainability assessment, as environmental, economic and societal. These very different forms of impacts, frequently characterized by reduction strategies in mutual disagreement, must be holistically taken into account by a proper balanced analysis in order to identify the optimal solutions in process design. Thus, a reliable *decision support system* is required to guide design activities, in particular for the development of new technologies, where significant risks may be overlooked due to a lack of previous experience (*emerging risks*).

With respect to the conceptual definition of sustainability and inherent safety, the literature reports an extensive discussion of the strategies, as well as sets of specific principles and guidewords. However, in the absence of quantitative assessment tools, these are not sufficient to develop effective strategies for the improvement of process and plant performance. As a matter of fact, the application of the principles or guidewords may result in contradictory indications on some possible hazard reduction actions. Therefore, the development and the introduction of a metric and of quantitative assessment tools is a necessary step in order to effectively introduce inherent safety and sustainability criteria in process and plant design.

Technical quantitative tools for development of sustainable processes and for the implementation of inherent safety principles in the design activities still need work to be fully defined. Several methodologies and techniques were proposed, mostly derived from a reorientation of traditional tools used in process engineering. However, these are poorly interfaced in an integrated system. The introduction of sustainability approaches in the practice of design (both *conceptual* and *basic*) and of process optimization is still a problem because of the specific characteristics of these design activities: limits in the amount and detail of the available information should be considered; the parameters actually measurable should be identified; time factor should be accounted; resorting to subjective or expert judgement in the analysis should be restrained. Current literature approaches are not fully suitable for applications that satisfy all these constraints. For instance, traditional risk assessment techniques rely on historical data and experience with risks (the *lagging risk indicators* used in e.g. assessment of environmental impact, quantitative risk analysis, etc.), and are therefore not always applicable to analyse early stages of process design. There is, thus, a need for a more pro-active approach on risk management. The development of *leading risk indicators* for performance assessment, to be used instead of or in combination with the traditional *lagging risk indictors*, is a key issue in this field. Moreover, comprehensive integrated approaches are required to limit the possibility of *risk shift*: the implementation of actions effective in the improvement of one aspect of the risk (e.g. inherent safety) may cause the uncontrolled increase of other risks (e.g. the environmental risk due to the process). In

particular, the clustering of the different quantitative indicators to a limited number of integrated indices is a critical point.
With regard to inherent safety assessment, existing methods are mainly based on empirical indexes. Moreover, they are concerned only with the selection of process alternatives during the conceptual stages of the lifecycle of process design (type of substances, selection of the catalyst and of solvents, etc.), while scarce attention is paid to the assessment of the possible options available in the other stages of project lifecycle, as in basic design or in lay-out definition. As a matter of fact, it has been recognized that the actions aimed to inherent safety improvement must focus not only on initial phases of process design, but also to all the initial phases of the different stages of the design lifecycle (process design, flow-sheet definition, P&ID definition, etc.). However, the different kind of information available in any of these stages requires the introduction of a modulated approach to inherent safety, that is not currently available.

The present work is aimed at the development of supporting tools for integrated industrial process design, specifically dedicated to the chemical industry or to industrial processes in which substances dangerous for humans and environment are used or stored.
The tools will be mainly devoted to the application in the stages of *conceptual* and *basic design*, for two main reasons. On one hand, the usual techniques of *project management* recognize in these stages a higher number of degrees of freedom. Thus, during conceptual and basic design it is still acceptable to consider and assess various and different technical solutions, also due to the reduced impact of the activity on the overall project costs. On the other hand, especially in the stage of conceptual design, the availability of a decision support system would be strategic to successfully address the decision process during design activities, that is too often only committed to unverified expert judgment.
The ultimate goal of current work is, thus, the development of a decision support system for conceptual design and basic design. In particular, a portfolio of tools, devoted to the analysis and assessment of process inventory, of process flow diagrams, and of preliminary plant lay-out, will be developed. The decision support system will be based on the use of a system of *leading key performance indicators* (KPIs), which will assure the assessment of economic, societal and environmental impacts of the process (referred to as the *sustainability profile* of the process). The integrated sustainability assessment will include both a normalization procedure, aimed to introduce in the analysis site-specific issues, and an aggregation procedure that will allow accounting for specific targets in the management policy of the site and of the surrounding area.
Particular attention will be devoted to the development of reliable criteria and tools for the assessment of inherent safety. The implementation of inherent safety in design activity is worth both for itself, since it leads to systems with a reduced hazard level, and as a key element for sustainable process development, since it can be linked to the social dimension of sustainability. A set of tools suitable for quantitative assessment of inherent safety in different stages of the process design was developed in current work.

The work was divided in 4 main sections:

- **Section 1** provides an introduction to the approaches for implementation of sustainability in design activity. A novel procedure developed for the definition and comparison of the quantitative sustainability profile for alternative process options is also described. The developed method is suitable for application as integrated decision support tool in early stages of process design.
- **Section 2** describes a portfolio of innovative tools for inherent safety quantitative assessment. The tools cover the specific aspects of different stages of process design

(material selection, process definition, plant design, layout definition). Objective criteria (e.g. expected possible consequence of accidents) were adopted in the definition of the methods. The methods provide a comprehensive support to the implementation of inherent safety principles in design stages previously poorly explored and a reliable indicator for societal aspects related to safety in the sustainability assessment.

- **Section 3** presents the results of an experimental survey aimed at exploring aspects related to the inherent safety of materials. In particular the thermal stability and the formation of hazardous decomposition products was studied. The activity was focused on the application of suitable experimental protocols for the analysis of isomers of chlorinated and non-chlorinated nitrobenzaldehyde.
- **Section 4** reports several case studies demonstrating the application of the developed methodologies. Moreover the case studies worked as validation tests for the methods, proving the ability to identify the expected critical issue of each case. The case studies concern the analysis of options for the production of chemicals (cyclohexanone, hydrogen), storage of materials (hydrogen), preparation and finishing of fine chemicals, disposal of wastes (electronic boards, exhausted solvents), hazard assessment of materials, layout definition for plant and storage farms.

Section 1: Sustainability

§1.0 - Introduction

In the last twenty years the chemical and process industry has been actively committed in reducing its impacts on the planet, aiming at the limitation of the environmental burdens and at the use of renewable resources. More recently, these actions were incorporated in a holistic perspective, referred to as sustainability, that promotes a common systematic approach to the investigation of economic, societal and environmental performances. The adoption of a sustainable behaviour is nowadays a core issue for process industry, representing the effective answer to problems like societal acceptability, pressure on the environment, efficiency, safety, etc. The development of specific guidelines and tools is required to effectively address sustainability at the different scales of industrial activity.

The design stages of production processes and plants strongly influence the sustainability profile of new installations. Process design activities are conventionally divided in several stages (conceptual design, basic design, detailed design, design of operative procedures). In particular, the early stages of the design (i.e. conceptual and basic process design) show a great potential for implementation of sustainability concepts, provided that adequate tools are available for the assessment. While several tools were introduced to support a life cycle approach to product and process design, the availability of widely accepted quantitative assessment tools providing a specific support to process design is still limited.

The present section aims at the development of an assessment tool specifically addressed to be used as a design support system. The tool will provide a quantitative sustainability metric for decision-making and improvement-assessing. The developed tool will be fully applicable since the early stages of design and it will include all the relevant aspects for the assessment of sustainability profile.

In §1.1.1 the basic principles underlying sustainability of industrial processes are reviewed. In §1.1.2 the existing quantitative approaches to sustainability assessment in industrial activities are discussed with respect to the applicability to process design support systems. In §1.2 the innovative procedure developed in current study is described in all its parts. Complementary information on the definition of normalization and weighting factors are presented in Appendix 1.1. The main conclusions on the section are briefly drawn in §1.3.

1.1 – Background

1.1.1 – Introduction to Sustainability

Sustainability aims to a balanced and respectful way to conduce human activities, so they can be maintained indefinitely. It is popular to define not the sustainability itself, but the collection of dynamic processes and activities that evolve in accordance to sustainability: this is the *sustainable development*. The well-known definition of this, from the Brundtland Commission - formally, the World Commission on Environment and Development *[WCED, 1987]* - is the development that "meets the needs of the present generation without compromising the ability of future generations to meet their own needs."
The natural resources of the Earth, in their broader sense, are limited in quantity and, once depleted, have their specific regeneration rates. This observation is the rationale of shifting to a development model that interfaces human activities with the Earth in a sustainable way, in order to allow long-term coexistence and prosperity.
In the analysis of sustainability of a system three main domains or spheres are identified as to require comprehensive addressing (*triple bottom line*): environment, economy and society.

As a matter of facts, human activities interest the whole crust and atmosphere of the Earth. Thus sustainability must account for the whole Earth system. However, in a complex system, the global performance deepens both on the performance of the single parts and on their interaction. Each part can be further divided in smaller elements and the procedure can be repeated. Sikdar *[2003]* identifies 4 system scales for the application of sustainability:

1. **Global concerns or problems** (e.g. global warming, ozone depletion, biodiversity, etc.): global treaties and agreements are effective tools on this scale.
2. **Systems characterized by geographical boundaries**: competencies about civil and environmental engineering, ecology, hydrology, urban planning, law and economics should act to address sustainability into this scale.
3. **Business** either localized or distributed: sustainability can be practiced by creating material and energetic exchange networks, reducing energy intensity, adopting cleaner technologies, recycling by-products, creating a safe and comfortable environment for employees.
4. **Sustainable technologies**: these are the technologies aimed at providing economic values and services through clean procedure/devices.

Operative tools and drivers are required to implement sustainability in each one of those scales. In the present study, the focus will be mainly on the last two levels of scale, since they are the ones of relevance for process and chemical engineering. However the connection with larger scales (global and geographical) will be a distinctive element in making the sustainability of technologies effective (see §1.2.4 and §1.2.5).
Being more specific, the focus of present study is on the design activity in the process and chemical industry. In fact, the design of a facility defines the sustainable performance of the technology, both as stand-alone (“sustainable technology” scale) and as interacting with other entities all across the temporal and spatial lifecycle (“business” scale and fallouts on larger scales).

Table 1.1.1 reports a brief list of guidelines, principles and conceptual tools that are suitable to provide theoretical support for the application of sustainability in process industry.

The Natural Step principles	*[TNS, WP]*
The Earth Charter principles	*[TEC, WP]*
The Hanover principles	*[THP, WP]*
The CERES (Coalition for Environmentally Responsible Economies) principles	*[CERES, WP]*
Industrial Ecology	*[Garner & Keoleian, 1995]*
Green Chemistry	*[Anastas & Kirchhoff, 2002]*
Green Engineering	*[Abraham & Nguyen, 2003]*
Life Cycle Thinking	*[Allen & Shonnard, 2002]*
Design for the Environment	*[DfE, WP]*

Table 1.1.1: List of guidelines providing theoretical support for the application of sustainability in process industry.

These guidelines were analysed and three common key-concept that characterize sustainability were identified:

- **Holism**: a system must be considered as a whole. A comprehensive and balanced perspective must be adopted with regard to the possible different point of view. The interactions of the system with the surroundings and the extension over time and space must be accounted. Analysis addressing a single aspect of the system must be avoided. Examples of holism are life-cycle thinking, combination of environment, economy and society in a tripe bottom line, “risk-shift” avoiding, etc.
- **Inherency**: the embedded proprieties of a system should be accounted, selected, designed and preferred. System should match their function without negatively affecting any other concern. Examples span from materials (safe, recyclable, bio-degradable, etc.), to processes (atom efficient, stable, safe, waste and by-product free, exploit renewable sources, etc.), to design for sustainable use and recycle phase (safe in use, requiring limited utilities/intervention for use and maintenance, safely disposable/recyclable, etc.).
- **Integration**: any system or element interacts with other systems. Systems must be designed to take advantage from such interactions, resulting in a shared and mutually profitable use of material energy and services and minimizing waste and inefficient use of resources. Industrial ecology, recycle and reuse policies, elimination of the concept of “waste” are example of this key-concept.

For sake of reference, a brief description of some of the principles and conceptual tools cited is reported in the following. For further details see the cited literature. Inherent safety will be extensively discussed in §2.

1.1.1.1 – Green Chemistry and Green Engineering

Green chemistry aims at the design of chemicals and of synthesis routes that are safe and that reduce or eliminate the formation of undesired materials and by-products. The approach is of particular concern among chemists and industrial chemists, but quite obviously extends its fallouts on all the competencies in the chemical and process industry.

Green chemistry features guidelines for the identification of chemical route and reactants. These are expressed through a collection of principles *[Anastas & Kirchhoff, 2002]*:

1. Prevent waste
2. Maximize atom economy
3. Design less hazardous chemical syntheses
4. Design safer chemicals and products
5. Use safer solvents and reaction conditions
6. Increase energy efficiency
7. Use renewable feedstock
8. Avoid chemical derivatives
9. Use catalysts, not stoichiometric reagents
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

Green chemistry has found a significant popularity among chemists and industrial chemists. To quote a few examples, outcomes of green chemistry concern the use o renewable raw materials *[Anastas & Kirchhoff, 2002]*, the identification of atom efficient reactions *[Trost, 2002]*, the development of solvent-free synthesis *[DeSimone, 2002; Allen & Shonnard, 2002]*, the use of supercritical solvents *[DeSimone, 2002]* and the development of innovative synthesis routes *[Allen & Shonnard, 2002; Bose et al., 2002; Trost, 2002]*.

Green chemistry alone is not sustainable chemistry. Though green chemistry is a good application of the inherency concept, the sustainability of an industrial chemical process is influenced also by design choices pertaining the scale-up of the laboratory chemical reaction. This introduces a number of further issues to be taken into account with regard to economic, environmental and social aspects.

Green engineering is the design, commercialization, and use of processes and products, which are feasible and economical while minimizing the generation of pollution at the source and the risk to human health and the environment. The green engineering encompasses all the branches of engineering activity, but is particular suitable for process engineering *[Abraham & Nguyen, 2003; Anastas & Zimmerman, 2003]*.

The principles of green engineering can be listed as follows *[Abraham & Nguyen, 2003]*:

1. Engineer processes and products holistically, use systems analysis, and integrate environmental impact assessment tools.
2. Conserve and improve natural ecosystems while protecting human health and well-being.
3. Use life-cycle thinking in all engineering activities.
4. Ensure that all material and energy inputs and outputs are as inherently safe and benign as possible.
5. Minimize depletion of natural resources.
6. Strive to prevent waste.
7. Develop and apply engineering solutions, while being cognizant of local geography, aspirations, and cultures.
8. Create engineering solutions beyond current or dominant technologies; improve, innovate, and invent (technologies) to achieve sustainability.
9. Actively engage communities and stakeholders in development of engineering solutions.

The principles are intended for engineers to use as a guidance in the design or redesign of products and processes within the constraints dictated by business, government and society such as cost, safety, performance and environmental impact. The vision provided by the principles is broad, outlining a similar perspective in addressing problems of different nature.

1.1.1.2 – Industrial ecology

Industrial processes are not stand-alone entities, but are connected one-another by material and energetic exchanges. The idea of industrial ecology is to optimize those exchanges making them efficient both from the ecological and economic sides *[Garner & Keoleian, 1995; Stanley & Manahan, 1999]*. It is essentially a system approach to the problem. Clearly enough the issues identified on the whole system scale should be reported to specific action in the design of the facilities (“Think globally, act locally” *[Garner & Keoleian, 1995]*).

Industrial ecology is named after the science of ecology, that studies the dynamic links among single organisms and their environment, accounting for physiologic feedbacks, population structure and dynamics, material and energy exchanges in the system, interaction and organization. Similarly industrial ecology studies the interactions among industrial facilities in the industrial systems and between the system and the surrounding environment.
Ecological systems are closed and fully-integrated systems, where a dynamic equilibrium exists. Materials and energy are continuously recycled and reused by the units of the system: wastes of an organism are the substrate for another. The only external contribution is a renewable source of energy, typically the sun. Feedback control systems exist to maintain the dynamic equilibrium of the system.
Industrial ecology strive to obtain the same for industrial systems, in order to reach the same proprieties of sustainability of the natural ecosystems. Closed material and energy cycles should be created. The fluxes among the components of the industrial system (industrial metabolism) should be completely integrated. A key element in industrial ecology is the elimination of the concept of “waste”. Waste is something that is not useful in any way and has to be disposed in order to be eliminated. According to industrial ecology wastes should not exist (or be largely reduced), since the unused streams of a process will be profitably exploited by some other system.
Of course integration of industrial processes poses problems with respect to the market issues, since links together industries with different demand of goods. Thus flexibility and redundancy of possible sources and sinks should be designed in order to let the system survive the single units. Moreover a continuous management and innovation/upgrade is required to maintain the dynamic equilibrium.

Some examples of real application of an industrial symbiosis already exist in the word. The most famous is Kalundborg, Denmark, where a network of connections and shared utilities links a power plant, a refinery, a plasterboard producer, a biotechnological industry, the nearby municipality, the farming activities, a cement industry, a sulphuric acid producer, fish farms and greenhouses. Another example can be found in the Gulf Coast of USA where a network exists between industries processing chlorine compounds *[Allen & Shonnard, 2002]*. Further examples can be found in some European countries *[Green & Randles, 2006; Garner & Keoleian, 1995]*.
The industrial symbiosis, in the general meaning, should involve different types of industrial activities. However, material and energy integration is in the culture of chemical industry since the oils crises. Heat and Material Exchange Networks (HEN and MEN) have been object of study and optimization, especially in oil-downstream and base chemical industry.

The creation of chemical and petrochemical industrial areas is another example of the natural tendency of integration in this industrial sector. Despite integration has always been pursuit in chemical industry, the present goal is to optimize the integrated system not only from the economic point of view, but including the environmental and the general sustainability perspective.

1.1.1.3 – Life-Cycle Thinking

The idea of lifecycle originates from comparing the "story" of a human-made object to the cycle of live beings: birth (creation/production), life (operation/use) and death (decommissioning/disposal). Any of the phases of the lifecycle involves interaction with the surrounding environment (exchange of materials, energy, release of emissions, generation of wastes, etc.). In particular they may involve the use of other goods (e.g. components for the production, energy for the use phase, means for transportation, etc.). Thus the analysis of the life-cycle of the base object may be extended to consider the lifecycle these goods as well. Eventually a complete lifecycle may extend from the extraction of the very raw materials (the "cradle") to the final disposal of non recyclable wastes (the "grave").

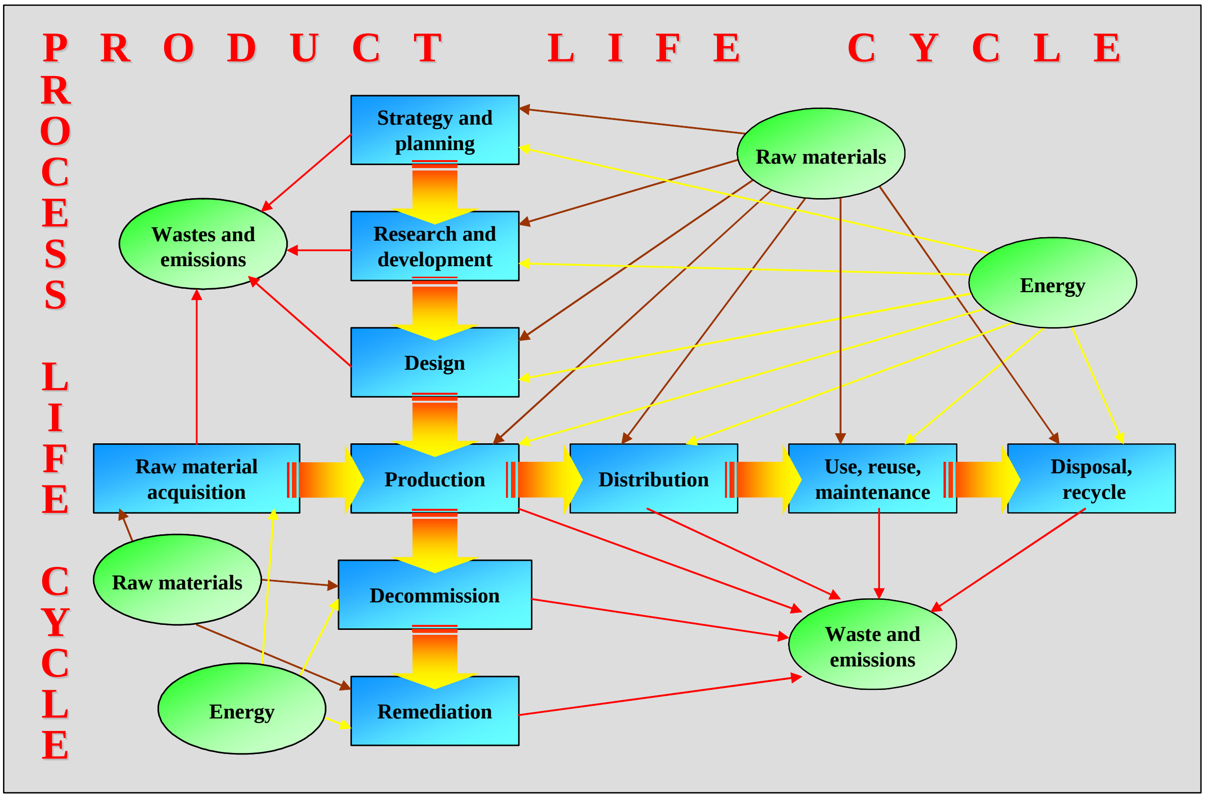


Figure 1.1.1: Product and process lifecycles.

Lifecycle concept is usually applied to a product, e.g. manufacturing, but also processes have their own lifecycle (Figure 1.1.1). The two are interrelated, since the impacts of the production of the product and of all the upstream phases of product lifecycle are defined by the production process. On the other hand, the product design influence the production procedure to fabricate it. Process design is thus a key stage in defining the impacts of production as well as of plant erection and decommissioning. The designer should be able to account all the phases of the lifecycle. In particular, this involve the responsibility of designer on impacts deriving from the operations that are outside of his direct control on the project. In fact, design activities should optimize the whole lifecycle and not only the current project *[Allen & Shonnard, 2002]*.

The operational counterpart of the life-cycle concept is the Life Cycle Analysis (LCA), a comprehensive and detailed study of the life-cycle. The procedure is defined in ISO 14040 to 14047. The first step of an LCA is the identification of the *scope* of the analysis; this defines the quality of the data required and, thus, the information and time necessary to accomplish it. The choice of the *functional unit* is an immediate consequence of the scope. The functional unit is the reference basis of the assessment. It is named after the idea that it should represent the function rather than the object itself: this allow easy comparison among LCA for items that are different, but fulfill the same ultimate function (e.g. plastic and paper shop-bags have different carrying capacities, number of reuses, weights, etc. so they can be compared effectively only with respect to absolving a certain function, e.g. carrying once a week a certain amount of shop-purchases).

The next step of LCA is the most time consuming, the compilation of the *Life-Cycle Inventory* (LCI): this is the list of all the material and energy fluxes entering or leaving the borders identified for the analysis. The values identified in this phase depend on the assumptions made in the definition of the scope and boundaries. The LCI may include a large number of items, in relation to the size of the lifecycle studied and of the classification that is made of the single fluxes. LCI are affected by availability and quality of the data reported. In particular when auxiliary processes or processes far away from the direct control of the analyst are studied, the gathering of information may rely on estimation and generic data reported by databases. As a consequence not all the studies have the same level of detail, extension of the boundaries or requirement of data quality. These elements are instead tailor-made according to the scope of the analysis and the availability of data.

Allocation is used when co-products are originated beside the one corresponding to the functional unit of interest. Allocation strategies may vary in function of the scope of the analysis: allocation of the items of the LCI for a mix of products can be done according to the commercial values, the mass or other criteria. Another option, used mainly for co-products have alternative ways of production, is the calculation of *avoided fluxes*, that corresponds at subtracting in the LCI the fluxes of the alternative production, which were “avoided” in by the adoption of the analysed lifecycle.

The information contained in the LCI is elaborated in the step of *Life-Cycle Impact Assessment*, where indicators and indices are usually calculated in order to summarize the quantitative information required by the scope of the analysis (e.g. assessment of greenhouse gases emissions, analysis of energy consumption, analysis of overall environmental impact). Many different approach were proposed for the life-cycle impact assessment; some of them are detailed and discussed in §1.1.2. However these indices usually refer to environmental impacts, though proposals for the inclusion of economic and societal aspects can be found in the literature *[Dhillon, 1989; LCWE, WSa]*.

The last step of an LCI is the *improvement analysis* or *interpretation step*. The results of the study are analysed and used to propose improvement of the lifecycle, in accordance to the initial scopes.

1.1.2 – Quantitative Assessment of Process Sustainability

The theoretical principles of sustainability reported in §1.1.1 point out the role of the design phase in defining the sustainability of the process. In particular early design stages of process show a great potential for the implementation of sustainability, since they define some core elements for the impact of production all over the lifecycle.

The principles of sustainability provide theoretical support and inspiration, but do not help an effective implementation of sustainability in the design activities. The practice of design requires the availability of adequate support tools for the quantitative assessment of the sustainability performance. These tools should be swift in application and able to cope the quality of available/estimable data during the design activity (in particular in early stages of design).

Although many significant efforts were made in this direction, the availability of widely accepted quantitative assessment tools suitable for supporting process design activities is still limited.
In the following a brief literature review of the principal quantitative tools that share elements applicable in supporting process design for sustainability is presented.

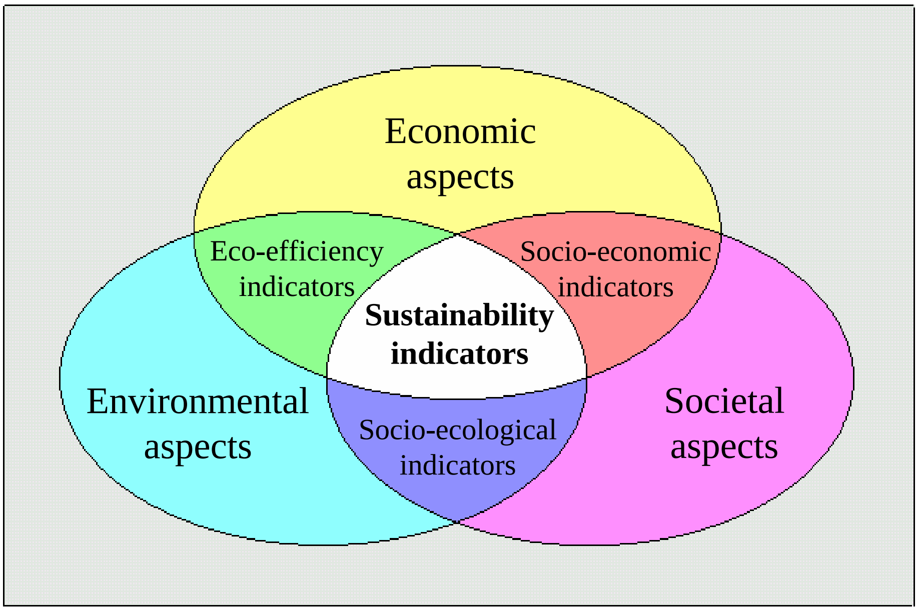


Figure 1.1.2: Sustainability as combination of three spheres.

Some Authors *[Gonzales & Smith, 2003; Sikdar, 2003b]* identified sustainability indicators in the evaluation of a set of critical parameters directly related to the process (non-renewable energy consumption, consumption of non-renewable raw materials, waste production, water use, CO_2 emission, yield, value creation, etc.). Though these parameters are the ones that define the sustainability profile of the process, the connection between their value and the impact of the process is not straightforward. Thus the size of positive effects on sustainability of marginal improvements on some of those parameters is difficult to recognize.

The indicators for the assessment of the impacts are usually calculated elaborating the raw process data. Several approaches were proposed in the literature to assess process sustainability by specific metrics or by a set of representative indicators *[IChemE, 2002b]*. However, most of these methodologies specifically address a single aspect of the problem (e.g. material and energy flow analysis *[Sikdar, 2003]*, exergy flows *[Heui-seok et al., 2004; Jorge & Bhavik, 2004]*, specific potential impacts through midpoint environmental indicators

[Allen & Shonnard, 2002; IPPC, 2006], endpoint environmental indicators derived from Life-Cycle Analysis *[Allen & Shonnard, 2002; Chen et al., 2002*; *Goedkoop & Spriensma, 2001; ISO 14040-43; Pennington et al., 2000]*), not featuring a complete and comprehensive assessment of the system.

Although a set of metrics for single aspects can be used to show the fingerprint of a system, comprehensive indexes are preferred for several applications, like optimization or decision-making. Numerical aggregation is usually proposed to obtain a single quantitative indicator of process performance that includes the different issues relevant to sustainability *[Chen et al., 2002; Goedkoop & Spriensma, 2001; ISO, 14040-43; Saling et al., 2002]*. However, the need to compare indicators of different nature, the completeness of their set and the subjective judgment in the aggregation process are critical and still need to be thoroughly investigated *[Sikdar, 2003]*.

Nevertheless various methods have been proposed to support the aggregation, as reported by Chen *[Chen & Shonnard, 2004]* (e.g. analytic hierarchy process *[Satty, 1980]*, multi-attribute utility theory *[Keeney & Raiffa, 1976]*, etc.). The problems relevant to the aggregation of indicators of different nature are only formally avoided in other approaches which use a common metric for all the elements involved (e.g. economic measures, exergy, emergy, etc. *[Figge & Hahn, 2004; Heui-seok et al., 2004; Jorge & Bhavik, 2004]*), since a criteria must be stated to measure the different issues through the common unit of measurement.

The concept of life cycle is central in sustainability assessment. However the conventional tools devoted to life cycle assessment (LCA) *[ISO 14040]* are not practically applicable to support process design. In fact a wide amount of data on the entire lifecycle (well apart from the process section to be designed) is required and the procedure can became significantly time consuming. The conventional applications of LCA is limited to the assessment of environmental impacts and no site-specific considerations are usually included, since the life cycle involves sources which are usually spatially spread. More recently, approaches accounting for lifecycle costs and societal impacts were proposed *[Dhillon, 1989; LCWE, WSa]*. Nevertheless, the indicators used in an LCA are not directly suitable for the analysis of the very specific features of process design assessment, that needs a dedicated approach.

BASF developed an eco-efficiency analysis tool that accounts for several categories of environmental and economic impact and that is based on the aggregation of the indices in a modular scheme that allows the comparison of alternatives *[Landsiedel & Saling, 2002; Saling et al., 2002; Shonnard et al., 2003]*. The methodology was later extended to consider societal impacts (SEEBalance). However the societal upgrade considers indicators mainly linked to the facility management (e.g. working conditions, local community) and to issues related to the entire lifecycle (e.g. child labour), fairly related to process design choices. Moreover, the use of internal normalization in the procedure may introduce biases in the assessment that somehow limit the suitability of the results for decision making.

A further approach was proposed by Narodoslawsky *[Krotscheck & Narodoslawsky, 1996; Narodoslawsky & Krotscheck, 2000]*, that suggested to base sustainability assessment on the estimation of the required area for process operability under sustainable conditions. This method is widely applicable and apparently avoids the issues related to normalization and weighting, although also in this case societal and economic aspects may not be easily integrated in the procedure.

Several assessment tools were promoted by EPA for supporting the development of greener processes. The Tool for the Reduction and Assessment of Chemical and Other Environmental

Impacts (TRACI) *[Bare et al., 2003]*, presents a wide set of environmental indicators for the analysis of industrial processes. However the assessment is limited to environmental aspects and aggregation is avoided. The Waste Reduction Algorithm (WAR) *[Mallick et al., 1996; Young et al., 2000]* proposes an aggregation strategy of the environmental indicators. However, a broad and organic coverage of all the sustainability domains is still missing.

Shonnard and co-workers *[Chen et al., 2002, 2003; Chen & Shonnard, 2004]* proposed and discussed the optimization of chemical processes for as concern economic and environmental performance. Their approach resort to a multi-criteria aggregation approach similar to the one discussed in the following. However no site-specific values are defined in the normalization of the indicators. The final aggregation of the economic and environmental indexes (no societal aspects are considered) is based on internal normalization and weight factors are evaluated there by AHP. These practices may introduce biases in the results, especially considering highly result-sensitive applications as design optimization.

Summarizing, the review of the literature evidenced the following features:

i) a dedicated approach is required for sustainability assessment in process design;
ii) specific indicators are necessary to match the information detail of early design stages;
iii) no specific methods encompassing all the sustainability aspects exist;
iv) combination and comparison of different indicators are critical element due to the possible introduction of biases and is not included in all the literature methods.

The methods proposed in the current work of thesis aims at filling these gaps. Elements from previous widely-accepted literature approaches (e.g. the general framework and some of the impact indices) will be included in the developed methods whenever possible, in order to make them consistent to the established practice. However, several new elements will be specifically developed, as discussed in the following of present text.

1.2 Proposed Assessment Method

1.2.1 Overview of the method

In this chapter a new sustainability assessment method is described. The developed procedure is specifically aimed at the quantitative assessment in the comparison of the impact on sustainability of process and plant options. The method is intended to be a tool within a design support system, accordingly to the general goals of the current work. As a consequence, the procedure is especially developed to be applicable with the limited amount of data available in early stages of process design (i.e. conceptual and basic design). Moreover, it is focused on assessing the aspects of sustainability that are influenced by design decisions in these stages of the process lifecycle.

The proposed methodology is aimed at identifying the best design alternative among a set of given options and to provide information on critical sustainability issues of the proposed options. The procedure is based on a classical multi-criteria analysis, but encompasses several innovative elements.

In particular, a comprehensive set of sustainability impact indicators addressing individual process performances in all the spheres of sustainability was defined. The indicators were chosen in order to match the data usually available in the early stages of process design. The indicators were either selected from widely accepted literature approaches, if suitable, or were developed within the present study. In particular, a specific method was developed to include inherent safety issues among the relevant sustainability parameters. Inherent safety, despite being a key element in sustainability, is seldom explicitly considered by other assessment approaches.

Innovative reference criteria were developed to compare and aggregate the impact indicators on the basis of the actual site-specific impact burden and sustainability policy. On the one hand this links the assessment of the process to the general sustainability management of the site and, on the other hand, it allows a straightforward comparison and aggregation of aspects belonging to economic, societal and environmental spheres. The proposed procedure resulted in a simple and flexible tool, that allows a straightforward application to practical situations.

The methodology consist of four main steps (Figure 1.2.1):

1. the selection of a common reference basis for the definition of compared options
2. the definition of a system of quantitative indicators
3. the development of a specific procedure for the normalization of the indicators
4. the aggregation of the indicators to define a final set of sustainability indices suitable for a comparative assessment of design options

In the following, the detail of each step of the procedure is described. The procedure is demonstrated by the application to several case-studies in Section 4. Some of the case-studies, as explained in Section 4, were also preliminary used to validate the method, checking the applicability and the ability to identify expected results.

1.2.2 Definition of the process alternatives

The starting point of the procedure is the definition, the characterization and the collection of the quantitative data necessary for the analysis of the possible process or plant option.

The effective comparison of different alternatives requires the specification of criteria to define common *reference basis* and *common boundaries* to be considered in the analysis.

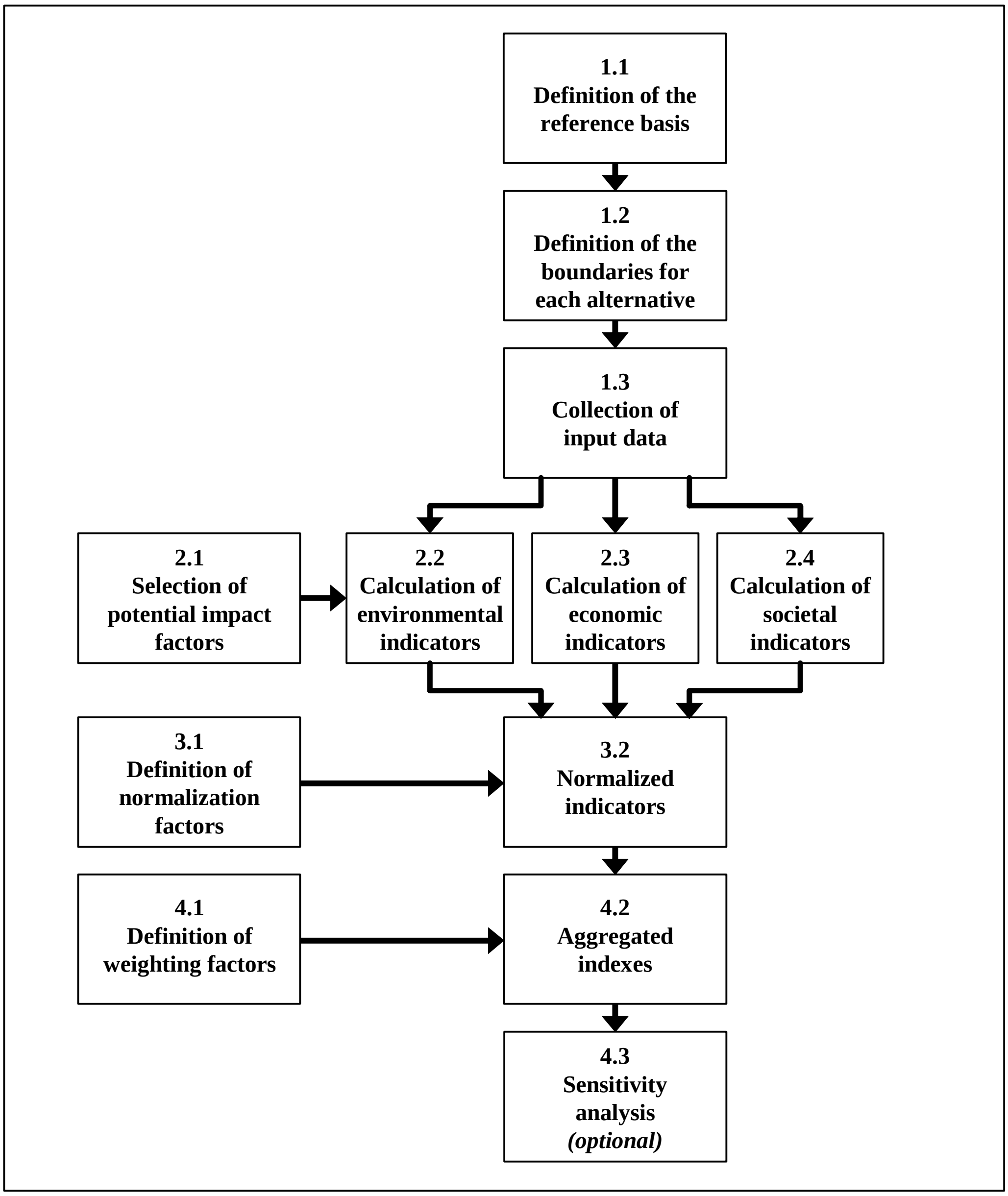


Figure 1.2.1: Flow diagram of the procedure developed for sustainability assessment.

A common *reference basis* may be easily introduced considering the same production potentiality for the different process alternatives. In the present framework, production potentiality may be defined as: i) the production rate of the main product of the process (e.g. the tons/year of ammonia for an ammonia production process); or ii) if the process is not aimed to obtain a product of interest but to the treatment of a raw material (e.g. the disposal of a waste), the amount of raw material processed. In case of multiple valuable products, the problem of allocation is generally avoided in current procedure by proper choices in the material flow assessment (see 1.2.3). If that is not possible, typical allocation rules used in LCA studies *[Allen & Shonnard, 2002]* can be followed.
The *reference basis* is the analogous to the *functional unit* of an LCA *[ISO 14040]*. However, for the current goals, the identification of the reference basis is generally more straightforward than in the typical life cycle analysis, since in the chemical and process industry it may be easily identified in the flow-rate of a key stream leaving (i.e. final product) or entering (i.e.

stream to be treated) the process. Thus, in order to have the same reference basis for all process alternatives, the flow rate and the composition of the key stream (i.e. the potential of the process) must be the same for all the alternatives.

The *boundaries* of the alternatives must be defined consistently among the options. The goal of the assessment is to analyze different design option for a process facility in a given site. Thus the boundaries of the analysis should be limited to installations present in the site. As a consequence, they should include the main process (i.e. the core process that is the central focus of the design activity and, consequently, of the analysis) as well as the on-site utilities that are necessary for the main process to operate (e.g. boilers for steam production, nitrogen separation facilities, wastewater treatments, etc.). The utilities must be accounted even if outside process design limits (e.g. utilities may be already in place, or may be designed independently since not dedicated only to a single process). However, in the analysis of the utilities, only the impacts allocable to the main process should be considered. For instance, an utility producing a material stream used by several facilities/section of a plant (e.g. steam), should be accounted only for the fraction of the stream employed by the process of interest.
The boundaries of the alternatives do not include the analysis the upstream and/or downstream operations not realized in the site under analysis. This correspond to a “gate to gate” analysis, in the LCA nomenclature *[ISO 14040]*. However the effect of the upstream and downstream operations is not fully neglected, but it is accounted through the assessment of input and output streams (indexes in the group *resource consumption*). This allows limiting to a practical and acceptable level the information input required in the analysis (see next section), while retaining the central value that belongs to life cycle perspective in the sustainability assessment.

Category	Data
Process	Simplified process flow diagram (list of units and characterization of process streams)
	Energy input/output data
	Raw materials flow rate, composition, temperature and pressure
	Products, Co-products and by-products flow rate, composition, temperature and pressure
	Waste streams / effluents flow rate, composition, temperature and pressure
	Fugitive emissions estimated rates and composition
	Hazardous proprieties of substances (flammability, instability, reactivity, toxicity)
	Operating conditions of equipment units (pressure and temperature)
	Preliminary definition of equipment types and geometry (taxonomy)
	Preliminary estimation of equipment inventories (quantity and average composition)
Economic	Preliminary estimate of capital cost
	Cost of raw materials
	Value of products
	Value or cost of disposal of co-products and by-products
	Number of employees
	Labour cost

Table 1.2.1: List of Data required for the application of the sustainability assessment procedure.

The data required to analyze each process alternative are summarized in Table 1.2.1. The method was specifically developed in order to allow the assessment in the early stages of process design (conceptual and basic design) that are notoriously critical with respect to this aspect. In the following a brief description of each data group of the table and suggestions on the tools to support data definition/estimation in the early stages of process design are provided.

i) Simplified process flow diagram (PFD). A diagram reporting the process equipment and the general flow patterns of the streams in the alternative. It is a core part of the definition and design of the alternative itself. The required information for the definition of the PFD may be obtained in early stages of design integrating the engineering practice/experience of the designer by the analysis of process literature and patents.

ii) Input/output material data. These are quantitative data on the flow rate, composition, temperature and pressure of the streams entering and leaving the boundaries of the process. The streams of raw materials, co-products and by-products, waste streams/effluents and fugitive emissions have to be accounted. Data on these streams, if not implicit in the process design, can be easily evaluated by material and energy balances or resorting to emission factors (in particular for micro-pollutants or fugitive emissions) from specific emission databases or reported in the literature. Several tools may be interfaced with the discussed methodology in order to support the collection of input/output material data. These include process simulation software (e.g. HYSYS) and tools for the evaluation of process emissions (e.g. FIRE *[EPA,WPa]*, fugitive emission estimation methods *[Allen & Shonnard, 2002]*, ChemSTEER *[EPA,WPb]*, etc.). Besides the material flows across the boundaries defined for the analysis, a preliminary evaluation of the main streams among the process units is required for inherent safety assessment.

iii) Input/output energy flow data. These data concern the useful energy flows entering or leaving the process boundaries. Thus, for instance, thermal energy dispersed in the environment is not accounted. As a matter of fact, these data include the evaluation of electric power and of thermal power exchanged with other users/suppliers (e.g. use of waste heat from another plant) outside of process boundaries. These data may be typically obtained in the early design stages of process design by material and energy balances; process simulation software may be used to support the evaluation.

iv) Operating conditions of equipment units. The definition of pressure and temperature in each equipment units is deeply related to the definition of the process alternative itself. Data can be obtained from the process literature and patents, as well as by material and energy balances.

v) Preliminary equipment taxonomy. It consists in a preliminary definition of the type of equipment used for each unit operation in the process. In particular, the definition of the geometry (shape and volume) of each unit is important for the identification of the inherent safety profile of the unit, characterizing both unit robustness (failure modes and their likelihood) and release potential. Furthermore, the definition of the equipment present supports the evaluation of capital costs. This kind of information is a key part of the basic design definition. In conceptual design, however, preliminary assumption may be done considering the type of equipment typically used for similar processes.

vi) Estimation of equipment inventories. This is an information strongly related to the equipment taxonomy *(v)*. It consists in an evaluation of the quantity and average composition of the material contained in each unit. Although a precise definition of these data require a detailed design of each unit, generally a rough evaluation based on simple rules of thumb, well known in the chemical engineering practice, is sufficient in the current analysis. The data are used in the assessment of the inherent safety of the process units and typical index methods (generally based on scoring) can easily cope with low precision data.

vii) Hazardous proprieties of materials. These parameters quantify the hazard related to the proprieties of the substances in the process (flammability, instability, reactivity, toxicity). These data are required for the inherent safety assessment and in general are needed only for the substances present or that may be accidentally formed in relevant quantities. This limits the actual number of substances to be considered. Information on these proprieties are usually found in the literature, and in particular are reported in the safety data sheets. Information on the toxic proprieties can also be found in dedicated databases (e.g. see *[EPA, WPb,WPc; CDC, WP]*).

viii) Economic data. This information is required to define the economic profile of the alternative. Data are required to define the operative costs, as for instance the input/output flow economics (cost of the streams crossing process boundaries) and labor cost. On the other side, a preliminary estimation of the capital costs should be done, according to the PFD of the alternative. Cost databases may be used to support the assessment (e.g. Matches' *[Matche, WP]*, Chemicals Cost Guide *[IChemE, 2002]*, Aspen Icarus Process Evaluator).

As showed in the earlier discussion of the data sources, several tools and software may be interfaced with the proposed methodology in order to support the collection of input data. However, the proposed method is of general applicability and the procedure does not pose restrictions in the approach used to obtain the required input data.

1.2.3 Definition of a system of quantitative indicators

The input data allow the quantification of the potential impacts of each process. A specific set of indicators must be defined to address the impact categories of process activities with respect to the three main issues of sustainability: *environmental*, *societal* and *economic impacts*.

A general set of indicators, suitable for the assessment of early stages of process design, is identified and listed in Table 1.2.2. As pointed out previously the set of indicators and, moreover, the evaluation rules have to cope with data availability. The approach proposed in current procedure is to identify a few critical parameters that can be related easily to the process or plant design of the assessed option. These parameters must be the core issues in affecting the sustainability performance of the future operation of the facility. Thus, considering the project lifecycle, the identified indicators are leading indicators. The name is borrowed from economic science, where it identifies indicators which tend to change before the general economy has changed (e.g. stock prices, building permits, unemployment insurance, etc.).

It must be remarked that the set of indicators reported in Table 1.2.2 was the result of an optimization aimed to define a set of quantitative indices useful in a generic application. Clearly enough, the set is open to the addition of further indicators in the context of a specific assessments.

As shown in the table, well-known and widely used *potential impact indicators* derived from the literature *[Allen & Shonnard, 2002; Azapagic, 2003; Bare, 2000; Chen et al. 2002; IPPC, 2006; ISO 14040-43; Pennington et al., 2000; Saling et al., 2002]* were selected for the assessment of *environmental impact*. The adoption of potential impact indicators is particularly useful in this context, since the selected indicators present a direct correlation among flows and impacts. Thus, their assessment is possible even in the initial stages of process or plant design, since it does not require the use of complex models of environmental fate, affected by a relevant uncertainty *[Bare, 2000]*. Moreover, potential impact indicators yield conservative impact values, thus reflecting a precautionary approach.

Standard procedures are available in the literature for the quantitative assessment of mid-point indicators, usually based on the reference to a benchmark substance *[Allen & Shonnard, 2002; Pennington et al., 2000]*. Thus, all the environmental indicators considered in Table 1.2.2 are assessed following the general equation:

$$I_{i,k} = \sum_j PIF_{i,j} \; m_{j,k} \qquad (1.2.1)$$

where $I_{i,k}$ is a generic indicator, $PIF_{i,j}$ is the *potential impact factor* for the i-th impact category for j-th material and $m_{j,k}$ the mass of j-th material crossing the boundaries of k-th alternative. The potential impact factor represents the ability of a material to cause a specific damage related to the reference material.

As previously mentioned, consolidated values of the potential impact factors for many emitted substances can be found in the technical literature with respect to several impact categories, such as *global warming*, *ozone depletion*, *acidification*, *smog formation*, *eutrophication*, *organic load* and *ecotoxicity* (e.g. *Allen & Shonnard [2002], IPPC [2006]).* For a few indicators (*toxic and carcinogenic releases*, *soil emissions* and *resource consumption*), an “ad-hoc” definition of the benchmark rule was required, since poorly standardized approaches suitable for the current procedure were found in the literature.

Thus, the development of assessment of *toxic* and *carcinogenic emissions* required particular attention. These impact categories are poorly standardized due to the complexity of the phenomena involved (e.g. different exposure pathways, lack of strong dose-response relations, non-linear effects). Several valuable proposal can be found in the literature (e.g. Human Toxicity Factors *[IPPC, 2006]*, DALY *[Goedkoop & Spriensma, 2001]*, etc.), but data are available only for limited groups of substances and are complex to estimate. However, easy and flexible impact indices on human health are required in early stages of design.

Thus, adopting a common approach in the definition of PIFs for midpoint indicators *[Pennington et al., 2000]*, in the present assessment the toxicity impact potential was assumed as the ratio of the toxicity parameters for the substance of concern and a benchmark substance (toluene). A similar definition of the PIF for toxicity, although corrected by environmental repartition coefficients, can be found in the literature *[Shonnard et al., 2003]*. Coherently, the carcinogenic potential was assumed as the ratio between the cancer potency slope factor for the substance of concern and that of benzene. The chosen approach ignores the fate of the compound in the environment (difficult and uncertain to estimate in many cases), but reflects the idea of the impact potential. Both carcinogenic and non-carcinogenic effects are separately assessed for releases in specific environmental media: inhalation data are employed for air release, ingestion data for water release. The toxicity parameters chosen in the present study are the inverse of 50% lethal doses and 50% lethal concentrations for rats:

$$IP_{airtox,j} = \frac{1/LC50_j}{1/LC50_{toluene}} \qquad IP_{watertox,j} = \frac{1/LD50_j}{1/LD50_{toluene}} \qquad (1.2.2)\ (1.2.3)$$

$$IP_{aircarcin,j} = \frac{CSF_{inh,j}}{CSF_{inh,benzene}} \qquad IP_{watercarcin,j} = \frac{CSF_{ing,j}}{CSF_{ing,benzene}} \qquad (1.2.4)\ (1.2.5)$$

The parameters selected for toxicity and carcinogenicity of the substances of concern are among the most available and may be collected for a wide number of substances from suitable databases *[EPA, WPb,WPc; CDC, WP]*. If the LC_{50} of the substance of interest is not reported, empirical correlation rules may be used for its estimation (e.g. see the diagram proposed in *[Koller et al., 2000]*).

The *solid waste disposals* are the material streams that leave the process boundaries in order to be disposed. The standard destination considered for these waste streams is landfill, since landfill is assumed to be the worst disposal option. As a working hypothesis, the ratio of the average disposal cost of the waste of concern to that of municipal waste is used as potential impact factor. The disposal cost is in general representative of the hazard due to the different standards necessary for landfilling a type of waste *[Saling et al., 2002]*.

The impact category of *resource consumption* is related to the valuable material and energy flows crossing process boundaries. Resource flows can both enter (raw materials) or leave (co-products) the system boundaries. The sign of the flow is defined respectively positive and negative. Material streams are generally divided in renewable and non-renewable, since this distinction will be useful in the weighting step in order to address the environmental policies (see § A1.1.3).
In order to compare in a single indices material fluxes of different nature, a potential impact factor is required. A good parameter to use in the definition of the PIF is the market value of the stream *[Krotscheck & Narodoslawsky, 1996]*; credit factor should be applied to consider the externalities. For renewable materials, the land-occupation for the crop grow can be used in alternative.
The consumption of electrical power is straightforward evaluated as an energy consumption rate. This is usually considered a distinct impact category for ease of data normalization and aggregation.
The *land use* indicator is related to the occupation of land. In particular, in the present case study, the impact is assessed for process alternative D, where the landfill facility occupies a significant land area for a long time span (virtually infinite). In that case, the area "consumed" per unit of disposed waste is evaluated by data of similar facilities.

With respect to *economic indicators*, a specific and simplified approach was developed to obtain an appropriate economic indicator to be used in the framework of the comparison of process sustainability issues. A "*net potential economic impact*" index (NPEI) was defined. Since the net present value (NPV) is typically adopted in the economic comparison of alternatives, NPEI was calculated as the NPV multiplied by –1. The change of sign was introduced since impact indices, used in the present approach, must have a higher value in the worst case. Thus:

$$NPEI = -NPV = -\left(\sum_{t=0}^{n} \frac{C_t}{(1+r)^t}\right) \qquad (1.2.6)$$

where C_t is the cash flow at time t, r the discount rate and n the expected life of the plant.

The identification of quantitative indices for the *societal impacts* relevant to the process sustainability is more difficult, as they involve subjective aspects that are not directly related to the process or that are not easy to quantify. In the following, as a working assumption, only two societal indices were considered, since they were identified as more directly related to the choices in process design: an *inherent safety index* and an *occupational index*.

The impact of process activities on population safety was evaluated using an *inherent safety* metric, since the inherent safety approach is described as a core issue in sustainability *[Abraham & Nguyen, 2003; Anastas & Zimmerman, 2003]*. Moreover inherent safety is particularly suitable to yield a numerical value representative of process safety performances in the analysis of early design stages. As a matter of facts, the hazards, that pertain to inherent

safety analysis, are almost completely defined since the early stages, while actual risk level requires an higher level of detail for to be assessed.
The definition of a specific consequence-based *inherent safety index* suitable for the framework of current procedure is extensively discussed in Section 2.

An *occupational index* was based on the assessment of the equivalent number of workers necessary for the specific process activity. If no specific data are available, the value of the equivalent number of workers may be derived from that of similar industrial processes. The occupational index used in the present study was defined as the specific equivalent number of persons necessary for process activities multiplied by –1. As in the case of NPEI, the change of sign was necessary since impact indices must have a higher value in the worst case.

1.2.4) Normalization of the indicators

The indicators listed in Table 1.2.2 yield important information on process performances and may allow the comparison of process alternatives with respect to specific aspects. However, they are not suitable for a direct comparison among the different categories of impact, since a normalization is required. Normalization is thus a necessary step both for the successive aggregation of indexes and the interpretation of the indicators. Normalization usually represents the comparison between the *impact value* and a *reference value* (or *normalization factor*) *[ISO 14040-43; Chen et al., 2002; Saling et al., 2002; Bare, 2006]*:

$$NI_{i,k} = \frac{I_{i,k}}{NF_i} \tag{1.2.7}$$

where $NI_{i,k}$ is the i-th normalized index for the k-th alternative, $I_{i,k}$ is the indicator value for the i-th impact category of the k-th alternative, and NF_i is the normalization factor for the i-th impact category. However, the selection of significant reference values, NF_i, is still an open

Aspects		Impact categories	Indicator	Scale
Environmental	Air emissions	Global warming	I_{GW}	National
		Ozone depletion	I_{OD}	National
		Rain acidification	I_{RA}	1500 km
		Smog formation	I_{SF}	100 km
		Toxicity in air	I_{TA}	100 km
		Carcinogenicity in air	I_{CA}	100 km
	Water emissions	Eutrophication	I_{EU}	Hydrographical basin
		Organic load	I_{OL}	Hydrographical basin
		Toxicity in water	I_{TW}	Hydrographical basin
		Carcinogenicity in water	I_{CW}	Hydrographical basin
		Ecotoxicity	I_{ET}	Hydrographical basin
	Soil emissions	Solid waste disposal	I_{WD}	Regional
	Resource consumption	Non renewable materials	I_{NR}	National
		Renewable materials	I_{RM}	National
		Electrical power	I_{EL}	National
		Land use	I_{LU}	Regional
Economic		NPEI	I_{NEPI}	National
Societal		Inherent safety index	I_{IS}	Regional
		Occupational index	I_{OC}	Regional

Table 1.2.2: Indicators used for the assessment of process impacts and characteristic scales used in the external normalization procedure.

problem. As a matter of fact, the choice of inadequate reference values in the normalization may introduce a relevant bias in the procedure, in particular if different processes are compared or if aggregated indices are calculated.

Usual normalization procedures heavily rely on *internal normalization*, that consists in the use of one of the $I_{i,k}$ index values calculated for an alternative option (in general the maximum or the more consolidated value) as the normalization factor NF_i (e.g. *[Saling et al. 2002]*). However this approach should be avoided, since it is likely to introduce biases in the calculations and requires, in the aggregation stage, the definition of weight factors specific for each set of considered options. On the other hand, when *external normalization* is used, it is commonly based on generic reference values that are not site specific. In the present study, a novel approach was developed, introducing a ***site-specific external normalization***. Where possible, a *target area* was defined for each impact indicator. The target area was defined as the area which properly accounts for the range of the impact of concern. A reference ‘external’ normalization factor was thus calculated accounting for the impacts of the industrial facilities within that area. The reference values may be collected from several available databases reporting widely accepted environmental data (see Appendix 1.1). Also in the case of the economic index it was possible to define an external normalization factor. The identified normalization factor is the gross domestic product in the area interested by the economic impact of the process considered. The target area generally corresponds to an administrative division of the territory (e.g. a province, a state, etc.) or even the entire national territory, depending on the economic impact of the installation with respect to its location. Data on gross domestic product on the impact area of concern are usually available by national statistics and conventional procedures exist to extrapolate, if necessary, future values according to the expected grow rate. With respect to societal indicators, the inherent safety and occupational metrics considered in this study allowed the definition of an external normalization value based respectively on potential life loss for technological risks and on the employment statistics in the area of concern.

The effects of process impacts occur on different spatial scales, thus a significant characteristic scale should be assumed for each category of impact. Table 1.2.2 reports the *characteristic scales* identified for the external normalization of each impact category. The target areas are defined in accordance to the spatial dimension that are affected by the impacts. These are evaluated for each impact category by suitable approaches (e.g. characteristic distances calculated by models for pollutant dispersion, administrative division of the land, etc.). Some impact categories concern phenomena having effects on a global scale (global warming, stratospheric ozone depletion, etc.). However the use of a national reference was preferred in these cases. As a matter of facts reliable national emission balances and reduction plans exist as a consequence of shared international agreements (e.g. Kyoto Protocol, etc.). Data from national references are generally easier to collect and closely reflect the emission policy in the chosen site, supporting the aggregation step.

All the facilities considered within the pertinent target area contribute to the normalization value for a given impact category. The normalization factors are straightforwardly calculated from the area data by the same rules used in the assessment of the corresponding indicator (see §1.2.3). Thus consistency of the indices for the assessed alternatives and normalization factor is warranted with respect to approximations possibly present. Since the impact scales are different for the different impact categories, normalization values are expressed per unit of area. The normalization factors for a specific site can be calculated by the simplified formula in Equation (1.2.8). The formula is valid under the assumption of background emission sources uniformly distributed in the target area:

$$NF_i = \frac{\sum_{s \in At} E_{s,i}}{At_i} \qquad (1.2.8)$$

where $E_{s,i}$ is the impact index for the i-th impact category from the s-th source belonging to the target area (*At*) and At_i is the size of the target area for the i-th impact category. The impact index $E_{s,i}$ is calculated from the data about the source, following the same rules defined for Level 1 indicators.

The *normalized indices* resulting from the use of these external reference values are a direct measure of the relevance of the additional impact from the process to the local conditions. This allows comparing the single indicators to a reference that is independent of the process alternatives assessed, but is dependent on the specific site. This reference represents the impact burden on the site generated by the other industrial activities. Thus the normalized indicators measure the relative contribution of the alternatives to the local impact loads.

1.2.5) Aggregation of the indicators and definition of overall sustainability indices

As shown in Table 1.2.2, a relevant number of different indicators may be necessary to correctly describe all the possible impacts of different process alternatives. However, in order to effectively compare the impacts of alternatives, the availability of a limited number of aggregated indicators would be important. In the present procedure a two stage multi-criteria weighted summation was adopted to generate a hierarchy of indices, as shown in Figure 1.2.2. The general structure of each *aggregation* stage is represented by the following expression:

$$I_{aggr,k} = \sum_i W_i NI_{i,k} \qquad (1.2.9)$$

where $I_{aggr,k}$ is the aggregated index for the k-th alternative, and W_i is the *weight factor* for the i-th impact category. *Weight factors,* summing up to 1, were chosen to represent the relative importance of the impact categories.

The normalized indexes resulting from the use of external reference values are a direct measure of the importance of the additional impact to the local conditions. Weight factor must be related to the background state accordingly: weight factors represent the relative importance of load reduction among the impact categories. This requires to refer to a sustainability policy for the site of concern, where the weights represent the result of long-term management perspectives that strive to reduce the critical effects in the area of concern. The sustainability policy belongs to a macro-scale level that is different than the technical domain of process design (§1.1.1). Weight factors must be defined within the macro-scale policy level, eventually creating a link between the general suitability policy and the process design. An important consequence of these assumptions is that weight factors should be independent from the assessed alternatives, but may depend on local conditions.

As shown in Figure 1.2.2, the developed procedure allows the calculation of a *hierarchy of indices* related to sustainability assessment. Level 1 indices are *impact indicators,* that may be used to compare a single impact of different process alternatives. Level 2 indices are a set of three normalized indices that represent the impacts of the process on the three main elements related to sustainability: *environmental impact*, *societal impact* and *economic impact*. Level 3 index is an *overall* value, obtained as the result of the above described aggregation procedure, suitable for a general comparison among alternatives.

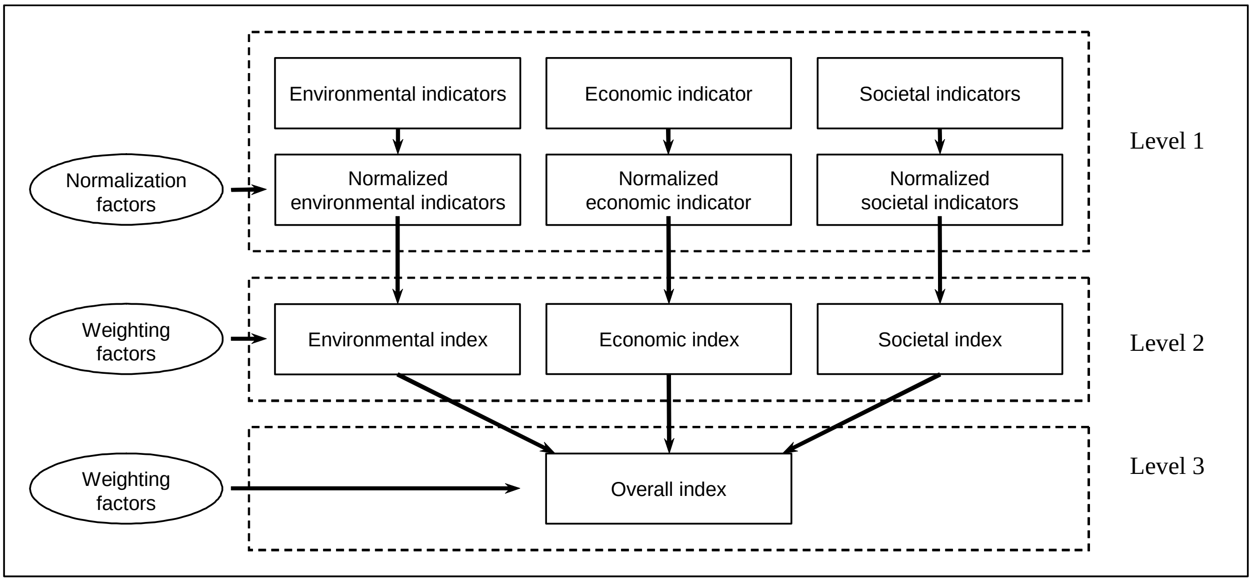


Figure 1.2.2: Set of indices selected for the representation of the impacts on sustainability of an assessed option.

1.2.6 Sensitivity Analysis

The results obtained for the overall (level 3) and level 2 indices are obviously influenced by the weight factors used in the procedure. Since these parameters refer to policy considerations that are inevitably affected by significant uncertainties, their value should be considered as less reliable than other parameters evaluated in the assessment. Thus, a sensitivity analysis is worth to check the influence of variation in the values of weight factors on the final values.
Of course, because of the mathematical structure of the procedure, a variation in the values of weight factors will change the numerical value of the aggregated indices. However in many practical applications it is not the absolute values of the aggregated indices that is of interest, but the relative performance of the indexes for the options or, more simply, the rank of the compared options.

The first step toward a sensitivity analysis is to identify a confidence interval for each weight factor. This will derive by an evaluation of the uncertainty of the data sources used in the definition of the weight factor. As a consequence it is generally possible to identify a maximum and minimum likely value for each weigh factors.
A sensitivity analysis would require to repeat several time the aggregation stage of the procedure with a variation of each single weight factor within the identified range and to assess the influence on the results. However this approach may result impractical and time-consuming in many cases. Thus, a possible option is the use of a software-aided Monte Carlo approach. The technique allow to automatically vary several parameters influencing the weight factors, obtaining a general feedback on the index results in a limited amount of time. Neither weight factor nor the parameters for their calculation are statistic variables and, thus, a distribution of probabilities of the weight values can not be strictly defined. However, in order to allow the application of the Monte Carlo method, it is possible to attribute to each parameter a conventional distribution of likelihood of the value within the identified confidence interval (e.g. uniform distribution, beta distribution, etc.). Monte Carlo runs of these distributions yield straightforward a distribution for of the aggregated indices.

As a matter of facts, if large variation of many weight factors are studied the aggregated indices of different options will likely result in spread distributions, that may partially overlap, making the interpretation of the results harder. In these cases the analysis of index differences can be applied, adapting the approach followed by Goedkoop & Spriensma *[2001]*. First the options are ranked according to the index of interest with the base set of weight factors. Then, by the Monte Carlo runs, the distribution of the difference among each couple of options with consecutive ranks is calculated. The analysis of these distributions yield important information on the inversions in the impact ranking of the options, since a change in the rank result in a change of sign in the index difference. Moreover, an information on the relative importance of the single weight factors on the aggregated values can be obtained by the analysis of the contribution of the different weight factors to the variance of the results. This can be easily expressed as a percentage contribution to the variance from the Monte Carlo analysis.

1.3 – Conclusions

In this section a sustainability assessment tool for design support for was presented and discussed.

The existing literature approaches were analysed in order to identify the elements useful for the development of the tool. The analysis evidenced that no existing method is suitable per se for the intended goal. In particular, limitations are related to the application in early stages of design (presence of uncertain data, specific impact categories to be addressed, etc.) and to the ability to encompass all the aspects required by a sustainability analysis.

Therefore, a dedicated quantitative assessment procedure was developed for the identification and comparison of the sustainability impact profile in early design stages. The aim of the proposed methodology is to identify the best alternative among a set of options and to provide information on critical sustainability issues of the proposed process options. The procedure will provide support for a sustainability oriented decision making in the design of industrial processes. A particular effort was devoted to develop a methodology based on a set of input data that may be easily evaluated in the early stages of process design (i.e. conceptual and basic design), since it is well known that the resulting impacts on sustainability are mostly influenced by decisions in these process design stages.

The developed procedure is based on a classical multi-criteria analysis, but encompasses several innovative elements. A comprehensive set of sustainability impact indicators addressing individual process performances in all the spheres of sustainability was defined. The indicators were chosen in order to match the data usually available in the early stages of process design. The indicators were either selected from widely accepted literature approaches, if suitable, or were developed within the present study. In particular, a specific method was developed to include inherent safety issues among the relevant sustainability parameters (see also §2). In fact, inherent safety, despite being a key element in sustainability, is seldom explicitly considered by other assessment approaches.

Innovative reference criteria were developed to compare and aggregate the impact indicators on the basis of the actual site-specific impact burden and sustainability policy. On the one hand this links the assessment of the process to the general sustainability management of the site and, on the other hand, it allows a straightforward comparison and aggregation of aspects belonging to economic, societal and environmental spheres.

The proposed procedure resulted in a simple and flexible tool, that allows a straightforward application to practical situations.

Appendix 1.1 - Approach to normalization and weighting

A1.1.1 – The normalization approach

As discussed in §1.2.4, normalization is a necessary step both for the aggregation of indexes and the interpretation of Level 1 indicators. In the proposed method the *internal normalization* (i.e. using one of the alternatives as normalization reference) is avoided, since it is likely to introduce biases in the calculations and requires a definition of weight factors specific for each set of the considered alternatives. Hence a *site-specific external normalization* is adopted. This allows comparing the single indicators to a reference that is independent of the process alternatives assessed, but is dependent on the specific site. This reference represents the impact burden on the site generated by the other industrial activities. Thus the normalized indicators measure the relative contribution of the alternatives to the local impact loads.

The definition of the normalization factors for a specific site requires to assess all the impacts on sustainability already present that are of pertinence for that site. The assessment is done independently for each category of impact. Once calculated, the normalization factors for a site are the same, no matter the process alternative assessed.
Assessing a normalization factor of a certain category of impact require three main steps:

1) Identify the *characteristic target area* for that impact;
2) Collect relevant impact data on that area;
3) Calculate the value of the normalization factor.

A1.1.1.1 – Identification of the characteristic target area

The *characteristic target area* must be identified for each impact category. The target areas are defined in accordance to the spatial dimension that are influenced by the impacts. The characteristic dimensions considered in the case studies of §4 are reported in Table 1.2.2.
The characteristic target areas are evaluated for each impact category by suitable approaches (e.g. characteristic distances calculated by models for pollutant dispersion, administrative division of the land, etc.). For instance, occupational impact acts on a local/regional area, since the creation of workplaces interest the job market in the area nearby. On the other side, rain acidification may interest target at considerable distance, since airborne transportation of acidic substances can interest a large meteorological phenomena (e.g. the characteristic dimension cloud systems over Europe is adopted in Table 1.2.2). In the case of some global issues, like global warming from greenhouse gases, alternative assumptions on the scale may be anyway adopted: in these cases the use of a national reference is preferred since national emission balances and reduction plans exist as a consequence of shared international agreements (e.g. Kyoto Protocol, etc.). Data from national references are generally easier to collect, more precise and closely reflecting the emission policy in the chosen site. Thus the assumption supports the weight definition in aggregation step.

A1.1.1.2 – Collection of relevant impact data

All the activities considered within the pertinent target area contribute to the normalization value for a given impact category. However it is practical (also in function of the decisions ion the assignment of the weights) to refer to the sole impacts from industrial facilities. This is because impacts from other activities (e.g. agriculture, financial business, transportation, etc.) have a completely different profile of sustainability impact to be considered, difficult to compare with industrial processes.

The impact data can be practically collected from the elaboration of databases. Several reliable databases may be used for gathering data on the emissions, consumptions, economics and social issues within the pertinent target area. The proper selection of data from databases is fundamental to obtain significant results. In particular the considered data must refer to homogeneous groups of activities in order to avoid biases (e.g. industrial facilities, power plants and waste treatment plants are considered in the discussed case studies of §4).

Some examples of available international and national database used as source for environmental normalization data are listed in the following:

- United Nations Framework Convention on Climate Change (UNFCCC), Greenhouse Gases Database, http://ghg.unfccc.int/
- UNECE/EMEP, Activity data and emission database, WebDab2005, http://webdab.emep.int/
- European Environment Agency dataservice, http://dataservice.eea.eu.int/dataservice/
- European Pollutant Emission Register (EPER), http://eper.cec.eu.int/eper/
- U.S. EPA, National Emissions Inventory Data & Documentation, 2002, http://www.epa.gov/ttn/chief/net/2002inventory.html
- U.S. EPA, Toxic Release Inventory: Public Data Release, 2005, http://www.epa.gov/triexplorer/
- U.S. Energy Information Administration, http://www.eia.doe.gov/
- Ministero dell’Ambiente e della Tutela del Territorio, Relazione sullo stato dell’ambiente 2001, http://www.minambiente.it/Sito/pubblicazioni/
- Ministero delle Attività Produttive, https://dgerm.attivitaproduttive.gov.it/dgerm/
- Autorità per l’energia elettrica e il gas, http://www.autorita.energia.it

Similar sources report economic and societal data of concern (e.g. the cases studies used data from some Italian statistical databases: Istituto nazionale di statistica (ISTAT), http://www.istat.it/ ; Istituto nazionale per l’assicurazione contro gli infortuni sul lavoro, http://www.inail.it/).

As it can be easily observed, most of the proposed sources of references offer public and free access to the data, that may be easily available through the world wide web.

A1.1.1.3 – Calculation of the value of the normalization factor

The normalization factors are straightforwardly calculated from the data available for the area of interest by the same rules used in the assessment of Level 1 indices (see §1.2.3). Thus, the consistency of the indices for the assessed alternatives and of the normalization factor is warranted with respect to approximations possibly present in impact evaluation.

Since the impact scales are different for the different impact categories, normalization values are expressed per unit of area. In the hypothesis of background emission sources uniformly distributed in the target area the following equation is valid for the calculation of the impact factors:

$$NF_i = \frac{\sum_{s \in At} E_{s,i}}{At_i} \qquad \text{(A1.1.1)}$$

where $E_{s,i}$ is the impact index for the i-th impact category from the s-th source belonging to the target area (At) and At_i is the size of the target area for the i-th impact category. The impact index $E_{s,i}$ is calculated for each source according to the rules for Level 1 indicators.

A1.1.2 – Example of Set of Normalization Factors

In the following an example of set of normalization factor is presented. It is actually the set used in most of the sustainability analysis of the examples in §4.
The set refers to a site localized in Northern Italy, in the in proximity of Bologna.

The characteristic target area were defined in function of the specific impact categories. Table 1.2.2 summarizes the dimensions considered.

Reference data for normalization were collected for the pertinent characteristic target areas surrounding the site. The emissions of the industrial plants located in the respective reference areas were obtained from the following databases:

- Global warming: United Nations Framework Convention on Climate Change (UNFCCC), Greenhouse Gases Database, http://ghg.unfccc.int/
- Rain acidification: UNECE/EMEP, Activity data and emission database, WebDab2005, http://webdab.emep.int/
- Smog Formation: European Pollutant Emission Register (EPER), http://eper.cec.eu.int/eper/
- Air toxicity: European Pollutant Emission Register (EPER), http://eper.cec.eu.int/eper/
- Air carcinogenicity: European Pollutant Emission Register (EPER), http://eper.cec.eu.int/eper/
- Solid waste disposal: Ministero dell’Ambiente e della Tutela del Territorio, Relazione sullo stato dell’ambiente 2001, http://www.minambiente.it/Sito/pubblicazioni/

The emissions for single substances of the different plants in the area were summed together. Then they were converted in equivalent emission for each category of impact by the same procedure described for the level 1 indicators (§1.2.4). Finally the total equivalent emission was divided by the spatial dimension (i.e. area) of the reference area, to yield the normalization factors reported in Table A1.1.2.
An example is provided in Table A1.1.1 for greenhouse gases responsible of global warming. The table reports the value of emission in equivalent unit of CO_2 for single substances over the time for a selected group of emission sources from UNFCCC database (emissions from industrial activities and energy production). The databases usually report recorded data till a certain year (e.g. 2002 in this case). Data for the successive years can be easily estimated by extrapolation of the trend in previous years. It is apparent the importance of all the reference data correspond to a standard reference year (i.e. 2005 in the example of the Table). The total equivalent of emissions for the reference year were divided by the reference area (the national area for this impact category) according to (A1.1.1).

	CO_2	CH_4	N_2O	HFCs	PFCs	SF_6	CO	NMVOC	Total
1990	2.52E+11	3.61E+10	3.30E+10	3.51E+08	1.81E+09	3.33E+08	7.62E+08	8.60E+08	3.28E+11
1991	2.44E+11	3.66E+10	3.43E+10	3.55E+08	1.42E+09	3.56E+08	8.50E+08	8.63E+08	3.21E+11
1992	2.42E+11	3.48E+10	3.38E+10	3.59E+08	7.99E+08	3.58E+08	7.74E+08	8.38E+08	3.15E+11
1993	2.34E+11	3.45E+10	3.40E+10	3.55E+08	6.31E+08	3.70E+08	9.20E+08	8.02E+08	3.08E+11
1994	2.36E+11	3.49E+10	3.36E+10	4.82E+08	3.55E+08	4.16E+08	8.85E+08	7.82E+08	3.09E+11
1995	2.57E+11	3.53E+10	3.43E+10	6.71E+08	3.37E+08	6.01E+08	8.37E+08	7.72E+08	3.32E+11
1996	2.48E+11	3.51E+10	3.37E+10	6.05E+08	2.43E+08	6.83E+08	7.37E+08	7.50E+08	3.21E+11
1997	2.53E+11	3.52E+10	3.49E+10	1.22E+09	2.52E+08	7.29E+08	8.33E+08	7.40E+08	3.28E+11
1998	2.58E+11	3.47E+10	3.44E+10	2.35E+09	2.70E+08	6.05E+08	7.91E+08	7.12E+08	3.33E+11
1999	2.53E+11	3.52E+10	3.49E+10	1.22E+09	2.52E+08	7.29E+08	8.33E+08	7.40E+08	3.28E+11
2000	2.63E+11	3.42E+10	3.50E+10	4.10E+09	3.46E+08	4.93E+08	8.05E+08	6.83E+08	3.39E+11
2001	2.65E+11	3.41E+10	3.60E+10	5.56E+09	4.52E+08	7.95E+08	7.98E+08	6.53E+08	3.45E+11
2002	2.66E+11	3.32E+10	3.54E+10	7.11E+09	4.14E+08	7.60E+08	7.53E+08	6.49E+08	3.45E+11
2003	2.67E+11	3.29E+10	3.55E+10	9.95E+09	4.26E+08	7.86E+08	7.41E+08	6.33E+08	3.47E+11
2004	2.68E+11	3.26E+10	3.57E+10	1.39E+10	4.39E+08	8.13E+08	7.30E+08	6.18E+08	3.49E+11
2005	2.70E+11	3.23E+10	3.58E+10	1.95E+10	4.52E+08	8.41E+08	7.19E+08	6.02E+08	3.51E+11

Table A1.1.1: Emission in equivalent unit of CO_2 (kg/y) for single substances from industrial activities and energy production (data from UNFCCC database); reference area: Italy.

A similar procedure was followed for the impact categories of use of resources. The data sources used in the definition of the reference values were, in this case:

- Land use: Ministero dell'Ambiente e della Tutela del Territorio, Relazione sullo stato dell'ambiente 2001, http://www.minambiente.it/Sito/pubblicazioni/
- Natural Gas: Ministero delle Attività Produttive, https://dgerm.attivitaproduttive.gov.it/dgerm/
- Electric Power: Autorità per l'energia elettrica e il gas, http://www.autorita.energia.it

With respect to economic normalization reference, data on the gross domestic product can be found in general statistics data (e.g. Istituto nazionale di statistica (ISTAT), http://www.istat.it/). Also in this case the data is expressed per unit of area, dividing for the pertinent area.

	Impact category	Normalization Factor	Unit
Environment	Global warming	$1.16 \cdot 10^6$	$kg_{eq} / (y \cdot km^2)$
	Rain Acidification	$4.83 \cdot 10^3$	$kg_{eq} / (y \cdot km^2)$
	Smog Formation	$5.63 \cdot 10^3$	$kg_{eq} / (y \cdot km^2)$
	Air toxicity	$3.79 \cdot 10^5$	$kg_{eq} / (y \cdot km^2)$
	Air carcinogenicity	$2.06 \cdot 10^1$	$kg_{eq} / (y \cdot km^2)$
	Solid waste disposal	$2.32 \cdot 10^5$	$kg_{eq} / (y \cdot km^2)$
	Land use	$2.34 \cdot 10^{-5}$	y^{-1}
	Natural Gas	$1.19 \cdot 10^{5}$	$kg_{eq} / (y \cdot km^2)$
	Electric Power	$1.10 \cdot 10^6$	$kWh / (y \cdot km^2)$
Economy	NPEI	$2.83 \cdot 10^6$	$€_{05} / km^2$
Society	Occupational index	$7.92 \cdot 10^1$	$people/ km^2$
	Inherent Safety	$6.00 \cdot 10^{-6}$	y^{-1}

Table A1.1.2: Example of set of normalization factors for a site in northern Italy (near Bologna). The data will be used in the case studies (§4).

The normalization reference for inherent safety depend on the index used in the assessment. In the case of the Hazard Index (HI) proposed in §2.3 the normalization factor must represent the average probability of death from industrial accident of people in the area surrounding the plant. This value is assumed as an average value of Potential Life Loss (PLL) from the analysis of social risk curves available in the literature *[Lees, 1996]* and national fatality statistics (Istituto nazionale per l'assicurazione contro gli infortuni sul lavoro, http://www.inail.it/).
The data on the occupation were got from "Istituto nazionale di statistica (ISTAT)" (http://www.istat.it/) and divided by the area of concern to obtain the desired normalization value.
Table A1.1.2 summarizes an example of set of normalization factors used in the case studies of §4.

A1.1.3 – Evaluation of the weight factors

As discussed in §1.2.4 and §1.2.5, normalization represents the first step towards aggregation. The normalized indexes resulting from the use of external reference values are a direct measure of the importance of the additional impact to the local conditions. On the other hand, weight factors represent the relative importance of load reduction among the impact categories. This requires to refer to a sustainability policy for the site of concern. The sustainability policy belongs to a macro-scale level that is different than the technical domain of process design. Weight factors must be defined within the macro-scale policy level, eventually creating a link between the general suitability policy and the process design.

Weight factors are defined in current method according to the hierarchy of the indexes described in §1.2.5 and pictured in Figure 1.2.2. Thus weights referring to each group to be aggregated (e.g. Level 1 environmental indicators) are assessed independently and sum up to 1. Since weight factors represent the sustainability policy, they are independent from the alternative assessed and should be defined also for those impacts that are not of interest for the specific process options considered in the analysis (e.g. also for water emissions, even no process has relevant emissions to water media). Thus in some case studies of §4 the weight factors used in some aggregation steps may not sum up to 1. This is intended to reward the processes that have not that do not address some categories of impact of potential impact.

A possible approach for the numerical determination of weight factors is based on the distance of present impacts from future target values. Weight factor can be evaluated as:

$$W_i = \frac{r_i^{\alpha}}{\sum_i r_i^{\alpha}} \qquad \text{(A1.1.2)}$$

$$r_i = f\left(IM_i(t=0),\ \ IM_i(t=n),\ \ n\right) \qquad \text{(A1.1.3)}$$

where W_i is the weight factor of the i-th impact category, r_i is the reduction rate and α is an aversion factor (generally assumed equal to 1). The function f describe the way impact loads are planned to be reduced from the present $IM_i(t=0)$ to the future value $IM_i(t=n)$ in the span of n years. The same structure for function f must be adopted for all the impact categories, in order to yield consistent rates. A simple example of function f is the linear reduction:

$$r_i = \frac{IM_i(t=0)\ -\ IM_i(t=n)}{n\ \ IM_i(t=0)} \qquad \text{(A1.1.4)}$$

In any case weight factors are limited to be greater or equal to zero.

Reliable values for the impact targets may come from large scale (i.e. regional/national) eco-system modeling of sustainability. Targets and trends are fixed for many categories by national policies or international agreements (e.g. Kyoto Protocol, Goteborg Protocol, etc.). Table A1.1.3 reports an example of reduction rate values at the Italian national level calculated by equation A1.1.4. The target data are derived from the Italian environment ministry *[MinAmb, 2001]*.

Media	**Impact Category**	**Reduction target over the time span (%)**	**Time span, *n* (y)**	**Reduction Rate, *r* (y^{-1})**
Air	Global Warming	1A1.1	12	0.0094
	Rain Acidification	66.7	13	0.0513
	Smog Formation	44.8	13	0.0345
Water	Eutrophication	10.0	20	0.0050

Table A1.1.3: Example of reduction rates from internationally agreed targets; values from *[MinAmb, 2001]*.

An alternative approach for weight estimation may be based on the judgment by a panel of experts. Resorting to an expert panel for weighting estimation is an approach common to several other assessment methods in the literature (e.g. BASF method *[Saling et al., 2002]*, the AHP procedure *[Chen et al., 2002, 2004]*, etc.). The panel should be composed by experts having different backgrounds and, preferably, include experts who are responsible of the definition of the local sustainability policy. Proper consistency checks must be made in order to limit the subjectivity introduced by the decisions of the expert panel. Table A1.1.4, reports an example of a set of weight factors decided by expert judgement that was derived from publications from BASF.

Group of categories	**%**	**Media**	**%**	**Impact category**	**%**	**Weight factors**
Emissions	20	Air	50	Global Warming	50	0.056
				Ozone Depletion	20	0.022
				Rain Acidification	10	0.011
				Smog Formation	20	0.022
		Water	35	Eutrophication	100	0.078
		Soil	15	Waste to disposal	100	0.033
Toxicity	20					0.222
Raw material consumption	25					0.278
Energy and Fuels	25					0.278
Other (non environmental)	10					-

Table A1.1.4: Example of weight factors for Level 1 environmental impacts from expert judgement; adapted values from *[Saling et al., 2002]*.

If the analysis has to account different criteria or point of view in the definition of weight factors (e.g. reduction targets, impact perception of the civil society, company policy etc.) a combination rule for different sets should be defined (see e.g. *Saling et al. [2002]*).
An example of combination rule is the arithmetic mean:

$$\overline{W}_j = \frac{\sum_k^n p_k W_{j,k}}{n} \qquad \text{(A1.1.5)}$$

$$W_j = \frac{\overline{W}_j}{\sum_j^m (\overline{W}_j)} \qquad \text{(A1.1.6)}$$

where $W_{j,k}$ is the weight factor for the j-th impact category in the k-th set out of n to be combined and p_k is the relative importance of the sets.
Another option is the use of the geometric mean, equation (A1.1.7) plus (A1.1.6). However arithmetic mean is advised, since effectively applicable also when some impact categories are not defined for certain weight sets.

$$\overline{W}_j = \sqrt[n]{\prod_k^n W_{j,k}{}^{p_k}} \qquad \text{(A1.1.7)}$$

Impact index			Weight Factor
Level 1 (normalized)			
Environment	Air	Global warming	0.051
		Ozone depletion	0.013
		Rain Acidification	0.066
		Smog Formation	0.049
		Air toxicity	0.095
		Air carcinogenicity	0.168
	Water	Eutrophication	0.041
		Organic Load	0.020
		Water toxicity	0.095
		Water carcinogenicity	0.168
		Eco-toxicity	0.033
	Soil	Solid waste disposal	0.030
	Resources	Land use	0.081
		Natural Gas	0.044
		Electric Power	0.064
Economy		NPEI	1.000
Society		Occupational index	0.200
		Inherent Safety	0.800
Level 2			
Environment			0.300
Economy			0.300
Society			0.400

Table A1.1.5: Example of set of weight factors used in the application of the proposed sustainability assessment procedure (§1.2 and §4).

No matter the approach chosen for the weights definition, a level of uncertainty always affect these values. As a consequence, a sensitivity analysis of the results is suggested §1.2.6.

Table A1.1.5 reports and example of set of weight factors used in the case studies of §4. The values were primarily derived from target data available from the site of the Ministry of the Environment, referring to international agreement and current impact reduction trends *[MinAmb, 2001; MinAttProd, WP]*. When the shortage of quantitative information about future targets did not allowed the full application of the procedure, expert judgement was followed for data integration on the basis of the available qualitative information on the national and local sustainability policy.

Section 2: Inherent Safety

2.0 – Introduction

Pursuing inherent safety is a key factor in the development of innovative chemical processes. Inherent safety promotes the elimination or the extensive reduction of process hazards by proper design choices. Moreover, it is broadly recognized that an integrated approach to the development of sustainable technologies requires the minimization of risk by the reduction of the causes and possible consequences of accidental events (§1.1).

The idea of limiting process hazards rather than controlling the risk was introduced in mid-70s by Tevor Kletz *[Kletz 1978]*. A well known schematization is based on five guidewords: minimization, substitution, simplification, moderation, and limitation.
The main advantage of a process design based on inherent safety is that the safety performance of the system is not influenced by active safety or mitigation devices (that may fail or have an ineffective action), or by safety procedures (subject to operational errors). Further relevant economic benefits may derive from the introduction of risk reduction strategies based on inherent safety, due the reduction of operational costs and of capital costs *[Lawrence & Edwards, 1993]*.

In spite of the relevant contributions dedicated to the subject of inherent safety in recent years, a well-accepted and detailed methodology for the assessment of the actions aimed to improve the inherent safety of a process is still missing. The absence of inherent safety among the approaches indicated for the control and the reduction of industrial risk in the European and Italian legislation is, at least in part, caused by the lack of tools for the quantitative assessment of inherent safety. A modulated inherent safety assessment methodology able to take into account the stage of process development and the detail of available information is still missing. It is also recognized that the available methodologies for inherent safety assessment are not able to identify some potential hazards (formation of undesired compounds in “out of control” conditions, specific modes of release from the equipment, domino hazard, etc.).

This section presents the approaches and the quantitative tools developed for supporting process design activities with regard to inherent safety aspects. Moreover, the tools introduced are a key element in the broader framework of sustainability assessment for design support, described in Section 1.
In §2.1 the theoretical background of inherent safety is reviewed and the tools proposed in the literature are analysed with respect to the goals of the current application. In the following chapters, the set of consequence-based quantitative tools developed for the inherent safety analysis in process and plant design is presented. The tools encompass three key features of the plant design: inherent safety of material (§2.2), inherent safety of process and plant schemes (§2.3) and inherent safety of plant layout (§2.4). In §2.5 the framework of a generalized approach for implementation of inherent safety in further stages of project lifecycle is presented.

2.1 – Background

2.1.1 - Definition

The CCPS *[CCPS, 1996]* defined a detailed scheme that classifies the different *strategies for the reduction of risk* in the industrial processes. Four different strategy levels were identified:

- *Truly inherent*: actions aimed to achieve process safety by a reduction of the hazard, e.g. by the use of less hazardous substances or of less hazardous reactions
- *Passive*: actions aimed to the reduction of risk by design procedures able to minimize the expected frequencies and the consequences of accidents without the introduction of any active device
- *Active*: actions aimed to achieve process safety by the introduction of active safety devices able to identify and correct process deviations from standard operating conditions, e.g. control and alarm systems, emergency shutdown systems, emergency cooling systems, etc.
- *Procedural*: actions aimed to control the risk by the introduction of procedures and management systems able to reduce the expected frequencies and the consequences of accidents

The concept of *"inherent safety"* was introduced for the first time by Kletz in 1976 *[Kletz, 1976]*. Inherent safety is an approach to industrial risk control and mitigation aimed at the elimination, or the 'reasonably practicable' reduction, of the hazards in a system *[Kletz, 1978]*. Thus, an inherent safety approach is considered to be based on the first category of actions (inherent) and, at least in part, on the second category (passive). The key idea of the inherent safety approach is the intuitive concept that a truly inherently safe system cannot possibly fail. This nullifies the requirement for safety devices to reduce the risk of accidents (likelihood and/or consequences) to acceptable levels. In principle, an approach to process safety based on "inherent safety" is more effective than the approaches based on active or procedural safety, since active devices may fail and procedures may be violated as a consequence of operational errors.

Although hazards cannot be completely eliminated in the process industries, a wide range of opportunities and improvements which lead to inherently safer systems are possible. Thus, inherent safety is usually considered in relative terms. Moreover, inherently safer systems can reduce the high costs usually associated with the full plant lifecycle – both operational (more simple procedures, reduced safety system maintenance, etc.) and capital costs (reduced investment in safety devices, easier hazard management and compliance to regulatory liabilities *[Edwards & Lawrence, 1993; Gupta et al., 2003; Khan & Amyotte, 2005; Kletz, 1984, 1991, 1998]*.

For all these reasons, the theme of inherent safety has received an increasing attention in recent years, as a possible alternative approach to process and plant safety *[Ashford, 1993; Bollinger et al., 1996; Carrithers, et. al., 1996; CCPS, 1993; Hendershot, 2002; IChemE & IPSG, 1995; Khan & Amyotte, 2003; Kletz, 1998],* that presently still relies mainly on active and procedural actions.

It is well known that the inherent safety of a process and/or of a plant is related to the properties of the substances, to the process conditions, and to the unit operations performed *[Ashford, 1993; Hendershot, 2002; Khan & Amyotte, 2003; Kletz, 1991]*. The actions aimed to the improvement of inherent safety should thus be addressed to the reduction of the hazards coming from these factors. Although similar in concept, the different possible actions toward inherent safety, the so called "*principles*" or "*guide-words*", may be formally classified or "labelled" in different ways depending on the various authors/practitioners (e.g. *CCPS, [1996]; Kletz, [1991]; Khan & Amyotte, [2004]*).

Since the terminology of inherent safety varies somewhat throughout the process safety community, the choice is made in current work to refer to the following guidewords: *minimization, substitution, attenuation, simplification,* and *limitation of effects*. The meaning of the five guidewords can be summed up as follows, according to their hierarchy:

1. *Intensification*: identifies the actions aimed to the minimization of plant and equipment inventory , thus reducing the hazard coming from the possible loss of containment
2. *Moderation*: consists in the promotion of actions aimed to the reduction of the hazards due to operating conditions (e.g. by the use of lower temperatures or pressures), that result in an inherently safer process due to the minimization of the energies involved and in a lower hazard associated to the substances present
3. *Substitution*: identifies the actions aimed to the development of substances, process schemes and equipment different from those conventionally used, but characterized by a higher inherent safety
4. *Simplification*: identifies the design actions aimed to reduce the complexity of the process and/or of the plant, thus reducing the possibility of errors and the probability of loss of containment
5. *Limitation of effects*: consists in actions aimed to the design of a process and/or of a plant in which the consequences of the possible loss of containment are effectively reduced and the possibility of escalation is minimized

The identified guidewords represent a roadmap of basic rules to improve the inherent safety of a system. They provide, for every stage of the design lifecycle, guidelines that help to categorize the possible actions for hazard reduction. However, in the absence of quantitative assessment tools, these are not sufficient to develop effective strategies for the improvement of process and plant inherent safety. As a matter of fact, the application of the keywords may result in contradictory indications on some possible hazard reduction actions *[Kletz, 1991]*. An example is given by the choice of less severe reaction conditions: this action is suggested by the moderation keyword, but may be in contrast with the intensification keyword, since the use of mild reaction conditions usually results in higher residence times and thus in a higher hold-up of process equipment. Therefore, the development and the introduction of a metric and of quantitative assessment tools is a necessary step in order to introduce inherent safety criteria in the process and plant design.

Furthermore quantitative indices for inherent safety are required to integrate the assessment in the general system of sustainability analysis of a project, as detailed in Section 1.

2.1.2 – Existing assessment tools: review of the literature

2.1.2.1 – Generalities on the methods for the quantitative assessment of inherent safety

It is widely recognized that the actions aimed to the improvement of inherent safety should be mainly concentrated during the initial steps of process development, since in the initial design phase changes and modifications are more easily introduced *[Kletz, 1976, 1991]*. Most of the available techniques for quantitative risk assessment are rather complex and require detailed information on the plant analyzed *[Khan et al., 2003]*. Thus, their application in the initial steps of process or of plant design is not possible, and the assessment of a high number of different solutions is extremely time consuming. A possible alternative is the use of simplified methods based on the estimation of risk indexes, that allow a quantitative assessment based on a limited amount of information. For this reason all the available methods for the quantitative assessment of inherent safety are based on the assessment of risk indexes *[Khan & Amyotte, 2003; Khan et al., 2003; Koller et al., 2001]*. Many contributions dedicated to the development of tools for inherent safety assessment focused on the modification of existing methods for the assessment of risk indexes or on the development of improved or original procedures for the assessment of inherent safety indexes.

An important problem that emerged in the use of inherent safety assessment tools during process design is related to the possible "risk shift" *[Koller et al., 2000; Shah et al., 2003]*: the implementation of actions aimed to improve inherent safety may reduce the risk of major accidents, but may cause the increase of other risks, e.g. of the environmental risk due to the process. Several publications evidenced the need of a comprehensive approach, that should take into account inherent safety jointly to the environmental and human health risk caused by the process *[INSIDE Project, 1997; Koller et al., 2000; Shah et al., 2003; Mansfield, 1994]*. However, the integrated tools proposed for the comprehensive assessment of all the different process impacts still need to overcome the problem posed by the clustering of the different indexes to a limited number of integrated indicators *[Gupta & Edwards, 2003]*. The development of specific aggregation tools, based on fuzzy sets or on hierarchical matrixes *[Gentile et al., 2003; Shah et al., 2003]*, seems to represent a promising perspective in order to achieve integrated methods for quantitative assessment.

Data Required	PIIS	ISI	i-safe Index	INSET (I , J)	ESH	I2SI	SWeHI	Dow F&EI	Dow CEI	Mond F,E&T	KPI (this study)
Chemicals and their proprieties	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Reactions and interactions	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
Operative conditions	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Process Flow Diagram		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Equipment inventory				✓	✓	✓	✓	✓	✓	✓	✓
Material balances						✓	✓	✓	✓	✓	✓
P&ID						✓	✓	✓		✓	
Layout definition						✓	✓	✓		✓	
Equipment design data								✓	✓	✓	

Table 2.1.1: Data required for the calculation of some quantitative indexes proposed for inherent safety assessment.

Most of the existing methods for the assessment of inherent safety are thus highly concerned with the selection of process alternatives during the initial steps of process development (type of substances, selection of the catalyst and of solvents, etc.), while often scarce attention is paid to the assessment of the possible alternatives available in the other steps of process development, as in flow-sheet or in lay-out definition. However, the analysis of the possible actions for hazard reduction deriving from the application of the inherent safety guidewords points out that many of these are related to flow-sheet optimization or to lay-out definition. As a matter of fact, has not been recognized that the actions aimed to inherent safety improvement should not be concentrated only in the initial step of process design (i.e. early stages of process lifecycle), but should be extended to all the initial steps of the different stages of project development (i.e. early phases of each stage of the process lifecycle: early process design, early flow-sheet definition, early P&ID definition, etc.) *[Carrithers et al., 1996]*. The different detail of information available in the different stages of project development requires a modulated approach to inherent safety, with a set of different tools for the quantitative assessment that may be integrated with the conventional tools used in process and plant design.

The existing tools for inherent safety assessment can be classified in function of the amount system of detail they require for the application. Table 2.1.1 depicts a summary this information level required by several inherent safety indexes proposed in the literature. In the following a quick review of the existing inherent safety tools and of their principal advantages and drawbacks in application is provided.

2.1.2.2 – Dow Fire and Explosion Index (F&EI) and Dow Chemical Exposure Index (CEI)

Commonly referred to as the Dow Index, the Dow Fire and Explosion Index is a well known and widely used hazard index *[Dow Chemical Company, 1994]*. It is primarily designed for operations in which a flammable, combustible, or reactive material is stored, handled or processed. The original procedure for the assessment of the index aims to take into account fire protection measures in combination with a damage factor to derive the maximum probable property damage (MPPD).

This method is not originally intended as a method for inherent safety assessment: in fact it is a simplified method for risk assessment. However it has been proposed as suitable for the assessment of inherent safety, provided that the assessment of loss control credit factors is skipped *[Etowa et al., 2002; Koller et al., 2001]*.

The assessment of F&EI includes a first step of calculation of a material factor (MF), which is a measure of the potential energy released from the material. It is determined by scoring the flammability and reactivity of the material. Then two penalty factors (F1 and F2), respectively accounting for general process hazards (penalties due to the type of reaction/process, type of chemical handled in the process unit, and spill control factors of the chemical) and special process hazards (penalties due to operation under hazardous conditions, quantity of chemical handled in the unit, and characteristics of the chemical) are calculated. These are combined to yield a process unit hazards factor (F3). The Dow Index is obtained as the product of the MF and the process unit hazards factor.

The Dow Chemical Exposure Index (CEI) is an index originally developed at Dow Chemical Company to measure relative acute toxicity risks *[Dow Chemical Company, 1993]*. It may be used for initial process hazard analysis, for health hazard ranking of units and for emergency response planning. Also in this case, the extension of the use to inherent safety assessment was proposed *[Etowa et al., 2002; Heikkilä, 1999; Koller et al., 2001]*.

The information needed for the calculation of the Dow CEI includes: a) physical and chemical properties of the material, b) a simplified process flow sheet, c) individual units showing vessels and major pipework with inventories, and d) an accurate plot plan of the industrial site and its surroundings. The CEI computation involves two key factors: the first is the Airborne Quantity (AQ) and second is the Emergency Response Planning Guidelines (ERPG) value. AQ is the rate at which the material can become airborne under process conditions. The ERPG represent the parameter assessing the toxic proprieties of released materials; in particular the index uses a threshold regarding to serious or irreversible health effects (ERPG-2).

Although both F&EI and CEI are widely accepted and validated methods for quick risk analysis, they suffer drawbacks for the use in inherent safety assessment. The complete calculation of the indices require the knowledge of several details on the plant (e.g. layout, material corrosion, indoor/outdoor, etc.) for the assignment of parameter values (Table 2.1.1). Since these characteristics are usually defined in late design stages, the method is applicable in earlier stages only in a simplified version that overrides the unknown aspects. Moreover the two indices assess separately the hazard of flammability/explosiveness and of acute toxicity. Thus a problem arises on the comparison of the two indexes results. No rules are defined for combining the values for single units in order to assess a plant/process.

2.1.2.3 – Mond Fire, Explosion, and Toxicity Index

The Mond Fire, Explosion, and Toxicity Index (referred to as the Mond Index) was developed by the Mond division of ICI *[ICI Mond Division, 1985; Tyler, 1985]*. The Mond Index makes an initial hazard assessment in a manner similar to that used in the Dow Index, but incorporates additional hazard considerations (wider range of applicability, processing of explosive chemicals, improved hazard consideration of hydrogen, inclusion of toxicity assessment, consideration of control and safety instrumentation). The potential hazard is expressed in terms of the initial value of a set of indices for fire, explosion, and toxicity. The material factor is determined as in the Dow method, but additional special material hazard factors are introduced. Again as in the Dow method, use is made of factors for general and special process hazards although some other necessary factors are different. A quantity factor, based on the inventory of material, and layout hazard factor are also introduced, as are toxicity hazards. The toxicity index is calculated using a health factor, the quantity of chemical in use, and the toxicological properties of the chemical. As in the Dow F&EI, also Mond Index allow to account for risk control measures by a system of offsetting factors; these ones should not be considered for the use in inherent safety assessment.

The Mond Fire, Explosion and Toxicity Index is a possible alternative to Dow Indexes, but it still retains some of the same limitations for the application in early stages, because of the required detail. On the other hand the improved factors considered in this index constitutes an advantage compared to Dow indices.

2.1.2.4 – Safety Weighted Hazard Index

SWeHI is the revised version of the hazard identification and ranking analysis proposed earlier by Khan and Abbasi *[Khan & Abbasi, 1998b]*. It aims at providing a “single frame” view of a desired process unit. The SWeHI represents the radius of the area under hazard (50% probability of fatality/damage) due to the given unit *[Khan et al., 2001]*. The SWeHI is the ratio of two factors: a quantitative measure of the damage that may be caused by a unit/plant, measured in terms of area under 50% probability of damage (B) and a factor representing the credits due to control measures and safety arrangements made to counter the undesirable situations (A). For inherent safety application this second factor can be ignored (i.e. considering it equal to 1).

The factor B is chosen as the maximum between the factor for damage due to fire and explosion (B1) and the factor for damage due to toxic release and dispersion (B2). The quantification of B1 is based on a few steps. First of all, the various units are classified in pre-defined groups (storage units; units involving physical operations; units involving chemical reactions; transportation units; other hazardous units (e.g. furnaces, boilers, direct-fired heat exchangers, etc.)). For each unit, within the rules specific for each group, a few energy factors (quantification of the potential of the system to release energy) are calculated. Then penalties are assigned for the operating conditions, material proprieties and unit/plant location. Finally B1 is calculated by group specific equations.

On the other hand, B2 is using the outcomes of the elaboration of derived using transport phenomena and empirical models based on the quantity of chemical(s) involved in the unit, the physical state of the chemical(s), the toxicity of the chemical(s), the operating conditions, and the site characteristics. The dispersion is assumed to occur under slightly stable atmospheric conditions, representing a median of high instability and high stability. The estimation of B2 is done for every unit by the combination of a core factor and several penalties. The core factor takes into account the condition for release (gas, liquid, two-phase, pyrophilic solids) by a proper factor.

Similarly to Dow and Mond Indices, SWeHI was initially developed for an evaluation of process safety requiring more detailed data. The index structure is equally based on the combination of factors by built-in rules. However the scoring rules were frequently calculated on the basis of physical phenomena concerning potential accidents. As in Dow F&EI, a relationship is claimed between the final result and a distance of damage, but, as pointed out, the physical relationship remains mostly embedded into the parameter scoring procedure. No combining rules are defined for whole plant/process assessment.

2.1.2.5 – Prototype Index of Inherent Safety

Edwards and Lawrence *[Edwards & Lawrence, 1993]* have proposed a Prototype Index of Inherent Safety (PIIS) to analyse, by a quick scoring, inherent safety potential of different process routes for the same product. The index attributes scores to 7 parameters related to the process and chemicals in use, that were select as key factors for the hazard potential of a process. The ISI computation procedure divides the complete process into various sub-steps based on the chemical route. A chemical score is calculated for inventory, flammability, explosiveness, and toxicity of each chemical used in the sub-steps. The highest score is considered the representative value for this sub-step. As well, the process score is computed for pressure, temperature, and yield of each sub-step. Chemical and process scores are combined to give a single value for each sub-step, and subsequently combined to produce a single index for a given process route. Finally, a ranking of process routes is done, implying that the higher the value of a process route, the less inherently safe is that route.

This index is a milestone in the field of inherent safety assessment, since it represents the first example of a quantification tool dedicated to inherent safety. Resorting to a scoring method allows an easily application even having limited details on the process. Nevertheless, this particular scoring approach has been criticized for including built-in judgments of the developers of the index on the relative importance of the terms *[Gupta & Edwards, 2003]*. All these assumptions may hardly retain their value when further information on the process become available in the further design steps. Another limit of index is that it is very reaction oriented and does not consider properly the other parts of the process even they usually represent the majority of equipment.

2.1.2.6 – Inherent Safety Index

Heikkilä *[Heikkilä, 1999; Heikkilä & Hurme, 1998]* has developed an Inherent Safety Index (ISI) to classify process alternatives during the preliminary process design. It is based on a scoring approach similar to the PIIS, as it can be considered an upgrade of the latter index. It consists of chemical and process inherent safety indices. Both contain revised sub indices with respect to both number of considered hazards and scoring rules. Noticeably enough, “chemical interaction” and “corrosiveness” are included in the chemical inherent safety index and “equipment safety” (i.e. possibility that a piece of equipment is unsafe) and “safe process structure” (i.e. inherent safety of the process configurations) are included in the process inherent safety index. The resulting tool can be easily applied within a very basic knowledge of the process. However it retains all the limits on subjective judgement and built-in assumptions typical of the simple scoring rules adopted.

2.1.2.7 – Inherent Safety Index based on fuzzy approach

According to Gentile and co-workers *[Gentile et al., 2003]* indices like the ISI and the PIIS are based on Boolean mathematics. Therefore each sub-range is like a set with sharp boundaries. So an element can belong only to one set at a time. This may bring a practical problem as regards sensitivity: an excessive sensitivity of the score is experienced when the value of a parameter is close to the limits of a range (the value of the parameter can have a big shift to former or later range even for a small change of the parameter) and, by converse, an insufficient sensitivity within the range (despite the reduction of the parameter within a range, no shift on the score is yield). In order to fix these limits, Gentile and co-workers proposed to improve the ISI method by using fuzzy set theory, where transition from one interval to the next is smooth. In fact, in a Boolean set, an element can only be inside or outside the set, but in a Fuzzy set, the element can be partially or totally inside or outside depending on the shape of membership function. In this method each factor is assessed by a Linguistic Variable. This variable is divided into sub-ranges, or fuzzy sets. The fuzzy sets for inputs are related to the output fuzzy sets through if-then rules, which describe the heuristic knowledge about the behaviour of the system. The final result can be defuzzyfied to yield a quantitative score.

2.1.2.8 – i-Safe Index

Palaniappan and co-workers have proposed the i-Safe index *[Palaniappan et al., 2002, 2002b]*. This index is part of a software-aided methodology for process chemical route selection and flow-sheet improvement; the approach includes a system of expert rules for inherent safety improvement in PFD design. For as regard the inherent safety index, it is practically an expansion of the approach from Heikkila *[Heikkilä, 1999]*, including further parameters. However the structure is similarly based on scoring of the proprieties for the chemical and the process. Thus the practical advantages, as well as the drawbacks, are similar to the ones discussed for ISI and PIIS.

2.1.2.9 –INSET Toolkit

The INSET toolkit *[INSIDE Project, 1997]* is the result of an European government/industry project aimed to promote inherently safer chemical process and plants (the INSIDE Project). The project has developed a set of tools to identify inherently safer design options through the life cycle of a process and to evaluate the options. Among these tools, indices aimed at the quantitative assessment of the safety health and environment (SHE) performance are defined. In particular tools I (ISHE performance indices) and J (multi-attribute ISHE comparative evaluation) concern aspects related to hazard assessment. The calculation of the indices relays on factors scored from the proprieties of substances (easily obtainable from material data sheets) and on an evaluation of inventories. However no particular rules are defined for the latter one. Tool J suggests a multi-attribute approach for combination of the indices calculated for single hazard aspects (e.g. fire and explosion, acute toxic hazard, reaction hazard, etc.), even if do not define strict rules for that, relying on case-specific expert judgement. No rules are provided for whole plant quantitative assessment. This method, along with the EHS Index, require an higher level of detail compared to the simper scoring methods like PIIS and ISI (Table 2.1.1). However the assessment procedure is still based on the evaluation of inherent safety scores, resulting in the same kind of limitations of the simpler approaches.

2.1.2.10 – EHS Index

Koller and co-workers proposed the EHS index for environment health and safety assessment of chemical processes, with particular attention to batch processes (e.g. fine chemistry) *[Koller et al., 2000]*. However the narrow application to inherent safety assessment is possible. The idea of the index is conceptually similar to the INSET tools, but the EHS Index has improved, but swift, assessment rules that account for a larger number of parameters influencing the hazard (the "dangerous proprieties"). Noticeably the rules for the scoring of dangerous proprieties are flexible in order to allow the use of different data sources. Also in this case the final index for each hazard aspect (the "potential of danger") scores from the material proprieties are combined with an estimation of the inventory. No general rules are defined for the quantification of the inventory for units of continuous processes. The approach allow to account, by proper factors, for technological and organizational measures for risk mitigation, but this is not the case for inherent safety assessment.

Also in this index the assignment of hazardous parameters is a scoring procedure, even if more refined then other scoring approaches, yielding the same practical limits discussed earlier. Moreover this method do not define a procedure for the aggregation or combination of the various sub-indices addressing specific hazard issues. Furthermore no combination of unit scores to a plant one is provided.

2.1.2.11 – Integrated Inherent Safety Index

Khan and Amyotte *[Khan & Amyotte, 2004, 2005]* have developed a tool for inherent safety evaluation, named Integrated Inherent Safety Index (I2SI). It consists of a comprehensive framework intended join hazard potential identification and assessment of hazard control measures with an economic evaluation of safety. I2SI is a function of Hazard Index (HI) and inherent safety potential index (ISPI). HI is a measure of the damage potential considering process and hazard control measures. The damage potential is based on scoring of expected damage distances for fire and explosion, acute toxicity, chronic toxicity and environmental damage. ISPI is a measure of the applicability of inherent safety's principles to the base process.

An I2SI value greater than unity, presents a positive response to inherent safety guideword application. The higher the value of the I2SI, the more pronounced the inherent safety impact. Thus, despite all the previous indices, that aimed at hazard evaluation, in this case the lower the value of the index, the less inherently safer is the option (i.e. it is more hazardous). According to the Authors, this indexing procedure required subjective judgment for certain aspects, and for this problem and other uncertainties they have suggested the use of fuzzy mathematics.

The methodology requires the calculation of damage distance, for some parameters, that may be obtained by a preliminary application of other approaches, like for instance SWeHI. Moreover the same Authors recognize that the procedure implies some extent of subjective judgement and some expertise on the processes should be suggested for a proper application. However it constitute the most comprehensive approach till now developed for inherent safety assessment.

2.1.3 – Limits of the existing methods

The analysis reported above identified several approaches that have been proposed in the literature for the assessment of the inherent safety performance in design activities. As discussed, despite the valuable research effort, some limitations exists in the effective applicability of the methodologies as support tool for process design. Hence, current work makes an effort to propose innovative tools for filling the gap. The principal limitations hindering conventional methodologies can be generalized as follows:

- Current assessment tools mainly focus on a single phase of the design lifecycle, generally the process selection. Though this is a key phase in the definition of the safety profile of a plant, the implementation of inherent safety should be generalized all over the design lifecycle.
- The simpler methodologies (i.e. requiring less process information) are heavily based on simplifications and built-in assumptions that strongly rely on the specific experience of the developers and may hardly retain their value when further information on the process become available.
- On the other side, some approaches resorts to scoring based on expert judgment of the analyst, thus introducing some subjective elements in the comparison of the alternatives.
- Only standard units are usually accounted. The rigid and sometimes unclear assessment structure of some index methods may lead to difficulties in the application to some specific cases (new technologies, minor and auxiliary equipment, etc.). In particular, some indexes were designed only for rather specific process applications, and their evaluation in other types of processes/units is not straightforward.
- Some methods yield unaggregated indexes for specific types of hazard. Moreover clear rules for the aggregation of the single unit indices to an overall plant profile are usually not defined.

2.2 – Proposed Method for the Inherent Safety Assessment of Materials

2.2.1 – Overview of the problem

Inherent safety principles recognize that an important part of the hazard involved in handling and processing of chemical substances is directly related to the substance characteristics and proprieties (toxicity, flammability, stability, etc.). Less attention is usually devoted to the potential dangers that may arise from the products that may be formed as a result of thermal decomposition or unwanted reactions of the primary material. Thermal decomposition can be triggered in anomalous conditions, as overheating or process runaway, or as a consequence of accidental scenarios. The unforeseen conditions may lead to the formation and to the release of extremely hazardous compounds, different from the normal reactants and products of the process.

It is well known that the loss of control of a chemical process may result in the formation of extremely hazardous compounds due to the unwanted conditions caused by the accidental event. Historical analysis results confirm that severe accidents in the manufacture of fine chemicals and pharmaceutical products, as well as, production and storage of commodities (plastics, fertilizers, etc.) were caused by the release of hazardous products formed as a consequence of the deviation of a process from the normal operating conditions *[Cozzani, et al., 1997a, 1997b]*. The dangerous substances “which it is believed may be generated during the loss of control of an industrial chemical process” must be considered by law in the analysis of industrial installations subject to the Directive (96/82/EC), named after the Seveso accident.

The particular aspect of hazardous substances that may be formed by unforeseen reactions is not considered in the currently available methods for the assessment of inherent safety. Accounting for the hazard from undesired decompositions is not a simple task, in particular if a comparative analysis among the hazards of different "primary" substances and the “secondary” products is pursued. As a matter of fact, a number of different products may be formed from a single "primary" substance, each having a different hazard.

Nevertheless the selection of less hazardous substances is a key issue for an inherent safety assessment method aimed at supporting the development of new chemical processes. Thus a specific tool for the assessment of the hazard profile of the decomposition products for a substance was developed in the current study.

The development of such a tool required to focus on two aspects: the first one concerns the identification of the expected “secondary” substances originated in anomalous condition and the second one concerns the definition of a comprehensive procedure for hazard assessment and comparison.

The problem of identification of the secondary substances requires dedicated experimental surveys. Experimental protocols may be adopted in order to reproduce the accidental conditions and to identify the products. A separated section (§3) of the current work will be specifically dedicated to this purpose.

In the following, the procedure specifically developed for the assessment of the hazard profile of “primary” and “secondary” materials is described. The procedure allows the comparison of the hazard profiles of the initial substances and the decomposition products, allowing the identification of potentially dangerous condition. This completes the outcomes of experimental surveys providing the elaboration and the interpretation of the results.

2.2.2 – Selection of hazardous proprieties

The first step in the development of the procedure for inherent safety of materials was the definition of a the hazard vector. This is a vector that contains the hazardous proprieties considered for a given material. The hazard vector represents the hazard related to the release of any identified substance into different environmental compartments. In particular the four targets of the hazard were considered:

i. acute effects on human health;
ii. long-term effects on human health;
iii. damages of ecosystems (both global balance and single species);
iv. environmental media contamination.

Physical and chemical hazards, as flammability or explosion, were not considered since the main concern of the present study was the possible formation and release in the environment of extremely toxic decomposition products. This choice is justified by the analysis of past accidental scenarios, that highlighted that the more critical aspects connected to the decomposition of substances are toxicity and environmental contamination.

The actual capability of a substance to reach a damage target was considered. A comprehensive study of the methodologies used to assess the risk for the human health, and for ecological and environmental media vulnerability, led to the identification of four categories of hazardous properties (Table 2.2.1).

The first category is represented by toxicological and eco-toxicological parameters, that express dose-response relationships, as acute toxicity and chronic reference doses (inhalation, oral and dermal), and cancer slope factors (inhalation, oral and dermal). In addition toxic effects on fish, daphnia and birds are taken into account in order to define the eco-toxicological behaviour.

Categories	Proprieties	Symbol
Toxicological and eco-toxicological properties	Acute toxicity on humans	P_{AT}
	Acute eco-toxicity on fauna and flora	P_{ET}
	Chronic toxicity on humans	P_{ChT}
	Carcinogenicity	P_C
Dispersion and environmental fate	Molecular weight	P_{MW}
	Henry's law constant	P_H
	Boiling point	P_{Bp}
	Water solubility	P_S
Uptake by humans and animals	Octanol-water partition coefficient	P_{Kow}
Persistence in the environment	Overall persistence time	P_{to}

Table 2.2.1: Potential impact categories and selected hazardous proprieties for the characterization of substances released into the environment.

The second category contains parameters influencing the dispersion and the environmental fate of substances (i.e. chemical and physical properties that describe the partition of chemicals between solid, liquid and gas phases). Molecular weight, melting point, boiling point, relative density (liquid, air), vapour pressure, Henry's law constant, water solubility, lipophilicity, air and water diffusivity belong to this group.

The third category is represented by the parameters influencing the uptake by humans and living organisms: octanol-water partition coefficient (K_{ow}), organic carbon partition coefficient, bioconcentration and bioaccumulation factors, soil-water partition coefficient, suspended solids-surface water partition coefficient, sediments-pores water partition coefficient. However, it must be remarked that reliable methodologies are available to derive all these parameters from the K_{ow} coefficient.

The fourth and last category consists of properties influencing the persistence in the environment: degradation coefficients or half-life times in air, soil and water.

Although many parameters can fit in these four categories, a selection of a small number of properties was possible (Table 2.2.1). The criteria for selection were based on the role they play in the risk modeling and the existence of predictive relations among the parameters belonging to the same category *[Allen & Shonnard, 2002; EPA, 2005]*.

2.2.3 – Definition and comparison of the hazard profiles

The parameters in Table 2.2.1 are the basis of the evaluation of the hazard profile. Thus the collection of the values for all these parameters is required for the application of the present methodology. The values of the proprieties will be converted in scores, the quantities actually used in the hazard vector. Table 2.2.2 reports the possible typology of data for assigning values at the parameters.

Two practical sources exist to obtain the values of the parameters: available databases reporting results from experimental data (suggested) or estimation on the basis of the structure of the chemical of concern.

Group of properties	#	Parameter	Data
1) Toxicological and eco-toxicological properties	P_{AT}	Acute toxicity	LC_{50}, LD_{50}, Risk Phrases
	P_{ET}	Ecotoxicity	LC_{50}, LD_{50}, EC_{50}
	P_{ChT}	Chronic toxicity	RfD, RfC
	P_C	Carcinogenicity	CSF
2) Dispersion and fate	P_{MW}	Molecular weight	M
	P_H	Henry's law constant	H
	P_{Bp}	Boiling point	T_b
	P_S	Water solubility	S
3) Uptake by organisms	P_{Kow}	Octanol-water partition c.	K_{ow}
4) Persistence	P_{to}	Overall persistence time	T_o

Table 2.2.2: Hazardous parameters and typology of data for the definition.

Examples of databases that can be used in the assessment are:

- CHEMEXPER, http://www.chemexper.com
- EPI SUITE, http://www.epa.gov/opptintr/exposure/pubs/episuite.htm
- SIRI, http://www2.siri.org/msds/index.php
- TOXNET (HSDB, IRIS, ITER), http://toxnet.nlm.nih.gov
- Lewis, R.J., Sax's Dangerous Proprieties of Industrial Materials, 1992, 8th Ed., Van Nostrand Reinhold, New York.

The predictive methods are generally described as group contribution methods, structure activity methods (SARs) or quantitative structure activity relationships (QSARs) *[Allen & Shonnard, 2002; EPA WPd; Perry 1997]*. As well, specific toxicological and eco-toxicological tests can be done where necessary.

In order to evaluate and compare the different hazards associated to a substance of concern, an arbitrary hazard ranking was derived from the substance parameters listed in Table 2.2.2. A score, integer between 0 and 3, was assigned to each property, on the basis of the value of the reference parameters. The 0 value (i.e. negligible effect) is assigned only for the first group parameters, that are related to toxicity, carcinogenicity and ecotoxicity, while for all the other parameters the lowest score is 1. Table 2.2.3 shows an example of this assignation procedure for the acute eco-toxicity for fauna and flora (P_{ET}). Scoring procedures similar to those described in figure were defined for all the other parameters, and are reported in Appendix 2.1. The scores assigned to each range of the parameters were defined on the basis of criteria depending on the specific parameter, considering typical values for a large number of substances as well as normative references (e.g. for the acute toxicity, the criteria were based on the classification given by Directive 67/548/EEC). Where more parameters contribute to the assignation of a single parameter score *[Koller et al.,2000; Allen & Shonnard, 2002]*, as in the example of Table 2.2.3, the overall score is conservatively assumed on the basis of the highest parameter.

All the parameter scores of a substance are listed in the "hazard vector" of the substance, that may be also represented using a radial graph, to give the "hazard footprint" of the substance, as shown in the examples of §4.5.

The scores of the hazard vector may be combined and aggregated in a limited number of hazard indexes, each expressing the potential impact towards a specific target, in order to allow a more identification of the hazards of a substance. The four impact indexes used to define the impact profile of each substance were defined in order to share the same generalized equation:

$$I = HF \cdot AF \cdot CPF \qquad (2.2.1)$$

where:

- HF (Hazard Factor) represents the ability of a substance to damage the target;
- AF (Availability Factor) represents the availability and the intensity with which the substance may actually reach the target;
- CPF (Contact Probability Factor) quantifies the likelihood of a target to come in contact with the substance.

	Fish $LC50_{96h}$ (g/m^3)	Daphnia $LC50_{48\ h}$ (g/m^3)	Birds $LD50_{oral}$ (mg/kg)	Algae $LC50_{72h}$ (g/m^3)	Score
Very toxic	< 1	< 1	< 10	< 1	3
Toxic	1 – 10	1 – 10	10 – 100	1 – 10	2
Harmful	10 – 100	10 – 100	100 – 1000	10 – 100	1
Negligible toxicity	> 100	> 100	> 1000	> 100	0

Table 2.2.3: Example of hazard ranking: acute eco-toxicity for flora and fauna (P_{ET})

Table 2.2.4 lists all the indexes considered by the method. The values of the specific impact indexes are between 0 and 27.

The first index, the Acute Toxicity Index (I_{AT}), assesses the hazards for the humans due to acute toxicity for the inhalation of a volatile compound. In this index, the HF is linked to the acute toxicity parameter (P_{AT}), but it refers to the specific acute toxicity for inhalation. The AF is represented by the tendency of the compound to be present in air. Thus, the AF was calculated as the mean of the scores for the boiling point and the Henry's law constant (H), expressed in $atm \cdot m^3/mol$. Finally, the CPF is related to the molecular weight, since diffusivity in air, which affects the dilution of a toxic cloud, is correlated to molecular weight by a decreasing function.

The second index (Ecotoxicity Index, I_{ET}) concerns the hazards for the ecosystem. Two sub-indexes were defined for the calculation: one for aquatic species (I_{ETaq}) and the other for avian ones (I_{ETav}). I_{ETaq} is obtained multiplying the scores of the following parameters: toxicity for algae, daphnia, and fishes (HF), solubility (AF) and persistence time (CPF). Toxicity for birds (HF), Henry's law constant (AF) and persistence time (CPF) are instead considered for I_{ETav} calculation. The higher value between the two indexes is chosen as I_{ET}.

The third index (Chronic Toxicity Index, I_{CT}), expresses the chronic toxic effects of a released substance on human targets. The three factors for the estimation of the Chronic Toxicity Index are the scores for chronic toxicity, the K_{ow} and the persistence.

Index	***Formula***
Acute Toxicity (I_{AT})	$I_{at} = P_{AT} \cdot ((P_H+P_{Bp})/2) \cdot P_{MW}$
Ecotoxicity (I_{ET})	$I_{et} = \max((P_{ETwater} \cdot P_S \cdot P_{to}) ; (P_{ETair} \cdot P_H \cdot P_{to}))$
Chronic Toxicity (I_{CT})	$I_{cht} = P_{ChT} \cdot P_{Kow} \cdot P_{to}$
Carcinogenicity (I_C)	$I_c = P_C \cdot P_{Kow} \cdot P_{to}$
Overall Index	$I_o = I_{at} + I_{et} + I_{cht} + I_c$

Table 2.2.4: Hazard indexes defined to describe the hazard profile of a substance.

The fourth index (Carcinogenicity Index, I_C), is similar to the previous, but the aspect of concern is the carcinogenicity. Therefore, the hazard factor is represented by the score for carcinogenicity (evaluated through slope factors or qualitative information), while the other two factors are the same of the I_{CT}.

The four indexes are added to calculate the Overall Hazard Index (I_O). Although this is useful for quick hazard comparison of different substances, its intrinsic limit due to the loss of detail in the information has to be recognized.

The loss of control of a chemical process may cause the contemporary release of many substances; therefore the development of an approach for the comparison of the hazard profiles of primary and secondary substances becomes a fundamental element for the comprehension of the consequences of an accidental scenario. The identification, possibly quantitative, of the substances released rely on the application of suitable experimental protocols, as described in Section 3.
When several substances are present in a mixture, the single hazard vectors, featuring the impact profile of the decomposition products, can be arranged in an hazard matrix.

The comparison of the hazard profile between the primary substance and the decomposition products is a starting point for the assessment of scenarios involving decomposition reactions following the loss control of the chemical system. The use of the hazard matrix allow a quick comparison among single substances (e.g. Table 2.2.5). Furthermore a graphical representation (radial diagrams and histograms, as in Figure 2.2.1) shows the new hazards that may arise in "loss of control" conditions.

Compound name	P_A	P_E	P_C	P_C	P_M	P_H	P_B	P_S	P_K	P_{to}
TBPB	1	3	1	1	2	2	1	2	1	2
Carbon Dioxide	0	0	0	0	3	3	3	3	1	3
Propanone	0	0	1	1	3	2	2	3	1	3
Methane	0	1	1	0	3	3	3	2	1	3
Toluene	1	2	2	1	3	2	2	2	1	1
Benzene	1	2	2	1	3	2	2	3	1	2
Butanone	0	0	2	0	3	2	2	3	1	2
Biphenyl	0	3	2	1	2	2	1	2	2	1
Ethyl benzene	1	2	1	1	2	2	2	2	1	1
1-phenyl-2-propanone	0	1	0	0	2	2	1	3	1	1
2-methyl-2-propanol	1	0	1	1	3	2	1	3	1	2

Table 2.2.5: Example of hazard matrix: the thermal decomposition of tert-butylperoxybenzoate (TBPB), (raw data from *CCPS, [1995]*)

In the case of mixtures, general rules can be defined for the identification of the hazard profile of the mixture. When quantitative data on the expected distribution of the weight fractions of the decomposition products are available, a significant information may be added up in the comparison of the hazard profiles, estimating the weighed average of the hazard profiles. Otherwise the range of variation of the values can be represented graphically, allowing a screening of the possibility of formation of more hazardous compounds and, through the analysis of the indexes, of the prevalent types of new hazard arising.

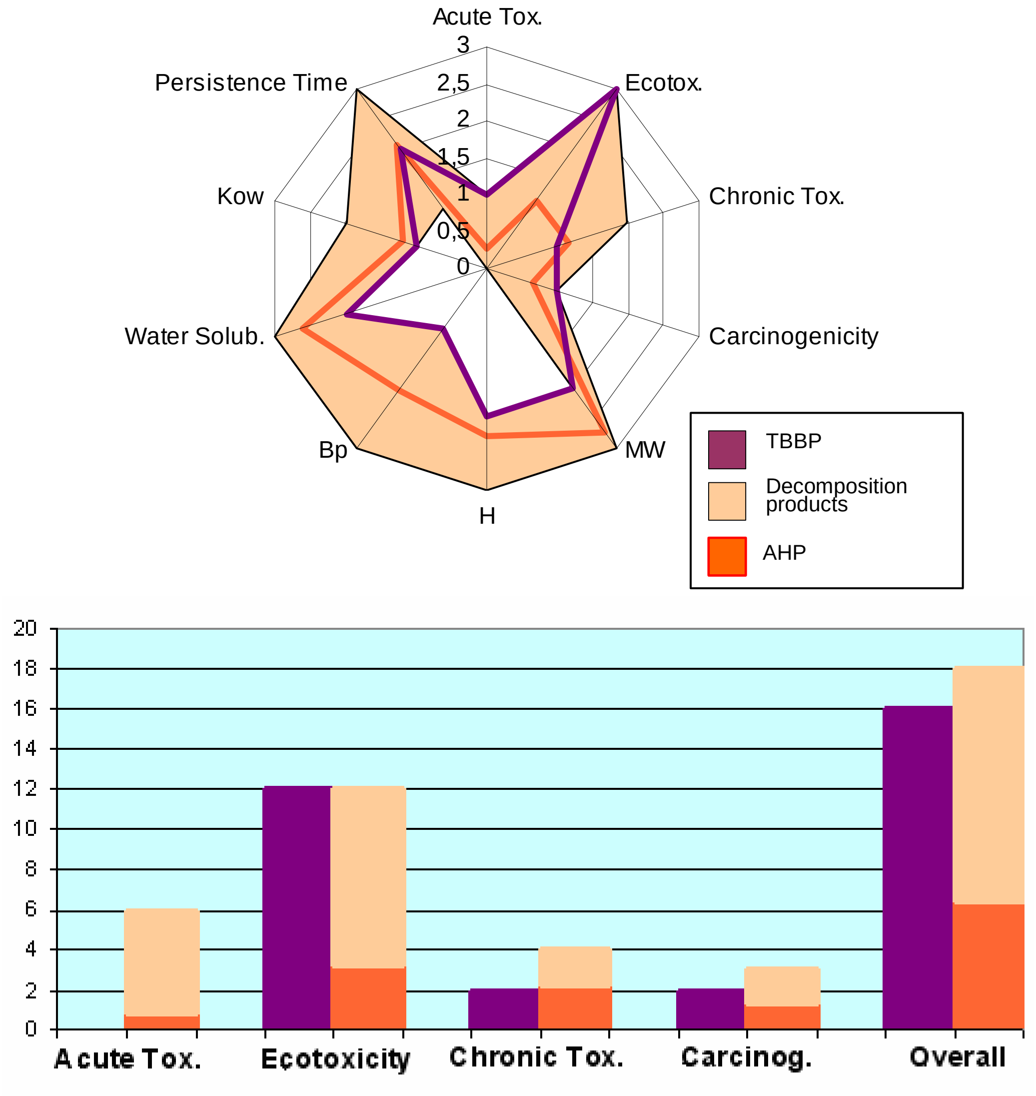


Figure 2.2.1: Example of hazard footprint: thermal decomposition of tert-butylperoxybenzoate (TBPB), (raw data from *CCPS, [1995]*)

2.3 – Proposed Method for the Inherent Safety Assessment of a Process

2.3.1 –Overview of the method

In the present chapter, a specific effort is made to develop an innovative method for quantitative inherent safety assessment in early process design. A few key performance indicators (KPIs) for inherent safety are defined and a procedure for their quantitative assessment is developed. These KPIs are particularly suitable for the use within the sustainability assessment introduced in §1.2.

In order to overcome the dependence of the scores on the experience and on expert judgement typical of other methods (see §2.1.2), the proposed procedure is strongly based on consequence assessment of potential accidents. A specific equipment classification and the related failure modes are identified, in order to define the potential accidental scenarios associated to each process unit. Rules for the calculation, by physical model runs, of reference

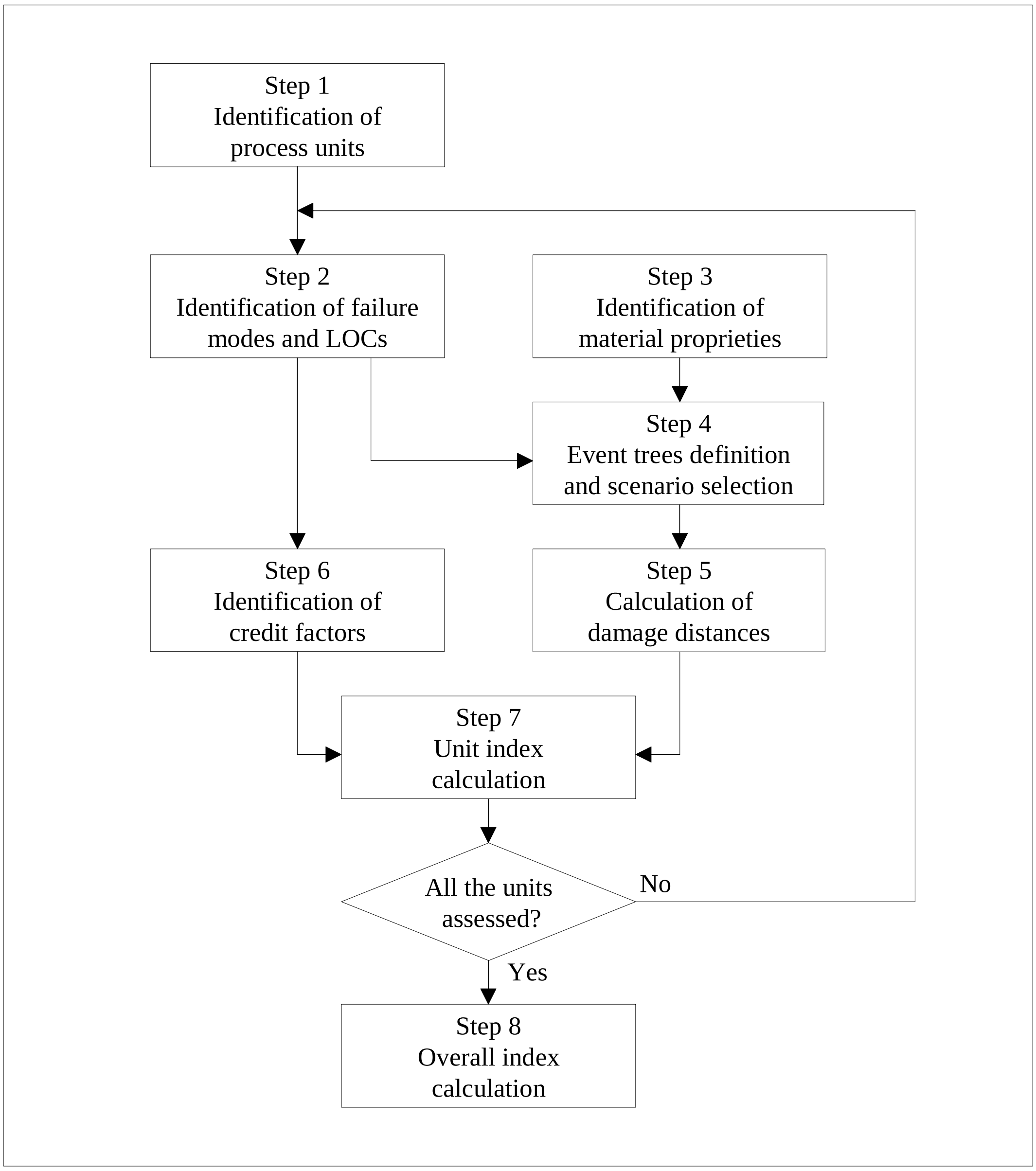


Figure 2.3.1: Flow diagram of the method.

damage distances are also defined. Credit factors to account for the safety score of the different equipment classes are introduced. The methodology is applied to a case study in order to demonstrate its suitability for the identification of safety critical units and for the assessment of the inherent safety of alternative processes.

The aim of the method is to compare the inherent safety of alternative process schemes by the calculation of quantitative hazard and risk indexes for single units and for the overall process. This is a purpose absolutely similar to the one of the sustainability assessment procedure (§1.2). Clearly enough, the inherent safety assessment for processes can be used both for providing societal indicators in sustainability assessment and for the category-specific assessment of the only inherent safety of process options.

The conceptual flow diagram of the inherent safety assessment method is reported in Figure 2.3.1. As most of the methods requiring the assessment of safety indexes, the procedure starts from the identification of the equipment units of each process, based on a specific equipment classification. KPIs are then calculated for each unit, based on the consequence analysis of credible scenarios. The single unit indexes may be further added in order to provide an overall hazard index.

The estimation of the KPIs of the single units is directly based on the assessment of the expected consequences of credible scenarios, whose straightforward calculation is presently possible with the aid of commercial software codes for consequence analysis. The use of a procedure based on consequence assessment contributes to limit the problems of built-in judgement on the relative importance of some parameters, that resulted a critical point in the application of score-based indexes (e.g. PIIS and ISI *[Gentile et al., 2003; Gupta & Edwards, 2003]*). Moreover, the rigid and sometimes unclear assessment structure of some index methods may lead to difficulties in their application. In particular, some indexes were designed only for specific process applications *[Khan et al., 2003; Koller et al., 2000]*, and their evaluation in other types of processes is not straightforward. In the methodology proposed, the approach introduced and the use of consequence analysis allow a more general application of the procedure.

The input data required for the application of the method to the process options of concern are preliminary data on process equipment and the data contained in a simplified process flow diagram (PFD):

- substances and operating conditions (pressure, temperature, phase) in each unit of the process;
- material flows in process lines;
- general technical specifications of the equipment units;
- a preliminary estimation of substance inventories in each process unit.

Thus they represent a subset of the data required for sustainability assessment of processes (§1.2.2).

2.3.2 – Identification of process units

As shown in Figure 2.3.1, the starting point for the application of the procedure is the identification of relevant equipment units to which the method should be applied. The units identified at this stage represent the basic elements of the assessment. Equipment units to be considered were sorted by a specifically defined classification, that was based on the geometrical structure of the units. Table 2.3.1 reports the main general unit categories defined for process equipment. For each unit category, sub-categories featuring the specific characteristics of the units related to their function/operative condition were also defined. Specific codes are given to each sub-category.

General Categories	*Sub-categories*	*Code*
Vessel-like equipment	Atmospheric vessel (storage, process, etc.)	EQ1.1
	Pressurized vessel (storage, column, reactor, etc.)	EQ1.2
	Mobile vessel (tank wagon, road tanker)	EQ1.3
Tube bundle equipment	S&T heat exchanger, reactor, etc.	EQ2.1
Plate and frame equipment	Filter, plate heat exchanger, etc.	EQ3.1
Pipe	Pipeline, manifold, etc.	EQ4.1
Pumping equipment	Pump (centrifuge, alternative, etc.)	EQ5.1
	Compressor (centrifuge, alternative, etc.)	EQ5.2
Warehouse	Packed materials (bags, barrels, etc.)	EQ6.1
	Spare materials (piles, etc.)	EQ6.2
Special equipment	Solid handling (conveyors, crushers, etc.)	EQ7.1
	Other	EQ7.2

Table 2.3.1: Main general categories proposed for the classification of process units.

2.3.3 - Definition of the failure modes and of the events leading to the loss of containment

The following step of the method consists in the identification of reference failure modes which lead to a loss of containment (LOC). Reference LOCs were associated to the more common classes of pieces of equipment, following the classification reported in Table 2.3.1, on the basis of approaches suggested in the technical literature *[Delvosalle et al., 2006; Lees, 1996; Uijt de Haag & Ale, 1999]*. Table 2.3.2 reports an example of the LOC events associated to different equipment categories on the basis of the approach suggested by the TNO "purple book" *[Uijt de Haag & Ale, 1999]*. When non-standard equipment needs to be considered in the analysis, Failure Mode and Effect Analysis (FMEA) may be applied to identify the credible events leading to loss of containment.

Several LOC events are possible for each piece of equipment. "*Credit factors*" may be determined in order to assess the credibility of the LOCs identified. In the present approach, the likelihood of the reference LOCs was estimated from statistical data. Reference failure frequency data may be easily used to evaluate the hazard linked to each class of equipment *[Heikkilä, 1999]*, and to represent the susceptibility to particular failure modes of the equipment class. Equipment frequency failure data are reported in several publications (e.g. *API, [2000]; Delvosalle et al., [2006]; MVG, [2004]; OREDA, [2002]; Uijt de Haag & Ale, [1999]*). The reference frequencies reported for a given equipment failure mode by the purple book *[Uijt de Haag & Ale, 1999]* or, if not available, by API publications *[API, 2000]* were used in the present approach as "credit factors" for standard technologies. Specific failure frequency data, e.g. derived from available statistical data or from conventional fault-tree analysis *[Delvosalle et al., 2006]*, were introduced to account for the credit factors derived from the adoption of technologies with higher safety standards. This approach allows the estimation of "standard" credit vectors for each reference class of equipment. The elements of the credit vector are the above defined credit factors for each LOC considered for the unit. Table 2.3.2 gives an example of credit vectors defined for some common pieces of equipment. Clearly enough, the standard credit vectors reported in Table 2.3.2 may be modified to account for improved safety standards of specific pieces of equipment.

LOC	*Horizontal gas storage (EQ1.2)*	*Floating roof tank (EQ1.1)*	*Centrifugal pump (EQ5.1)*	*Centrifugal compressor (EQ5.2)*	*Shell and tube heat exchanger (EQ2.1)*
R1: small leak, continuous release from a 10 mm equivalent diameter hole	$1x10^{-5}$	$1x10^{-4}$	*n.a.*	*n.a.*	$1x10^{-3}$
R2: catastrophic rupture, release of the entire inventory in 600 s	$5x10^{-7}$	$5x10^{-6}$	*n.a.*	*n.a.*	$5x10^{-5}$
R3: catastrophic rupture, instantaneous release of the entire inventory and release from the full-bore feed pipe	$5x10^{-7}$	$5x10^{-6}$	*n.a.*	*n.a.*	$5x10^{-5}$
R4: pipe leak, continuous release from a hole having 10% of pipe diameter	*n.c.*	*n.c.*	$5x10^{-4}$	$1x10^{-3}$	*n.c.*
R5: pipe rupture, continuous release from the full-bore pipe	*n.c.*	*n.c.*	$1x10^{-4}$	$1x10^{-4}$	*n.c.*

Table 2.3.2: LOCs and related "credit factors" for different categories of process equipment (data for credit factors derived from the literature *[API, 2000; Uijt de Haag & Ale, 1999]*). *n.a.*: not applicable; *n.c.*: not considered.

	FB	JF	VE	FF	TD	PF	BV
Continuous releases							
Gas or vapor		✓	✓	✓	✓		
Pressurized liquefied gas		✓	✓	✓	✓		
Cryogenic / Boiling liquid			✓	✓	✓	✓	
Non-boiling liquid					✓	✓	
Instantaneous releases							
Gas or vapor			✓	✓	✓		
Pressurized liquefied gas	✓		✓	✓	✓		✓
Boiling liquid			✓	✓	✓	✓	
Cryogenic liquid	✓		✓	✓	✓		
Non-boiling liquid					✓	✓	

Table 2.3.3: Summary of conventional scenarios considered by the reference set of event trees for the more common LOC events involving flammable or toxic fluids, listed as a function of release conditions. Fireball (FB), jet fire (JF), vapor cloud explosion (VE), flash fire (FF), toxic dispersion (TD), pool fire (PF), BLEVE (BV).

2.3.4 - Event tree definition and scenario selection

As discussed above, the present methodology is based on the calculation of equipment hazard indexes derived from the consequences of the accidental scenarios that may be associated to each unit. Thus, a necessary step in the application of the procedure is the identification of the accidental scenarios that may be associated with each unit. A set of reference event trees, derived from conventional approaches proposed in the technical literature *[Delvosalle et al., 2006; Lees, 1996; Uijt de Haag & Ale, 1999]*, were defined to identify the expected incidental scenarios associated with each LOC. An example of standard reference event tree is reported in Figure 2.3.2. The selection of the proper event tree follows the criteria used in conventional risk analysis, that are based on the characteristics of the LOC event, and on the hazard, the physical state, the physical properties, the temperature and pressure of the stream released. Further details on the criteria for event tree definition and selection are reported in the literature *[CCPS, 2000; Lees, 1996]*. Table 2.3.3 summarizes the scenarios associated with the different release categories considered for flammable/toxic substances.

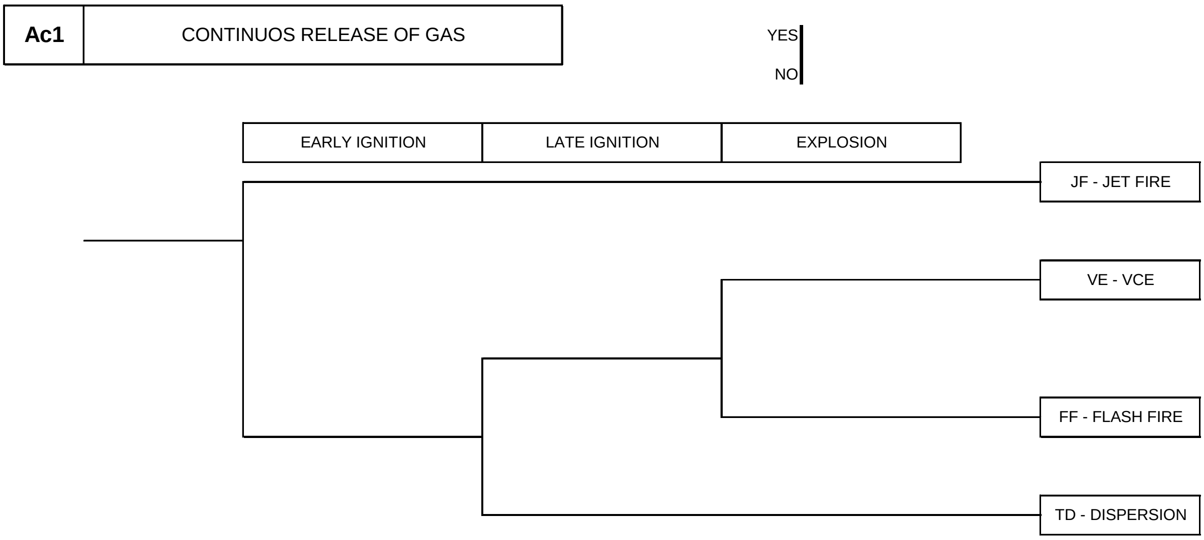


Figure 2.3.2: Example of reference event tree for the continuous release of a flammable gas.

2.3.5 - Calculation of damage distances

The calculation of the equipment hazard indexes requires the estimation of a parameter representing the severity of each scenario that may be triggered by the identified LOC events. Different types of physical effects (thermal radiation, overpressure or toxic concentration), are taken into account and compared in the analysis. Thus, in order to obtain a homogeneous severity parameter of each scenario, the damage distances corresponding to a given effect threshold were calculated. The effects on humans were taken into consideration to define threshold values for each physical effect. Table 2.3.4 shows an example of homogenous-effect threshold values, that are suggested in technical documents as representing the 1% mortality level of exposed population *[Christou et al., 1999; Lees, FP.; 1996; Planas et al., 2006; TNO, 1992]*. Damage distances are thus defined as the maximum distance where at a fixed height (1m in the present study) the physical effect of the scenario (thermal radiation, overpressure or concentration) reaches the threshold value. Damage distances may thus be calculated for each scenario using consequence analysis models, on the basis of the LOC characterization performed in the previous steps. Several models and commercial software tools are available in the literature for consequence analysis, and may be used for the purpose. The only limitation is that the same model should be used in the comparative assessment of different LOC events to obtain coherent results and to avoid at least the possible “bias” in the comparison derived from model differences. In the case study discussed in the following, the set of consequence analysis models reported by the TNO “yellow book” *[Van Den Bosh & Weterings, 1997]* were used.

Physical effect	*Threshold Value*
Flash Fire	½ LFL
Fireball	7 kW/m^2
Jet Fire	7 kW/m^2
Pool Fire	7 kW/m^2
Vapor cloud explosion	14 kPa
Physical/mechanical explosion	14 kPa
BLEVE	14 kPa
Toxic exposure	IDLH

Table 2.3.4: Threshold values assumed for damage distance evaluation (LFL: lower flammability limit; IDLH: toxic concentration immediately dangerous to life and health).

Thus, for each unit it is possible to calculate an impact matrix, having a number of rows equal to all the credible LOC events and a number of columns equal to the maximum number of accidental scenarios related to each LOC event. Each element of the impact matrix for the k-th unit, $m_{i,j,k}$, is related to the expected damage distance calculated for the j-th scenario of the i-th LOC event by the following expression:

$$m_{i,j,k} = \max\ (\ d_{i,j,k}\ ,\ c\ ) \tag{2.3.1}$$

where $d_{i,j,k}$ is the calculated damage distance and c is a constant. The use of the constant c in Equation (2.3.1) allows the definition of a “near field” zone, in which the consequences of the event are neglected. This takes into account the unreliability of conventional consequence assessment models in describing correctly the consequences of the events in the “near field”, thus avoiding biases in the analysis due to these uncertainties.

Starting from the impact matrix, a unit hazard vector h may be defined, whose elements are the maximum damage distances calculated for each LOC event considered in the analysis:

$$h_{i,k} = \max_j (m_{i,j,k}) \tag{2.3.2}$$

where $h_{i,k}$ is the maximum damage distance of the i-th LOC event considered for k-th unit.

2.3.6 - Calculation of hazard indexes

The Key Performance Indicators (KPIs) are obtained starting from the hazard and credit vectors calculated for each unit. A *unit potential hazard index* may be defined as follows:

$$UPI_k = \max_i (h_{i,k})^2 \tag{2.3.3}$$

where UPI_k is the unit potential hazard index of the k-th unit and $h_{i,k}$ is the corresponding hazard vector. The unit hazard index is thus representative of the maximum impact area that may derive from the worst case scenario considered for the unit.

Credit factors may be introduced in the analysis in order to take into account the safety scores of the equipment, and to consider differences in inherent safety performance deriving from equipment technology:

$$UHI_k = \sum_{i=1}^{n_k} cf_{i,k} \cdot h_{i,k}^2 \tag{2.3.4}$$

where UHI_k is the *unit inherent hazard index* of the k-th unit, n_k is the number of LOC events considered for the k-th unit, $cf_{i,k}$ and $h_{i,k}$ are respectively the credit factor and the maximum damage distance calculated for the i-th LOC event. The value of the index is higher for units having higher potential hazards or a higher record of LOC events.

The *overall indexes* of a group of N units (e.g. the entire plant) are calculated as follows starting from the unit indexes:

$$PI = \sum_{k=1}^{N} UPI_k \tag{2.3.5}$$

and:

$$HI = \sum_{k=1}^{N} UHI_k \tag{2.3.6}$$

Thus, the methodology developed allows the calculation of indexes representing the inherent safety performance of the plant, based either on a direct assessment of potential worst-case scenarios (*PI*) or of likely safety performance and release scenarios of process units (*HI*). Both indexes represent a quantification of the inherent safety of a process, having lower values as the inherent safety of the process is increased.

2.3.7 – Notes on the main features of the method

The proposed method for inherent safety assessment presents several advantages, compared to existing literature approaches. The case studies will help to underline these features (see §4).

- The method is based on the consequence assessment of reference accidental scenarios, taking advantage of the progress in the availability of user-friendly commercial software, that significantly reduced the time requirements for consequence analysis. The use of consequence modelling of reference accidental scenarios and of credit factors derived from statistical data limit the requirements for built-in expert judgement and for the introduction of subjective elements within the analysis. The final result is expected to be a more realistic and sound representation of the inherent safety performance.

- Through the use of credit factors, the method considers the inherent safety performance of the single pieces of equipment (i.e. the credibility of the LOCs). This feature is not present in most of the other methods in the literature.
- The method is extremely flexible allowing the application of the more appropriate model for the analysis of each specific scenario. As a consequence, built-in assumptions and generalizations typical of other tools are avoided, yielding a more specific assessment of the expected accident severity. On the other hand, the method has no limitations in considering specific and non-standard pieces of equipment, since LOCs and credit factors may be determined by the application of well-known specific methods (e.g. FMEA). This possibility is not present in most of literature tools, due to built-in assumptions that may not be easily modified by the user.
- The method yields quantitative indexes that allow an easy interpretation and communication of the results. Transparent rules are defined for the combination of the KPIs of the single units to give overall indexes for the process. Moreover, the results are obtained on a fixed scale. Therefore, it is possible to compare the inherent safety indexes obtained even for very different units or processes. This is an important feature in order to address the absolute ranking of the inherent hazard, and the requirements for add-on safety devices or other risk control and risk management measures.

2.4 – Proposed Method for the Inherent Safety of Layout

2.4.1 – Overview of the problem

In this chapter the implementation of inherent safety in the design of plant layout plots is discussed and specific decision support tools for layout design are proposed.

The plant layout plays an important role in defining the safety of a facility. The spatial arrangement of process units influences the ability of an accidental event to propagate from one unit to another (domino effect), resulting in escalation of the magnitude of the accident consequences *[Cozzani et al., 2005,2007; Khan & Abbasi, 1999]*. As well, the position of populated targets (e.g. buildings) with respect to possible sources of hazard is of major concern due to the possibility of exposure and fatalities. Moreover, layout design affects the accessibility of the different areas in a plant, which is a critical element for both accident risk (e.g. easy, regular operations and maintenance) and accident management (e.g. fire-fighting operations and evacuation).

Plant layout design involves several different issues that have to be considered at the same time: constraints on process requirements, cost, safety, services and utilities availability, plant construction, regulations, etc. Layout design is usually performed in successive steps of increasing detail. Design strategies and computer aided-tools have been developed to assist in the various steps (see, for example, *[Mecklenburgh, 1985; Lees, 1996]* and the references cited therein). Current research worldwide on design analysis tools is focused primarily on optimization of the economic aspects of the facility plot (see, for example, *Barbosa-Pòvoa et al., [2002]; Deb & Bhattacharyya, [2005]; Georgiadis et al., [1999]; Papageorgiou & Rotstein, [1998]*). From the safety point of view, early layout design is mainly based on industrial practice and simple guidelines or empirical rules. Tables of conventional segregation distances for various equipment units are traditionally used in this framework *[Mecklenburgh, 1985; Lees, 1996]*. Some attempts to include safety aspects in layout optimization have been made *[Nolan & Bradley, 1987 Penteado & Ciric, 1996 Patsiatzis, D.I.; Knight, G.; Papageorgiou, L.G.; 2004]*; these are aimed mainly at economic optimization of layout design, including the assessment of safety aspects (e.g. cost of safety devices and of losses). A more detailed safety analysis, involving evaluation of possible accidental scenarios and consequence analysis, is generally confined to the final stages of the design lifecycle when the risk performance of the whole plant is verified. There are, however, limited margins for layout improvement left at this final stage. Hence, there exists a need for an engineering tool that is applicable in the early stages of each step of the process design lifecycle.

Inherent safety can be effectively implemented in the layout structure beginning with the early stages of layout design. However no comprehensive inherent safety assessment tool specifically addressing the assessment of early layout design is currently available: the analysis of the literature reported in §2.1.2 evidences that the attention in developing tools was manly focused on the phases of chemical route selection and conceptual process design.

This chapter is divided in two main sections: in the first is specifically aimed at the analysis of domino hazard, including the discussion of the possible design actions to limit the escalation potential and the proposed methods for the quantitative assessment of this hazard during design activities; the second deals with the overall problem of inherent safety in layout and with the method developed for the safety assessment in the design of layout plans.

2.4.2 – Domino Hazard reduction in layout design

2.4.2.1 – The domino hazard and the risk reduction strategies: introducing an inherent approach

A *domino accident* (also known in the literature as escalation or *knock-on event*) may be defined as an accident in which a primary event propagates to nearby equipment, triggering one or more secondary events. Four elements characterize this phenomenon:

- a *primary accidental scenario*, which triggers the domino event;
- the propagation effect following the primary event, due to the physical effects (*escalation vectors*) caused by the primary event on secondary targets;
- one or more *secondary accidental scenarios*, involving the same or different plant units
- an *"escalation" effect*, that is an increase of the overall severity of the domino event with respect to that of the primary accidental scenario

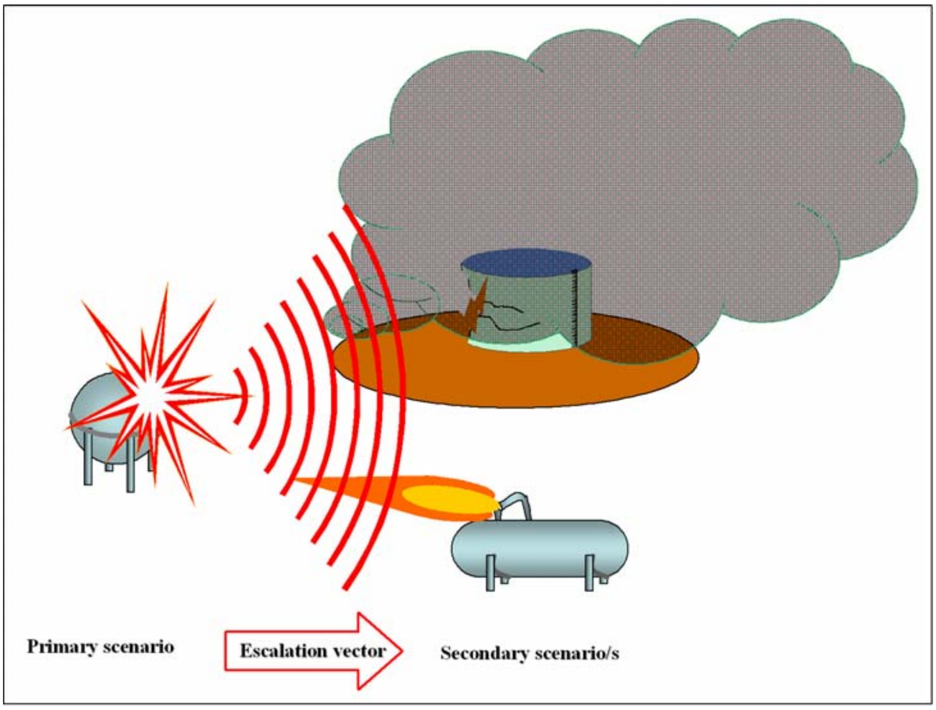


Figure 2.4.1: The domino escalation accident.

Escalation sequences for atmospheric and pressurised equipment are only possible when highly energetic primary scenarios occur. Table 2.4.1 shows the primary scenarios that are likely to trigger escalation effects, and the escalation vectors identified for each scenario. The list of primary scenarios included in Table 2.4.1 derived for the analysis of more than 100 domino case-histories performed in a previous study *[Cozzani et al., 2006],* and was extended to comprehend all the categories of accidental scenarios that were responsible of at least an escalation event. Definition, modelling details and physics of the scenarios listed in Table 2.4.1 are widely described elsewhere *[Baker et al., 1983; CCPS, 1994; Lees, 1996]*. Table 2.4.1 reports also the physical effects responsible of escalation identified for each scenario, which may be defined as the escalation vectors of the scenario.

Primary scenario	Escalation vector
Fireball	Heat radiation
Jet fire	Heat radiation
Pool fire	Heat radiation
Vapour cloud explosion (VCE)	Overpressure
BLEVE	Overpressure Fragment projection
Mechanical Explosion	Overpressure Fragment projection

Table 2.4.1: Escalation vectors for the primary scenarios identified as potential initiator of domino escalations.

Accidents in which a domino effect takes place are among the more severe events that may affect industrial processes and storage sites. Hence, strong efforts should be addressed by the safety management to the prevention of domino accidental scenarios, which is currently mainly pursued by active and passive safety strategies.

The passive safety approach to domino limitation consists in the proper design of physical barriers and protection systems (e.g. thermal insulation of process equipment) whose effect, when needed, is available without any external intervention. This strategy is widely used for the reduction of accident consequence, although the cost of passive protection systems may be relevant *[Hendershot, 1997]*. Active strategies to prevent escalation events are usually considered less reliable in the hierarchy of safety but, at least for some primary scenarios as pool or jet fires, these approaches may be effective (e.g. sprinklers protecting pressurized storages), and are often compulsory in the national legislation of several countries as well as in international design standards.

Although the two approaches cited above are of great relevance, it is of fundamental importance to explore the possibility of an inherent safety approach to the prevention of domino accidental events.
An inherent approach to domino prevention may be easily applied in early plant design, taking into account the possibility of domino events during lay-out definition. In this case, escalation events may be avoided simply by introducing appropriate safety distances between the more hazardous process units (those having large inventories of flammable or toxic substances) and other process installations. However, distances between process units are usually defined on the basis of industrial practice and simple guidelines or rule of thumbs, without specific reference to the prevention of domino events *[Mecklenburgh, 1985]*.
Thus, the possibility of an inherent approach to escalation prevention, based on lay-out definition during early design, is seldom taken into account, and no well accepted procedure or guideline is available. Moreover, the possibility of an inherent approach to escalation prevention in existing plants, where lay-out modifications are usually not possible and only limited changes may be introduced, has never been explored.

The assessment of escalation requires, in the case of domino effect prevention, the analysis of the possible primary scenarios and of the possible domino targets, and thus may not be carried out in detail before the preliminary design of equipment. On the other hand, at this stage, limited changes may be introduced in the process, although the lay-out definition still leaves some degrees of freedom. Even less modifications are possible on existing plants. The feasibility of inherent safety actions addressed to the prevention of domino effect and classified by the inherent safety guidewords should thus be carefully evaluated.

The guide word *intensification* is mainly referred to the reduction of the inventory in single equipment items or of the number of equipment items. Since the inventory involved is often a significant parameter in determining the escalation of a primary scenario (e.g. for BLEVEs or VCEs), the minimization of quantities stored or processed is an effective measure for the reduction of hazard, though the revision of equipment design is needed. Also actions related to *moderation* would lead to important reduction in escalation possibilities. The use of less hazardous conditions, as the shift to safer storage technologies (as, in general, the use of cryogenic instead of pressurized storages), is effective in reducing on one hand the hazard of the primary event, on the other the vulnerability of equipment to escalation as well as the severity of the possible secondary scenarios.

However, also in this case the revision of equipment design and mainly of storage strategies is required. Thus, actions falling under the *intensification* and *moderation* guidewords, when introduced specifically for escalation prevention issues, may be considered mainly for equipment items having relevant inventories, as storage tanks (e.g. reducing storage capacity or changing storage conditions). Their applications will actually lead to complex design modifications that are hardly acceptable in the final stages of plant design. Similarly, *substitution* of substances with others having less hazardous proprieties, and *simplification* of processes, although effective in reducing the possibilities of escalation, would require relevant modification in process design, that are scarcely applicable in the stage of lay-out definition during plant design or in existing plants. Indeed, the actions identified by these guidewords require, in general, important process modifications or changes in plant design, usually not affordable in the stage of lay-out definition during plant design or in existing plants. Thus, actions related to the *moderation, intensification, substitution* and *simplification* guidewords are usually hardly applicable to the prevention of escalation, and should be considered in other steps of process development.

Limitation of effects is sometimes considered as a "minor" guideword, as it accepts that a negative effect will somehow take place. However, in the perspective of escalation, this guideword should assure that no secondary event will be caused by domino effects, thus pursuing the prevention of domino accidents by an effectively inherent approach.

It may be concluded that the application of an inherent safety approach to the prevention of escalation events will mainly lead to identify actions that fall under the *limitation of effects* guideword, specific to the prevention of damage and of escalation.

2.4.2.2 – KPI for domino hazard assessment: proposed method based on models for consequence analysis

As previously reported in several points of this work, the implementation of inherent safety strategies in layout design requires quantitative key performance indicators to support design activity. Several methods were proposed for the assessment and the comparison of inherent safety of alternative processes, as showed in §2.1. However, most of these methods do not include the assessment of possible domino events. Moreover, none of the literature methods for inherent safety assessment includes consequence-based criteria to consider the actual hazard posed by escalation *[Khan et al., 2003]*.

In the following, such an approach, based on the modeling of expected consequence, will be presented. The method conceptually mirrors the approach proposed in chapter §2.3 for the analysis of inherent safety of processes. The flow diagram of the method is shown in Figure 2.4.2. The typical inputs required by the method are:

1) Definition of substances and operative conditions in each unit of the process
2) Quantification of flows in process lines and piping
3) General technical specifications of the equipment units
4) Evaluation of inventories in the equipment units of each process alternative

As shown in Figure 2.4.2, the first step of the methodology is the identification of process units to be considered in each alternative scheme, which are classified on the basis of their structural and geometrical features. Different failure modes related to loss of containment (LOC) are thus associated to each unit on the basis of literature data analysis *[API, 2000; Uijt de Haag & Ale, 1999]* (step 2). A simplified Failure Mode and Effect Analysis (FMEA) is used to obtain data for non-standard equipment *[Tugnoli et al., 2007]*.

In steps from 3 to 5 of the procedure, the consequence analysis of each possible scenario following the LOC is performed. Standard event trees are used to identify the scenarios, while loss intensities and consequences are calculated by conventional literature models *[Lees, 1996; Van Den Bosh & Weterings, 1997]*. The threshold values for damage to equipment units (*escalation thresholds*) are derived from previous studies *[Cozzani et al., 2006, 2007]*. These data are used to calculate the conventional *escalation distances* for each LOC and scenario. The escalation vector (i.e. array of the escalation distances for the possible scenarios) is used in the following step to provide specific Key Performance Indicators (KPIs) (step 7). Some KPIs require a credibility factor to be assessed for each LOC, on the basis of the expected release and failure frequency data reported for standard technologies in several publications *[Delvosalle et al., 2006; Uijt de Haag & Ale, 1999]* (step 6).

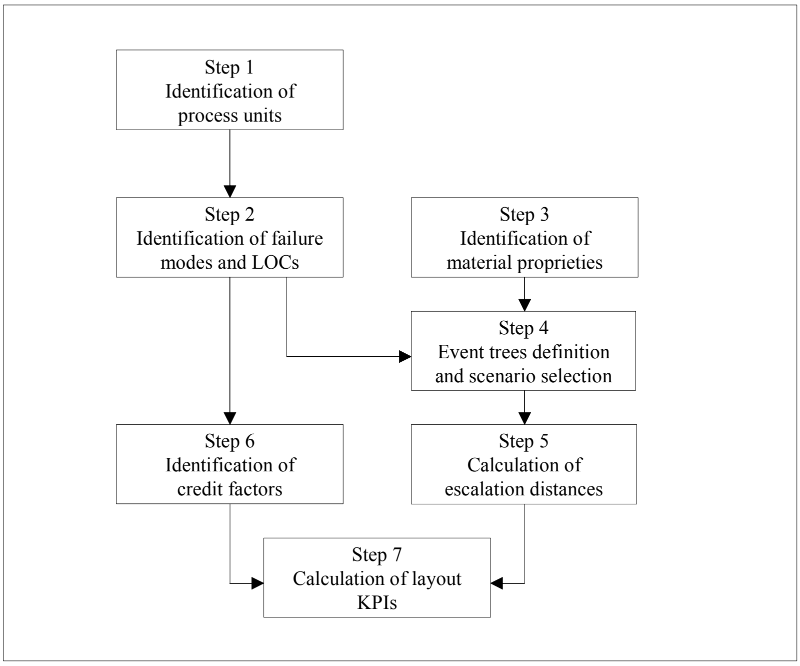


Figure 2.4.2: Flow diagram of the method used for the calculation of the inherent safety key performance indicators.

The key step of the method is the definition of a physical parameter quantifying the *intensity of* each *escalation vector*. This parameter is identified as the *escalation distance*, that is the maximum distance form the primary unit at which escalation effects may be considered credible. Escalation distance coincides, as well, with the *inherent safety distance*, since no escalation event is expected for target units located at distances larger than this one. The escalation distance (i.e. intensity of escalation vector) for each possible escalation scenario triggered by a given primary unit, depends on the total amount of energy (or substance) which is possibly released from the primary system of containment (reactor, storage tank, etc.). Table 2.4.2 reports the definition of the escalation distance for each primary scenario likely to result in escalation.

Further details about the definition of the intensities of the escalation vectors (escalation distances) and about the possible inherent strategies to reduce domino hazard can be found in Appendix 2.2.

Primary scenario	**Escalation vector**	**Escalation distance**	**Equipment category**	**Safety criterion**
Fireball	Heat radiation	Fireball Radius	atmospheric	Fireball radius
			pressurized	0
Jet fire	Heat radiation	Distance at which heat radiation equals threshold value	atmospheric	Flame length + 50m
			pressurized	Flame length + 25m
Pool fire	Heat radiation	Distance at which heat radiation equals threshold value	atmospheric	Pool border + 50m
			pressurized	Pool border + 15m
Vapour cloud explosion (VCE)	Overpressure ($F \geq 5$; $M_f \geq 0.35$)	Distance at which peak pressure equals threshold value	atmospheric	$\underline{R} = 1.75$
			pressurized	$\underline{R} = 2.10$
BLEVE	Overpressure	Distance at which peak pressure equals threshold value	atmospheric	$\underline{R} = 1.80$
			pressurized	$\underline{R} = 2.00$
	Fragment projection	Maximum projection distance	Any	undefined
Mechanical Explosion	Overpressure	Distance at which peak pressure equals threshold value	atmospheric	$\underline{R} = 1.80$
			pressurized	$\underline{R} = 2.00$
	Fragment projection	Maximum projection distance	Any	undefined

Note: $\underline{R}$, is the Sachs energy-scaled distance ($\underline{R} = r\cdot(E/P°)^{1/3}$, where r is the effective distance, P° is the ambient pressure and E is explosion energy calculated by means of the total combustion heat of the flammable cloud), F is the strength factor as in the Multi-Energy Method [Van den Berg, 1985] and M_f is the flame Mach number in the Baker-Sthrelow-Tang methodology [Tang & Baker, 1999].

Table 2.4.2: Escalation vectors and definition of escalation distances for domino propagation.

The escalation distance is determined on the basis of the threshold values for escalation (step 5). Table 2.4.3 reports escalation threshold values identified for various types of target equipment *[Cozzani et al., 2005, 2006; Cozzani & Salzano, 2004; Salzano & Cozzani, 2004, 2006]*. A generalized value of escalation distance, independent from the target unit can be obtained conservatively assuming thresholds for the more vulnerable categories of process equipment (i.e. the escalation criterion); these values are reported in Table 2.4.3 (i.e. the escalation criterion).

Appendix 2.2 also reports a simplified approach, based on generalized graphs, for a quick estimation of the escalation distances in early screening. An example is reported in Figure 2.4.3, for jet fires of pressurized hydrocarbons. In more precise assessments, it is however suggested the use of suitable consequence modes for the calculation of escalation distances.

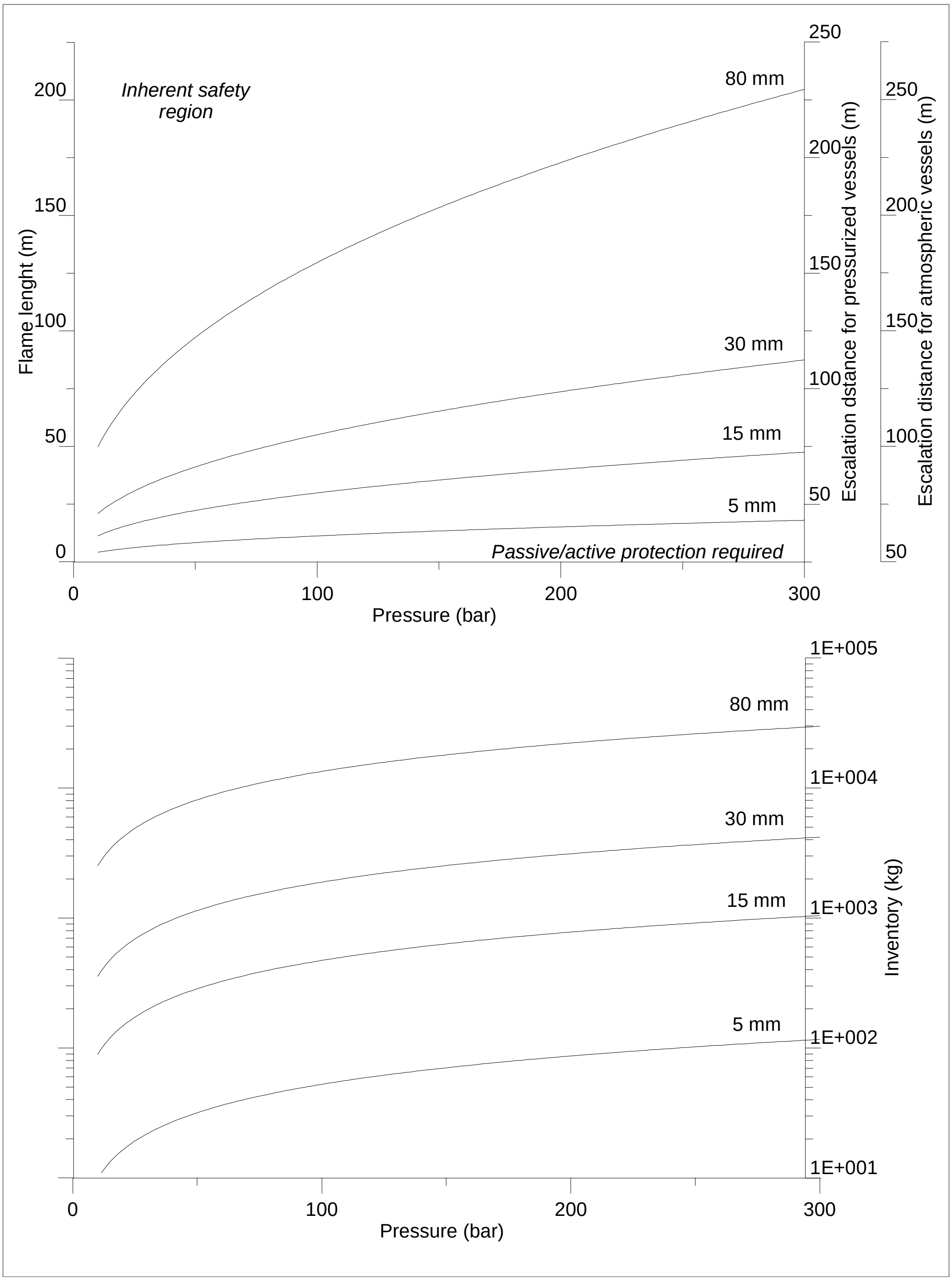


Figure 2.4.3: Example of generalized graph for evaluation of escalation distances: escalation distances (a) and critical primary vessel inventory (b) for different release diameters in the case of jet fires from hydrocarbon gases at ambient temperature. See Appendix 2.2 for further details.

Table 2.4.2 shows the safety distances identified for different categories of target equipment on the basis of the specific escalation thresholds listed in the Table 2.4.3, as derived by the quick generalized approach *[Cozzani et al., 2005, 2006, 2007]*. The safety distances and the threshold values reported in the table are specific to escalation assessment, thus they are derived also taking into account the severity of the secondary scenarios that are likely to follow the damage of the primary equipment *[Cozzani et al., 2006; Salzano & Cozzani, 2006]*. It is also important to evidence that Tables 2.4.2 and 2.4.3 report general conservative results that are not affected by substance-dependent parameters.

Primary scenario	Escalation vector	Equipment category	Threshold Value	Escalation criterion
Fireball	Heat radiation	atmospheric	15 kW/m^2	Engulfment
		pressurized	50 kW/m^2	
Jet fire	Heat radiation	atmospheric	15 kW/m^2	15 kW/m^2
		pressurized	50 kW/m^2	
Pool fire	Heat radiation	atmospheric	15 kW/m^2	15 kW/m^2
		pressurized	50 kW/m^2	
Vapour cloud explosion (VCE)	Overpressure ($F \geq 5$; $M_f \geq 0.35$)	atmospheric	22 kPa	16 kPa
		pressurized	16 kPa	
BLEVE	Overpressure	atmospheric	22 kPa	16 kPa
		pressurized	16 kPa	
	Fragment projection	Any	undefined	Fragment impact
Mechanical Explosion	Overpressure	atmospheric	22 kPa	16 kPa
		pressurized	16 kPa	
	Fragment projection	Any	undefined	Fragment impact

Table 2.4.3: Escalation threshold for the definition of escalation distance for different primary scenarios.

The above defined escalation distances may be used for a preliminary evaluation of the inherent domino hazard in a lay-out. Since several specific issues are of interest in the layout design an extensive set of key performance indicators may be defined for this purpose:

- a *Unit Potential Domino index*, UPD, that may be used for a preliminary ranking of the worst-case hazard of the primary units independently of the definition of a layout
- a *Unit Hazard Domino index*, UHD, that may be used for a preliminary ranking of the expected hazard of the primary units independently of the definition of a layout
- a *Domino Chain Actual hazard index*, DCA, that may be used to assess the hazard of a specific escalation between a primary and a secondary unit
- a *Unit Domino actual hazard Index*, UDI, that expresses the hazard due to escalation scenarios triggered by a given primary unit
- a *Target Domino actual hazard Index*, TDI, that expresses the hazard for a given target unit due to escalation scenarios triggered by other primary units

The *unit potential domino index*, UPD, was defined as the area potentially affected by worst-case escalation effects, estimated on the basis of the intensity of the escalation vector.

$$UPD_i = \left(\max_{h,j=1}^{p_i,t_i} \left(D_{IS\ h,i,j} \right) \right)^2 \qquad (2.4.1)$$

where UPD_i is the unit potential domino index for the i-th primary unit and $D_{IS\ h,i,j}$ the escalation distance (or inherent safety distance) for the h-th scenario with respect to a generic j-th target. In equation (2.4.1) the maximum inherent safety distance is selected among the p_i possible scenarios and the t_i possible typologies of generic targets which the i-th unit can potentially trigger. The index represents a leading indicator of the domino hazard potential of the unit generating the escalation vector. It allows a preliminary screening of domino hazard and the identification of critical potential sources of escalation events, independently on the actual lay-out configuration.

The *unit hazard domino index*, UHD was defined similarly to UPD; however in this case the credibility of the LOC is taken into account, similarly to the approach described in §2.3.6. The UPD index was defined as the sum of the squares of the maximum escalation distance calculated for each LOC multiplied by the respective credit factor:

$$UHD_i = \sum_{k=1}^{n_i} cf_{k,i} \cdot \left(\max_{h,j=1}^{p_i t_i} \left(D_{IS\ k,h,i,j} \right) \right)^2 \qquad (2.4.2)$$

where UHD_i is the unit hazard domino index for the i-th primary unit, $D_{IS\,k.h,i,j}$ is the escalation distance for the h-th scenario of the k-th LOC with respect to a generic j-th target and $cf_{k,i}$ the credit factor for the k-th LOC of the possible n_i LOC events considered the i-th unit.
The index represents a leading indicator of the domino hazard of the unit that accounts for the credibility of the loss and, thus, the inherent safety of the containing equipment. The index value is a reference independent on the actual lay-out configuration.

In order to evaluate the specific escalation hazard between two units in a given layout, the *domino chain actual hazard index*, DCA, was defined as the ratio of the inherent safety distance to the actual distance among the two units considered:

$$DCA_{h,i,j} = \frac{D_{IS\ h,i,j}}{D_{i,j}} \qquad (2.4.3)$$

where $DCA_{h,i,j}$ is the hazard index for the h-th primary scenario of the i-th unit, considered as a domino trigger towards the j-th unit.
The actual equipment distance ($D_{i,j}$) is available only if a layout plan, either in a preliminary form, is defined. If separation distances and plant lay-out are not available (e.g. in the early steps of plant design), conventional safety distances may be used to provide at least a preliminary estimation of the expected chain propagation hazard. As a matter of facts, these distances reflect the current practice in layout design and are those more likely are adopted in a standard layout design. Such distances are reported in several technical publications and standards *[Lees, 1996; Mecklenburg, 1973; and references cited therein]*.

The chain escalation index, DCA, concerns specific escalation scenarios and target units. In order to obtain a synthetic representation of the critical primary units with respect to domino hazards in a given lay-out, a *unit domino actual hazard index*, UDI, may be defined:

$$UDI_i = \sum_{j=1}^{u_i} \max_{h=1}^{m_i} \left(DCA_{h,i,j} \cdot \alpha_{h,i} \right) \qquad (2.4.4)$$

where u_i is the total number of units considered for possible escalation caused by the i-th unit, m_i is the total number of primary escalation scenarios of the i-th unit that may trigger escalation and $\alpha_{h,i}$ is an inventory parameter. The inventory parameter takes into account that the escalation hazard may depend on the inventory of the primary unit, in particular for escalations triggered by stationary radiation. As a matter of fact, in these scenarios a higher duration of the fire may be a consequence of a higher inventory in the primary unit. Thus, the inventory parameter, $\alpha_{h,i}$, was defined as follows:

$$\alpha_{h,i} = \begin{cases} DCF_{h,i} & if\ DCF_{h,i} < \eta \\ \eta & if\ DCF_{h,i} > \eta \\ 1 & if\ DCF_{h,i}\ not\ defined\ for\ h \end{cases} \tag{2.4.5}$$

where η is a parameter proportional to the maximum time of interest for the accidental scenario, that identifies the time for effective emergency actions to be enforced (a suggested value for η is 10, corresponding to a time of interest of 2.5h), and $DCF_{h,i}$, the domino inventory factor, is the ratio among unit inventory I_i and the critical inventory for the h-th escalation scenario $CI_{h,i}$:

$$DCF_{h,i} = \frac{I_i}{CI_{h,i}} \tag{2.4.6}$$

The target *domino actual hazard index*, TDI, was defined similarly to UDI but, in this case, the focus is on the hazard is on the target:

$$TDI_j = \sum_{i=1}^{q_j} \max_{h=1}^{m_i}\left(DCA_{h,i,j} \cdot \alpha_{h,i}\right) \tag{2.4.7}$$

where TDI_j is the target domino hazard index for j-th target unit, q_j is the total number of units considered for possible escalation scenarios having j-th unit as a target and the other parameters are defined as in Equations (2.4.6) to (2.4.7). The index is aimed at the definition of the actual risk for a target unit within the assessed layout. Clearly enough it may be calculated as well for external units, in order to assess the escalation hazard toward other facilities.

2.4.2.3 – Proposed scoring system for domino hazard: the Domino Hazard Index

In the following a scoring system for domino hazard, the *Domino Hazard Index* (DHI), assessment is presented. This indexing system is useful for a swift quantification of domino hazard to be used in the more general framework of the proposed layout safety assessment described in §2.4.3. In fact, that approach requires a single indexing parameter based on a scoring scale, in order to keep the method quick and simple.

The Domino Hazard Index (DHI) is specifically aimed at assessing the domino effect hazards caused by a unit in a specific layout. For each unit of the layout, the DHI considers the actual consequences of possible escalation scenarios and scores or ranks the accident propagation potential. The index is able to consider the effects of both inherent and passive measures on the domino escalation potential, as required by the framework of I2SI for layout assessment (§2.4.2). The specific use of the index as a reference within I2SI for layout assessment decides whether to account for the effects of passive measures in the DHI calculation.

Figure 2.4.4 illustrates the assessment procedure for the Domino Hazard Index. The starting point is the plant layout plan, from which the relative distances of the geometric centres of each possible pair of units are evaluated. The distances can be arranged for ease of use in a matrix form ($D_{i,k}$). In subsequent steps of the procedure, each single unit is analyzed, with the ultimate goal being to evaluate the DHI_i for a particular unit.

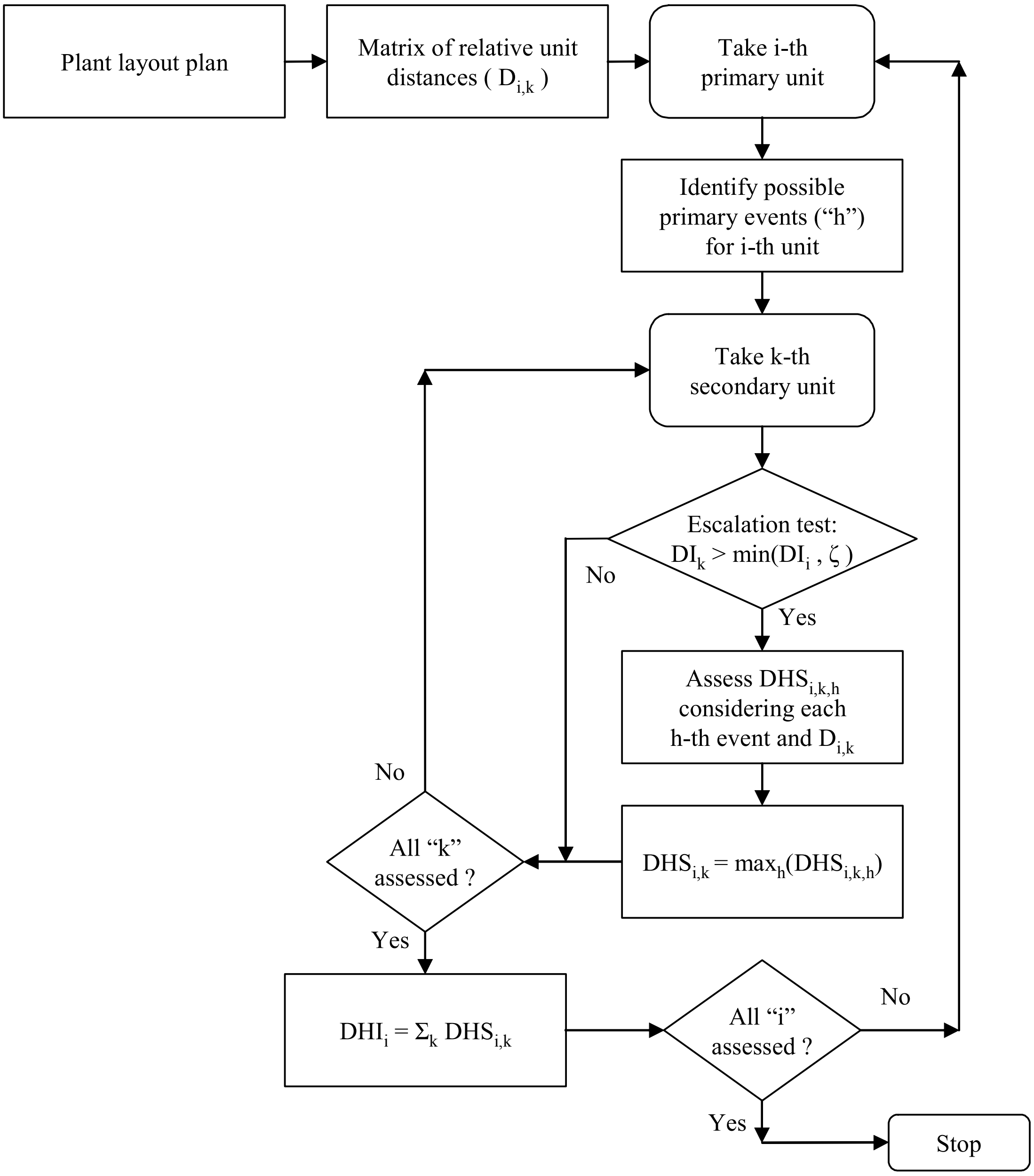


Figure 2.4.4 Conceptual flow diagram of DHI assessment.

The primary accidental events that may result in domino effects arising from the assessed unit (i-th unit) must be identified. These events, as previously outlined, depend on the chemical characteristics, inventory and operating conditions relevant to the primary unit. Methods for primary event identification are widely available in the literature (e.g. *[Delvosalle et al., 2006; Lees, 1996]*). Table 2.4.4 provides an overview of the possible primary events which can trigger domino effects. Table 2.4.5 classifies the accidental events according to the involved escalation vector (i.e. the physical phenomenon that causes the escalation from one unit to another).

	Material Classification		
	Flammable	*Explosive/reactive*	*Stable & non-flammable*
Physical State			
Liquid	Pool fire, Flash fire, VCE	Condensed phase/ confined explosion	-
Liquefied gas	Pool fire, Jet fire, VCE, Flash fire, Fireball, BLEVE, Physical explosion	Condensed phase/ confined explosion, Physical explosion, BLEVE	Physical explosion, BLEVE
Gas	Jet Fire, Flash fire, VCE, Physical explosion	Condensed phase/ confined explosion, Physical explosion	Physical explosion
Solid/dust/mist	Fire, Dust explosion, Confined explosion	Condensed phase/ confined explosion	-

Table 2.4.4: Possible primary events likely to give domino escalation as a function of material hazardous proprieties and operative conditions.

Escalation Vector	**Accidental Event**
Flame impingement/heat radiation	Pool fire, Jet fire, Flash fire, Fireball, VCE
Blast wave	Condensed phase explosion, Confined explosion, Physical explosion, BLEVE, VCE
Fragment projection	Condensed phase explosion, Confined explosion, Physical explosion, BLEVE

Table 2.4.5: Accidental events likely to give rise to domino escalation (classified according to the escalation vector involved) *[Cozzani et al., 2007]*.

Each possible pair of units ('i' being the assessed primary unit and 'k' the secondary unit) that can potentially result in a domino escalation scenario is analyzed. A selection criterion is defined in order to account only for the units that have significant potential for an increase in accidental adverse consequences, or that are considered highly hazardous 'per se'. The Damage Index (DI) of the original I2SI approach *[Khan & Amyotte, 2004]* is used as the hazard indicator for the units in this procedure (Equation (2.4.8)):

$$\begin{array}{lll} \text{If } DI_k > (\min(DI_i\,;\,\zeta\,)) & \text{then} & k\text{-th unit is assessed as a secondary unit} \qquad (2.4.8) \\ & \text{else} & k\text{-th unit is skipped (i.e. minor consequences)} \end{array}$$

where ζ is an arbitrary threshold value that defines the lower limit of DI for units considered highly hazardous 'per se'; in the section 3 case study, ζ is taken as having a value of 25.

For each identified primary accidental event (h-th event) of the assessed unit (i-th unit), a Domino Hazard Score ($DHS_{i,k,h}$) is evaluated for each of the secondary targets (k-th unit). $DHS_{i,k,h}$ is therefore a ranking that represents the score given to the hazard in terms of an escalation from unit 'i' to unit 'k' by event 'h'. The maximum value for DHS is 10, meaning that escalation is highly probable; the minimum value, 0, represents the inherently 'safest' level for domino escalation (i.e. elimination of the escalation hazard). The value of $DHS_{i,k,h}$

for each possible event is derived by comparison of the physical effect distances associated with that particular event to the actual distance between units on the layout plan. The rules for assigning $DHS_{i,k,h}$ values are summarized in Table 2.4.6 and are discussed in detail in Appendix 2.2.

Escalation Vector		Secondary Unit	Inherent DHS	Protective Device	Passive DHS
Flame impingement /radiation	*Flash fire, thermal effect VCE*	Free flammable vapors	10	-	
		Other cases	0		
	Fireball	Impinged atmospheric vessel	10	Fire insulation	5
		Other cases	0		
	Pool fire	Impinged equipment	10	Fire resistance wall Bund	1 + 1
		Thermal radiation as distant source	Fig. A2.2.9	Fire insulation	Fig. A2.2.9
	Jet fire	Impinged equipment	10	Fire resistance wall / mounding	1
		Thermal radiation as distant source	Fig. A2.2.10	Fire insulation	Fig. A2.2.10
Blast wave		Unprotected equipment	Fig. A2.2.11	Barricade	1
Fragment projection		Unprotected equipment	Fig. A2.2.12	Barricade	1

Table 2.4.6: Summary of rules for assignation of Domino Hazard Score (DHS) as a function of the escalation vector. Inherent DHS and passive DHS refer to the possibility of accounting for passive protection devices in DHS evaluation. The figures cited in the Table are reported in Appendix 2.2.

Once the $DHS_{i,k,h}$ values have been assessed, the worst possible scenario is selected as a reference among all the possible scenarios, yielding $DHS_{i,k}$ for every pair of considered units (Equation (2.4.9)):

$$DHS_{i,k} = \max_h (DHS_{i,k,h}) \tag{2.4.9}$$

where subscript h identifies the scenario.

The final index (DHI_i) for the i-th primary unit is the sum of the scores ($DHS_{i,k}$) for all possible secondary target units (Equation (2.4.10)):

$$DHI_i = \sum_k DHS_{i,k} \tag{2.4.10}$$

An upper limiting value of 100 is imposed on DHI_i for practical applications.

2.4.3 – The proposed layout assessment method

The goal of layout design for safety is to bring inherent safety concepts into the early stages of layout design by means of an easy-to-use approach. This requires consideration of the role of both strictly inherent as well as passive safety measures in achieving layout safety. An index-based assessment tool specifically aimed at the comparison of preliminary alternative layout options was developed to support layout design for safety. Although the potential of domino effect is a key issue in the design for layout safety, as discussed in §2.4.2, further aspects should be taken into account in this index. Thus, the evaluation of the index is based on an integrated analysis of the different aspects concerning hazard of process units, applicability of inherent safety guidewords, requirement for safety devices and safety economics. A scoring method was adopted because it is suitable for quickly considering at once such a different array of issues and because it is particularly suitable for the early stages of design when a limited amount of information is available.

The framework of the Integrated Inherent Safety Index (I2SI) proposed by Khan and Amyotte *[Khan & Amyotte, 2004, 2005]* was chosen for the newly proposed layout assessment tool. This is in keeping with an overall objective of providing a portfolio of tools with a common structure for the assessment of inherent safety aspects in both process design (previous applications of I2SI as described in *Khan & Amyotte, [2004, 2005])* and layout design (present contribution). Furthermore, such an approach shows other features matching the needs of the layout assessment:

- I2SI is an indexing approach structured to assess in a comprehensive manner various aspects of inherent safety, with particular reference to applicability of inherent safety guidewords.
- It can be easily adapted to the specific design issues of different phases of the design lifecycle, such as layout design in this case, while maintaining the same general structure.
- The application is simple and quick, requiring details that are ready available or estimable.
- I2SI employs inherent safety guidewords in a manner similar to the well-accepted and practiced HAZOP methodology.
- Quantitative scores are provided to help with the interpretation of results and design decision-making.

- *Inherent Safety Index (ISI)* is reviewed to consider the specific issues of layout design.
- A new *ISI for attenuation* is defined to account for domino hazards.
- *ISI for simplification* is extended to account for increase of complexity.
- Three new sub-indices are defined for *ISI for limitation of effects*.
- Reference indices are provided to reduce subjectivity in the evaluation of the extent of applicability of inherent safety guidewords.
- The index *PHCI* in *ISPI* is limited to the hazard control measures (*HCI*).
- Explicit accounting of *costs of domino effect escalation* is implemented in cost indices.
- *LSI* is introduced for a better evaluation of costs of losses.

Table 2.4.5: Modifications of the former I2SI methodology introduced for the analysis of layout safety.

The sub-indices of the original I2SI have been revised in the current work to match the unique issues of layout safety assessment. Table 2.4.5 provides a summary of the main modifications introduced to the original I2SI.

The framework of the Integrated Inherent Safety Index (I2SI) relies on the assessment of the applicability of inherent safety guideword. Thus a preliminary analysis of the guideword applicability in layout design was essential for the index development. The principal outcomes of that analysis are presented in the following. Then, a brief illustration of I2SI and a more detailed description of the specific features developed for layout assessment are presented in the following chapters.

2.4.3.1 - Inherent Safety Guidewords for layout plans

The basic principles of inherent safety can be expressed by a few guidewords, as discussed in §2.1.1. However terminology of inherent safety varies somewhat throughout the process safety community, resulting in the same conceptual principles being expressed with alternate labels. In the framework of I2SI the key guidewords employed are: *minimization*, *substitution*, *attenuation*, *simplification*, and *limitation of effects*. The guidewords can be applied at the different levels of the hierarchy of inherent safety strategies (§2.1.1), for example leading to add-on measures that are more reliable, effective and thus – in a broad sense – inherently safer. In the developed layout assessment index both *strictly inherent* measures as well as *passive* measures have been investigated for their ability to improve the safety performance of the layout plot. The perspective of layout design considered here, therefore, is one in which the entire set of items placed in the facility (no matter if they are pieces of equipment or blast walls) contributes in defining the global hazard of the plant as a system (e.g. the potential for maximum domino effect escalation). This shift in perspective justifies the choice to consider both safety strategy levels (inherent and passive) in the current analysis. *Active* and *procedural* safety strategies are not considered here because, by their definition, they do not generally belong to the first stages of layout design.

As earlier mentioned (§2.4.1), constraints related to previous design steps (e.g. chemical route choice, process design, equipment selection, etc.) exist in layout design. These constraints limit the applicability of measures aimed at enhancing inherent safety in the layout options. The inherent safety principles are reviewed below with respect to their applicability in layout design:

- The *minimization* guideword is generally not applicable because equipment characteristics and material inventories have already been selected in previous design phases. If options of changing inventories are still open, they are likely to principally affect storage sections. In the design of equipment layout, the application of this guideword is fairly impractical.

- The *substitution* guideword in layout design, both for equipment and materials, is affected by limitations similar to *minimization*. Thus, *substitution* applicability is generally limited.

- The *attenuation* guideword, in its usual reference to changes in unit operating conditions, has limited applicability as these conditions will have been fixed in previous design steps. However, this guideword may be applied to changes in the arrangement of units. Changing unit arrangement and/or increasing unit segregation reduces, if not eliminates, the potential of domino effects and thus the hazard within the system. This is a key point because accident escalation by domino effect has been identified as the most important hazard source related to process layout design *[Cozzani et al., 2007]* (§2.4.2). The effectiveness of layout in reducing this hazard is thus the application of the guideword *attenuation* for the plant considered as a system (i.e. from the perspective of layout analysis). Further justification for this viewpoint can be found in the work of Kletz *[Kletz, 1998]*. His original definition of *attenuation* in process design (processing hazardous materials under less hazardous conditions – e.g. low pressure and temperature) can be revised in the case of layout design as 'using hazardous units in the least hazardous form' (i.e. the layout which limits the domino potential). The present approach is proposing that as the materials being processed are the building blocks of process design, the process units may be considered the building blocks of layout design.

- The *simplification* guideword is readily applicable to layout design. The choice of unit spatial organization has great potential to affect the simplicity of a plant. Complexity can easily arise as the disposition of units diverts from the logical process flow order, or as further items (e.g. walls, equipment of other production lines, and buildings) are added to the plan. Therefore, it is quite likely that layout design choices, even if oriented to satisfy the other inherent safety guidewords, eventually result in a negative feedback with respect to *simplification*.

- *Limitation of effects* is a guideword that deals with the reduction of the extent of negative consequences arising from accidental events. Accepting that a negative effect may somehow occur, this guideword implies a consideration of the measures aimed to limit consequences. In early layout design both inherent and passive strategies can be implemented to pursue this goal. Thus, the *limitation of effects* guideword has been considered in the safety analysis of both inherent and passive measures. Three main applications of *limitation of…* in layout design were identified:

  i) limitation of the effects of domino escalation: reduction of the effects and consequences of domino escalation events, considering the integrated action of inherent and passive strategies. Note that this is a different aspect than the one considered for the applicability of the *attenuation* guideword. With *attenuation*, the focus was on reduction of the embedded hazard, such reduction being attained only by inherent measures. With *limitation of effects*, the focus is on the effects themselves that can be controlled by both inherent and passive strategies.

  ii) limitation of the damage potential to target buildings: appropriate location of buildings (workshops, administrative buildings, trailers, etc.) and control or emergency structures (control room, medical centre, etc.) in the layout plan so as to limit harm to people and impairment of accident response.

  iii) limitation of the affected area: limitation (generally by passive measures) of the spatial area affected by the consequences of an accidental event, regardless of the effects on other units, buildings, etc.

The conclusion from the above examination is that out of the five guidewords, three (*attenuation*, *simplification* and *limitation of effects*) are of particular interest for the safety assessment of layout plans.

2.4.3.2 - The I2SI for Layout Safety

The conceptual framework of the Integrated Inherent Safety Index (I2SI) is given in Figure 2.4.5, according to *[Khan & Amyotte, 2004, 2005]*. The first step of I2SI assessment for safety in layout is the identification of the units in a given option. For each unit, the I2SI is comprised of two main sub-indices: a Hazard Index (HI) and an Inherent Safety Potential Index (ISPI). The Hazard Index is a measure of the damage potential of a single unit after taking into account the process and hazard control measures. The Inherent Safety Potential Index, on the other hand, accounts for the applicability of the inherent safety principles (or guidewords) to the unit. The HI is calculated for the units of an arbitrary reference layout option – called the base case – and the values remain the same for the corresponding units in all other possible options. The HI and ISPI are combined to yield a value of the Integrated Inherent Safety Index (I2SI) as shown in Equation (2.4.11).

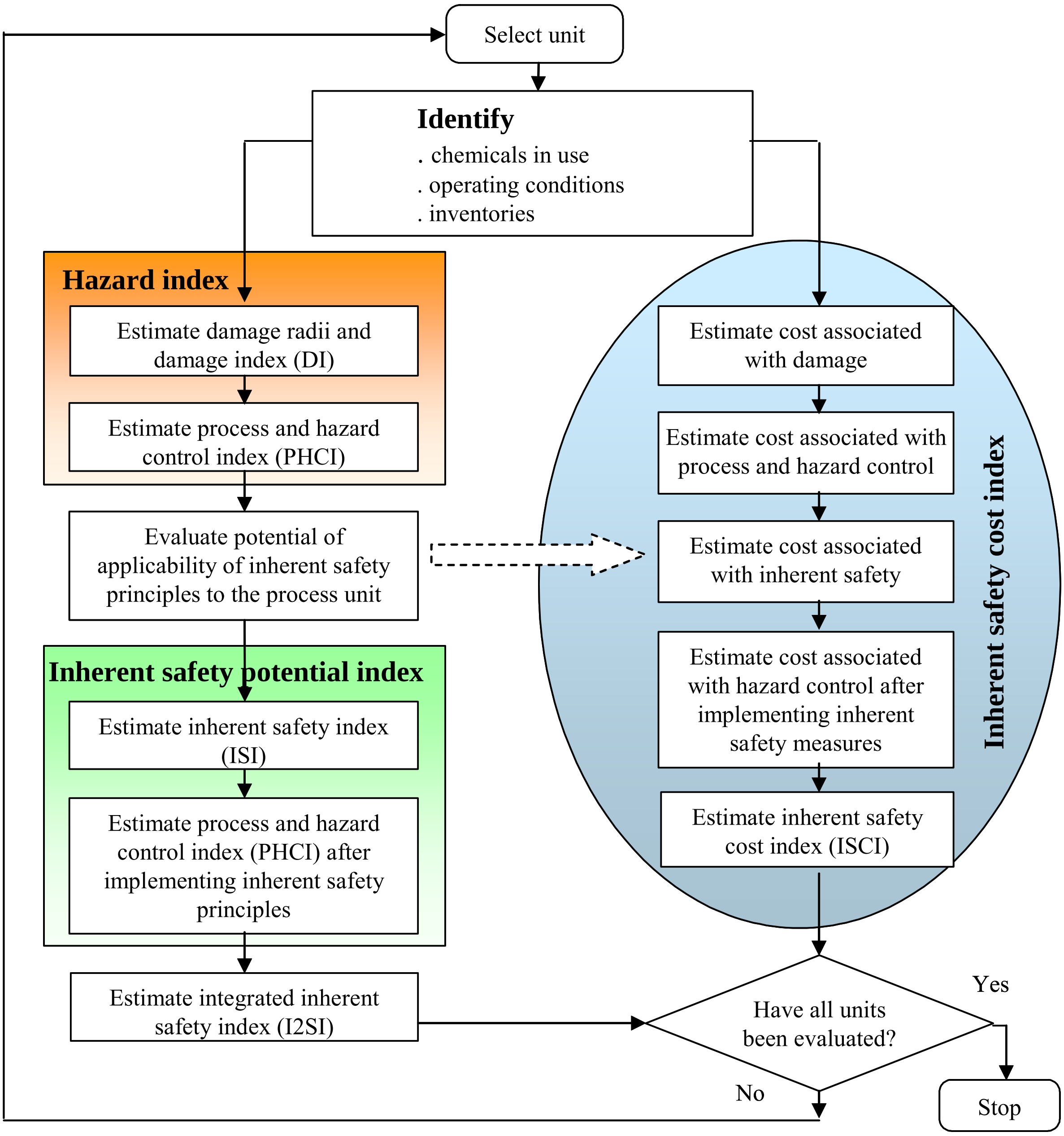


Figure 2.4.5: Conceptual flow diagram of the I2SI assessment method.

$$I2SI = \frac{ISPI}{HI} \tag{2.4.11}$$

As evident, an I2SI value greater than unity denotes a positive response of the inherent safety guideword application (i.e. an inherently safer option). The higher the value of I2SI, the more pronounced the inherent safety impact.

To evaluate alternative layout options for the same plant, the I2SI values for all the N considered single units are combined according to Equation (2.4.12):

$$I2SI_{system} = \left(\prod_{i=1}^{N} I2SI_i \right)^{1/2} \tag{2.4.12}$$

The Hazard Index (HI) for layout assessment is evaluated for each unit following the same procedure as for process assessment *[Khan & Amyotte, 2004]*. The HI is comprised of two sub-indices: a Damage Index (DI) and a Process and Hazard Control Index (PHCI). The numerical value of HI for the unit being considered is calculated by dividing the DI by the PHCI, as shown in Equation (2.4.13):

$$HI = \frac{DI}{PHCI} \tag{2.4.13}$$

The Damage Index (DI) is a function of four hazard parameters, namely: fire and explosion, acute toxicity, chronic toxicity, and environmental damage. These are estimated as a function of the expected damage radii for each scenario and have values ranging up to 100. Damage radii may be calculated using simple, validated approaches such as the Safety Weighted Hazard Index, or SWeHI, methodology developed by Khan et al. *[Khan et al., 2001]*.

The Process and Hazard Control Index (PHCI) is calculated for various add-on process and hazard control measures that are required or are present in the system. This index is quantified on a scale mutually agreed upon by process safety experts. The index ranges from 1 to 10 for any control arrangement and is quantified based on the necessity of this control arrangement in maintaining safe operation for the unit.

The Inherent Safety Potential Index (ISPI) is comprised, similarly to the Hazard Index (HI), of two sub-indices: an Inherent Safety Index (ISI) and a Hazard Control Index (HCI). The ISPI for single units is computed as shown in Equation (2.4.14):

$$ISPI = \frac{ISI}{HCI} \tag{2.4.14}$$

The ISI is calculated by using scores based on the applicability of the inherent safety guidewords. A detailed description of the procedure for ISI computation in layout assessment is reported in the next section.

The original version of ISPI *[Khan & Amyotte, 2004]* used *PHCI after the implementation of safety measures* as the denominator in Equation (2.4.14). For layout considerations, the denominator in Equation (2.4.14) is redefined as *HCI (Hazard Control Index) after the implementation of safety measures*. In the assessment of HCI, the requirement to install further add-on hazard control measures after the previous analysis and implementation of safety measures in the layout option is assessed. Process controls are not considered here, since they are not effective in layout safety. The scores of HCI are evaluated by the same rules as PHCI *[Khan & Amyotte, 2004]*.

2.4.3.3 - The ISI index

The ISI calculation follows the same procedure as a HAZOP study in which guidewords (in the present case, the identified inherent safety guidewords) are applied to the assessed system. Based on the extent of applicability and the ability to reduce the hazard, an index value is computed for each guideword. *Attenuation*, *simplification* and *limitation of effects* were earlier identified as the relevant guidewords for layout design. For each guideword a specific value of ISI is estimated. For *attenuation* and *limitation of effects* these values are estimated by conversion monograph (Figures 2.4.6 and 2.4.7) that relate the quantification of the extent of applicability of the guideword in the assessment option to an ISI score. The extent of applicability was evaluated, in the original I2SI, on a linguistic variable scale resulting from the agreement of a panel of experts *[Khan & Amyotte, 2004]*. Since the evaluation of the extent of applicability is admittedly subjective, specific guidelines are proposed here to facilitate the quantification of this parameter. These guidelines are discussed in the following paragraphs with respect to each guideword. For the guideword *simplification*, where the current authors experienced objective difficulty in quantifying this subjective parameter, an arbitrary reference table is proposed for the direct assessment of the index value by linguistic guidelines (Table 2.4.6).

The specific values of ISI for the single guidewords are combined together to yield the final ISI for the assessed unit, according to Equation (2.4.15):

$$ISI = [\, Max(\, \eta^2 \,,\, ISI_a^2 + ISI_{si} * \| ISI_{si} \| + ISI_l^2 \,)\,]^{1/2} \qquad (2.4.15)$$

where the subscripts refer to the considered guidewords (*a* for *attenuation*, *si* for *simplification* and *l* for *limitation of effects*). Equation (2.4.15) allows negative values for the simplification parameter, although limiting to $\eta \geq 0$ the lowest value of the final ISI. In the subsequent analysis, η is set equal to the minimum of the corresponding HCI in ISPI calculation ($\eta = 5$); hence ISPI is equal to 1 for base case units (i.e. ISI = 5) that do not require any hazard protection device (i.e. HCI = 5).

2.4.3.3.1 - Attenuation

Figure 2.4.6 reports the monograph proposed to convert the extent of applicability of the guideword *attenuation* into an ISI value. This is in accordance with the monograph approach used in the original version of I2SI *[Khan & Amyotte, 2004]*. The extent of applicability of this guideword is assessed mainly as the ability of the layout option to reduce the hazard potential from domino effects.

To overcome the subjectivity in assessment of the extent of applicability, an approach based on the Domino Hazard Index (DHI) is used. The DHI is specifically aimed at assessing the domino effect hazards caused by a unit in a specific layout. The DHI values for a unit range from 0 to 100. The maximum value means that the unit can affect multiple other units, triggering severe domino consequences; the zero-value indicates no domino possibility from the unit (i.e. the highest degree of inherent safety). Detailed discussion of the index and its development is reported in §2.4.2.3. The DHI of each unit of the layout being assessed is compared with the base option. In this case, the protection provided by passive devices is not accounted for in DHI as the focus is on the domino escalation potential (i.e. hazard) that can be reduced only by inherent measures. The estimation of extent of applicability by DHI may be done using Equation (2.4.16):

$$E_a = Max\left[0\ ,\left(1-\frac{DHI_{option}}{DHI_{base\ option}}\right)\times 10\right] \tag{2.4.16}$$

This proposal is in line with that suggested in the original I2SI formulation for the assessment of toxicity within the *moderation* guideword (i.e. use of reduction in LC50 values as $LC50_{intial}$/ $LC50_{changed}$) *[Khan & Amyotte, 2004].*

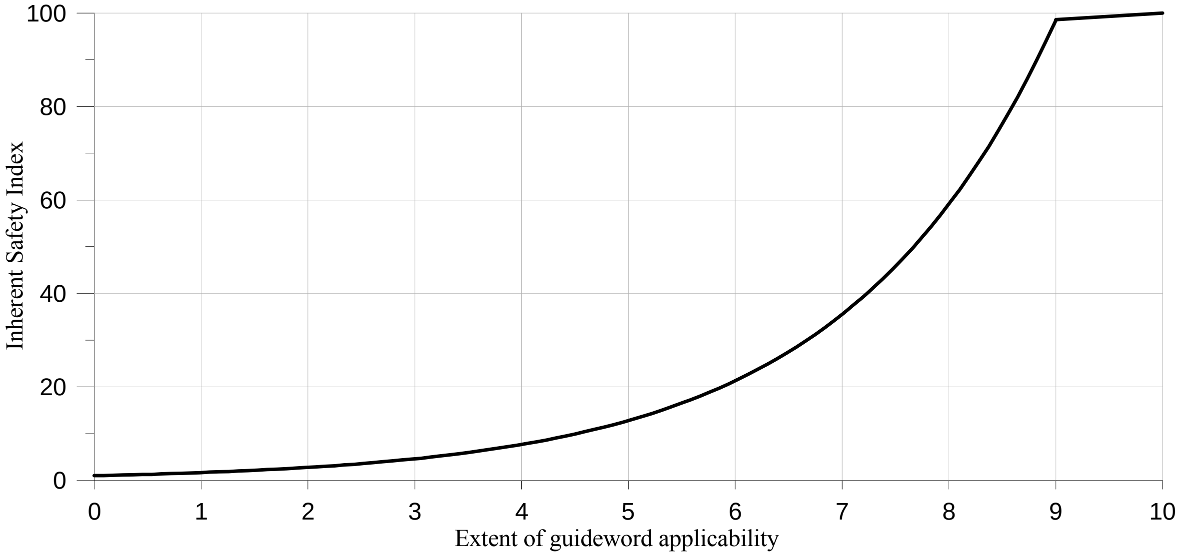


Figure 2.4.6: Inherent Safety Index for the *attenuation* guideword.

2.4.3.3.2 - Simplification

As previously discussed, layout options aiming at safer performance with respect to *attenuation* and *limitation of effects* usually cause an increase in layout complexity. Some important factors that may result in an increased complexity are:

- Complication of pipe connection among units – the displacing of units from the logical process-flow arrangement makes the piping network, pumping and control more complicated.
- Complication of pipe connection among units – the need for longer pipelines to connect units provides additional sources of release that are not strictly related to the units themselves. This situation may create additional units (transportation units) that may undergo failure.
- Increase in the number of items in a plant – in addition to the process units, other elements (e.g. blast walls, fire walls, etc.) contribute to the number of items present on the site. As the number of items increases, the requirements for management and maintenance increase, thus complicating procedures and increasing the probability of errors. Moreover, a non-linear disposition of a high number of units and the presence of obstacles (blast walls, dikes, etc.) limit the ease of access to the units. The access limitation further complicates regular operations (e.g. maintenance) as well as emergency response operations (e.g. fire-fighting).

To assess the complexity introduced by both inherent and passive measures, the former ISI of *simplification* was extended to account for negative values (Table 2.4.6). This is based on the idea that complexity can be defined as negation of simplicity. Pursuing *simplification* indeed limits the increase in complexity up to values that are overbalanced by the positive effects from the application of other guidewords.

It is worth remembering that *simplification* is a matter of interrelation among process units. It must be judged not by focusing only on a single unit, but with respect to the whole plant (or occasionally a plant section). The extent of this guideword applicability should be assigned with respect to groups of units.

Description	**ISI**
Process simplified to large extent and hazard eliminated	100
Process simplified to large extent and most significant hazard reduced	90
Process simplified to large extent and hazard reduced	80
Process simplified to large extent and hazard reduced moderately	70
Process simplified and hazard eliminated	60
Process simplified and hazard reduced	50
Process simplified moderately and hazard reduced	40
Process simplified moderately and hazard reduced moderately	30
No significant process simplification and hazard reduced moderately	20
No significant process simplification and no substantial hazard reduction	10
Non-applicable	0
No significant process complication and no substantial hazard increase	- 10
No significant process complication and hazard increased moderately	- 20
Process complicated moderately and hazard moderately increased	- 30
Process complicated moderately and hazard increased	- 40
Process complicated and hazard increased	- 50
Process complicated and new hazards introduced	- 60
Process complicated to large extent and hazard moderately increased	- 70
Process complicated to large extent and hazard increased	- 80
Process complicated to large extent and hazard significantly increased	- 90
Process complicated to large extent and hazard highly increased	- 100

Table 2.4.6: Extended guidelines to decide on the ISI value for the guideword *simplification*.

2.4.3.3.3 - Limitation of effects

Analysis of the applicability of *limitation of effects* to layout design involves three different elements that must be considered in the assessment: i) *limitation of the effects of domino escalation* (ISI_{le}), ii) *limitation of the damage potential to target buildings* (ISI_{lb}), and iii) *limitation of the affected area* (ISI_{la}). Monographs for converting the extent of applicability of each parameter to an ISI value are defined in Figure 2.4.7, again by an approach in accordance with *[Khan & Amyotte, 2004]*. These parameters are combined by Equation (2.4.17):

$$ISI_l = Min\{\, 100\ ,\ [(ISI_{le})^3 + (ISI_{lb})^3 + (ISI_{la})^3\ ]^{1/3}\ \} \qquad (2.4.17)$$

Also in this case, suggestions are provided for guidance in the evaluation of extent of applicability, striving to reduce the degree of subjectivity in the analysis:

i) Limitation of the effects of domino escalation can be estimated by resorting to the Domino Hazard Index (DHI) as a reference. The approach is similar to that followed for *attenuation*, but the focus, as discussed earlier, is different in this case. In *limitation of the effects of domino escalation*, the DHI is calculated considering the synergistic effect of passive and inherent measure protection on domino consequence limitation. The extent of applicability of *limitation of the effects of domino escalation* may be evaluated using Equation (2.4.18):

$$E_{le} = Max\left[0\ ,\left(1-\frac{DHI_{option}}{DHI_{base\ option}}\right)\times 10\right] \qquad (2.4.18)$$

ii) Limitation of the damage potential to target buildings aims to assess the location of the facility's populated buildings (control rooms, laboratories, workshops, offices, etc.) in relation to the hazardous units of the process. A proposal for this assessment is based on the grouping of the buildings into hazard-susceptible areas (i.e. areas affected by fire, explosion and acute toxic effects). The assessment has to take into account the combined effect of different primary units on the same building, since they may change from one layout option to another. Thus a reference index (A_j) is calculated for each target building (j) according to Equations (2.4.19) and (2.4.20):

$$a_{i,j} = Max\left(1-\frac{D_{i,j}}{B_i}\ ;\ 0\right) \qquad (2.4.19)$$

$$A_j = \sum_i a_{i,j} \qquad (2.4.20)$$

where $D_{i,j}$ is the distance between the i-th unit and the j-th building, and B_i is the maximum damage distance of the i-th unit for fire, explosion and acute toxic effects. The estimation of the extent of applicability of ISI_{lb} is defined by Equation (2.4.21):

$$E_{lb,i} = \begin{cases} Max\left[0\ ,\left(1-\dfrac{\sum_j A_{j,option}}{\sum_j A_{j,base\ option}}\right)\times 10\right] & if\ a_{i,j,option} > 0\ \ or\ \ a_{i,j,base\ option} > 0 \\ 0 & otherwise \end{cases} \qquad (2.4.21)$$

iii) Limitation of the affected area accounts for the effects of passive measures to decrease the area susceptible to dangerous consequences, no matter if particular structures are located there (e.g. units or buildings), but simply because final targets (e.g. people, environment) can potentially be present. The suggested guideline for quantitative assessment of this aspect is based on the percentage decrease of damage area compared to the same unit in the base option:

$$E_{la} = Max\left[0\ ,\left(1-\frac{AA_{opion}}{AA_{base\ option}}\right)\times 10\right] \qquad (2.4.22)$$

where *AA* is the affected area exposed to the consequence from the considered unit (e.g. if no protective devices exist, this is the area encompassed by the damage radius; if protective devices exist, the upwind protected areas are subtracted).

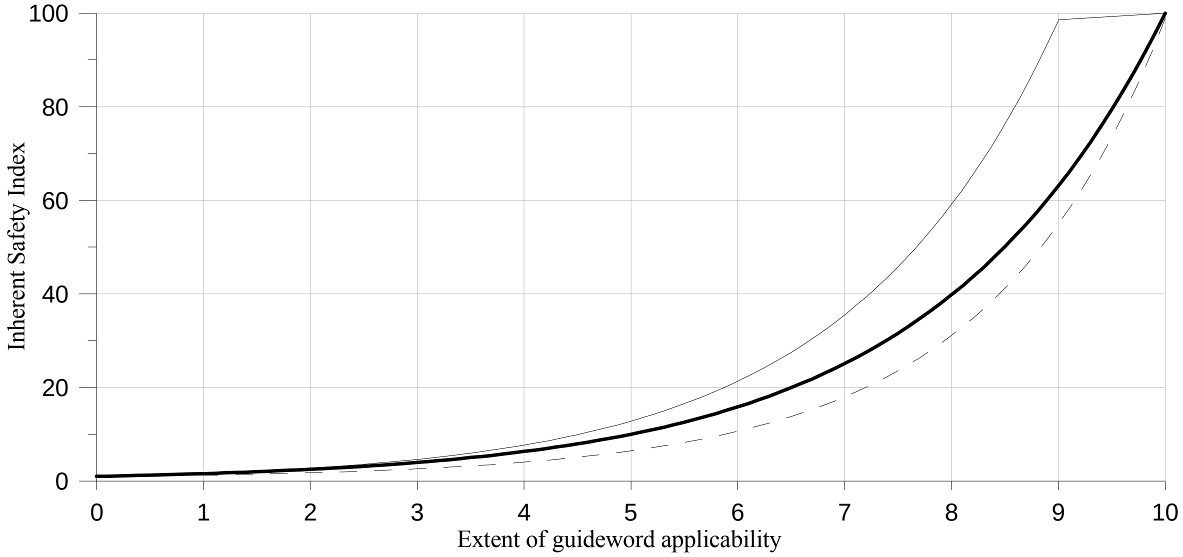


Figure 2.4.7: Inherent safety index for the *limitation of effects* guideword: *limitation of effects of domino escalation* (thin solid line), *limitation of the potential to target buildings* (thick solid line), *limitation of the affected area* (dashed line).

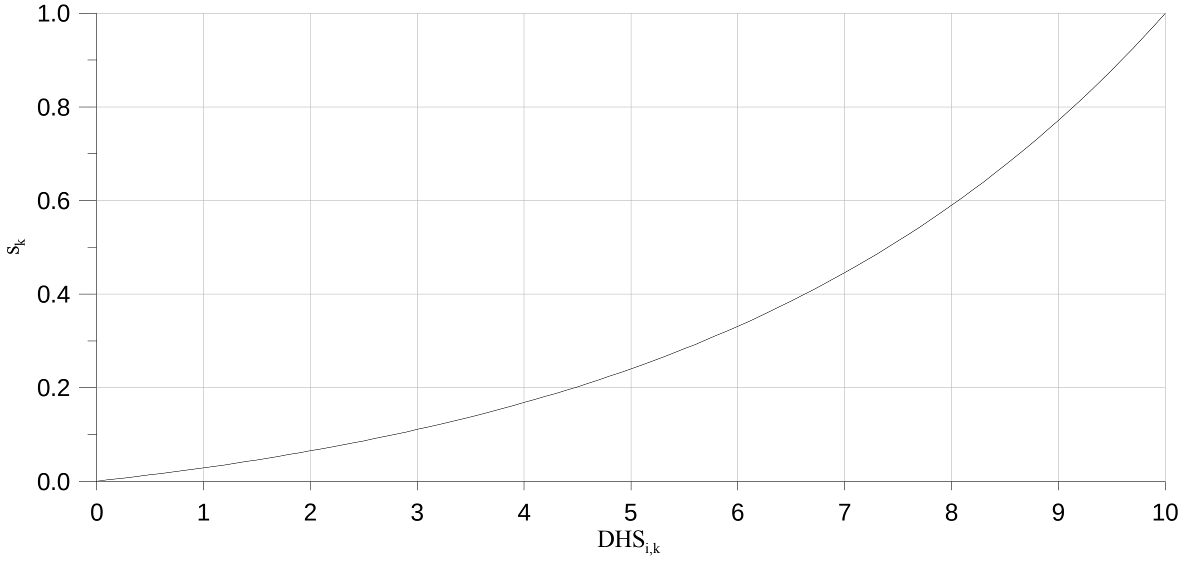


Figure 2.4.8: Credit factor for domino escalation as a function of $DHS_{i,k}$.

2.4.3.4 - Cost indexing

The cost indexing procedure of I2SI accounts for and evaluates the economic aspects of inherent safety. The costing system (right-hand side of Figure 2.4.5) is comprised of two sub-indices: a *conventional safety cost index* (CSCI) and an *inherent safety cost index* (ISCI). A further index specific to layout analysis, the Loss Saving Index (LSI), is introduced to account for the savings on potential losses due to a reduction of domino escalation possibility.

2.4.3.4.1 - Conventional Safety Cost Index (CSCI)

The *conventional safety cost index* (CSCI) is computed as shown in Equation (2.4.23):

$$CSCI = \frac{C_{ConvSafety}}{C_{Loss}} \tag{2.4.23}$$

The numerator in Equation (2.4.23), $C_{ConvSafety}$, is the sum of the costs of process control measures and add-on (end-of-pipe) safety measures (i.e. $C_{ConvSafety} = C_{Control} + C_{Add\text{-}on}$). It can be estimated by the number of measures required and their representative reference costs (see e.g. Khan and Amyotte *[Khan & Amyotte, 2005]*).

The denominator in Equation (2.4.23), C_{Loss}, represents the dollar value of expected losses caused by accidental events in a unit. It is comprised of five components, as shown in Equation (2.4.24):

$$C_{Loss} = C_{PL} + C_{AL} + C_{HHL} + C_{ECC} + C_{DEC} \tag{2.4.24}$$

Production Loss (PL) is the economic consequence of production shutdown (i.e. business interruption). *Direct Asset Loss* (AL) represents the value of the physical unit itself which is depleted by the accidental event (e.g. fire or explosion). *Human Health Loss* (HHL) is calculated in terms of the cost of fatalities/injuries directly caused by the accident at the unit. However there can be a high degree of subjectivity and discomfort associated with assigning a dollar value to fatality and/or injury. While the value of a human life is immeasurable, it is still possible to employ indicators such as insurance costs, rehabilitation costs, worker compensation rates, etc. *Environmental Cleanup Cost* (ECC) is associated with the mass or volume of soil, water and air that were contaminated by the accidental event. Reference costs for the estimation of this parameter are adapted from *[Khan & Amyotte, 2005; Khan et al., 2004b]*. *Domino Escalation Cost* (DEC) is a cost term explicitly introduced in the present approach to account for the loss consequences of the possible chain of accidents. It represents the sum of the loss related to the secondary units involved, weighted by a parameter that features the probability of being involved, as expressed by Equation (2.4.25):

$$C_{DEC} = \sum_k s_k \left(C_{AL,k} + C_{HHL,k} + C_{ECC,k}\right) \tag{2.4.25}$$

where $C_{AL,k}$, $C_{HHL,k}$ and $C_{ECC,k}$ are respectively the additional direct asset loss, human health loss and environmental cleanup costs for the failure of each k-th secondary unit, as a result of escalation from the primary unit under assessment. The production loss cost is not accounted for a second time in C_{DEC} because the target units are considered to be in the same production line as the primary unit. The factor s_k accounts for the credibility that the failure of the considered unit affects the k-th secondary unit. It can be evaluated as a function of the maximum Domino Hazard Score ($DHS_{i,k}$), an intermediate index in the DHI calculation (see §A2.2.4 in Appendix 2.2). The correlation between s_k and $DHS_{i,k}$ is reported in Figure 2.4.8.

2.4.3.4.2 - Inherent Safety Cost Index (ISCI)

The inherent safety cost index (ISCI) is computed by Equation (2.4.26):

$$ISCI = \frac{C_{InhSafety}}{C_{Loss}} \tag{2.4.26}$$

The denominator in Equation (2.4.26), C_{Loss}, is the same as in Equation (2.4.23) for the CSCI. However, the numerator, $C_{\mathrm{InhSafety}}$, is the sum of the costs of inherent safety implementation, of process control measures, and of add-on (end-of-pipe) safety measures required in the inherently safer layout option (i.e. $C_{\mathrm{InhSafety}} = C_{\mathrm{Inherent}} + C_{\mathrm{Control}} + C_{\mathrm{Add\text{-}on}}$). The costs of process control and of add-on safety measures are calculated following the same procedure as for CSCI.

The costs for inherent safety implementation are estimated considering the extent of application of the inherent safety guidewords and the costs associated with their application. A cost value is calculated for the application of each guideword. For example, the cost of extra space required for increased unit segregation is estimated and referred to as the cost of implementing the guideword *attenuation*, as earlier discussed. This cost is divided by a factor called the extent of applicability, which denotes the extent to which the guideword will eliminate/reduce the hazards. Hence, the total cost of inherent safety implementation is represented by Equation (2.4.27):

$$C_{Inherent} = C_A / E_A + C_{Si} / E_{Si} + C_L / E_L \qquad (2.4.27)$$

where the C variables are the costs and E the extents of applicability of, respectively, *attenuation (A)*, *simplification (Si)*, and *limitation of effects (L)*.

2.4.3.4.3 - Loss Saving Index (LSI)

The possibility of escalation by domino effects, assessed by C_{DEC}, is frequently a prevailing term within the cost of loss. This value can have a significant variation for different layout options because of the choices specifically aimed at inherent safety improvement. A new index is proposed to map out the economic effect of escalation reduction deriving from inherently safer layout design:

$$LSI_{option} = \frac{C_{InhSafety,option} + (C_{Loss,option} - C_{loss,base\ option})}{C_{loss,base\ option}} \qquad (2.4.28)$$

This index compares inherent safety costs with a parameter that represents the savings from avoided loss by domino escalation, since it considers loss variations between the base case and assessed options.

2.3.4 - Conclusions

This chapter presents several support tools for the implementation of inherent safety in the design of layout. The tools are integral part of a research effort aimed at the implementation of inherent safety practice throughout the whole design life-cycle of a project.

A common element of the proposed tools is the definition of escalation distances. Escalation distances are identified as an objective parameter for the assessment of the escalation potential of a unit within a layout. The distances are calculated by mathematical models for the simulation of the consequences. Generalized rules are provided for swift application. Several Key Performance Indicators (KPIs) are calculated combining the escalation distances with the layout distances and credit factors of equipment failure. These KPIs provide a quantitative information on specific safety aspects for escalation hazard (e.g. ranking of the escalation potential of a unit; identification of critical units in a given layout, both as an escalation

initiator and as a vulnerable target; etc.), which may be used to support a detailed design of the process. Examples of application for identification of the critical units and analysis of the configurations in the definition of plant layout plot are provided in §4.4.5, §4.7.3 and §4.7.4.
In a second step, a comprehensive screening tool for the assessment of the safety performance in layout plans is proposed. The tool is suitable for the comparison of alternative options for layout plan, especially in preliminary stages of the design. Process unit hazards, domino hazard, inherent safety guideword applicability, requirement of safety devices and safety economics are the principal features accounted by the tool. The information in the output indices of the method allows a comprehensive analysis and comparison of the alternative options and provides suggestions for the improvement of the single layout options. Demonstration of the application is reported in §4.7.1 and

2.5 – Proposed Approach for Inherent Safety through the Project Lifecycle

2.5.1 - Introduction

The application of inherent safety principles throughout the lifecycle of process design and management is not yet a current practice. Several reasons may be attributed to this lack, the main being a limited awareness of the potential benefits of the inherent safety strategy within each level of engineering activities, and the shortage of suitable tools to support the implementation. In particular, there is a general tendency to focus inherent safety efforts only on the early stages of the process design lifecycle. It is well-understood and agreed by practitioners that inherent safety can make significant contributions in the early design stages. However, the systematic application of inherent safety concepts at other stages of the process design and risk control-measure selection lifecycle has yet to be fully explored.

In the following a conceptual framework for supporting the application inherent safety throughout the project lifecycle is presented. The procedure is named *design assistance method for inherent safety implementation*. The work described herein is largely conceptual at present, but outlines the general structure where the tools described in chapters from §2.2 to §2.4 should be located.

The research endeavours to incorporate three key ideas: (i) the process design lifecycle, (ii) the hierarchy of risk control strategies, and (iii) inherent safety. Although some of these concepts have been already introduced in §1.1.1 and §2.1.1, they are refreshed and detailed in the following.

i) Process Design Lifecycle

The process design lifecycle represents the evolution of a design over time. The lifecycle can be divided into stages, with more detailed and specific elements being designed at each successive stage. The lifecycle stage terminology used in the present work is shown in Table 2.5.1 along with the stage classifications proposed by other workers. Phases such as upgrading, management of change and decommissioning were not explicitly considered at this stage of the work. However this does not affect the concepts proposed, nor does it limit the applicability of the suggested method to design guidance.

Activities involved in the design stages include selection and determination of:
Process Research & Development: process technology, raw materials, intermediate products, byproducts and wastes, chemical synthesis route (after *Mannan*, *[2005]*).
Conceptual Design: specific unit operations, types of reactors and other units, operating conditions, recycle, product purification, waste treatment (after *Mannan, [2005]*).
Basic Design: size and number of production lines, general material and energy balances, size of storage facilities, specific equipment types, process control philosophy, location of the facility.
Detailed Design: design of all equipment, pressure rating of all equipment and piping, inventory in process equipment, location of equipment in the plant, size and routing of piping, utilities, layout, control system, plant/operator interface.
Procedure Design: procedures and codes of rules for normal operation, emergencies, inspections and maintenance.

Present Work	**Mannan, 2005**	**CCPS, 1996**	**BSI 7000:4**
Process research & development	Conceptual process research & development	Research	Inception
			Feasibility
Conceptual design	Process research & development	Process development	Conceptual design
Basic design	Preliminary plant design		Scheme design
Detailed design	Detailed plant design	Design and construction	Detail design
			Production information
Procedure design (operation & emergency)			
	Operation	Operation, maintenance, modification	
		Decommissioning	

Table 2.5.1: Equivalence Among Various Lifecycle Stage Classifications

ii) Hierarchy of Risk Control Strategies

The hierarchy of risk control strategies (or simply *hierarchy of controls [Hopkins, 2005]*) is a classification of measures that can be taken to accomplish loss prevention and mitigation. As one progresses downward through the hierarchy, the reliability of the strategy decreases and possible failure modes increase in number. From most to least effective, the hierarchy of controls consists of safety measures that are: (i) inherent, (ii) passive (engineered), (iii) active (engineered), and (iv) procedural in nature. As described by *Amyotte et al., [2007]* engineered or add-on safety involves the addition of safety devices typically at the end of the design. These safety devices do not perform any fundamental operation, but are designed to act when a process upset occurs. The division of engineered safety into passive and active measures indicates that the devices accomplish their intended aim either without active functioning (*passive* – e.g. a machine guard), or only upon detection and initiation of action (*active* – e.g. emergency shutdown systems). Procedural safety measures, or administrative controls, use safe work practices and procedures to reduce risk. On the other hand, inherent safety uses the properties of a material or process to eliminate or reduce the hazard. The fundamental difference between inherent safety and the engineered and procedural categories is that inherent safety seeks to remove the hazard at the source as opposed to accepting the hazard and aiming at mitigation of the effects.

iii) Inherent Safety Guidewords

Inherent safety is clearly a distinct category in the hierarchy of risk control strategies. Inherent safety can also be thought of as an enabling measure and as being applicable to the other hierarchy levels, so that it works to enhance the effectiveness of passive, active and procedural strategies. This is the broader view of inherent safety that the current work seeks to advance.

As discussed extensively in previous sections, inherent safety involves consideration of a number of principles, of which the four most general and widely applicable are given in Table 2.5.1 as a set of guidewords. The principle/guideword descriptions are purposely brief and are focused on materials, process routes, equipment and procedures.

Guideword	Description
Minimize	Use smaller quantities of hazardous materials when the use of such materials cannot be avoided. Perform a hazardous procedure as few times as possible when the procedure is unavoidable.
Substitute	Replace a substance with a less hazardous material or processing route with one that does not involve hazardous material. Replace a hazardous procedure with one that is less hazardous.
Moderate	Use hazardous materials in their least hazardous forms or identify processing options that involve less severe processing conditions.
Simplify	Design processes, processing equipment, and procedures to eliminate opportunities for errors by eliminating excessive use of add-on (engineered) safety features and protective devices.

Table 2.5.2: Inherent Safety Principles *[CCPS, 1996]*.

The guidewords and descriptions shown in Table 2.5.2 are usually invoked by designers familiar with these concepts at the inherent safety level in the hierarchy of controls and at the early lifecycle stages of process research & development and conceptual design. This is where there is general agreement that major changes can be undertaken with the greatest opportunities for cost-effective risk reduction. Extension of the applicability of inherent safety throughout the complete design lifecycle may require a more general expression of the guidewords in Table 2.5.2; suggestions in this regard are:

- *Minimize (Minimization):* reduce the size of the hazard and therefore its potential to cause harm.
- *Substitute (Substitution):* reduce the hazard by changing the type of hazardous elements.
- *Moderate (Moderation):* reduce the ability of the (present) hazard to result in negative impacts.
- *Simplify (Simplification):* eliminate unnecessary complexity, make operating errors less likely, improve error tolerance.

2.5.2 - Design Assistance Method for Inherent Safety Implementation

The following discussion presents a method for guiding the introduction of inherent safety at any level or stage of process design. The method is based on the systematic implementation of the concepts of inherent safety in each point of the design space.

The *design space* is a rational representation of the safety choices in design, according to their position with respect to several hierarchies of elements. Figure 2.5.1 gives one possible depiction of the design space as an oriented space that illustrates the applicability of inherent safety in process design. A design choice within a given project is represented by a unique point in the space. With this representation, it is clear that inherent safety can be successfully implemented at any single point in the space. As previously mentioned, it is universally recognized that some zones of the design space may yield better effects (e.g. early design stages coupled with use of inherent control strategies). Any point in the space, however, is available for safety measure implementations that contribute positively to the overall inherent safety performance of the project.

As previously mentioned, the basic idea of the design assistance method is the rigorous exploration of inherent safety applicability within the design space. The framework of the methodology is shown in Figure 2.5.2. By means of nested cycles, the analysis proceeds systematically through the design lifecycle stages, risk control levels and inherent safety guidewords. Application of this methodology will eventually result in an inherent safety-optimized design for each stage of the lifecycle.

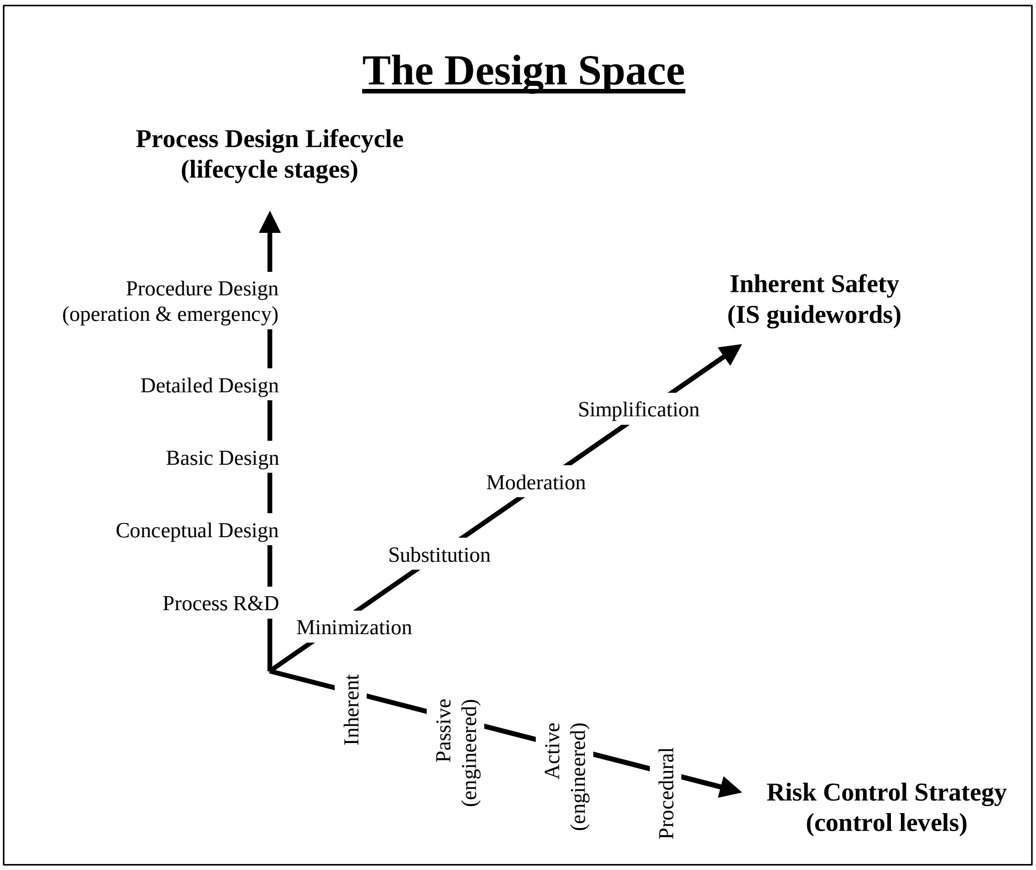


Figure 2.5.1: The Design Space – A Representation

Figure 2.5.3 is a graphical representation of the design space (Figure 2.5.1) and how it is systematically filled, point-by-point through application of the methodology given in Figure 2.5.2. On the other hand, Figure 2.5.4 provides an example of an incomplete filling of the design space, as would be obtained in the traditional design approach claiming to apply inherent safety. The application of inherent safety guidewords is non-systematic and occurs only at the early design stages with little consideration given to other risk control strategies. The more detailed (i.e. more advanced) stages of design rely on higher control levels with no application of the inherent safety guidewords (as represented by the shape *A*, which has no dimension on the inherent safety axis).

Key blocks in the methodology shown in Figure 2.5.2 are described below:

Hazard identification: The first step to design for safety is to identify the hazards present. This identification is based on checklists, brainstorming activities (e.g. What-If? analysis), analyst experience, and is supported by the information recorded in the knowledge bank.

Generate a base option: As the proposed methodology is intended to lead to incremental design improvements, a base option is necessary to initiate the procedure. The base option can be generated from information in the knowledge bank, is pertinent to a given lifecycle stage, and may include several levels of risk control strategies. It is in the successive *Analysis* phases of *Assessment*, *Interpretation* and *Improvement* that the control strategies are considered level by level and inherent safety guideword by inherent safety guideword.

Assessment: In this phase, a safety index is developed for the considered point of the design space. One possible safety index is the KPI approach described in §2.3 and §2.4. The input to the assessment phase is a design option for the given lifecycle stage, including the cumulative safety measures up to the given control level. In each application of the overall *Analysis* block (i.e. *Assessment*, *Interpretation* and *Improvement*), the credit and consequence calculations are updated as required by the subsequent modifications in safety measures.

Interpretation: As suggested by its name, this step is aimed at recognition of the main elements defining the safety index or measure of risk assessed in the previous phase. A weighting analysis of fault tree elements, for example, can help determine the most important features that characterize the risk profile of the analyzed option.

Improvement: Once the role of each of the safety measures introduced is identified in the previous step, actions can be taken to improve the inherent safety of the system. These actions should involve the elements identified as critical and should be driven by the inherent safety guidewords, which are systematically applied. Suggestions for system improvements can be provided by the knowledge bank that should contain information on possible safety measures as well as hazards.

Knowledge Bank: This element represent an extensive database listing expected hazards, process technologies and safety measures for the analyzed kind of process (i.e. specific industrial sector). It is an advisory element in the method that provide information and checklists to the analysis. It is compiled resorting to the knowledge of several expert and practitioners (e.g. brainstorming activities, What-If? Analysis, etc.). It is intended as a live-database, as it can be enriched by the outcomes of the method itself. The basic form of this database contains the information of hazard and barriers classification.

As shown in Figure 2.5.2, the design assistance method moves *forward* along the axes of the design space with no explicit feedback routes to previous phases. This is reflective of the usual approach to design (especially within the lifecycle stages) in which, although design is clearly an iterative process, *backward* steps are generally infeasible due to practical, time and economic constraints. A comprehensive knowledge bank is a key requirement, therefore, to ensure that the impact on later stages of decisions made at a given stage on are well-understood (e.g. a reduction in number of flanges, which is an inherent measure in detailed design, will have implications for procedure design with respect to inspections).

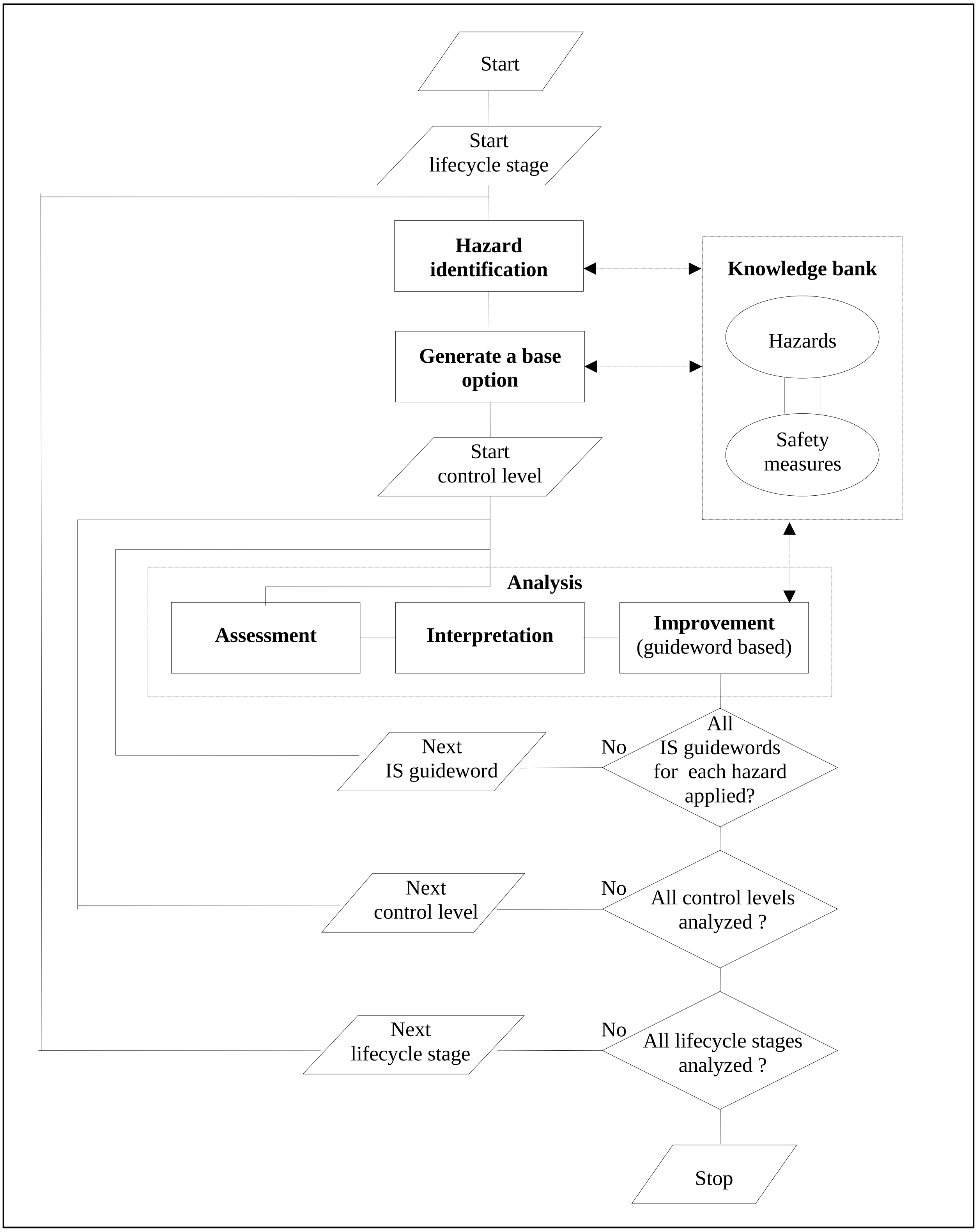


Figure 2.5.2: Flow Diagram of the Design Assistance Method

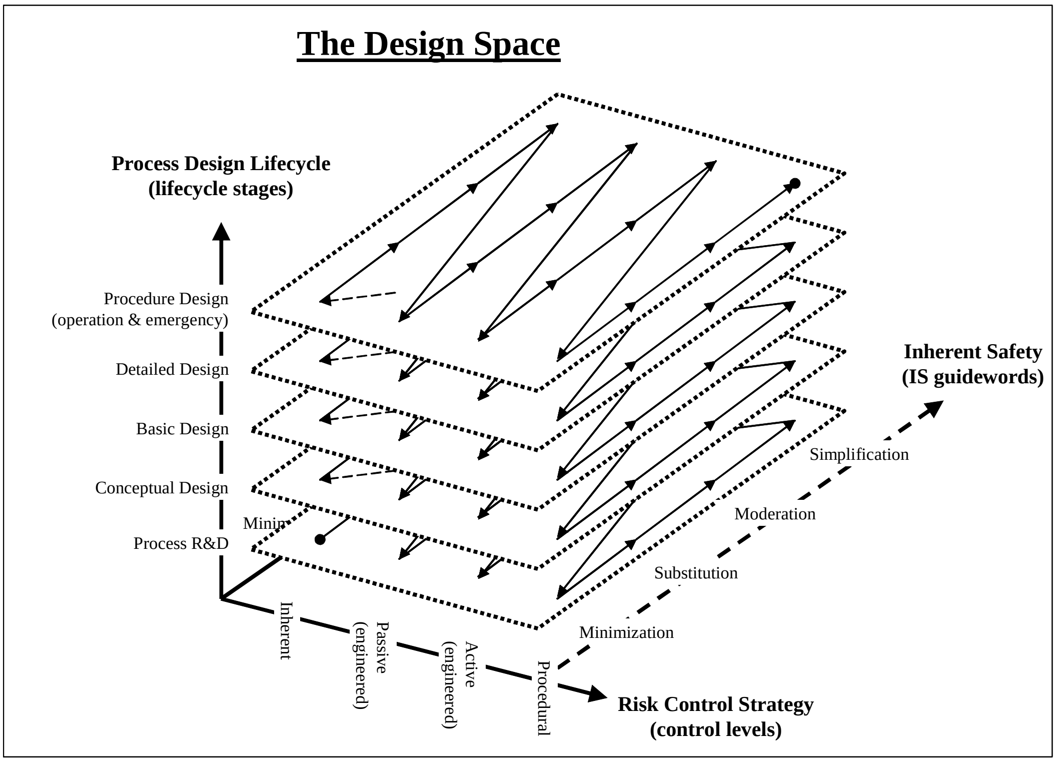


Figure 2.5.3: The Design Space – Systematically Filled by the Design Assistance Method

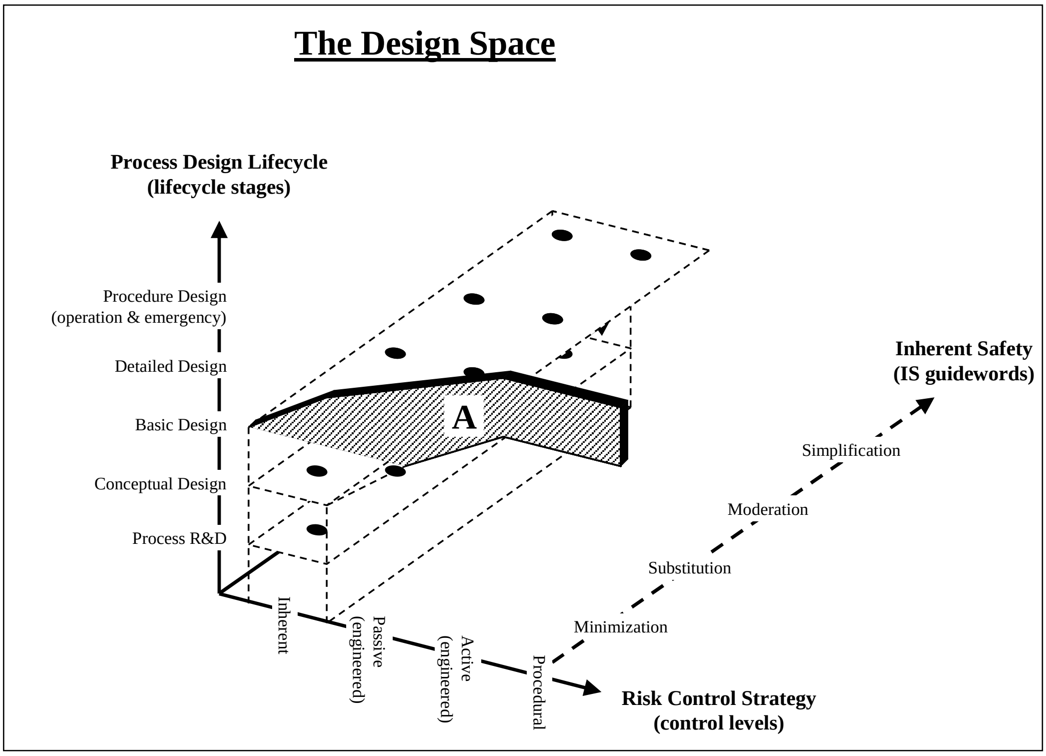


Figure 2.5.4: The Design Space – Non-Systematic Application of Inherent Safety Considerations

2.6 - Conclusions

The implementation of inherent safety within a design support system was pursued through the development of a portfolio of dedicated tools.

The review of the scientific literature on inherent safety assessment evidenced the limitations of tools currently available: applicability restrained to specific cases, presence of non-transparent build-in assumptions, large use of arbitrary parameters based on expert judgement, etc..

A portfolio of quantitative assessment tools was proposed to overcome these limitations:

- A procedure for the definition of the hazard profile of the decomposition products of a material was developed. The approach, joined with experimental protocols for the identification of expected decomposition products, allows the screening of the accidental scenarios may follow the emission in the environment of the decomposition products released in the loss of control of a chemical process. These scenarios should be assessed in the next step of evaluation of process safety.
- A consequence-based method for the quantitative assessment of the inherent safety of processes was developed. The method is based on the evaluation of two KPIs, related to the severity of potential accidents and to the recorded safety scores of process equipment. In the framework of a comparative assessment of the inherent safety of alternative processes, the developed method overrides several problems of literature methods. Introducing a direct relation among hazard factors and consequence analysis of potential scenarios, the proposed method avoids the use of arbitrary indexes.
- A consequence-based method, derived from the previous one, for the assessment of the hazard of chain effects leading to catastrophic consequences by escalation (domino effect). The index allow identification of the critical units and configurations in the definition of plant layout plot.
- A screening tool for the comprehensive assessment of the inherent safety in early phases of plant layout design. The proposed tool is based on the framework of former literature methods, in order to produce a common approach for both process and layout assessment. However the application within the constraints and specific characteristics of layout design required a throughout update of the indexing system. The assessment is based on the integrated analysis of the various aspects: process unit hazards, domino hazard, inherent safety guideword applicability, requirement of safety devices and safety economics.

The developed approaches listed above are integral part of a research effort aimed at implementation of inherent safety practice throughout the whole design life-cycle of a project.

Appendix 2.1 – Tables for the scoring of hazardous proprieties of materials

In the following, the correlation tables for the scoring of the hazardous proprieties of substances required by the procedure described in §2.2 are reported.

A2.1.1 – Toxicological and eco-toxicological properties

Score		0 Negligible toxicity	1 Harmful	2 Toxic	3 Very toxic
Inhalation gas o vapour	LC_{50} (4h) inhalation rat (mg/l)	> 20	2 ÷ 20	0,5 ÷ 2	< 0,5
	Risk phrase	-	R20	R23	R26
Inhalation aerosol o particles	LC_{50} (4h) inhalation rat (mg/l)	> 5	1 ÷ 5	0,25 ÷ 1	< 0,25
	Risk phrase	-	R20	R23	R26
Dermal contact	LD_{50} dermal rabbit (mg/kg)	> 2000	400 ÷ 2000	50 ÷ 400	< 50
	Risk phrase	-	R21	R24	R27
Ingestion	LD_{50} ingestion rat (mg/kg)	> 2000	200 ÷ 2000	25 ÷ 200	< 25
	Risk phrase	-	R22	R25	R28

Table A2.1.1: Score ranking for acute toxicity

Score	0 Negligible toxicity	1 Harmful	2 Toxic	3 Very toxic
LC50 (96 h) fish (mg/l)	> 100	10 – 100	1 – 10	< 1
LC50 (48 h) daphnia (mg/l)	> 100	10 – 100	1 – 10	< 1
LC50 (72 h) algae (mg/l)	> 100	10 – 100	1 – 10	< 1
LD50 oral birds (mg/kg)	> 1000	100 – 1000	10 – 100	< 10

Table A2.1.2: Score ranking for eco-toxicity

RfD - reference dose (mg/kg·d)	RfC - reference concentration (mg/m3)	Chronic toxicity	Score
-	-	None	**0**
> 0,1	> 0,35	Low	**1**
0,001 – 0,1	0,0035 – 0,35	Medium	**2**
< 0,001	< 0,0035	High	**3**

Table A2.1.3: Score ranking for chronic toxicity.

CSF - Cancer Slope Factors $(mg/kg \cdot d)^{-1}$	**Carcinogenicity**	**Score**
$> 10^3$	High	**3**
$1 - 10^3$	Medium	**2**
< 1	Low	**1**
-	None	**0**

Table A2.1.4: Score ranking for carcinogenicity.

A2.1.2 – Dispersion and fate

Score	**1**	**2**	**3**
Molecular weight (kg/kmol)	> 300	100 – 300	< 100
Henry's law constant $(atm \cdot m^3/mol)$	$< 10^{-6}$	$10^{-6} - 10^{-2}$	$> 10^{-2}$
Boiling point (°C)	> 150	50 – 150	< 50
Water Solubility (mg/l)	< 1	$1 - 10^3$	$> 10^3$

Table A2.1.5: Score ranking for dispersion and fate parameters.

A2.1.3 – Uptake by organisms

Octanol-water partition coefficient	**Bio-accumulation potential**	**Score**
$4.3 < \text{Log } K_{ow} < 8.0$	Alto	**3**
$3.5 < \text{Log } K_{ow} < 4.3$	Moderato	**2**
$\text{Log } K_{ow} < 3.5$	Basso	**1**

Table A2.1.6: Score ranking for bio-accumulation factor.

A2.1.4 – Persistence

Overall persistence time (h)	**Score**
> 1000	**3**
100 - 1000	**2**
< 100	**1**

Table A2.1.7: Score ranking for persistence.

Appendix 2.2 – Escalation vectors in domino scenarios

A2.2.1 – Overview

In this Appendix the accidental scenarios that can result in domino escalation are discussed. According to the main text, the scenario will be classified on the basis of the escalation vector (i.e. the physical effects causing the propagation) as in Table 2.4.1. The possible inherent strategies to reduce domino will be discussed, starting from the definition of the escalation vector and of the escalation radii of each accidental scenario. The assessment of the intensity of the escalation vector yields, as discussed in §2.4.2, the definition of inherent safety distances and of critical inventories. In the following discussion, the rule of thumbs developed for the quantification of reference values for these parameters are presented. Finally the developed rules for the assessment of the Domino Hazard Scores (DHS) required for the calculation of the Domino Hazard Index (DHI, §2.4.2.3) are presented.

A2.2.2 – Escalation scenarios caused by fire

In the chemical and process industry, fires are the more frequent accidental event. It is well known that escalation may be caused by fire scenarios due to:

i) damage of the secondary unit caused by radiation;
ii) ignition of flammable vapours at the secondary unit due to direct flame impingement or to the heat of the primary fire.

Consequently, relevant efforts are usually addressed to the reduction of fire hazards, mainly by avoiding the presence of ignition sources and installing mitigation devices. A number of well-known active and passive systems for fire prevention are typically installed in process plants. The strategies and the details of fire prevention and fire fighting measures are widely discussed in the literature (e.g. see *[Lees, 1996; NFPA, 2003; Nolan, 1996]* and references cited therein) and are not reported here for the sake of brevity. However, it is important to remark that several alternative actions may be considered in order to apply an inherent safety approach to the prevention of escalation events caused by fires. The more effective are related to the *substitution*, *intensification* and *moderation* guidewords: using non flammable substances, reducing stored quantities, and shifting to less hazardous storage conditions (in general, lower pressure and lower temperature) are well known measures aimed to the reduction of fire hazard. If these are not applicable or, more frequently, if after the application of these measures an escalation vector is still present, inherent safety may be obtained by *limitation of effects*. The limitation of the effects of the escalation vector should be related to the vulnerability of the possible target equipment. This principle suggests two categories of actions: i) the proper design of the possible targets of escalation events (e.g. buried or mounded tanks are not exposed to external fire radiation), and ii) the adoption of appropriate safety distances. A specific study dedicated to the analysis of the behaviour and to the assessment of the time to failure of atmospheric and pressurized vessels exposed to fires *[Cozzani et al. 2005, 2006; Salzano et al., 2003]* evidenced that safety distances are strongly dependent on target vulnerability and on the primary fire scenario. Nevertheless, conservative envelope correlations were obtained for the time to failure of different categories of unprotected vessels with respect to the radiation intensity and the radiation mode.

In these cases, the escalation distance is dependent on the fire intensity, that may be related to the type of fire scenario, to geometrical parameters (release diameter, pool radius, etc.), and to the inventory involved in the fire. The latter is in turn related to the equipment item at which the fire takes place and to the fire prevention measures introduced in equipment design. The estimation of fire intensity starting from the previous parameters is a standard procedure in the consequence assessment of fire scenarios within conventional QRA studies *[Uijt de Haag & Ale, 1999]*. Thus, the intensity of the escalation vector of each fire scenario may be calculated estimating the distance at which the radiation thresholds reported in Table 2.4.1 are obtained. Inherent safety may be achieved reducing the escalation distance and/or limiting the possible escalation effects of fires.

The primary fire scenario is therefore the key element both in the evaluation of the escalation vector and in the assessment of the safety distances for limitation of effects. Thus, the inherent safety actions applicable to the fire scenarios listed in Table 2.4.1 will be separately discussed in the following.

A2.2.2.1 – Fireballs

A fireball is a diffusive combustion of a gas cloud originated by the sudden release of relevant amounts of pressurized and/or liquefied gases, followed by ignition. Several models are available for the calculation of the maximum flame diameter, of the duration of the fire and of radiation intensities *[CCPS, 1994; Van Den Bosh & Weterings, 1997]*. The fireball diameter and duration mainly depend on the mass released after the vessel rupture, which is usually (and conservatively) assumed to be equal to the whole vessel content.

The fireball duration is usually limited (in general of the order of 5 s to 20 s), and this should be taken into account in order to define the possibility of escalation. However, it must be recalled that the limited duration of the fireball scenario excludes the possibility of active protection systems in the prevention of escalation.

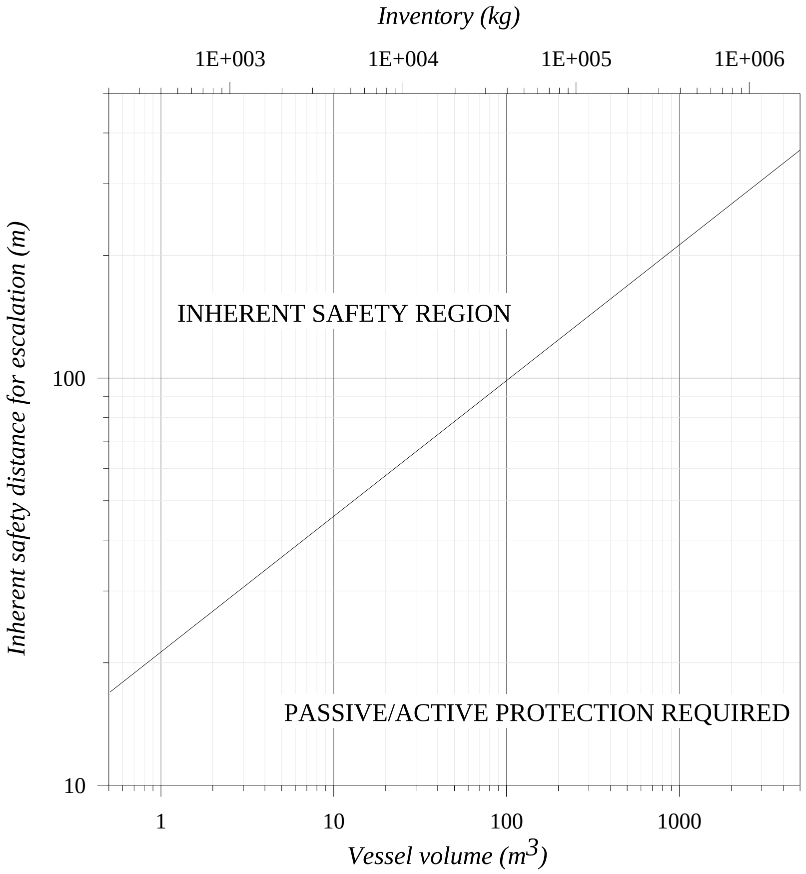


Figure A2.2.1: Escalation distance for fireballs with respect to inventory (= mass released) and volume of propane vessel, fill level = 80%.

It is well known that the fireball scenario is typical of flammable liquefied pressurized gases, although it is also possible for any flammable pressurized gases. Thus, an inherently safer condition with respect to escalation would be obtained by eliminating this scenario, by changing operating conditions (e.g. introducing low pressure cryogenic storage), or by reducing the escalation distance by limiting vessel inventory.

The results of a study concerning the behaviour of unprotected atmospheric and pressurized vessels exposed to fireball radiation evidenced that the possibility of escalation due to radiation may be reasonably excluded for pressurized vessels, even in the absence of passive protections *[Cozzani et al., 2005, 2006]*. With respect to atmospheric equipment, escalation resulted as well unlikely, unless a direct engulfment in the flame takes place.

Figure A2.2.1 reports the escalation distance with respect to inventory and mass released from a pressurized vessel containing propane. The plot was obtained using the simple approach recommended by CCPS *[CCPS, 1994]* for fireball radius calculation. In Figure A2.2.1, the separation distances necessary to prevent escalation involving atmospheric equipment are given. Indeed, the upper region is the inherently safer zone, where escalation may reasonably be excluded. On the other hand, the lower region corresponds to the zone where passive protection measures may be required to prevent escalation due to fireball radiation. The figure also evidences the influence of actions towards process *intensification* (thus leading to lower process inventories) on safety distances.

A2.2.2.2 – Jet fires

A jet fire is a turbulent flame that may have a relevant length in the direction of the release. It is well known that escalation is always possible when any fire engulfs or impinges target equipment. Indeed, recent experimental studies confirmed that even in the presence of active mitigation systems (e.g. water deluges) and passive protections (e.g. thermal insulation), hot spots may cause the failure of vessels exposed to jet fires *[Roberts, 2004a,b; Shirvill, 2004]*. As a consequence, the escalation distance depends mainly on the maximum flame length, i.e. the maximum distance from the flame source at which the damage of the more vulnerable category of unprotected vessels results credible. As shown in Figure 2.4.2, the escalation vector may be obtained adding a constant distance to the jet flame length, below which the radiation intensities are unlikely to cause an escalation due to vessel damage. Horizontal directions of the flame should be conservatively assumed.

Figures A2.2.2 to A2.2.4 may be used for a preliminary conservative assessment of flame length for the three more common types of jet fires that are likely to take place in industrial installations: i) jet fires from compressed flammable gases at high pressure and ambient temperature; ii) jet fires from liquefied gases at ambient temperature (e.g. propane and butane in storage conditions); and iii) jet fires from hot saturated liquids (e.g. butane or higher molecular weight hydrocarbons in process conditions, as in distillation columns or in pressurized batch reactors). The plots were obtained applying the Shell jet fire model *[Chamberlain, 1987]*, extensively described in the TNO “yellow book” and by Lees *[Lees, 1996; Van Den Bosh & Weterings, 1997]*. The model was applied to different hydrocarbons and considering different wind velocities, selecting the worst case results.

An inherently safer condition with respect to escalation may be obtained eliminating or reducing the escalation distance, and/or limiting the possible effects of the event. Pressure is the main operating variable that influences the flame length and thus the escalation possibility of a jet fire. As shown in Figures A.2.2.2 to A.2.2.4, the flame length is highly dependent on the internal pressure. Temperature may also be an important factor in the case of saturated liquids, since it influences the vapour pressure and thus the severity of the jet fire. However, if the application of the *moderation* guideword to these process variables is not possible or not sufficient to eliminate the hazard, the *limitation of effects* guideword may lead to an effective reduction of the escalation hazard.

Escalation due to jet fire heat radiation only (i.e. target equipment is not directly impinged) is dependent both on radiative heat load and on the duration of the flame exposure. Several criteria were proposed to identify critical heat radiation values for jet fires. In a recent study, the minimum heat loads leading to vessel failure in a critical time (15 minutes) were estimated for several vessel categories *[Cozzani et al., 2005, 2006]*. Figures A.2.2.2-(b), A.2.2.3-(b), and A.2.2.4-(b) report the value of the inventory of the primary vessel above which the jet fire duration is at least equal to the critical time assumed for secondary vessel failure. Thus, the plots in Figures A.2.2.2 to A.2.2.4 allow on one hand the identification of the range of release diameters that may lead to escalation given the inventory of the primary vessel and the distance of the secondary target. On the other hand, given the maximum credible release equivalent diameter, the data reported allow the identification of the safety distances for the

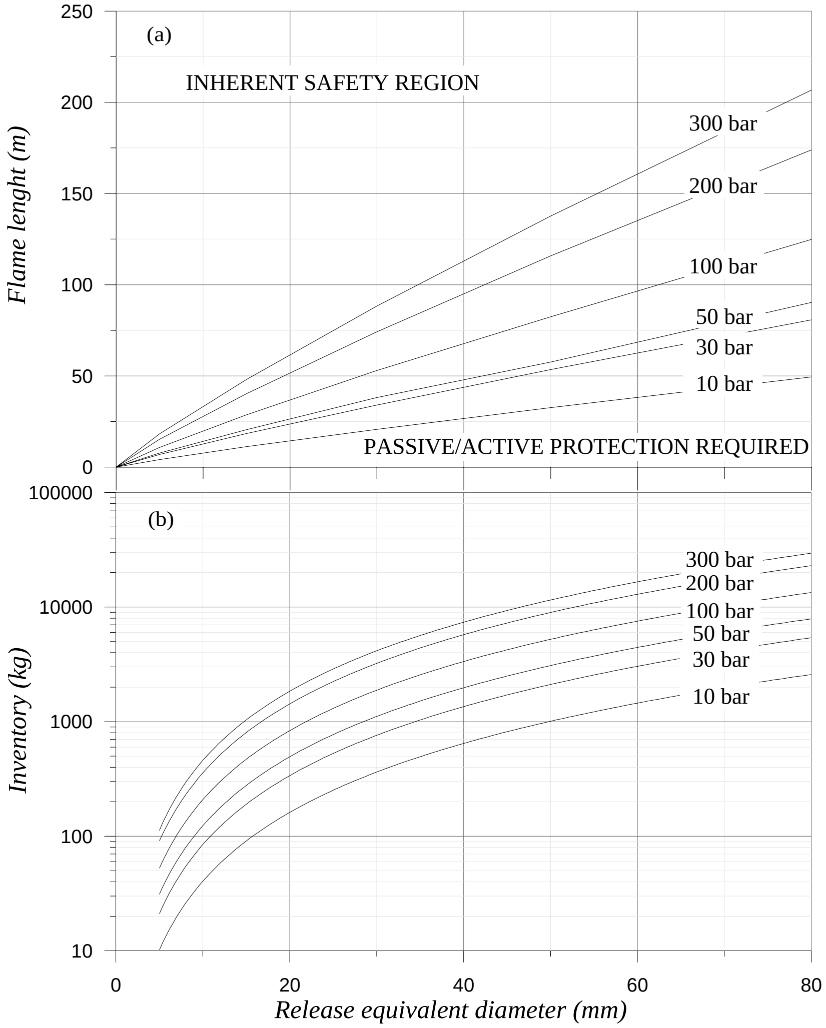


Figure A2.2.2: Jet-fire flame length **(a)** and critical vessel inventory for a 15 minutes release **(b)** with respect to the equivalent release diameter for hydrocarbon gases at ambient temperature and high pressure. To obtain safety distances, 50 m for atmospheric vessels and 25 m for pressurized vessels should be added to the flame length.

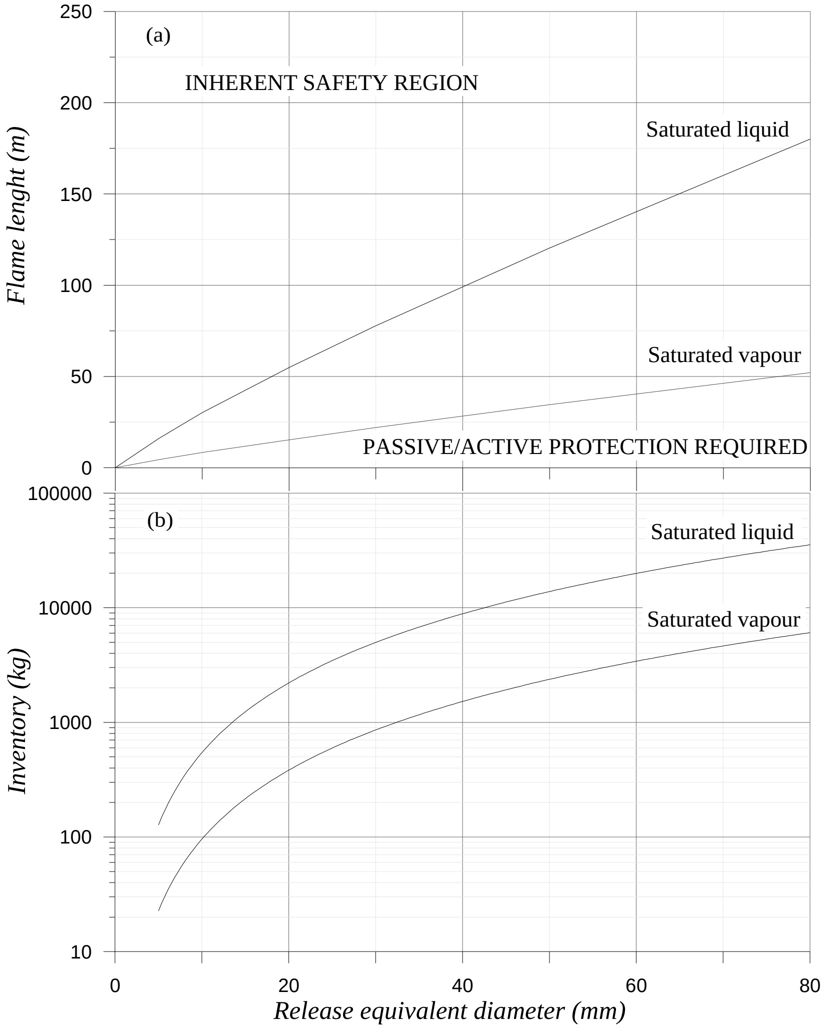


Figure A2.2.3: Jet-fire flame length **(a)** and critical vessel inventory for a 15 minutes release **(b)** with respect to the equivalent release diameter for propane releases at ambient temperature. To obtain safety distances, 50 m for atmospheric vessels and 25 m for pressurized vessels should be added to the flame length.

limitation of effects with respect to different categories of secondary vessels (Figures A.2.2.2-(a), A.2.2.3-(a) and A.2.2.4-(a)), and the critical inventory of the primary vessel, above which the duration of the jet fire may be sufficient to cause the failure of the secondary target (Figures A.2.2.2-(b), A.2.2.3-(b), A.2.2.4-(b)).

Thus, the upper sections of Figures A.2.2.2-(a), A.2.2.3-(a) and A.2.2.4-(a) identify the inherently safe regions of secondary targets with respect to escalation caused by jet fires: escalation involving a secondary target falling in this region may be considered unlikely. On the other hand, the lower region of the figures identifies the region where passive and active protection systems are required. Targets having a distance from the primary event that falls inside this region are not inherently safe, and require the installation of protections to prevent domino accidents, in particular in existing plants. Similarly, Figures A.2.2.2-(b), A.2.2.3-(b), and A.2.2.4-(b) point out that an inherently safer region may be identified for vessel inventory with respect to the possibility of generating primary jet fires resulting in escalation.

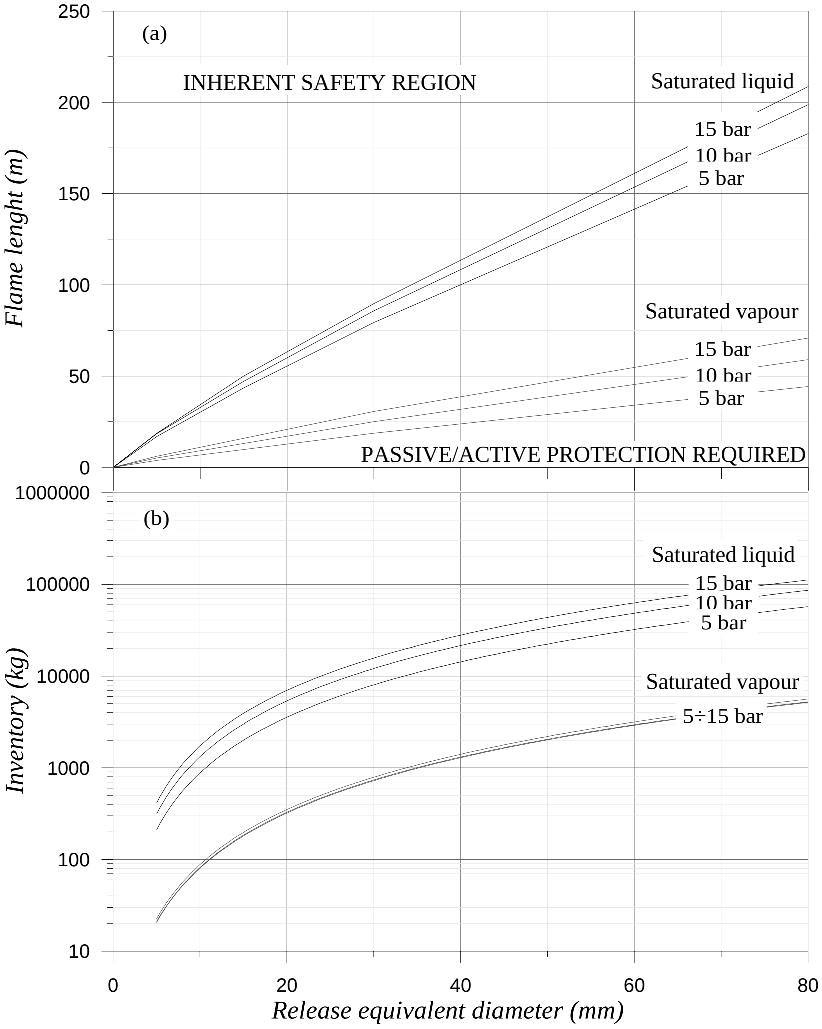


Figure A2.2.4: Jet-fire flame length **(a)** and critical vessel inventory for a 15 minutes release **(b)** with respect to the equivalent release diameter for hot saturated hydrocarbons at high temperature and pressure. To obtain safety distances, 50 m for atmospheric vessels and 25 m for pressurized vessels should be added to the flame length.

Finally, it must be recalled that the safety distances obtained from the data in Figures A.2.2.2 to A.2.2.4 and in Figure 2.4.2 refer to unprotected vessels, thus may be considered as conservative values. The use of active (fire sprinklers, water curtains) and, preferably, of passive (thermal insulation, fire walls) protection systems may greatly improve the resistance of the secondary targets, thus lowering the probability of escalation.

A2.2.2.3 –Pool fires

A pool fire is formed by the combustion of the vapour from a pool of a flammable liquid *[CCPS, 2000; Van Den Bosh & Weterings, 1997]*. Escalation caused by pool fires is mainly due to the full engulfment of a vessel in the flames, although the stationary radiation caused by the fire may as well cause the failure of a secondary vessel. Therefore, the escalation distance depends on the area of the pool fire and on the distance from the border of the pool fire. As in the case of jet-fires, the escalation distance was assumed as the maximum distance from the flame at which the damage of the more vulnerable category of unprotected vessels (atmospheric storage tanks) is credible. The parameters that mainly influence the escalation distance are two: i) the surface emissive power of the flame, that in turn depends by the characteristics of the flammable substance that forms the pool, and ii) the pool dimension or equivalent diameter. Pool fires in fixed installations are most likely to take place inside the catch basin of the primary vessel at which a loss of containment takes place. Thus, in the case of severe pool fires, the pool extension may be often coincident with that of the catch basin, if present. In the case of unconfined pool fires, the maximum pool diameter should be considered. A number of literature models are available for the calculation of pool fire radiation and of pool fire radius (e.g. see *[CCPS, 1994; Lees 1996; Van Den Bosh & Weterings, 1997]* and references cited therein), and may be used for the assessment of the escalation distance. The results reported in the present study were obtained using the models reported in the TNO "yellow book" *[Van Den Bosh & Weterings, 1997]*. As shown in Figure 2.4.2, the escalation distance may be estimated as the maximum radius of the liquid pool added of a constant distance over which the radiation intensity falls below the threshold values discussed above.

Inherently safer conditions with respect to escalation are obtained also in this case eliminating the escalation vector or reducing the escalation distance, and/or limiting the possible effects of the event. Also in this case, provided that the substitution guideword is not applicable, the *moderation* guideword applied to temperature and pressure would be effective at least in the reduction of the ignition probability. However, quite often the liquid forming a pool fire is above the flash point even at ambient conditions. Thus, the *limitation of effects* guideword seems to identify the only effective actions that may lead to the reduction of the escalation hazard.

As for jet-fires, escalation possibility depends on the radiation intensity and on the fire duration. Figure 2.4.2 shows the safety distances from flame border for pool fire damage of atmospheric and pressurized vessels derived from a previous study [*Cozzani et al., 2005, 2006]*. In the case of pool fires, the safety distances may be expressed as the distance from the pool border. The presence and a proper design of the catch basins are thus important elements towards inherent safety. Individual catch basins having a high height/surface ratio lead to an inherently safer layout with respect to escalation. This is evidenced in Figure A2.2.5, where the critical inventory for escalation is reported.

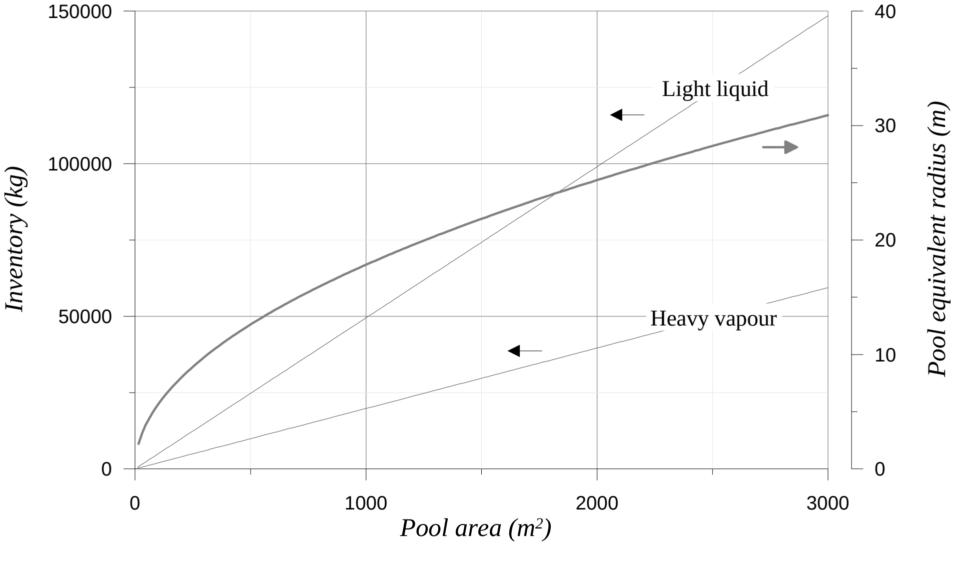


Figure A2.2.5: Critical inventory (black lines) for pool fire scenarios with respect to catch basin surface area. Grey line relates pool area with an equivalent radius. To obtain safety distances, 50 m for atmospheric vessels and 15 m for pressurized vessels should be added to catch basin equivalent radius.

The figure shows the inventory involved in the pool fire required to obtain a pool fire duration equal to the critical time for escalation (15 minutes) as a function of the pool surface and of the burning rate of the liquid. The critical inventory was calculated on the basis of literature data for the burning rate [*Van Den Bosh & Weterings, 1997]*, assuming a constant area of the pool.

The plot shows conservative results for two categories of flammable liquids: "heavy liquids", having a burning rate lower than 0.055 kg/m^{2}s (e.g. kerosene, fuel oil, etc.), and "light liquids", having a burning rate higher than 0.055 kg/m^{2}s (e.g. gasoline, n-heptane, etc.). Pool fires involving liquefied gases are characterized by higher burning rates (typically higher than 0,078 kg/m^{2}s), thus the results obtained for "light" liquids are sufficiently conservative to be extended also to these compounds.

As in the case of jet fires, also in Figure A2.2.5 the section below the solid lines may be considered an inherently safer region for the inventory of the primary vessel as a function of separation distances. On the other hand, the upper region of the plot is that where passive or active protection of possible targets is required. Thus, in particular in the case of existing plants, the installation of passive (e.g. thermal insulation, fire walls) or active systems (e.g. sprinklers, fire curtains) are required to protect the possible target vessels that fall in these zones with respect to primary pool fire scenarios.

A2.2.3 – Escalation scenarios caused by overpressure

It is well known that escalation may be triggered by pressure waves as a consequence of the damage of secondary vessels containing hazardous substances. The interaction of pressure waves with process equipment is rather complex, involving pressure wave reflection, flow separation, drag forces, and being influenced by the mechanical characteristic of equipment. However, in industrial explosions (thus excluding the explosions due to condensed high explosives or nuclear weapons), damages to equipment in the far-field are mainly related to the incident peak overpressure and to the positive impulse, while the effects of the drag forces (the explosion wind) may be neglected. Furthermore, many literature approaches relate the damage intensity to the maximum peak static overpressure only *[Baker et al., 1983; Cozzani et al., 2005, 2006]*. As a matter of fact, pressure-impulse data related to equipment damage are lacking and theoretical difficulties arise in the description of the interaction unless ideal and unrealistic blast waves are considered. Thus, a conservative assumption often used in the design criteria is to assume that the equipment damage is mainly related to the peak overpressure. Following this approach, the escalation vector due to overpressure is related to overpressure thresholds above which the damage of the more vulnerable equipment items may be expected. Figure 2.4.3 shows the threshold values derived from a previous study *[Cozzani et al., 2005, 2006]* for different overpressure scenarios. Blast waves from confined explosions, i.e. gas, vapour and dust explosions or runaway reactions within equipment, producing blast wave propagating in the external atmosphere through vents and openings (even formed for the partial failure of shell) were not included in the discussion due to low distances run by low-energy blast waves (see Forcier and Zalosh analysis *[Forcier & Zalosh, 2000]* and *[Cozzani et al., 2006]* for further details) and considering the usually associated damages due to fragment projection and jet fires.

The escalation distance for each overpressure scenario may be calculated estimating the distance at which the specific threshold reported in Figure 2.4.3 is obtained by the use of standard literature models *[CCPS, 1994; Uijt de Haag & Ale 1999; Van Den Bosh & Weterings, 1997]*. Inherent safety may be obtained reducing the escalation distance and limiting the possible escalation effects that may be triggered by the blast wave.

A number of active safety devices (alarms, safety interlock system, automatic remote safety valves, water curtains, foam sprinklers) and passive systems (pressure release valves, vents, etc.) are used to prevent the different explosion scenarios possible in the process industry (e.g. see *[Baker et al., 1983; Lees 1996; Nolan, 1996]* and references cited therein). An inherent approach may however suggest several possible actions, related to the *substitution, intensification* and *moderation* guidewords: using non-flammable or non-volatile substances, reducing stored quantities, and shifting to less hazardous operating conditions (in general, lower pressure and lower temperature that may limit the explosion energy and/or the amount of substance forming a vapour cloud). As in the case of fires, if after possible actions compatible with the process under examination an escalation vector is still present, the *limitation of effects* guideword may suggest further actions leading to an inherently safer plant lay-out with respect to escalation. However, the features of the primary scenario generating the blast wave are of fundamental importance in the identification of the more effective actions. These will be thus separately discussed in the following for the explosion scenarios listed in Figure 2.4.3.

A2.2.3.1 - Vapour Cloud Explosion (VCE)

When partially confined or unconfined gas or vapour cloud explosions (VCE) occur as a primary scenario, large destruction is usually expected in the surroundings due to the heat effects and the blast wave which characterize this scenario. Provided that heat radiation is unlikely to produce damage to equipment, escalation effects are usually caused by the mechanical damage followed by loss of containment of target equipment. The escalation distance is thus related to the distance at which the blast wave peak overpressure equals the threshold value in Figure 2.4.3. This may be calculated by the standard approach used in QRA *[CCPS, 1994; Uijt de Haag & Ale, 1999]*, estimating the explosion energy and evaluating the “strength” of explosion on the basis of plant lay-out and fuel reactivity, i.e. the “strength factor F” for the Multi-Energy method (MEM, see *[Eggen, 1998; Van den Berg, 1985]*), or the flame Mach number, M_f, in the Baker-Sthrelow methodology (BS, see *[Tang & Baker, 1999]* for details).

Figure A2.2.6 shows the escalation distance with respect to the estimated explosion energy, and the correspondent fuel air mass and volume, for two categories of target equipment (atmospheric vessels and pressurised equipment). The escalation distance was defined as the threshold distance with respect to the fuel-air cloud border at which damage is expected for the category of process equipment more likely to trigger escalation events (pressurised vessels). The plot was obtained using the threshold values for escalation given in Figure 2.4.3, starting from the following assumptions: i) the cloud was considered hemispherical (release at ground level), homogeneous and at stoichiometric concentration; ii) a mean combustion energy typical of air/hydrocarbon mixtures was assumed (3.6 MJ/m^3 of mixture); and iii) the strength factor and the flame Mach number for the VCE were assumed as for intense deflagration ($F > 7$ and $M_f > 3.5$). The latter assumption is justified comparing the energy-scaled plots for the propagation of blast waves in the region where escalation effects are of concern: either by the MEM or by the BS approaches, no differences may be observed for more intense explosion (i.e. the peak pressures are superimposed whatever is the initial pressure). The mass-volume-energy conversion was obtained considering the total combustion of fuel to water and carbon dioxide.

Quite obviously, several actions may be identified to improve inherent safety by the minimization of the escalation distance. This may be obtained decreasing the explosion energy and the explosion strength. Explosion energy may be reduced by the *substitution* of process substances with less volatile compounds or by the *moderation* of operating conditions (e.g. using lower pressure and temperature), thus minimizing the total fuel available for the explosion. On the other hand, the explosion strength may be reduced again by the *substitution* of substances with less reactive compounds, e.g. gases or vapours with minor specific combustion energy, and/or minor laminar burning velocity. However, also the *limitation of effects* may also be effective in reducing the explosion strength, by a proper lay-out design, aimed to the reduction of the geometrical congestion and confinement, which strongly affect the violence of explosions.

If an escalation vector is still present after the application of the above discussed actions that resulted compatible with the process under examination, the *limitation of effects* guideword indicates the necessity of adopting appropriate safety distances in lay-out design. As in the case of fires, in Figure A2.2.6 the section above the solid lines may be considered as the zone of inherent safety separation distances with respect to the flammable cloud border. On the other hand, the lower region is that where passive protections, as barricades and/or blast wall, should be considered for application.

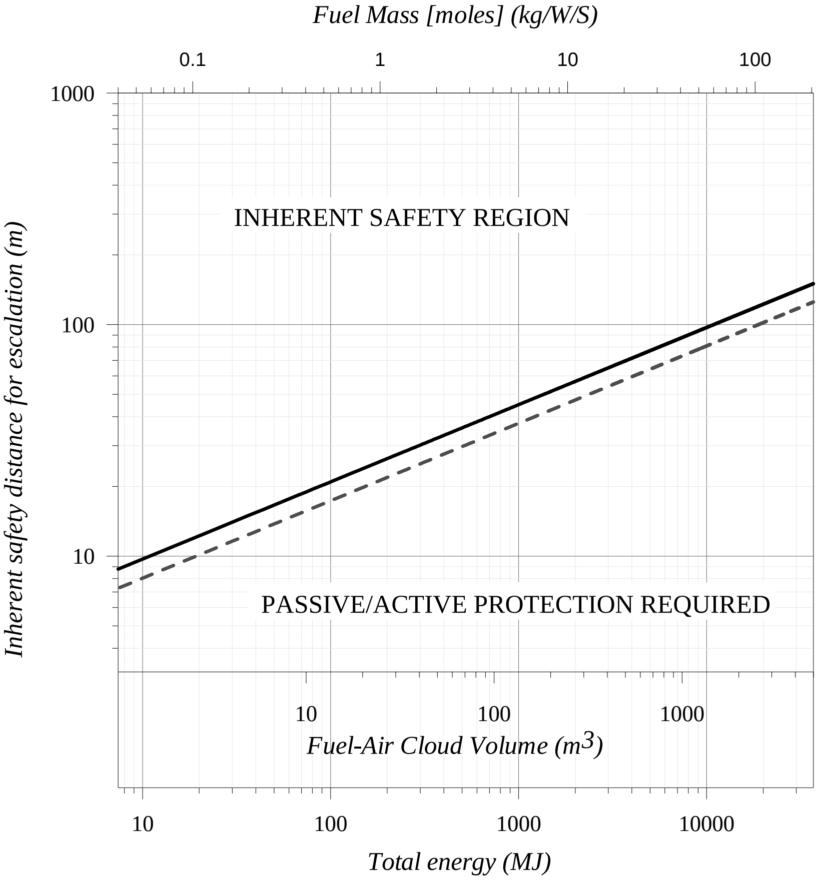


Figure A2.2.6: Escalation distance and inherent safety distances for escalation effects on equipment loaded by VCEs generated by the more common hydrocarbons. (W = molecular weight; S = stoichiometric concentration expressed in volume percent of fuel air mixture combustion). Distances should be calculated from the flammable cloud border. For more reactive fuels a factor 1.2 should be used to correct energy values based on cloud volume. Target vessel: i) Solid line: pressurised; ii) Dashed line: atmospheric.

A2.2.3.2 - Boiling Liquid Expanding Vapour Explosion (BLEVE)

The catastrophic failure of a vessel containing a pressurized liquefied gas, due to the external heating of vessel wall or to other causes of overpressure, may result in a sudden evaporation of the vessel content and in the formation of a blast wave. The conditions necessary for the blast wave formation, usually related to a superheat temperature, as well as the procedure for the evaluation of the explosion energy are widely discussed in the literature *[CCPS, 1994; Salzano et al., 2003]*. In the present section, escalation effects triggered by the blast wave originated from the sudden expansion of the vessel content are only considered.
As for Vapour Cloud Explosion, the escalation distance may be defined as the distance from the explosion centre at which damage is expected for pressurised equipment and vessels (see Figure 2.4.2). A preliminary estimate of the escalation distance may be obtained from Figure A2.2.7, which reports the inherent safety radii for either atmospheric or pressurised target equipment vessels with respect to the explosion energy, starting from the explosion of typical propane vessel with failure pressure of 20 bar, and 80% filling level, as conservative choice.

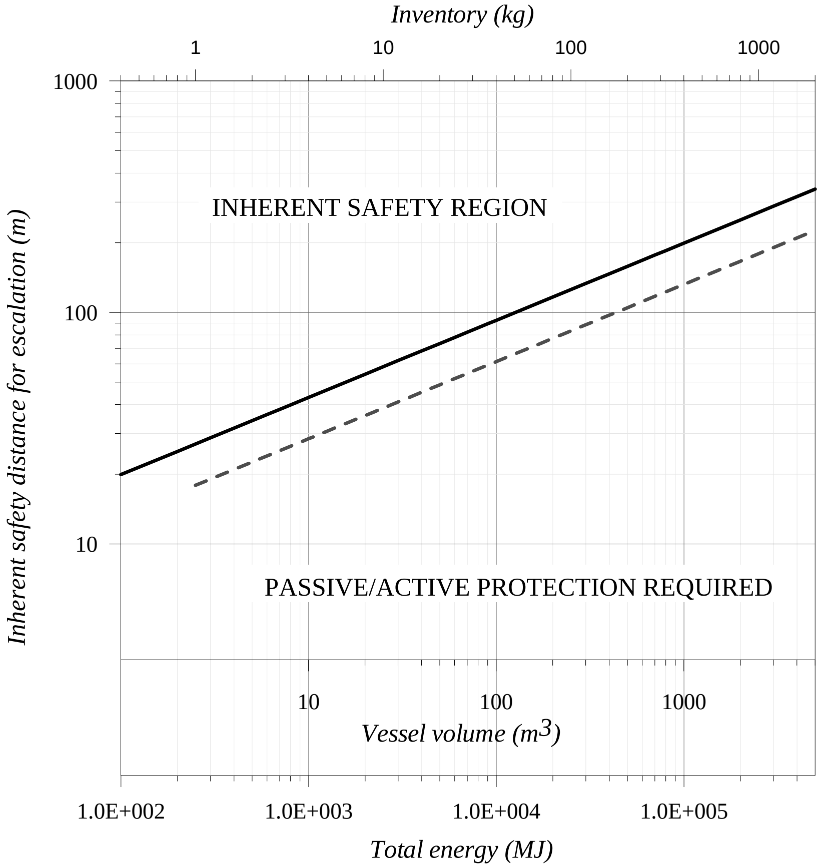


Figure A2.2.7: Escalation distance and inherent safety distances for escalation caused by blast wave produced by BLEVE with respect to the total explosion energy and to the corresponding volume and mass of a propane vessel having an 80% filling level. Distances must be calculated from the vessel border. Target equipment/vessel: i) Solid line: pressurised; ii) Dashed line: atmospheric.

The explosion effects have been calculated from the assumption that the expanding boiling liquid is at the superheat temperature (about 237 K for pure propane) at the moment of failure of vessel shell. Keeping constant the filling level and the initial and final thermodynamic states (corresponding to the expansion from 20 bar to the atmospheric pressure), the correlation of the escalation distance with respect to vessel volume and inventory is also obtained, as the boiling liquid and the vapour specific energies can be scaled to any amount or vessel volume. Eventually, as the pressure threshold values for target equipment and the total available energy for the explosion of both expanding liquid and vapour are known, the effective safety distances are easily obtained (see the methodology given in *[CCPS, 1994]*, where specific energy-scaled plot for the evaluation of peak overpressure are also given). To this regard, it’s worth considering that the results obtained for propane are conservative with respect to butane and LPG, as detailed in *[Salzano et al., 2003]*.

Several actions may be considered in order to eliminate or reduce the escalation distance. The *intensification* and *moderation* guidewords suggest to reduce the vessel volume or to shift to less hazardous storage conditions (e.g. use of lower storage pressure and temperature). If these actions are not applicable to the process of interest, inherent safety may be obtained by the *limitation of effects* guideword. The analysis of Figure A2.2.7 evidences that also in this case the upper region of the plot identifies the zone of inherent safety, where no damage to secondary equipment is expected to be caused by the blast wave. The lower zone of the plot is the region where protection measures are required. As in the case of VCE, the more effective protections are blast walls or barricades, or vessel mounding. However, since the BLEVE is likely to take place after a few minutes of heat loading, active systems as vessel dumping may be effective in the prevention of escalation following the damage of secondary equipment.

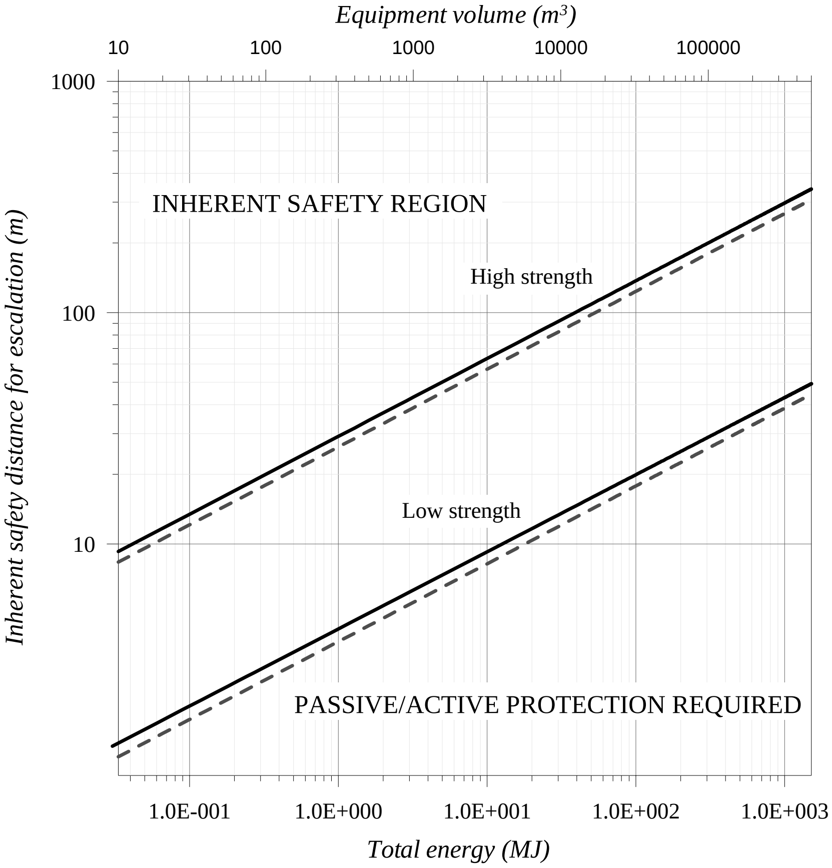


Figure A2.2.8: Escalation distance and inherent safety distances for escalation caused by mechanical explosion of high strength and low strength equipment/enclosure with respect to total explosion energy. Distances must be calculated from the vessel border. Target vessel: i) Solid line: pressurised; ii) Dashed line: atmospheric.

A2.2.3.3 - Mechanical Explosion

Mechanical failure of an equipment item, followed by the sudden expansion of the compressed gas phase may result in the generation of a blast wave, which may trigger escalation events. The explosion energy may be estimated by standard literature approaches on the basis of vessel volume and of conservative assumptions for energy calculation, e.g. by using the Brode equation *[CCPS, 1994; Lees 1996]*. In particular, following conventional approaches, two categories may be introduced for vessel failure pressure *[NFPA 68, 2002; NFPA 69; 1997]*: low strength equipment behaviour (failure pressure of 0.03 bar g) and high strength equipment behaviour (failure pressure higher than 1 bar g). Also in this case, the escalation vector may be defined as the distance from the explosion centre at which damage is expected for the more vulnerable target category (see Figure 2.4.2). This is plotted in Figure A2.2.8 with respect to the total explosion energy. The escalation distance may be reduced following the *moderation* guideword, thus considering the adoption of lower operating pressures. Figure A2.2.8 also reports the inherent safety threshold distances for pressurized and atmospheric equipment, whose application is suggested by the *limitation of effects* guideword. Also in this case, the lower region of the plot identifies the zone where passive protection systems, as blast walls or barricades, are required to prevent escalation.

A2.2.4 – Escalation scenario caused by fragments

Fragment projection is among the more frequent causes of domino effect in industrial accidents. The primary scenarios that are likely to generate this escalation vector are BLEVEs, mechanical and more generally confined explosions. The escalation distance may be defined as the maximum fragment projection distance for the primary scenario of interest. Several approaches were proposed in the literature for the assessment of fragment projection distances and of damage to process equipment following fragment impact *[Baker et al., 1983; Baum, 1984; Gubinelli et al., 2004]*. In all these approaches, the fragment projection distances are dependent on the initial explosion energy. In many scenarios involving the burst of pressurized vessel, the projection distances may be higher than 500 m. This is in accordance with the experience from past accidents, in which fragment projection up to 800 m was reported *[Holden & Reeves, 1985; Westin, 1971]*. Therefore, in the framework of the identification of actions towards inherent safety with respect to escalation events caused by fragment projection, the *limitation of effects* guideword has a limited utility.

As discussed above, no safety distance of practical use in lay-out design may be identified for fragment projection on a deterministic basis. Actions towards inherent safety should be oriented to the elimination of the escalation vector or to the reduction of its intensity. The *substitution*, *intensification* and *moderation* guidewords may lead to the identification of the more appropriate actions. Among these are: the introduction of vessel having lower volumes and the use of lower operating pressures, that contribute to the reduction of the available explosion energy; the substitution of vessel technology (e.g. the shift from fixed roof to floating roof tanks), that may reduce the possibility of confined explosions leading to fragment projection). However, in most applications, the above listed actions towards inherent safety are effective in the reduction of the escalation distance, but often not sufficient for the complete elimination of the possibility of fragment projection. Thus, conventional actions based on passive protection either of the primary vessel (venting devices, thermal insulation) or of the critical targets (blast walls, mounding, etc.) should be also applied to prevent the escalation due to the projection of fragments.

A2.2.4 – Assessment of Domino Hazard Scores

The assessment of Domino Hazard Scores ($DHS_{i,k,h}$) of each single primary accidental scenario is required in the calculation of Domino Hazard Index (DHI, §2.4.2.3). $DHS_{i,k,h}$ is a ranking that represents the score given to the hazard in terms of an escalation from unit 'i' to unit 'k' by event 'h'. The maximum value for DHS is 10, meaning that escalation is highly probable; the minimum value, 0, represents the inherently 'safest' level for domino escalation (i.e. elimination of the escalation hazard). The value of $DHS_{i,k,h}$ for each possible event is derived by comparison of the physical effect distances associated with that particular event to the actual distance between units on the layout plan.

The rules for assigning values for Domino Hazard Scores ($DHS_{i,k,h}$) of each single primary accidental scenario are presented in the following according to the classification of escalation vectors given in Figure 2.4.1 and used in the previous discussion of escalation scenarios. Table 2.4.6 reports a summary of these scoring rules.

A2.2.4.1 - Flame Impingement/Heat Radiation

Fire could cause escalation due to equipment overheating (by direct flame impingement or by far-field heat radiation effects from the flame surface), or due to direct ignition of flammable vapors. Different fire scenarios therefore need to be analyzed in detail, as each scenario would have different flame properties and heat loads – thus influencing the escalation mechanism.

A2.2.4.1.1 - Short duration scenarios

In short duration scenarios (i.e. flash fire and the thermal effects associated with vapor cloud explosions, VCEs), escalation is likely to occur only by direct ignition of flammable vapors (*[Cozzani et al., 2006, 2007]* and references cited therein). Thus, only secondary units likely to release vapors (e.g. a floating-roof tank) are considered in the analysis. Affected secondary units within a distance ($D_{i,k}$) that can possibly be reached by the flame, receive a score of $DHS_{i,k,h} = 10$; otherwise $DHS_{i,k,h} = 0$. In usual industrial practice, passive measures are not considered to be effective in limiting this mode of escalation.

Fireballs involve high thermal radiation levels in the area occupied by the flames, even if the duration of the event is short. Previous work concerning escalation likelihood has shown that escalation is reasonably possible only for impinged atmospheric vessels, while pressurized vessels are generally unaffected. Moreover, escalation phenomena are unlikely to occur for radiation from a distant source without impingement (*[Cozzani et al., 2005, 2006, 2007]* and references cited therein). The fireball radius (d_f) is the key dimension for evaluation of escalation possibility. Thus, the presence of an atmospheric unit within the fireball area ($D_{i,k} < d_f$) means a score of $DHS_{i,k,h} = 10$; otherwise $DHS_{i,k,h} = 0$.

Fire insulation is a passive measure that is effective in protecting vessels from fireball effects. It should be noted, however, that in general practice fire insulation protects only the lower 10 m of a vessel *[Lees, 1996]*, and fireballs can reach significant heights because of the lift forces involved. Similar considerations apply when protection is provided by fire resistant walls. Nevertheless, if the insulation is complete, some degree of protection is afforded to atmospheric vessels and the appropriate value is $DHS_{i,k,h} = 5$.

A2.2.4.1.2 - Pool fires and jet fires

Escalation scenarios triggered by pool fires or jet fires involve both flame impingement and continuous heat radiation from a distant source. Impinged unprotected vessels are reported to undergo failure in a relatively short time *[Cozzani et al., 2005, 2006]*, and the distances occupied by the flame envelope (d_f) encompass an area where escalation is highly possible ($DHS_{i,k,h}$ = 10). The flame dimension (d_f) can be roughly considered equivalent to the pool radius for a non-tilted pool fire. For jet fires, the worst case of horizontal-axis release directed toward the secondary equipment is considered. Thus, the distance enveloped by flames (d_f) is the sum of the characteristic dimension of the primary unit on the layout plan (i.e. the distance of the leaking boundary from the geometric centre) and the maximum flame length. Diagrams are available for a quick estimation of flame length (§A2.2.2).

Concerning the effects of heat radiation, a correlation can be identified between the distance from the flame boundary and the expected time to failure of exposed units *[Cozzani et al., 2006]*. Elaboration of these data results in the DHS values reported in Figures A2.2.9 and A2.2.10. The distance from the flame envelope, or radiation-impacted distance (d_r), can be calculated as:

$$d_r = D_{i,k} - d_f - d_s \qquad \text{(A2.2.1)}$$

where d_s is the characteristic dimension of the secondary unit on the layout plan (i.e. the distance of the failing unit boundary from the secondary unit geometric centre). $DHS_{i,k,h}$ can be evaluated by entering d_r from Equation (A2.2.1) in the graphs on Figures A2.2.9 and A2.2.10, according to the scenario and the secondary unit characteristics.

Fire insulation is a passive measure that is suitable for protecting equipment from these types of escalation events. In the case of flame impingement, however, even small defects in insulation continuity nullify the protective behavior *[Birk et al., 2006; VanderSteen & Birk, 2003]*. Defects can easily originate from damage or ripping, but also from incorrect operations (e.g. removal for inspection and missed replacement). Thus, even for protected targets, no

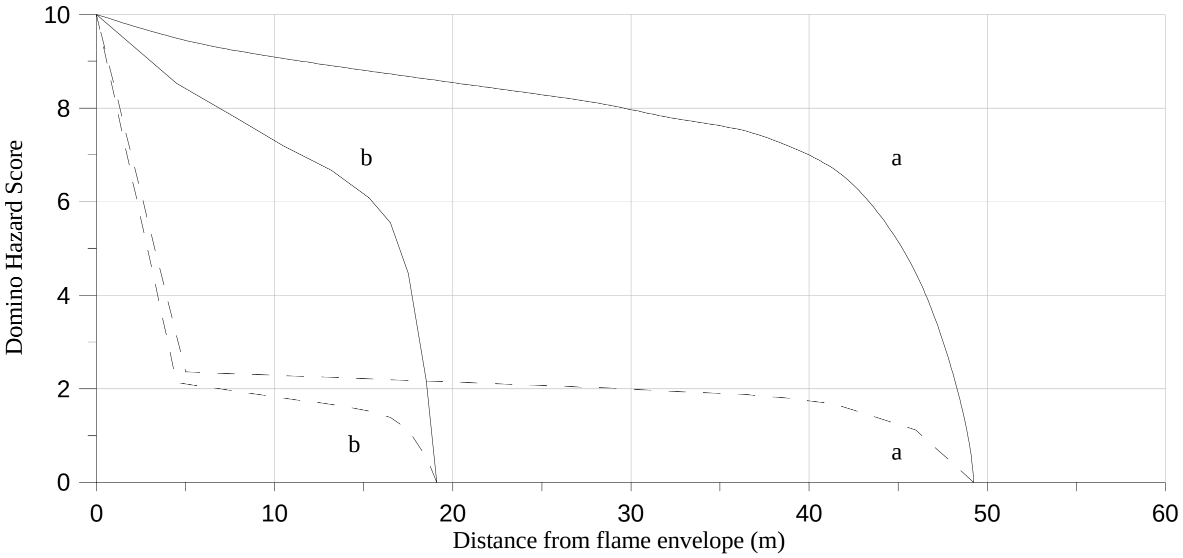


Figure A2.2.9: DHS as a function of the distance from the flame envelope for pool fire scenarios. Solid line: unprotected vessels; dashed line: fire-insulated vessels; atmospheric equipment (a); pressurized equipment (b).

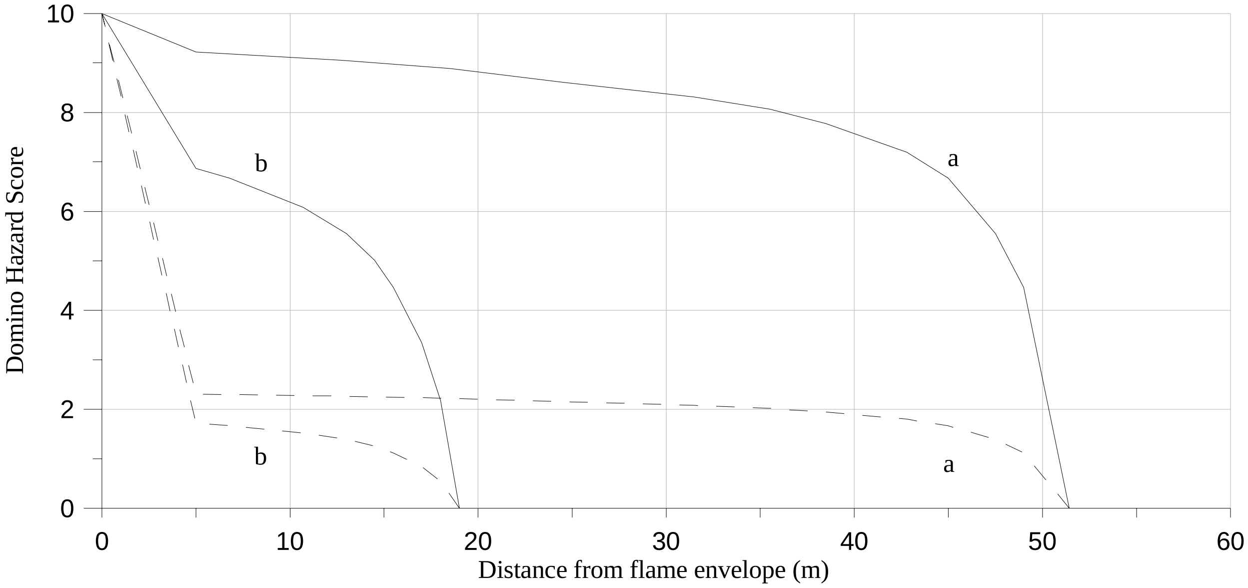


Figure A2.2.10: DHS as a function of the distance from the flame envelope for jet fire scenarios. Solid line: unprotected vessels; dashed line: fire-insulated vessels; atmospheric equipment (a); pressurized equipment (b).

reduction of DHS is accounted for in the case of fire impingement (i.e. $DHS_{i,k,h} = 10$). On the other hand, in the zone of radiation from a distant source, fire insulation is considered to effectively decrease the risk of escalation by heat load and the values of DHS can be derived from Figures A2.2.9 and A2.2.10.

Fire resistant walls provide effective protection from both flame impingement and radiation, and the DHS value is reduced to $DHS_{i,k,h} = 1$ for equipment in the protected area. The hazard is not completely eliminated because passive devices have an intrinsic probability of failure on demand *[AIChE, 2001]*. Mounded equipment is considered in the present analysis to have a protection value equivalent to fire resistant walls.
For pool fires, a bund limits the area subjected to flame engulfment. However, as with any passive protection measure, bunds are not fully reliable and a one-point increase of DHS (a penalty of +1 to the DHS value in the radiation zone) is assigned if units can be reached by flames in the event of bund failure.

A2.2.4.2 - Blast Waves

Blast wave consequences are affected by numerous parameters including the explosion characteristics, blast wave characteristics and reflection phenomena. When far-field interaction between the explosion source and the target equipment is of concern, or when low pressures are considered (static peak overpressure less than 50 kPa), the static peak overpressure can be effectively used to assess the damage caused by the overpressure wave. Hence, it is possible to identify overpressure threshold values for different levels of damage for typical classes of equipment *[Cozzani et al., 2006; Salzano & Cozzani 2006]*. DHS scores have been defined using these thresholds for different magnitudes of loss-of-containment in target vessels, and are reported in Figure A2.2.11. Using a suitable blast wave model (e.g.

Multi-energy or Baker-Strehlow), the static peak overpressure can be related to the distance (d_b) from the explosion source once the energy released by the explosion is estimated. The distance (d_b) is defined as:

$$d_b = D_{i,k} - d_e - d_s \qquad \text{(A2.2.2)}$$

where d_e is the distance of the explosion source from the centre of the primary unit, d_s is the characteristic dimension of the secondary unit (as previously defined), and $D_{i,k}$ is the relative distance between the two units. The distance of the explosion from the primary unit (d_e) can be considered as the geometric position on the layout plan of a failing boundary (e.g. a wall) or a vent in the case of confined explosions, physical explosions and BLEVEs. In the case of VCEs, since weather conditions play a direct role in cloud dispersion, conservative assumptions may be adopted; e.g. considering a hemispheric stoichiometric cloud centered on the unit and assuming the flammable cloud radius to be the explosion source distance (d_e).

Passive measures for limitation of escalation due to overpressure waves mainly consist of barricades such as blast walls or cubicles. These passive devices, within the extent of their feasibility and reliability *[AIChE, 2001]*, are considered effective in limiting overpressures in the desired propagation direction (i.e. $DHS_{i,k,h} = 1$ in the protected zone).

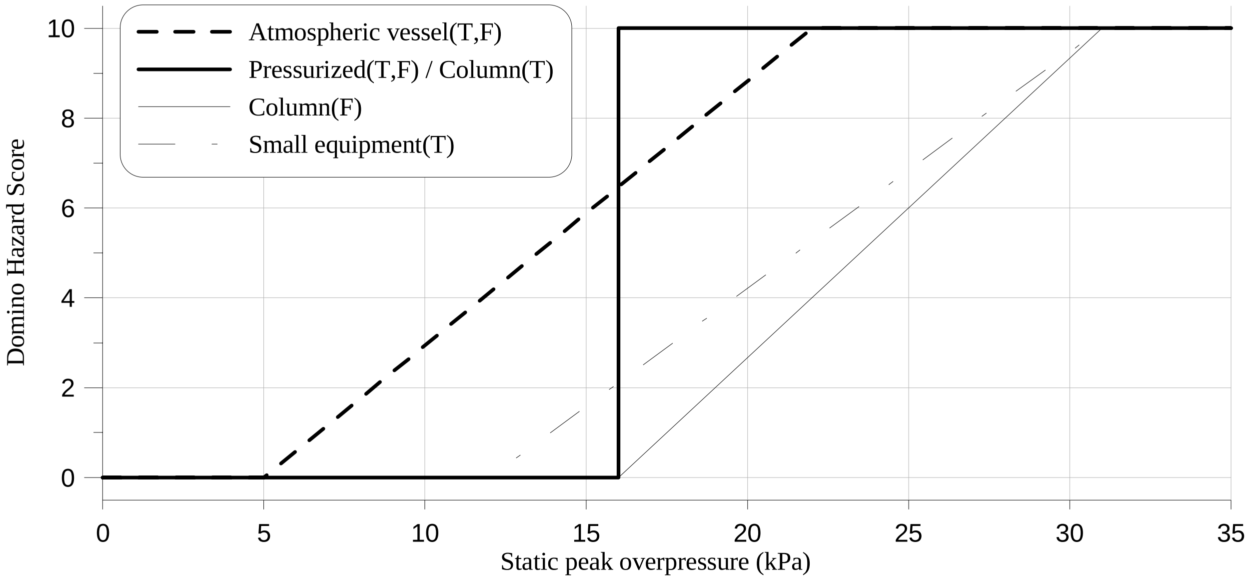


Figure A2.2.11: DHS as a function of the static peak overpressure for blast wave scenarios for different classes of equipment (T: handling toxic material; F: handling flammable material).

A2.2.4.3 - Fragment Projection

The projection of fragments is considered an important cause of domino effects in industrial accidents *[CCPS, 2000; Gubinelli et al., 2004; Khan & Abbasi, 1998; Lees, 1996; Pula et al., 2007]*. Detailed analysis of the cinematic records of missile projection has enabled the identification of probabilities of hitting targets of a given size as a function of distance *[Cozzani et al., 2007; Gubinelli et al., 2004]*. From these data, values for DHS as a function of distance and vessel size were derived and are reported in Figure A2.2.12. These cited studies on missile projection, as well as reports from industrial accidents *[Holden & Reeves, 1985; Westin, 1971]*, show that fragments are capable of generating secondary accidents at large distances from the primary source. Thus, no practical action in layout design (e.g. segregation) can result in a complete negation of escalation possibility. This is recognized in the DHI assessment by a lower limit of unity for the DHS score (see Figure A2.2.12).

The same passive protection measures used for limiting blast wave effects (e.g. blast walls) can also be designed to be effective in blocking missiles. Thus, in the protected area, the appropriate value is $DHS_{i,k,h} = 1$.

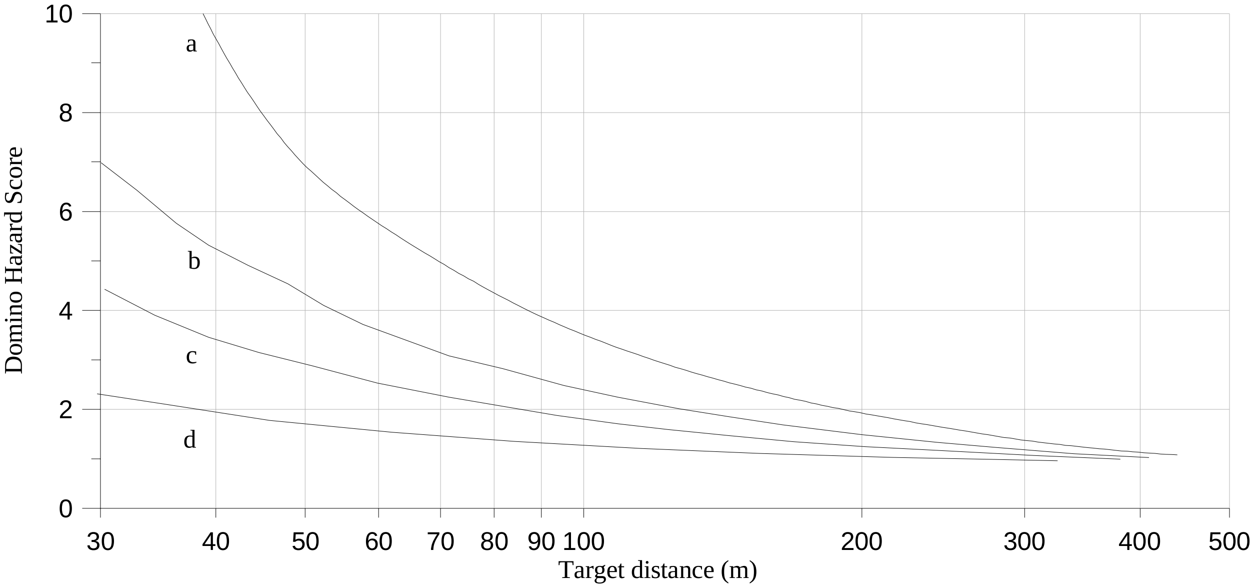


Figure A2.2.12: DHS as a function of the secondary unit distance for fragment projection; curves for different geometrical size of target unit are presented (very large storage vessel (a), large storage vessel (b), medium storage vessel (c), process vessel or small storage vessel (d)).

A2.2.4.4 - Toxic Release

In the present study, only primary events that result in physical effects likely to cause direct escalation were considered. Toxic releases may exert an escalation influence because of indirect effects on emergency procedures and crisis management *[Khan & Abbasi, 1998]*. Such considerations are, however, beyond the scope of the present analysis.

Section 3: Experimental Results

3.0 Introduction

Handling and processing of chemical substances may directly cause important hazards due to the substance characteristics (toxicity, flammability, stability, etc.). However, the formation of dangerous compounds by unwanted or unforeseen reactions in the deviation of a process from the normal operating conditions is reported to be an important cause of severe accidents *[Cozzani & Zanelli, 1997b; Cozzani et al., 1997, 1998]*, as in the case of the Seveso accident (1976). These events are usually associated to loss of containment, thus resulting in a toxic release.
The dangerous substances "which it is believed may be generated during the loss of control of an industrial chemical process" must be considered by law in the analysis of industrial installations subject to the Directive (96/82/EC), actually named after Seveso. However the section of Material Safety Data Sheets dedicated to this information usually reports only scant and vague data. This is probably a consequence of the complexity of the problem. The chemical effects of "out of control" conditions are difficult to foresee, since a wide number of chemical substances and of chemical systems are involved in industrial operations.

The intuitive analysis of historic databases reporting past accidents (e.g. *[Cozzani et al., 1997; Cozzani & Zanelli, 1997b]*) is limited to long-experience applications involving well-known substances and can not be used proactively.
A few approaches were proposed for the prediction of hazardous substances that may be formed in the loss of control of a chemical were proposed in the literature, based on lumping schemes *[Cozzani & Zanelli, 1997, 1999b; Cozzani et al., 1997]* and on stochastic approaches *[Nomen et al., 2003; Gigante et al., 2004]*.
However the presently more reliable routes for the analysis of the hazardous substances that may be formed in a chemical system of interest require experimental surveys. These kind of studies are required also for the validation and the improvement of predictive approaches. Therefore, adequate and specific reference experimental techniques are needed to define the more likely products formed during an accident, if no specific data are available in the literature. Moreover, these techniques should also allow an estimation of the expected quantities of substances that may be formed in "out of control" conditions.

The development of laboratory-scale experimental techniques to allow the identification of degradation and/or combustion products called for a relevant technological and scientific effort since the '70s. Several experimental techniques are now available to simulate the operating conditions during the loss of control of a chemical system, and several methodologies were proposed to identify the decomposition products formed. The applications in the field of process safety are summarized and revised in several comprehensive publications *[CCPS, 1995; Molag et al., 1992]*.
The results obtained in the application of the proposed techniques to chemical systems of industrial interest pointed out that operating conditions such as pressure and heating rate may become critical factors if a quantitative characterization of products formed is required. Thus, beside the development of calorimetric devices, attention is required on the development of specific experimental techniques for the sampling, the identification and the production of quantitative data on products formed in the simulation of the accidental scenarios *[Gigante et al., 2004; Marsanich et al., 2004]*.

The current section of the thesis describes some results of experimental tests on the behaviour of materials in "loss of control conditions". The goal of the presented tests is to illustrate a typical application of experimental techniques in the collection of data for sustainability and inherent safety assessment. In fact, the assessment methods proposed in Sections 1 and 2 require data on the thermal stability of substances (§2.3) and on the formation of undesired products in deviations from the normal process conditions (§2.2).

3.1 – Experimental Techniques and Procedures

3.1.0 – Overview

This paragraph describes the techniques used and the procedures followed in the experimental activity. This activity has been aimed at the demonstration of the collection of the information about the behaviour of materials in a chemical system undergoing “out of control” conditions. This information is necessary for the application of the assessment procedures described in Sections 1 and 2. In particular data on the thermal stability (useful for process inherent safety assessment §2.3) and on decomposition products (useful for material inherent safety assessment §2.2) are discussed here.

In the following, the experimental protocols proposed for the identification of products formed in the loss of control of chemical systems are discussed (§3.1.1). Then the experimental configurations and devices used in the experiments are introduced (§3.1.2).

3.1.1 – Experimental Protocols

The definition of specific protocols is required because of the poor standardization of the procedures, as previously discussed. A set of reference experimental techniques is defined to approach the problem of hazardous substances formed in "out of control" conditions. Calorimetric techniques, as thermogravimetry (TG), differential scanning calorimetry (DSC), differential thermal analysis, and adiabatic calorimetry were explored for the simulation of operating conditions taking place during accidental scenarios. Complementary and integrated experimental techniques were used for the achievement of experimental data on the products formed in the loss of control of a chemical system. The potential application of specific couplings between techniques for the simulation of operating conditions taking place during industrial accidents and analytical methodologies for the identification and the analysis of the products of interest are explored. The main analytic techniques considered are Fourier transform infrared spectrometry (FTIR), gas chromatography (GC) and mass spectrometry (MS).

The experimental protocols proposed were applied and validated on several chemical systems of industrial interest *[Andreozzi et al, 1997; Barontini et al., 2004a, 2004b, 2005, 2008; Lunghi et al, 2002; Marsanich et al., 2004]*.

Table 3.1.1 summarizes the main features of the experimental protocols defined in the present study.

3.1.1.1 – Thermogravimetry-Differential Scanning Calorimetry (TG-DSC) and Fourier Transform Infrared spectrometry (FTIR)

A first protocol based on the use of thermal analysis coupled with Fourier Transform infrared analysis of evolved gases (TG-DSC-FTIR technique) was defined for the analysis of gaseous products formed in the simulation of thermal degradation or combustion scenarios.

Thermal analysis coupled with Fourier Transform infrared analysis of evolved gases may be advantageously used for the characterization of gaseous products formed in thermal degradation processes, i.e. combustion or pyrolysis *[Bhandare et al., 1997; Materazzi & Curini, 2001; Pitkanen et al., 1999; Wilkie & Mittleman, 1993; Zanier, 1999]*. Several coupling devices are commercially available. Low-volume gas cells have been specifically

		TG-DSC-FTIR	DTA	Adiabatic calorimeter
Scenario simulation		Thermal degradation, combustion (fire)	Thermal degradation	Runaway
Operating mode		Isotherm, constant heating rate	Isotherm, constant heating rate	“heat-wait-search”, “open cell”, “closed cell”
Max. heating rate		100°C/min	2°C/min	-
Temperature range		25-1600°C	25-400°C	25-400°C
Pressure range		1 bar	0-200 bar	0-140 bar
Sample size		1-50 mg	0.5-5g	0,5-50 g
Data on products formed	***Gas phase***	Quail/quantitative data from on-line FTIR	Quail/quantitative data from off-line FTIR	Quail/quantitative data from off-line FTIR
	high MW products	Non suitable	Quail/quantitative data from off-line GC analysis	Quail/quantitative data from off-line GC analysis

Table 3.1.1: Main features of the experimental protocols developed for the identification of products formed in the loss of control of chemical systems

developed for these applications. The main use of TG-DSC-FTIR data is the qualitative identification of decomposition or reaction products formed during the TG run *[Bhandare et al., 1997; Cai & Shen, 1999; Fisher & Dunn, 1999; Pitkanen et al., 1999]*. However, several authors proposed the use of the TG-DSC-FTIR system for quantitative determinations of the compounds evolved in the TG experiments *[Bassilakis et al., 2001; Charpenay et al., 1996; Liau et al., 1997; Seebauer et al., 1997]*. This requires the use of a calibration procedure to obtain quantitative data from FTIR on-line gas-phase measurements.

Experimental protocols based on these techniques start from the definition of the accidental scenario to be reproduced, which implies the definition of temperature range, temperature-time profile and reaction environment of experimental run, the latter one being controlled by the use of a specific purge gas. Preliminary thermogravimetric (TG) and/or differential scanning calorimetry (DSC) runs may be performed on the material to be tested in order to obtain indicative values on sample decomposition temperatures and on the extent of volatile loss. On the basis of the preliminary information obtained, it is possible to define specific conditions to carry out the TG-DSC-FTIR experimental runs. The analysis of the experimental data should yield specific results on sample thermal stability and decomposition kinetics (TG data), thermal effects related to the decomposition process (DSC data), and evolved gas composition (FTIR data). FTIR spectra analysis affords a qualitative identification of gaseous products evolved, and the use of calibration data *[Marsanich et al., 2002]* allows the achievement of quantitative results. The application of FTIR spectra deconvolution methods may further improve the FTIR results *[Bassilakis et al., 2001]*. Data are commonly obtained at atmospheric pressure, though high pressure devices have been specifically developed *[Seebauer et al., 1997]*.

The limited amounts of sample needed for experiments (of the order of milligrams), which turns out in a reduction in costs, safety and disposal problems, joined to the relatively short times required by the procedure, are very attractive features of the protocol. However, the concurrent formation of a wide number of volatile compounds may complicate the interpretation of FTIR data. On the other hand, it should be reminded that homodinuclear molecules (e.g. hydrogen and chlorine) are transparent to infrared radiation, thus they cannot be detected. Moreover, it should be recalled that TG devices are mainly oriented to the study of primary decomposition reactions, and not of gas-phase secondary reactions processes. A further limitation of the technique is that the data are commonly obtained at atmospheric pressure, and, though high pressure devices have been specifically developed, it is not possible to simulate a specific time-pressure profile.

A spin-off of the current protocol is the coupling of DSC with off-line Gas Chromatography (GC). In fact, the study of the apparent kinetic of a decomposition reaction requires information on the conversion of the initial substance over time and temperature. These can be combined with calorimetric data in order to identify the thermal parameters of the reaction (i.e. the heat of reaction as a function of a key compound). For this purpose, an experimental technique was specifically developed. It is based on the interruption of DSC tests by rapid

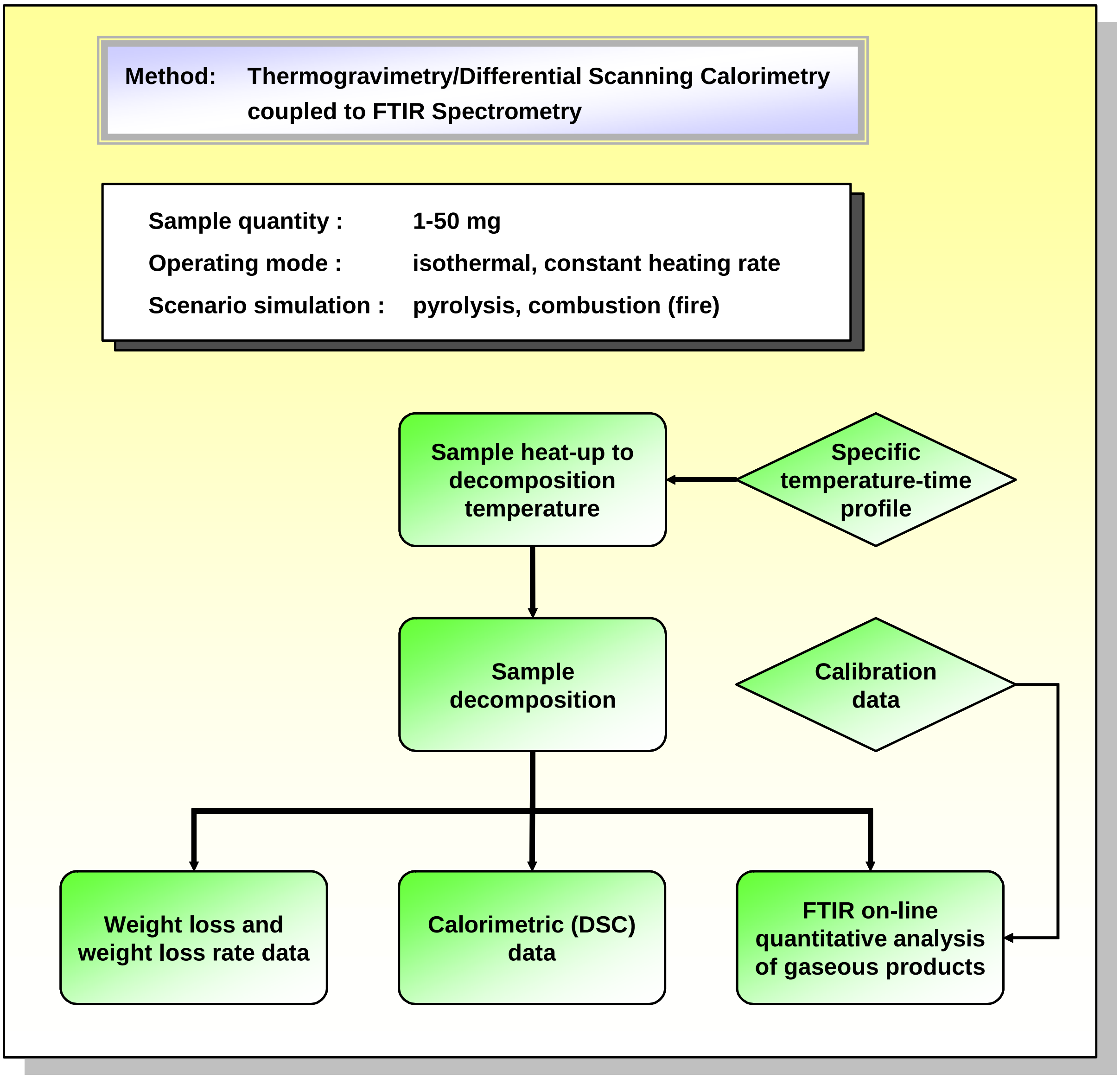


Figure 3.1.1: Main features of the TG-DSC-FTIR experimental protocol.

quenching of the samples. The partially-converted samples are then recovered and a solution is prepared with a fixed amount of solvent. This solution is then analysed by gas-chromatography.

The DSC allows monitoring the thermal behaviour of the sample: the thermal profile of the reaction and the heating rate will be used to characterize the temperature and the heat of reaction since test interruption. The chromatographic test on the sample, will provide the corresponding information on the quantity of unconverted initial substance and, thus, on the conversion. This requires, of course, a calibration by solutions of known concentration in the initial substance.

The use of a DSC for conversion tests, compared to other similar laboratory tests (e.g. *[Andreozzi et al. 1999]*), allows the use of minimum quantities samples in the tests (in the order of milligrams), still maintaining a precise control of the reaction behaviour. This turns out in a reduction in costs, safety and disposal problems, that, joined to the relatively small times required by the procedure, are very attractive features. However limits due to transport phenomena may affect the results, in particular at high conversions.

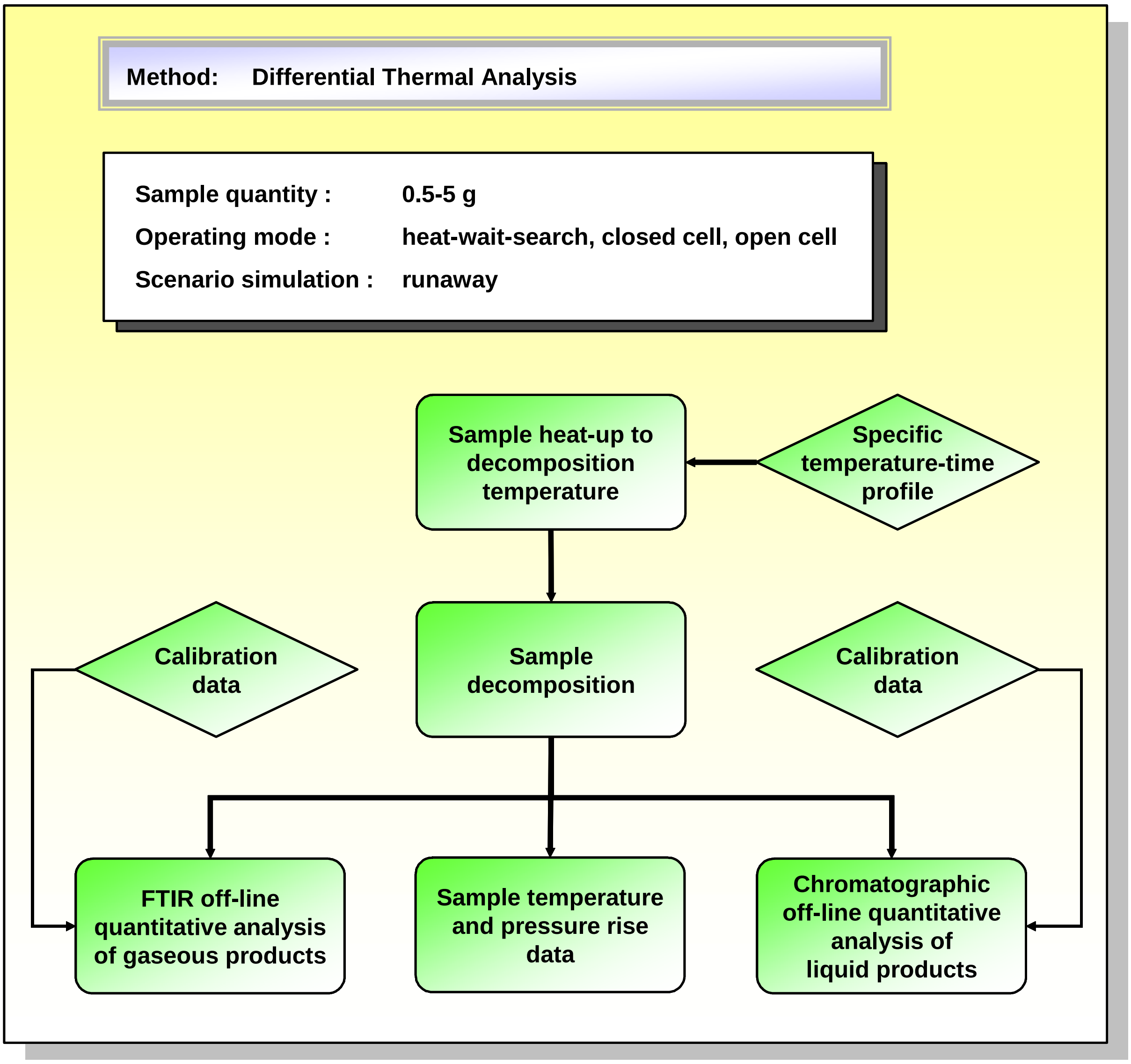


Figure 3.1.2: Main features of the TGA experimental protocol.

3.1.1.2 – Differential Thermal Analysis (DTA)

Thermal analysis of materials by DSC and TG is limited to atmospheric pressure and small samples. A scanning differential thermal analysis (DTA) in closed vessel, with continuous pressure recording is proposed as a test method to integrate or confirm DSC data *[Andreozzi et al., 1997; Syvret, 1999]*. This allows to monitor the pressure profile and its influence on the decomposition, since both rates of pressure generation and temperature increase are recorded as a function of temperature during the thermal decomposition event. The analysis of data yields the identification of the decomposition thermal steps, of the onset temperatures and of the decomposition pressure profile. If a reference calibration is available, the heat flux can be measured in the form of temperature difference between sample and inert reference.

The decomposition products formed can be sampled and weighted at the end of the test. In this case the analysis is suitable for both the gaseous and the high molar weight phases. Off-line FTIR and GC-MS techniques are used for the qualitative and quantitative identification of these phases.

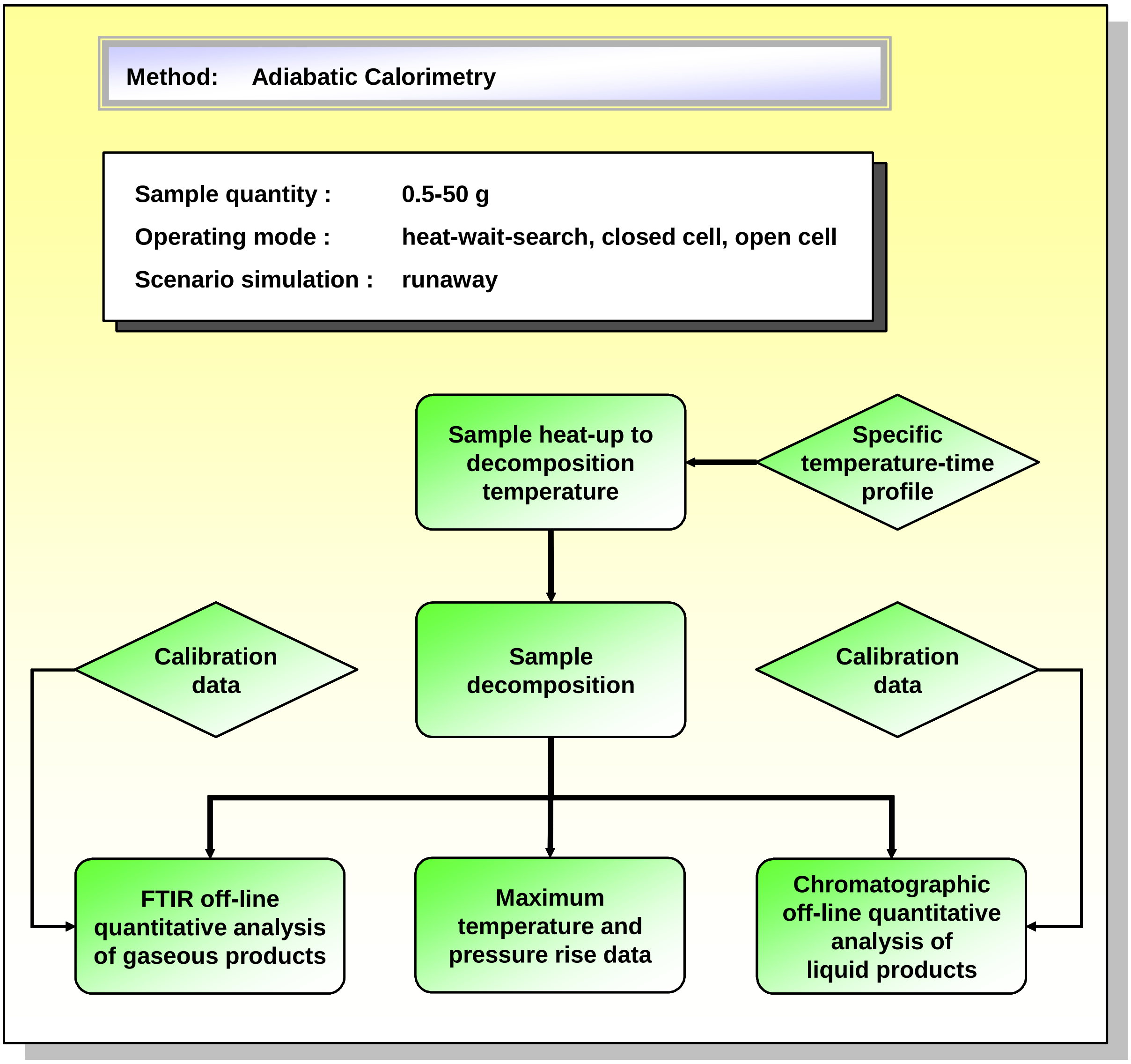


Figure 3.1.3: Main features of the Adiabatic Calorimetry experimental protocol.

3.1.1.3 – Adiabatic Calorimetry

Adiabatic calorimetry is a standard technique used for the simulation of runaway scenarios *[Benuzzi & Zaldivar, 1991; Cardillo, 1998]*. Low phi-factor calorimeters are among the devices currently used to assess the thermal stability and the expected severity of exothermic runaway reactions. This allows an efficient simulation of runaway conditions in full-scale chemical reactors. Thus, an experimental protocol was defined for the analysis of gaseous and high molecular weight products formed during the simulation of runaway scenarios by adiabatic calorimetry.

Preliminary data are needed with respect to the onset reaction temperatures and the expected adiabatic temperature rises, and may be obtained by DSC runs (§3.1.1.1). Conventional data obtained by adiabatic calorimetry in the simulation of a runaway scenario are the maximum temperature and pressure rise, the maximum temperature and pressure rise rate, the reaction heat and the apparent reaction kinetics. The use of a specifically developed sampling strategy joined to FTIR calibration data allows for a qualitative and quantitative determination of gaseous products generated in the experimental run by off-line FTIR analysis *[Marsanich et al., 2004]*. Off-line chromatographic analysis of the high molecular weight products which are recovered from the test cell at the end of experimental run affords a qualitative and quantitative characterization of this product fraction. A significant highlight of the technique is the efficient simulation of the expected operating conditions, as temperature and pressure, present during the runaway of an industrial chemical reactor.

3.1.2 - Experimental configurations and devices

Some different scale experimental devices were used to study an exothermic thermal decomposition process, according to the defined protocols (§3.1.1): thermogravimetry (TG), RADEX oven and low phi-factor adiabatic calorimetry. The products formed in the experimental runs were identified and quantified by analytical techniques as FTIR spectrometry and Gas Chromatography-Mass Spectrometry (GC/MS). Quantitative analysis of decomposition products required the development of calibration methods and of specific couplings between the analytical devices and the facilities used to simulate "out of control" conditions.

3.1.2.1 – Thermogravimetry-Differential Scanning Calorimetry (TG-DSC) and Fourier Transform Infrared spectrometry (FTIR)

Simultaneous data on the thermal degradation behaviour and on the products formed in the thermal degradation of chemical systems of interest were obtained using a Netzsch STA 409/C thermoanalyzer coupled to a Bruker Equinox 55 spectrometer. The FTIR spectrometer was linked to the thermal analyzer using a transfer line with a 2mm internal diameter teflon tube, heated at a constant temperature of 230°C to limit the condensation of volatile decomposition products. FTIR measurements were carried out with a MCT detector in a specifically developed low volume gas cell (8.7ml) with a 123mm pathlength, heated at a constant temperature of 250°C. These temperatures were chosen in order to limit the condensation of volatile decomposition products and to avoid the further degradation of volatile compounds in the transfer line.

Constant heating rates between 1 and 50°C/min were used in experimental runs. Tests were carried out using a purge gas flow (60ml/min at 25°C) of pure nitrogen or air. A residence time of 30s in the transfer line could be evaluated for the evolved gases. This value was assumed as the time delay correction to be used for the comparison of TG and IR results. Typical sample weights of 2 to 50 mg were employed. Experimental runs were performed using open or closed low-pressure aluminium crucibles, open alumina crucibles or open platinum crucibles. Closed crucibles were used to limit evaporation phenomena at low temperatures. In these runs, the crucible lid opened due to the internal pressure at the beginning of the decomposition process.

Evolved products were identified by the analysis of recorded FTIR spectra. During TG-FTIR runs, spectra were collected at $4 cm^{-1}$ resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.5s, more than sufficient to follow the gas evolution rates characteristic of TG runs at the heating rates used in the present study. A residence time of 30s in the transfer line could be evaluated for the evolved gases. This value was assumed as the time delay correction to be used for the comparison of TG and IR results.

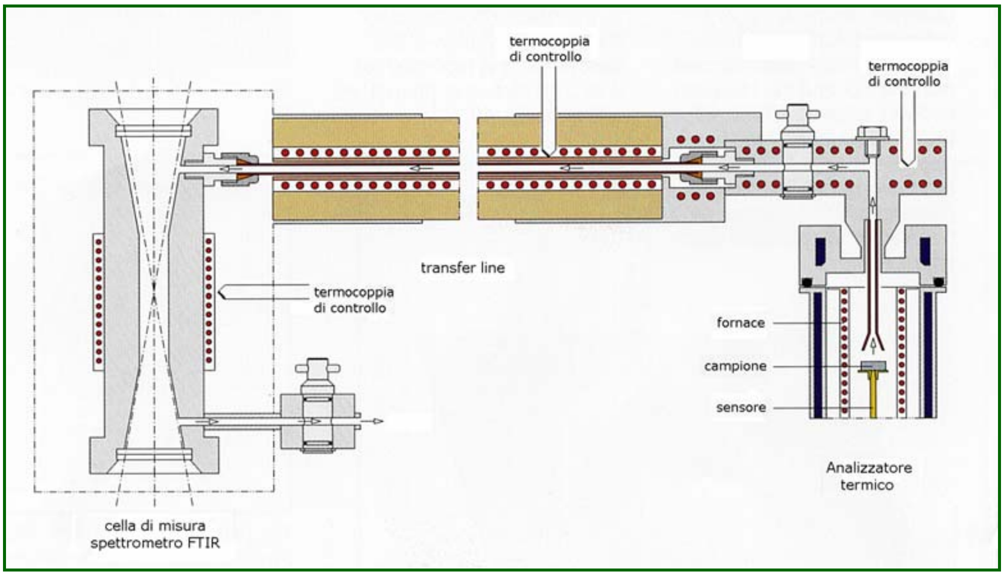


Figure 3.1.4: Configurations of the transfer line used in TG-DSC-FTIR experiments.

The quantitative use of FTIR analysis requires a calibration. A few techniques were actually applicable for the setups of interest (concentration-based calibration, gas-pulse calibration, vaporization-based calibration). The equivalence of the various approaches and the typical measurement error were discussed and demonstrated by *Marsanich et al., [2002]*. In the present study, gas-pulse calibration, vaporization-based calibration were used.

a) Gas-pulse Calibration

This is a pulse calibration technique *[Lopez-Anreus et al., 1998; Maciejewsky et al., 1997; Perez-Ponce et al., 1998a,b,c]*. In pulse methods a known quantity of the gaseous compound of interest is sent to the IR measurement cell using the gas injection device and the system configuration shown in Figure 3.1.5-(a). The gas injection system used is directly derived from that used in gas chromatography to supply known volumes of gas samples *[Skoog & Leary, 1992]*. It consists in a rotary sample valve allowing a carrier gas to purge a known-volume loop, previously filled with a calibration gas of known composition. Thus the system allows a known quantity of gas to be carried to the measurement cell by the carrier gas flow. Volumes of available loops were: 1.15, 3, 12, 50, and 200ml. A 100% nitrogen carrier gas flowrate of 60ml/min (25°C) was used.

Clearly enough, this method is limited to substances that are in gas or vapour state at ambient temperature. It is not applicable in present form to liquids.

b) Vaporization-based Calibration

This is a pulse calibration technique, thus similar to the previous one, but complementary since it is suitable for liquids or liquid solutions (including water solution of soluble gases, like HCl).
TG-FTIR measurements is performed vaporizing water solutions of the compound of interest in the TG analyzer (see Figure 3.1.5-(c)). At the beginning of each calibration run, a quantity of solution in the range of 15-45μl is inserted in an alumina crucible using a chromatographic syringe. A pierced lid is positioned on the crucible, to limit evaporation caused by gas-phase diffusion at the beginning of the TG run. The initial weight of the sample and the composition of the solution allow the calculation of the quantity of the compound of interest vaporized in

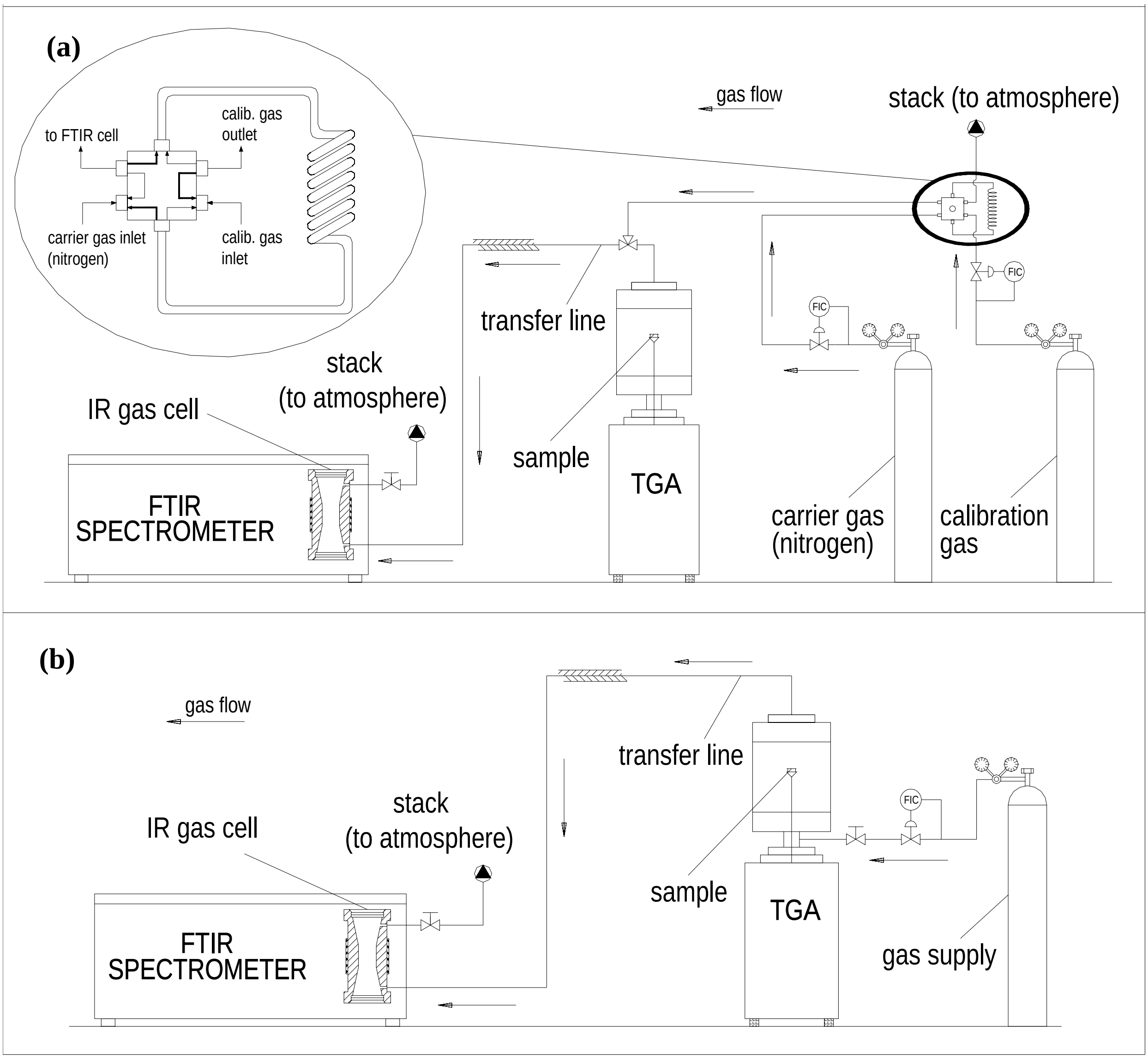


Figure 3.1.5: Configurations of the TG-DSC-FTIR coupling used for: (a) concentration-based calibration, (b) gas-pulse calibration and (c) vaporization-based calibration.

the TG run. The use of solutions of different concentration and of samples of different weight allows the vaporization of different quantities of the compound of interest, that are carried to the IR measurement cell by the carrier gas flow. A constant heating rate of 5°C/min from 25°C to 200°C is generally used for experimental runs. The carrier gas is 100% nitrogen, and a gas flowrate of 60ml/min is used.

3.1.2.2 – DSC-GC conversion tests

In the DSC-GC coupled conversion tests a Mettler DSC-25 calorimeter was used. Constant heating rates between 1 and 50°C/min were used in experimental runs. Tests were carried out using a purge gas flow (300 ml/min at 25°C) of pure nitrogen. Typical sample weights of 2 to 10 mg were employed. Experimental runs were performed using closed low-pressure aluminium crucibles, in order to limit sample evaporation. The use of small samples usually prevented crucible opening by pressure development.

After quenching the crucibles were opened and the partially-converted samples are recovered preparing a solution with a fixed amount of solvent. The solution was then analysed by the ThermoQuest Trace GC 2000 gas chromatograph, as described in §3.1.2.5.

3.1.2.3 – Differential Thermal Analysis (RADEX)

A PC-Combilab (by Systag) equipped with a RADEX-Solo oven *[Syvret, 1999]* is used for scanning runs. In all the runs, the RADEX oven is equipped with a closed high pressure (up to 100 bar) stainless steel (316 SS) reactor ($V = 0.004$ dm^3). Basically, the Radex is similar to a system described in ASTM E476-87; “Thermal Instability of Confined Condensed Phase systems (Confinement Test)”, but has a greater ease of use and flexibility in test parameters. The Radex test cell is connected to a transducer to measure the internal pressure, thus providing the gas generation data which is not available from DSC. Information on gas generation during decomposition is crucial in assessing the overall hazard associated with a given material. Radex uses larger sample sizes than DSC (0.1 to 5g).

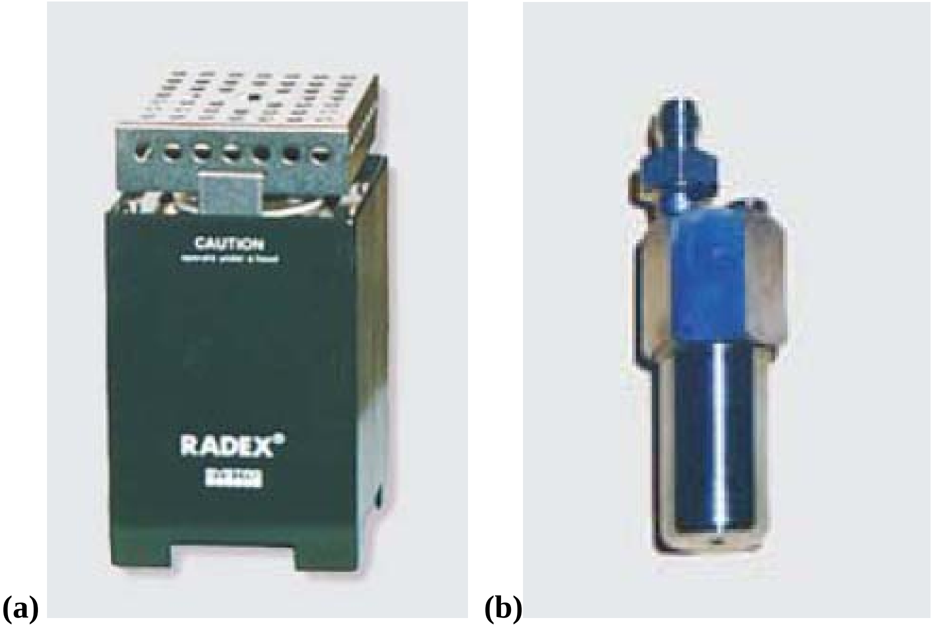


Figure 3.1.6: RADEX-Solo oven by Systag. (a) oven case; (b) closed high pressure stainless steel reactor.

In scanning mode, Radex is typically operated at a constant heating rate (0.5 to 2°C/min), and it can measure heat flux, in the form of temperature difference between sample and inert reference. Since Radex has a single measurement thermocouple, the reference data must actually be obtained in a separate run. The subtraction of this “baseline” is done via software.
However, if thermal data are not of interest, the analysis of data from a single run with no calibration on the reference, allow identifying the behaviour of the decomposition (i.e. single or multiple steps), the onset temperatures of the different decomposition steps and the decomposition pressure profile.

The material can be scanned over the whole temperature range encompassed by the device (25-400°C) or the scanning can be stopped at any temperature of interest by reactor extraction from the oven and rapid quenching. At the end of the test, or after the cool down of the system, gaseous compounds can be sampled for off-line FTIR analysis and condensable fraction may be recovered from the reactor for chromatographic analysis (§3.1.2.4).

3.1.2.4 – Adiabatic Calorimetry (PHI –TECH II)

A Phi-Tec II adiabatic calorimeter developed by Hazard Evaluation Laboratory was used to obtain data on products formed during adiabatic decomposition runs. Samples within the range of 0.5-50g can be used in experimental runs. Tests were performed in stainless steel cells magnetically agitated, with a thermal mass of 15.23J/K. Runs were performed in a heat-wait-search mode. A threshold of 0.02°C/min was arbitrarily chosen as the start of the exothermic activity.

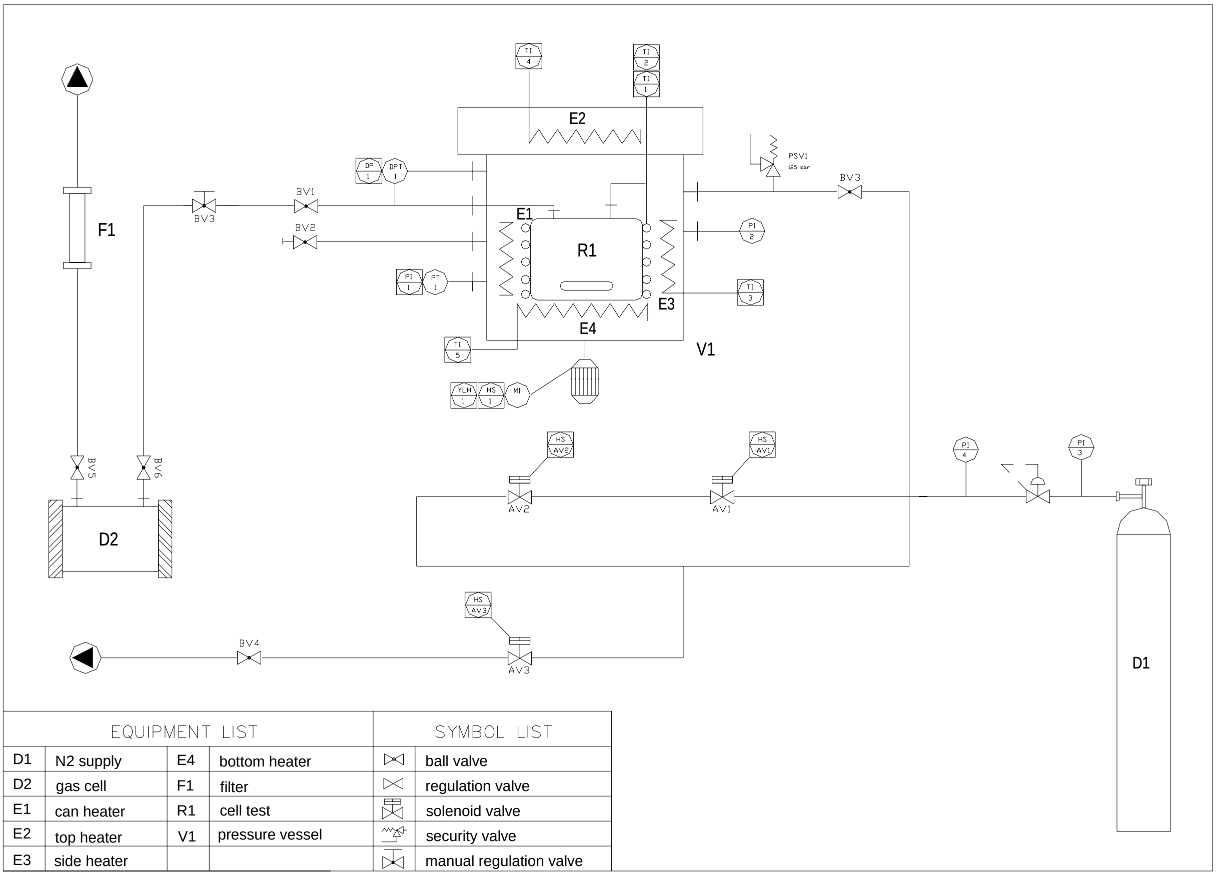


Figure 3.1.7: Scheme of the Phi-Tec II gaseous products sampling system.

In order to allow the sampling and the analysis of the gaseous products formed during the experimental runs, a specifically developed sampling line was connected to the Phi-Tec device. Figure 3.1.7 shows a scheme of the equipment assembly. The sampling line was equipped with a manual pressure reduction valve and a removable cell for FTIR gas analysis. This system allows gas-phase sampling both during or at the end of the exothermic decomposition.

Quantitative data on gaseous decomposition products could be obtained using a specifically developed sampling strategy. At the end of the exothermic decomposition, the test cell was cooled to ambient temperature, in order to limit the solvent concentration in the vapour phase. The residual pressure, due to the presence of gaseous decomposition products, was used to force the gas phase through the sampling line. The FTIR analysis of the gas inside the sampling cell was performed by a Bruker Equinox 55 spectrometer. Calibration curves, may be obtained using known concentration gas mixtures of the compounds of interest *[Marsanich et al., 2002]*, allowed the determination of the molar concentration in the gas cell of each gaseous species identified. The total number of moles discharged during each sampling interval could be roughly estimated from the pressure decrease in the test cell by ideal gases volumetric correlation:

$$\mathrm{N_i} = (\mathrm{P_{i\text{-}1}} - \mathrm{P_i}) \cdot \frac{\mathrm{V_f}}{\mathrm{R} \cdot \mathrm{T}} \qquad (3.1.1)$$

where n_i are the total moles discharged from the test cell during the i-th sampling, P_{i-1} and P_i are the pressure of the Phi-Tec test cell respectively at the beginning and at the end of the i-th sampling, V_f is the free volume of the test cell and T the cell temperature during the sampling. Thus, an approximate estimation of the total number of moles of the compound of interest discharged from the test cell during the sampling interval could be performed, assuming a plug-flow in the sampling line:

$$\mathrm{n_{j,i}} = \left(\frac{C_{j,i-1} + C_{j,i}}{2} \right) \frac{\mathrm{N_i} \cdot \mathrm{R} \cdot \mathrm{T_s}}{\mathrm{P_s}} \qquad (3.1.2)$$

where $m_{j,i}$ are the total moles of compound j discharged during the i-th sampling, $C_{j,i-1}$ and $C_{j,i}$ are the concentrations of compound j measured by FTIR analysis respectively at the beginning and at the end of the i-th sampling, T_s and P_s are respectively the temperature and the pressure of the sampling cell. Obviously this method yields only a rough estimate of the quantities of products formed in the thermal decomposition. However, validation runs performed using gaseous mixtures of known composition showed that a mean relative error of less than 5% should be expected, in spite of the assumptions performed in the analysis *[Calvani, 2002]*.

Decomposition products present in the residue inside the cell at the end of experimental runs were quantified by the differential weight of the cell before and after the test. The soluble part was recovered by washing with acetone. The solution is suitable for qualitative and quantitative identification by a chromatographic analysis, as described in §3.1.2.5.

In the current study, a non conventional use of the PHI-Tech device was explored. This was suggested by some experimental results emerged in the study activity (§3.5). In this sub-protocol, small sample quantities (lower side of the range, 0.5-0.7 g) are tested in small stirred cells (15.9 J/K), so to deliberately obtain high pi-factors (10-15). This will limit the final temperature of the system after decomposition. Intermediate decomposition products, that will further convert to other substances at higher temperatures, can thus be sampled. These compounds can be measured and analysed by the same procedure described above for regular runs. The pressure increase rate and temperature increase rate are, as well, recorded during the test. However it should be considered that both are affected by larger errors than in usual tests due to the smaller sample size and the larger phi-factors.

3.1.2.5 – Gas Chromatography (GC) and Mass Spectrometry (MS)

The analysis of high molecular weight decomposition products collected from calorimetric tests (e.g. Adiabatic Calorimetry (§3.1.2.4), Differential Thermal Analysis (§3.1.2.3)) was performed with chromatographic techniques.

A Fisons MD 800 quadrupole mass spectrometer interfaced to a Fisons GC 8060 gas chromatograph was used for *gas chromatography/mass spectrometry* (*GC/MS*) analysis. A Mega SE30 fused silica capillary column (25m length, 0.32mm internal diameter, cross-bonded, 0.25μm film thickness) was employed for the chromatographic separation, with helium as carrier gas. The column temperature programme was the following: 5min isothermal at 40°C, heating to 250°C (6°C/min), then 20min isothermal. Splitless injection with the injector at 220°C was used.
Mass spectrometric detection was performed in full scan conditions (scan range, *m/z* 10-819) in electron impact ionization mode.

Quantitative gas chromatographic analysis (*GC*) was carried out using a ThermoQuest Trace GC 2000 gas chromatograph equipped with a Flame Ionization Detector. The capillary column and the experimental conditions were identical to those used for GC/MS analysis, detector temperature was fixed at 280°C. Thus data obtained from both chromatographic systems are comparable.

More details on GC quantitative determinations are reported elsewhere *[Barontini et al., 2004a,b]*.

3.2 – Chemical Systems Analyzed

3.2.1 – Overview

This chapter presents the materials and the chemical system analysed in the experimental survey.

3.2.1 – Chemical Systems

The thermal decomposition and formation of decomposition product was investigated on 6 chemical systems:

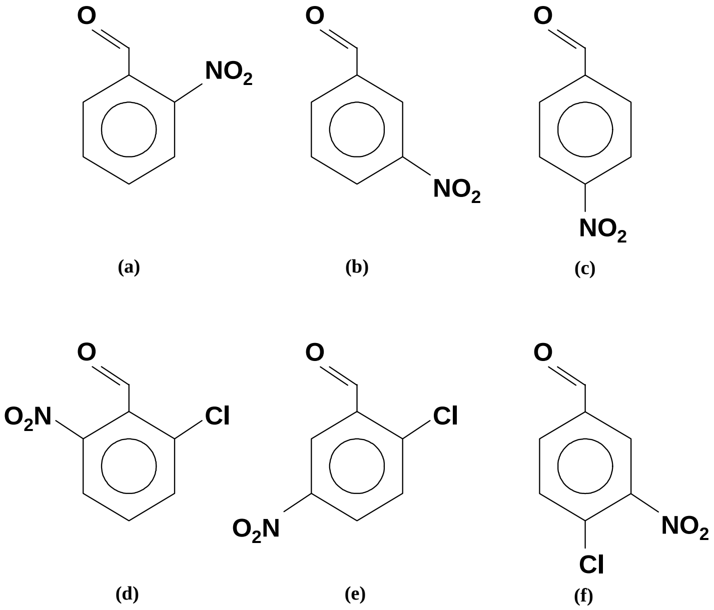
a) 2-nitrobenzaldehyde (*o-nitrobenzaldehyde*)
b) 3-nitrobenzaldehyde (*m-nitrobenzaldehyde*)
c) 4-nitrobenzaldehyde (*p-nitrobenzaldehyde*)
d) 2-Chloro-6-nitrobenzaldehyde
e) 2-Chloro-5-nitrobenzaldehyde
f) 4-Chloro-3-nitrobenzaldehyde

The chemical structure of the substances analysed is quite similar, since they are two groups of the three isomers of the nitrobenzaldehyde and of a chorine-substituted nitrobenzaldehyde (Figure 3.2.1). Proprieties derived from the Material Safety Data Sheets (MSDS) or estimated by predictive methods (e.g *[EPA, WPd]*) are reported in Table 3.2.1.

These compounds are the intermediates of organic synthesis for the production of dyes and biologically active products (pharmaceuticals, agrochemicals, etc.). In particular, 2-nitrobenzaldheyde is a feedstock for the synthetic production of indigo.

Name	**CAS**	**Molar mass**	**Melting point**	**Predicted boiling point**	**Vapour pressure**	**Predicted vapour pressure at 25°C**
			(°C)	*(°C)*	*(kPa)*	*(Pa)*
2-Nitrobenzaldehyde	552-89-6	151.1	42-43	270	3.1 (at 152°C)	0.8
3-Nitrobenzaldehyde	99-61-6	151.1	55-58	270	3.1 (at 164°C)	0.60
4-Nitrobenzaldehyde	555-16-8	151.1	103-106	270	n. a.	0.19
2-Chloro-6-nitrobenzaldehyde	6361-22-4	185.57	69-71	295.6	n. a.	0.12
2-Chloro-5-nitrobenzaldehyde	6361-21-3	185.57	72-77	295.6	n. a.	0.11
4-Chloro-3-nitrobenzaldehyde	16588-34-4	185.57	61-65	295.6	n. a.	0.15

Table 3.2.1: Selected physical proprieties of the materials used in the experimental activity as reported in the Material Safety Data Sheets; the predicted values were obtained by the tested by EPI Suite *[EPA, WPd]*; n.a.: not available.



(a) (b) (c)

(d) (e) (f)

Figure 3.2.1: Chemical structure of the 6 substances analysed in the experimental studies. **(a)** 2-nitrobenzaldehyde; **(b)** 3-nitrobenzaldehyde; **(c)** 4-nitrobenzaldehyde; **(d)** 2-Chloro-6-nitrobenzaldehyde; **(e)** 2-Chloro-5-nitrobenzaldehyde; **(f)** 4-Chloro-3-nitrobenzaldehyde.

3.2.2 – Information Available on the Chemical Systems

The data on the thermal stability and decomposition product formation of the materials of interest are extremely scant.
A survey of the Material Data Sheets available by different producers and suppliers is summarized in Table 3.2.2. As shown in the table, the information are quite scant, both on the stability and the product formation. Some sources report the materials as "stable" or more prudently "stable under normal temperatures and pressures". The decomposition products, when reported, are intuitively expected from the structure of the chemicals (i.e. carbon dioxide, carbon monoxide, nitrogen oxides and, for chlorinated isomers, hydrogen chloride).

Ando and co-workers *[Ando et al., 1991]* report the three isomers of nitrobenzaldehyde to be thermally instable if heated. They provide thermal data on the decomposition, obtained by a differential scanning calorimetry (DSC) (Table 3.2.3).
The data show relatively high onset temperatures (> 200°C) for all the isomers, but with the 2-nitrobenzaldehyde decomposing at lower temperatures than the other two. The heat of decomposition are quite high, as well as he steepest increase rate.

Cardillo *[Cardillo, 1998]* reports the results for self-heating curves of the isomers of nitrobenzaldehyde (Figure 3.2.2).
For 2-nitrobenzaldehyde, a 2 stage decompositions, at 176°C and 194°C was identified.
For 3-nitrobenzaldehyde also 2 stages were identified at 166 and 210°C.
Finally 4-nitrobenzaldehyde is reported to decompose in a single stage at 226°C.
The decomposition takes place for all the materials jointly to the generation of high quantities of gases and high thermal effect (above 1500 J/g).

Name	Stability	Hazardous decomposition products
2-Nitrobenzaldehyde	"Stability: The product is **stable**. Instability Temperature: Not available. Conditions of Instability: Not available"	---
	"**Stable at room temperature** in closed containers under normal storage and handling conditions. Conditions to Avoid: Incompatible materials, **excess heat**, strong oxidants."	Nitrogen oxides, carbon monoxide, irritating and toxic fumes and gases, carbon dioxide, nitrogen.
	"**Stable**"	Carbon monoxide, Carbon dioxide, Nitrogen oxides.
3-Nitrobenzaldehyde	"Stability: The product is **stable**. Instability Temperature: Not available. Conditions of Instability: Not available"	---
	"**Stable** under normal temperatures and pressures."	Nitrogen oxides, carbon monoxide, carbon dioxide, nitrogen.
	---	Carbon monoxide, Carbon dioxide, Nitrogen oxides.
4-Nitrobenzaldehyde	"Stability: The product is **stable**. Instability Temperature: Not available. Conditions of Instability: Not available."	---
	"**Stable** under normal temperatures and pressures"	Nitrogen oxides, carbon monoxide, carbon dioxide, nitrogen gas.
2-Chloro-6-nitrobenzaldehyde	---	Carbon monoxide, Carbon dioxide, Nitrogen oxides, Hydrogen chloride gas.
2-Chloro-5-nitrobenzaldehyde	---	Carbon monoxide, Carbon dioxide, Nitrogen oxides, Hydrogen chloride gas.
	"**Stable** under normal temperatures and pressures. Conditions to Avoid: Incompatible materials, dust generation, **excess heat**, strong oxidants."	Hydrogen chloride, nitrogen oxides, carbon monoxide, irritating and toxic fumes and gases, carbon dioxide, nitrogen.
4-Chloro-3-nitrobenzaldehyde	"**Stable** under normal temperatures and pressures. Conditions to Avoid: Incompatible materials, dust generation, **excess heat**, strong oxidants."	Hydrogen chloride, nitrogen oxides, carbon monoxide, irritating and toxic fumes and gases, carbon dioxide, nitrogen gas.
	"**Decomposition**"	Carbon monoxide, carbon dioxide, hydrogen chloride (hydrochloric acid), oxides of nitrogen, nitric acid, hydrogen cyanide.
	"**Stable**"	Carbon monoxide, Carbon dioxide, Nitrogen oxides, Hydrogen chloride gas.

Table 3.2.2: Summary of outcomes the survey of the "stability and reactivity" section in Material Safety Data Sheets of the substances of interest.

Nome	**Onset temperature** *(°C)*	**Heat of decomposition** *(cal/g)*	**Power increase rate** *(cal/(min^2 g))*
2-Nitrobenzaldehyde	223	506	141.0
3-Nitrobenzaldehyde	262	594	∞
4-Nitrobenzaldehyde	285	670	∞

Table 3.2.3: Data from *Ando et al., [1991]* on the thermal stability of nitrobenzaldehyde isomers.

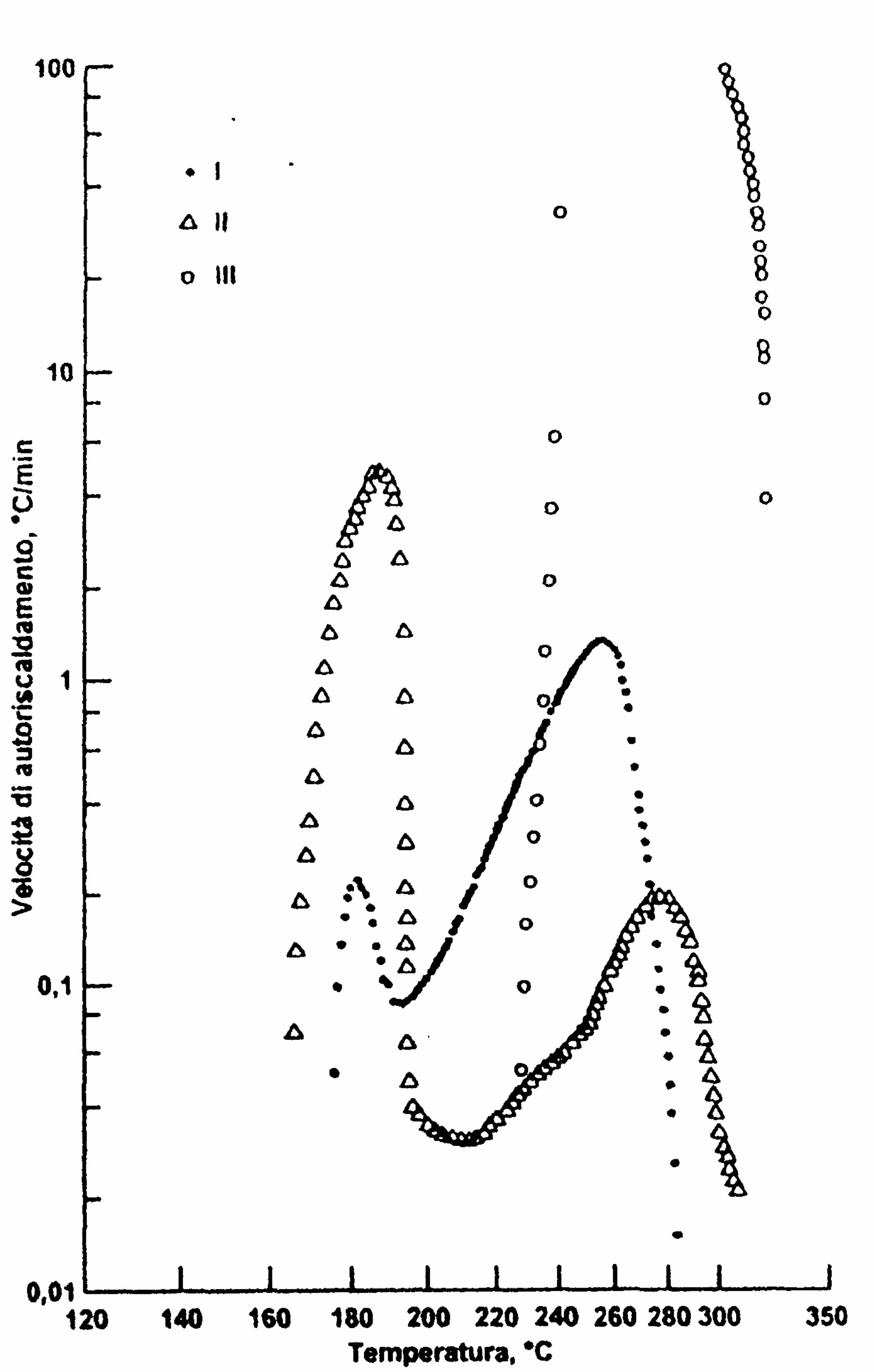


Figure 3.2.2: Self-heating curves for the isomers of nitrobenzaldehyde. I: 2-nitrobenzaldehyde, II: 3-nitrobenzaldehyde, III: 4-nitrobenzaldehyde. Heating rate on the y-axis and Temperature on the x-axis. From *Cardillo, [1998].*

3.2.3 – Materials Used

The experimental studies were performed on the material listed in Table 3.1.4. The compounds were supplied by Sigma-Aldrich (Milan, Italy). The table reports also the purity declared and tested by the supplier.

Name	CAS	Purity
2-nitrobenzaldehyde *(o-nitrobenzaldehyde)*	552-89-6	98% (99.1%)
3-nitrobenzaldehyde *(m-nitrobenzaldehyde)*	99-61-6	99% (99.3%)
4-nitrobenzaldehyde *(p-nitrobenzaldehyde)*	555-16-8	98% (n.a)
2-Chloro-6-nitrobenzaldehyde	6361-22-4	97% (n.a)
2-Chloro-5-nitrobenzaldehyde	6361-21-3	97% (97.8%)
4-Chloro-3-nitrobenzaldehyde	16588-34-4	98% (99.1%)

Table 3.1.4: Materials used in the experimental activity; the purities, as declared and the tested by the Supplier (in brackets), are reported; n.a.: not available.

3.3 – Results from experimental studies: TG – DSC – FTIR

3.3.0 – Overview

In the following some of the results of the experimental survey on the group of materials identified in §3.2 are presented. In particular the current section deals with the results obtained within the TG-DSC-IR experimental protocol (Figure 3.1.1).

As evidenced in §3.2.2 scant data are available on the thermal stability and decomposition products of the materials of interest. This protocol is particularly suitable for a first screening of the thermal stability of the materials whose decomposition behaviour is unknown, since it is applicable to small quantities (order of few milligrams) at ambient pressure (no high pressure build-up is possible). The information obtained will allow to better design further experiments within this or others protocols.

3.3.1 – Thermogravimetric (TG) tests

Simple thermogravimetric tests were performed for a first characterization of the materials.

As shown in Figure 3.3.1 for 3-nitrobenzaldehyde, the use of open crucibles, even in inert atmosphere (pure nitrogen) results in the evaporation of the sample, not allowing to investigate the decomposition phenomena. Thus, to limit evaporative losses, a closed crucible was used. Evaporation is not allowed due to the presence of the sample in a closed cell. When decomposition occurs, pressure will build-up inside the cell, causing the opening of the lid. From that instant on, the crucible behaves more or less as an open cell.

Thus the experimental setup will allow to test:

i. The thermal stability of the materials
ii. The presence of decomposition steps occurring at different temperatures
iii. The formation of a non-volatile residue (char) after decomposition

The typical quantity of material used in the tests was between 5 and 10 mg.

All the materials resulted to be thermally instable in the interval 25 - 500 °C. Table 3.1.1 reports the average temperature of lid-opening in the different tests. The temperature is not expected to be a precise indicator of the decomposition range, since there is no control on the opening pressure of the cell. However it appears to be reproducible (typical scattering of few °C) among different tests on the same material.

The decomposition appears to be limited to one stage. The typical behaviour of the mass loss with respect to temperature is similar to the one showed in Figure 3.3.1 for all the materials. After lid opening a progressive weight loss is experienced, that shows a low steep trend at the higher temperatures (400-500°C).

This leads to the formation of a stable char as a result of the decomposition process. Average values for the char formation are reported in Table 3.1.1. The visual inspection of the char reveals it as a black porous solid.

The main conclusions that can be draw from the preliminary TG tests are:

- All the materials studied are thermally unstable at temperatures higher than 200°C. Expected onset temperature for the decomposition, estimated through the temperature of lid opening, are relatively similar among the two groups of nitrobenzaldehyde isomers and chloro-nitrobenzaldehyde isomers. Chlorinated isomers have slightly higher decomposition temperatures.
- The decomposition yields the formation of a char. The fraction of the final char is around 35 – 40% of the initial weight of the sample for many of the analysed

materials. The 2-nitrobenzaldehyde appears to be an exception, yielding a lover residue. This hints a different decomposition behaviour of this isomer, with an higher expected formation of volatile compounds.

- Evaporative phenomena occur in open cell tests, since decomposition temperatures are high (above 200°C). This represents a constraint for the design of the experimental tests on these materials.

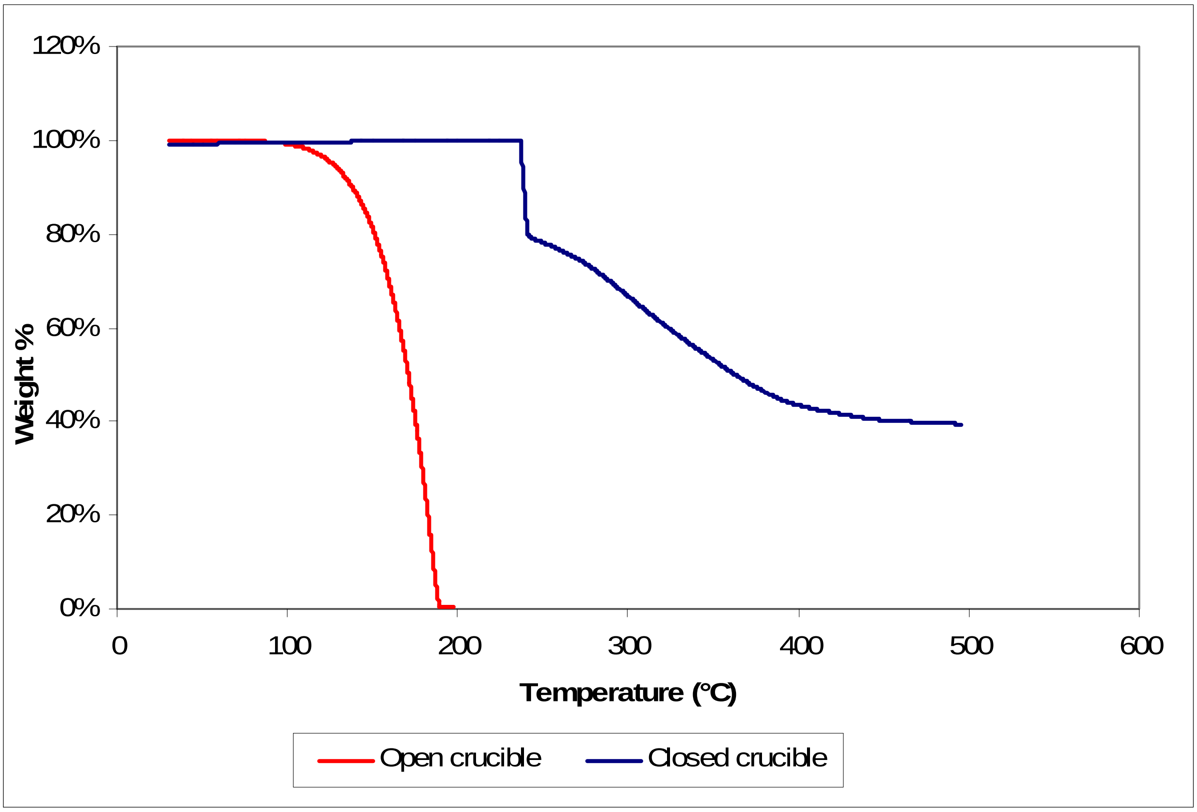


Figure 3.3.1 Weight loss in TG tests with open and closed crucibles for 3-nitrobenzhaldehyde.

Name	CAS	T lid-opening °C	Residue at 500°C %
2-Nitrobenzaldehyde	552-89-6	241	23.3
3-Nitrobenzaldehyde	99-61-6	237	39.4
4-Nitrobenzaldehyde	555-16-8	236	38.2
2-Chloro-6-nitrobenzaldehyde	6361-22-4	249	37.5
2-Chloro-5-nitrobenzaldehyde	6361-21-3	266	38.5
4-Chloro-3-nitrobenzaldehyde	16588-34-4	233	42.1

Table 3.3.1 Experimental results of the TG tests.

3.3.2 – Differential Scanning Calorimetric (DSC) tests

The six materials object of the study were analysed by Differential Scanning Calorimetry (DSC) in order to quantify the thermal effects related to the decomposition. More in detail, this experimental setup will allow obtain new information on :

- The onset temperature of the materials
- The presence of decomposition steps occurring at different temperatures
- The quantification of the thermal effects related to the decomposition steps
- The formation of a non-volatile residue (char) after decomposition

As shown by the TG data, open cells are not suitable for the analysis of these substances, since the evaporative phenomena are not negligible at the decomposition temperatures. Thus closed aluminium crucibles were used. Similarly to what described for TG, the closed crucibles used are not suitable for holding the built-up of pressure, so they will eventually open when decomposition occurs.

The temperature profile used in the tests was a ramp having a constant slope of 10°C/min. Average sample size was between 5 and 2.5 mg.

Several tests were performed for each of the substances of interest. Reproducibility resulted good for all the investigated materials. Data on heat fluxes were integrated to yield the decomposition effects of the thermal phenomena. The average among the different test runs was considered in further data analysis.

Table 3.3.2 reports a summary of the principal results of DSC analysis. Table 3.3.3 compares the results with the available literature data. Figures 3.3.2 and 3.3.3 show the profiles of the heat fluxes with respect to temperature as obtained in one of the runs for each substance.

	Heat of melting (J/g)	**Melting temp. (°C)**	**Onset temp. (°C)**	**Heat of decomposition (J/g)**	**Residue at 500°C (%)**
2-Nitrobenzaldehyde	-82	42	236	1106	23%
3-Nitrobenzaldehyde	-126	53	242	699	40%
4-Nitrobenzaldehyde	-164	101	239	630	38%
2-Chloro-6-nitrobenzaldehyde	-74	65	223	936	36%
2-Chloro-5-nitrobenzaldehyde	-93	66	265	541	33%
4-Chloro-3-nitrobenzaldehyde	-113	60	203	839	43%

Table 3.3.2 Summary of the experimental results of DSC tests.

The results in Table 3.3.2 confirm the outcomes of the TG runs. In particular the fraction of the residue is frequently in line with TG results. This was expected, due to the similar conditions of the two tests in terms of heating rate, material quantity and cell structure. However it should be remembered that after lid opening, uncontrolled evaporative phenomena occur and the residue fraction varies in the different tests.

The temperature of lid opening introduced in the discussion of TG runs is confirmed to be an estimator of the decomposition temperature, even if a strong correlation does not exist, because thermal and gas generation effects can not be contemporary.

The 2-nitrobenzaldehyde shows two main stages of decomposition (Figure 3.3.2). The first one at 236°C and the second one around 246°C. The two main peaks partially overlap. The second peak is relatively broad and slightly exothermic phenomena can be identified around 281°C. However it is expected that the test cell has already opened at that temperature and, thus, the peak is not clearly identificable in all the tests, due to material losses. The char formed from decomposition appears to be thermally stable up to 500°C.

The 3-nitrobenzaldehyde shows a single decomposition stage, quite sharp (Figure 3.3.2). The average onset temperature is 242°C, thus higher than the first peak of 2-nitrobenzaldehyde, but very similar to the second peak. The chemical structure of 2- nitrobenzaldehyde (Figure 3.2.1) suggested an higher reactivity of the molecule, that may be responsible of the first stage of decomposition for the ortho-isomer. In 3-nitrobenzaldehyde the char formed from the first decomposition does not appear to be fully stable, since modest exothermic effects occur between 275 and 355 °C. However these effects are quite low, although they appear reproducible in the tests.

The 4-nitrobenzaldehyde has a behaviour very similar to 3-nitrobenzaldehyde, with respect the onset temperature, profile of heat fluxes, heat of decomposition and final residue. This seems to suggest similar decomposition mechanism for the two isomers. The similarity with the second stage of 2-nitrobenzaldehyde is interesting too.

With respect to the chlorinated isomers, the behaviour appears quite different among the different materials (Figure 3.3.3). In all the cases decomposition occurs in a single stage, but onset temperatures are rather different.

The 2-chloro-6-nitrobenzaldehyde starts decomposition at 223°C, thus lower than the correspondent non-chlorinated nitrobenzaldehyde. The peak is however centered on the same temperatures as the non-chlorinated nitrobenzaldehyde isomers. The char formed does not yield other detectable thermal effects.

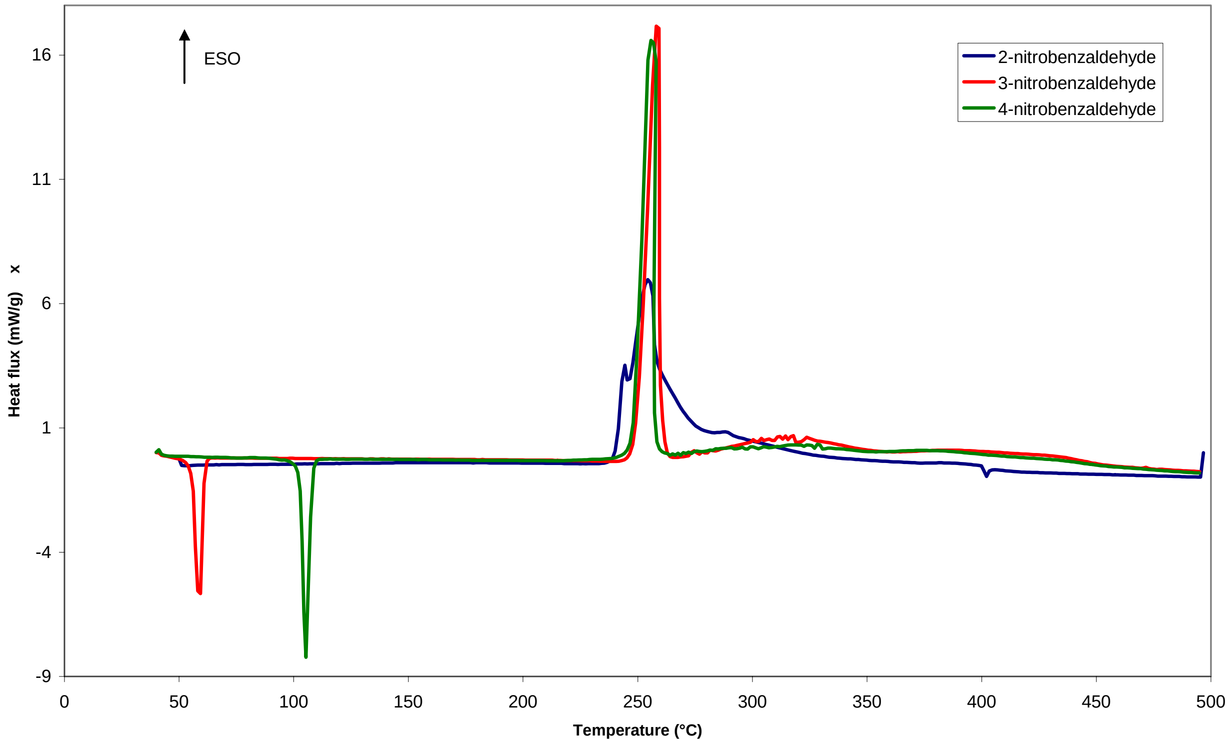


Figure 3.3.2: Profile of the heat fluxes as to temperature at DSC for the isomers of nitrobenzaldehyde.

For 2-chloro-5-nitrobenzaldehyde the detected onset is at 265°C, higher than that of any other isomer. The char shows a slightly exothermic flux between 290 and 355°C. This is an interesting similarity with the non chlorinated isomers, 3-nitrobenzaldehyde and 4-nitrobenzaldehyde. The other chlorinated isomer with meta-oriented nitro-group shares this peak too. However the behaviour of 4-chloro-3-nitobenzaldhyde is peculiar with respect to the other exothermic effects: the main decomposition peak has a very sharp and steep heat flux rise at a relatively low onset temperature (203°C) and a second low peak is observed for char decomposition between 340 and 390°C. While the secondary peak is reproducible among the tests, the primary peak was occasionally found at lower onset temperatures (in one test was as low as 158°C). The geometric shape and the heat release of the drifted peak however is similar independently on the temperature. This, together with the sharp steepness of the peak suggest that specific issues (e.g. catalytic effects of impurities, etc.) influence the activation of the decomposition of this compound.

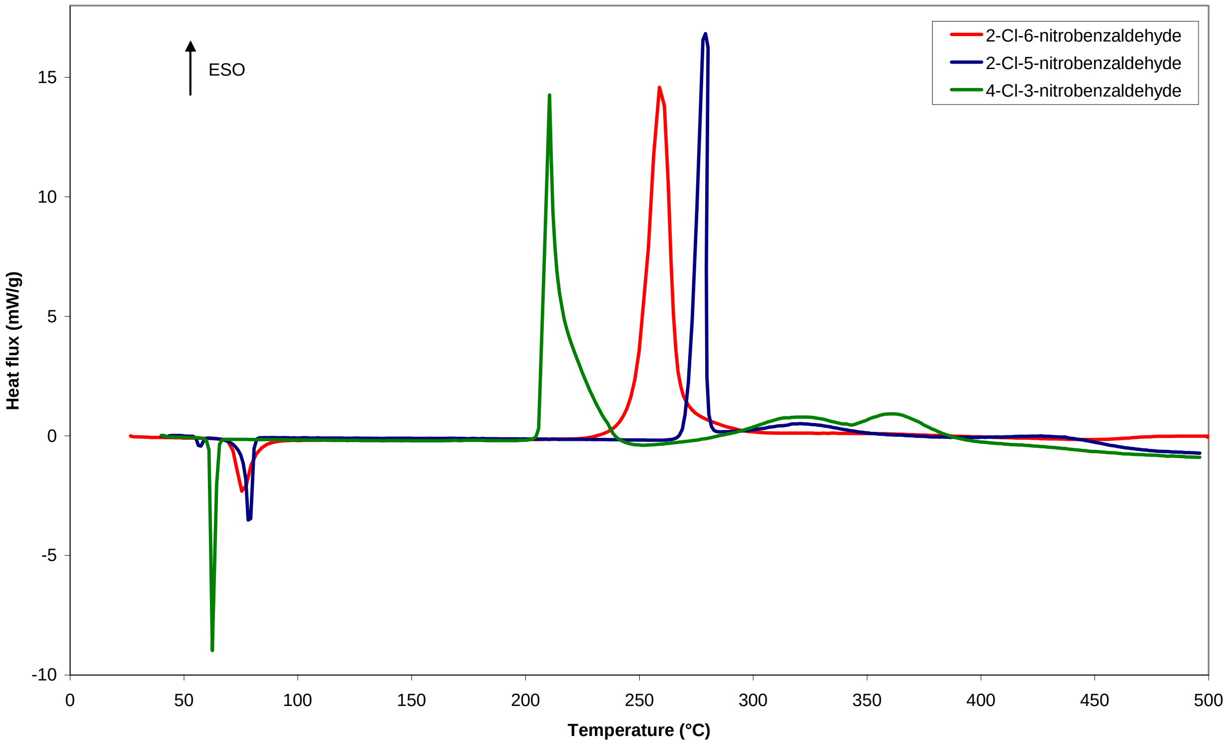


Figure 3.3.3: Profile of the heat fluxes as to temperature at DSC for the considered isomers of chloro-nitrobenzaldehyde.

The comparison of the decomposition behaviour of nitrobenzaldehyde isomers with the few literature data available (Table 3.3.3) is difficult due to the different experimental techniques used by the different authors.

With respect to the onset temperature, all the sources agree in identifying the ortho-isomer as the less stable. However both the literature sources describe the meta- and para-isomers as largerly different than they appear in the current survey.

The onset temperature determined by DSC test is, as well known, influenced by the temperature profile of the test. For the sake of clarity, Figure 3.3.4 reports the curves of 3 tests on 3-nitrobenzadheyde.

In the comparison of the heats of decomposition with literature data (Table 3.3.3), the results of the current study appear to be systematically lower than the values reported from other sources. This can be partially interpreted as a consequence of the uncontrolled loss of material after lid opening in the DSC tests. This aspect is expected to be common also to chlorinated materials. A properly designed test will be discussed in order to provide more accurate estimation of the heat of reaction (§3.3.6).

	Onset temperature (°C)			**Heat of decomposition (J/g)**		
	c. s.	***Ando***	***Cardillo***	***c. s.***	***Ando***	***Cardillo***
2-Nitrobenzaldehyde	236 (~246)	223	176 (194)	1106	2119	> 1500
3-Nitrobenzaldehyde	242	262	166 (210)	699	2487	> 1500
4-Nitrobenzaldehyde	239	285	226	630	2805	> 1500
2-Chloro-6-nitrobenzaldehyde	223			936		
2-Chloro-5-nitrobenzaldehyde	265			541		
4-Chloro-3-nitrobenzaldehyde	203			839		

Table 3.3.3 Comparison of the experimental results of DSC tests with literature data. c.s.: current study; Ando: Ando et al. 1991; Cardillo: Cardillo 1998.

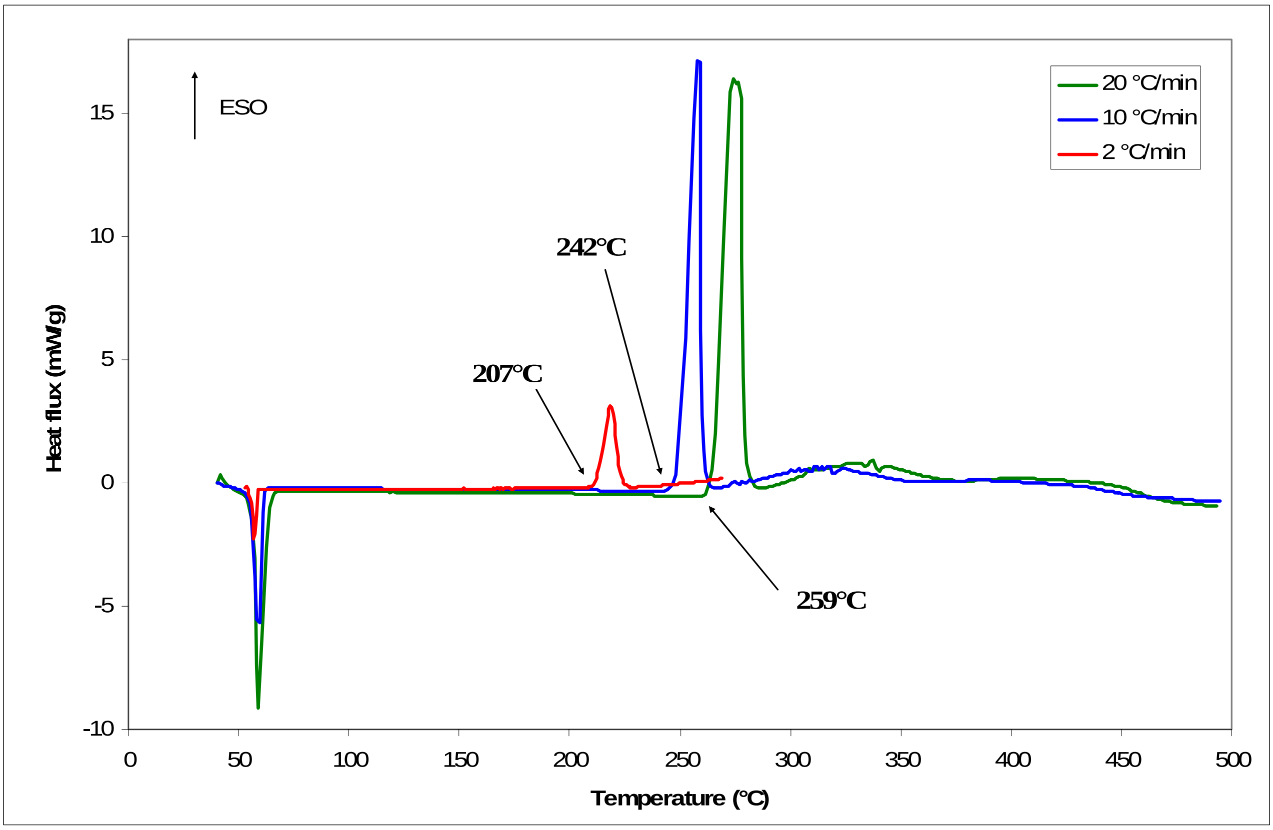


Figure 3.3.4: Heat fluxes as to temperature at DSC for 4-nitrobenzaldehyde. The curves were obtained by tests with different temperature profiles.

3.3.2 – TG and DSC combined tests

The developed experimental protocols (§3.1.1.1) and the equipment used (§3.1.2.1) allow the coupling of TG with DSC results (NETZSCH STA 409 C). In the case study of interest, these tests do not yield new results compared to what discussed earlier. However, for sake of completeness, the data obtained for only two materials out of six are presented in the following.

The test used a closed cell as described in the previous DSC test; the lid of the cell will open when pressure is built-up from decomposition. The use of larger crucibles allowed to test material quantities around 10 mg. The heating rate is the same as previous tests (10°C/min) and the instrument head is flushed by a 60 ml/min flow of nitrogen.

Figure 3.3.5 reports a typical result for a TG-DSC test on 2-nitrobenzaldehyde. The conclusions that can be drawn from the graph are similar to those discussed for single TG and DSC experiments. From the graph it is evident that, after lid opening, decomposition and evaporation phenomena are concomitant, as shown by the trend of the DSC curve at lid opening temperature. Another interesting effect is showed among 300 and 400°C, where a weight loss is experienced with negligible thermal effects: this is due to the volatilization of the char. This justifies expressing the data as a char fraction at a fixed temperature (500°C in Tables 3.3.1 and 3.3.2).

Similar comments can be done on Figure 3.3.8, later in the text, featuring a TG-DSC test on the 2-chloro-6-nitrobenzaldehyde.

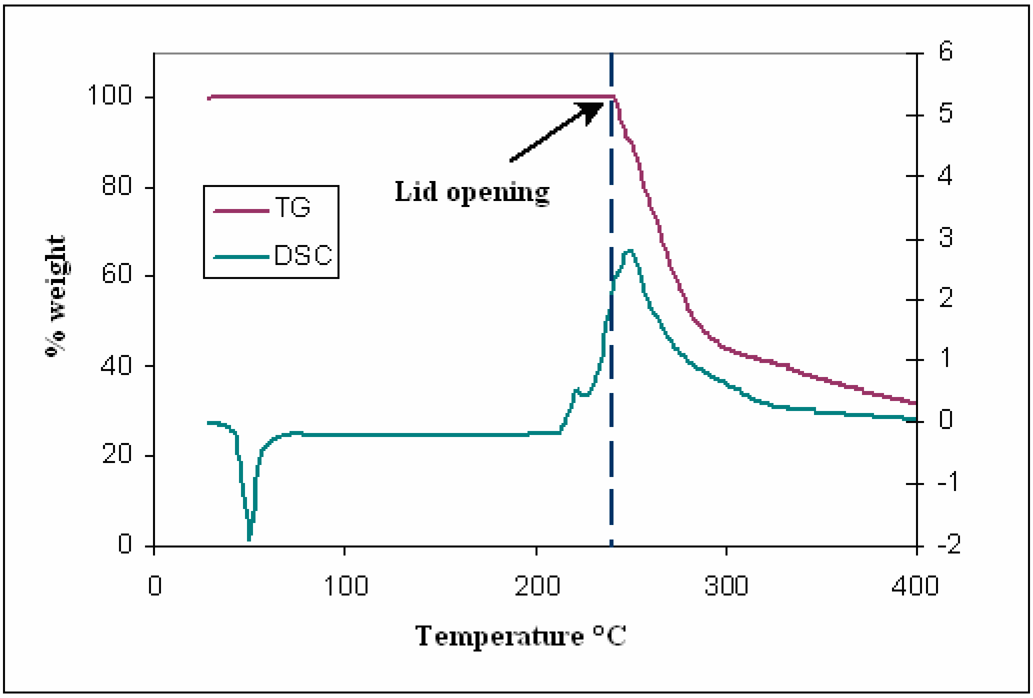


Figure 3.3.5: Heat fluxes as to temperature in a DSC-TG test on 2-nitrobenzaldehyde.

3.3.4 – TG-DSC-FTIR combined tests

The experimental protocol (§3.1.1.1) and the equipment used (§3.1.2.1) allow to integrate TG, DSC and FTIR tests at once (NETZSCH STA 409 C + transfer line + Bruker Equinox 55). This allow the identification of some the gaseous products formed in the decomposition. The

technique has obvious limits related to the IR detection (i.e. minimum detectable concentrations and IR transparent molecules).
Results are presented here for the 2-nitrobenzaldehyde and the 2-chloro-6-nitrobenzaldehyde. The TG-DSC part of the test for these substances was actually discussed in §3.3.3.
Figure 3.3.6 reports a typical IR spectrum obtained for 2-chloro-6-nitrobenzaldehyde. The bands of carbon monoxide, carbon dioxide and hydrogen chloride can be can be recognized in the spectrum. Water can be recognized too, but it is related with issues of the experimental setup.

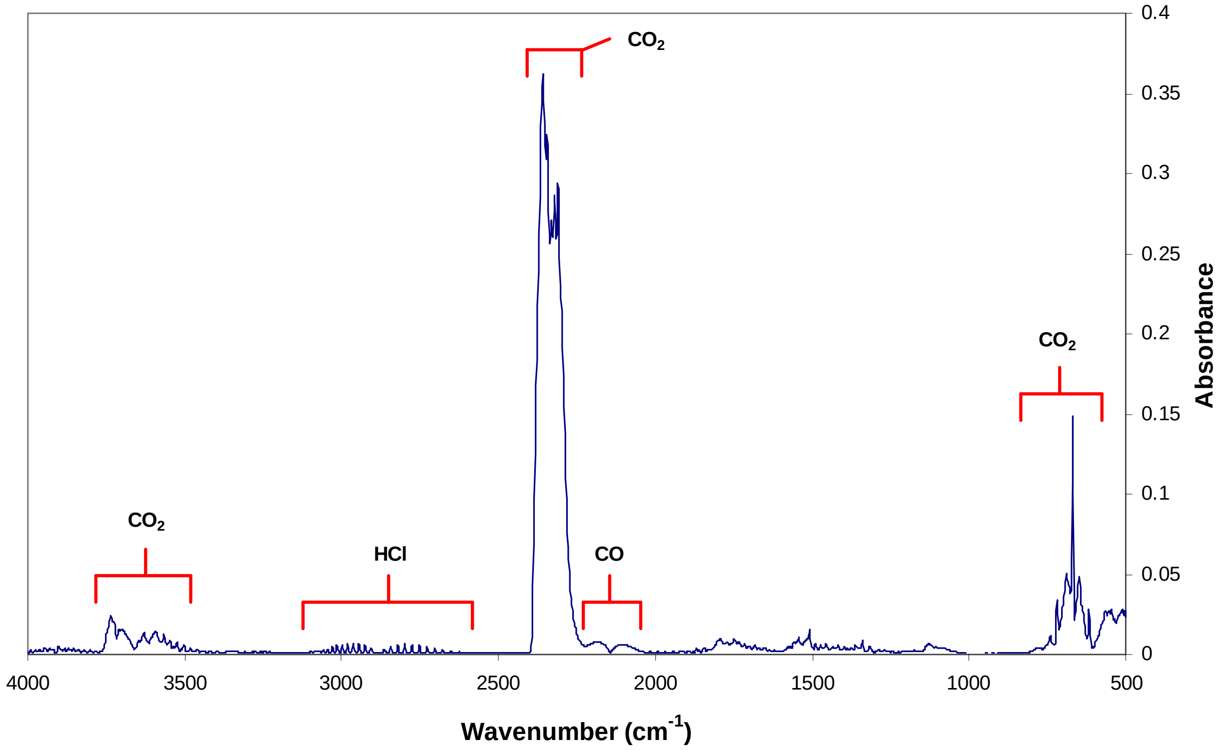


Figure 3.3.6: Example of an IR spectrum obtained in a TG-DSC-FTIR test for 2-chloro-6-nitrobenzaldehyde.

Furthermore the TG-DSC-FTIR technique yields a profile of the product formation along the test. By a proper calibration, quantitative data can be obtained. Calibration was obtained for carbon dioxide, carbon monoxide and hydrogen chloride by the gas pulse method described in §3.1.2.1.

Figure 3.3.7 reports the profile of carbon monoxide and carbon dioxide signal as a function of the cell temperature in the case of 2-nitobenzaldehyde. Data are corrected for the lag time of the transfer line. The figure reports the TG graph registered in the test. It can be observed that both the gases are released when the lid of the cell opens. They are both formed in the decomposition, even if it is not possible to know from this test if they originated since the first stage or only in the second.
A secondary carbon dioxide release peak is detected between 310 and 370°C.

The calibration data allow to quantify the integral quantity released, that correspond to an average of 192mmol of CO_2 and 27mmol of CO per mol of initial sample. This quantity is likely to be an underestimation of the potentially releasable gases, due to the evaporative phenomena that may occur after lid opening.

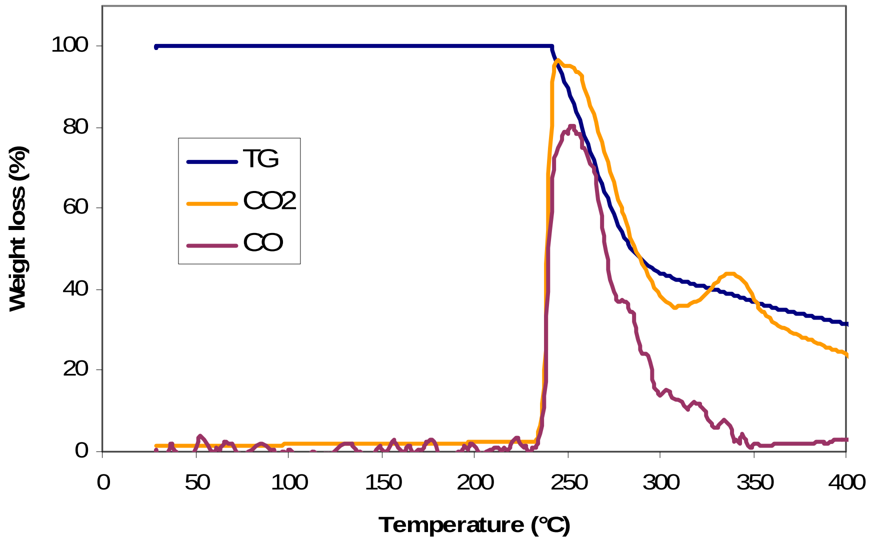


Figure 3.3.7: Release curve for carbon dioxide and carbon monoxide in TG-DSC-FTIR tests on 2-nitrobenzaldehyde. The weight loss curve from TG is reported too. Both CO_2 and CO signals were rescaled by an arbitrary factor to improve visualization.

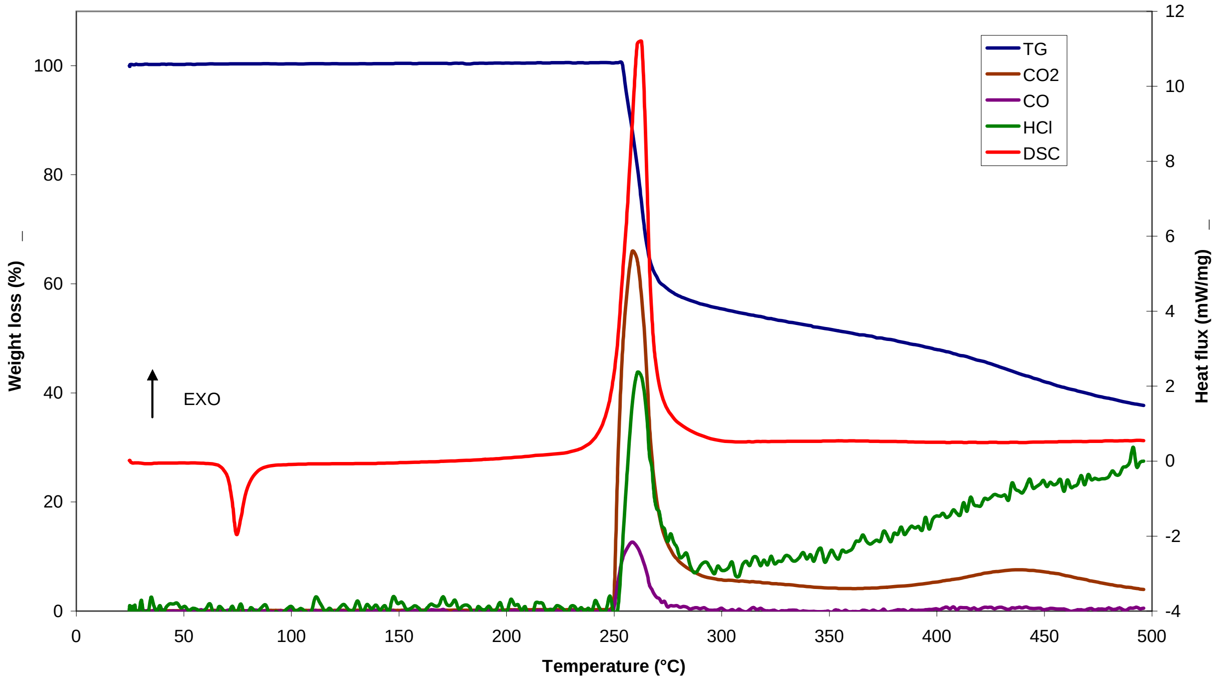


Figure 3.3.8: Release curve for carbon dioxide, carbon monoxide and hydrogen chloride in TG-DSC-FTIR tests on 2-chloro-6-nitrobenzaldehyde. The weight loss curve from TG and the heat fluxes from DSC are reported too. All the substance release signals were rescaled by an arbitrary factor to improve visualization.

The behaviour of chlorinate isomers in TG-DSC-FTIR tests is quite similar to what previously described. Figure 3.3.8 summarizes the curves obtained for 2-chloro-6-nitrobenzaldehyde. Carbon monoxide, carbon dioxide and hydrogen chloride are all released in the main decomposition step.
Important releases of hydrogen chloride from the char are detected at temperatures higher than 300°C. A temperature cycle test was also performed (Figure 3.3.9): temperature is risen till 300°C as in a regular test than the sample is cooled down and the transfer line purged. A new test with the regular temperature profile shows hydrogen chloride release at temperature higher than 300°C with non appreciable release of other compounds, as e.g. carbon dioxide.

The use of calibration data yield the released quantities of the three substances: 600mmol of CO_2, 54mmol of CO and 474 mmol of HCl per mol of initial sample. Also in this case, this quantity is likely to be an underestimation of the potentially releasable gases, because of the evaporative phenomena that may occur after lid opening.

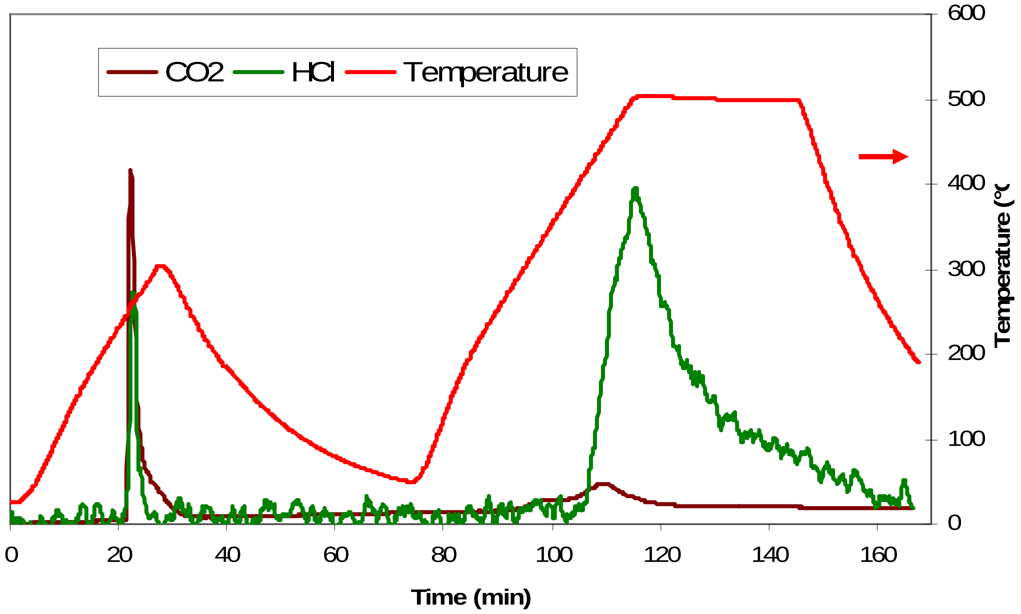


Figure 3.3.9: Release curve for carbon dioxide and hydrogen chloride during a cyclic TG-DSC-FTIR tests on 2-chloro-6-nitrobenzaldehyde. The temperature profile is reported too. Both CO_2 and HCl signals were rescaled by an arbitrary factor to improve visualization.

3.3.5 – DSC-GC combined tests

The off-line combination of the DSC and GC techniques allows to monitor both the thermal effects of reaction and the reagent conversion. The final goal of the test is to identify the overall heat of decomposition without limitations by evaporative effects.

The DSC runs were performed in a Mettler DSC-25. Tests were carried out using a purge gas flow (300 ml/min at 25°C) of pure nitrogen. Aluminium closed test cells were used (160µl). Typical sample mass is of 3-4 mg; this leaves some free volume in the test cell to prevent cell opening from pressure build-up, at least in the earlier phases of the decomposition. At pre-identified temperatures test runs were stopped and the cell was quenched. Weight loss was checked to verify any appreciable weight loss due to gas/vapour release from the cell. Cells were opened and an acetone solution of the content was prepared and injected in the gas chromatograph.

In order to obtain quantitative data, a calibration is needed among the concentration of the solution and the output signal of the GC. This was obtained injecting solutions having known concentration. Figure 3.3.10 shows an example of calibration line for 3-nitrobenzaldehyde. The calibration correlation is linear in the range of interest.

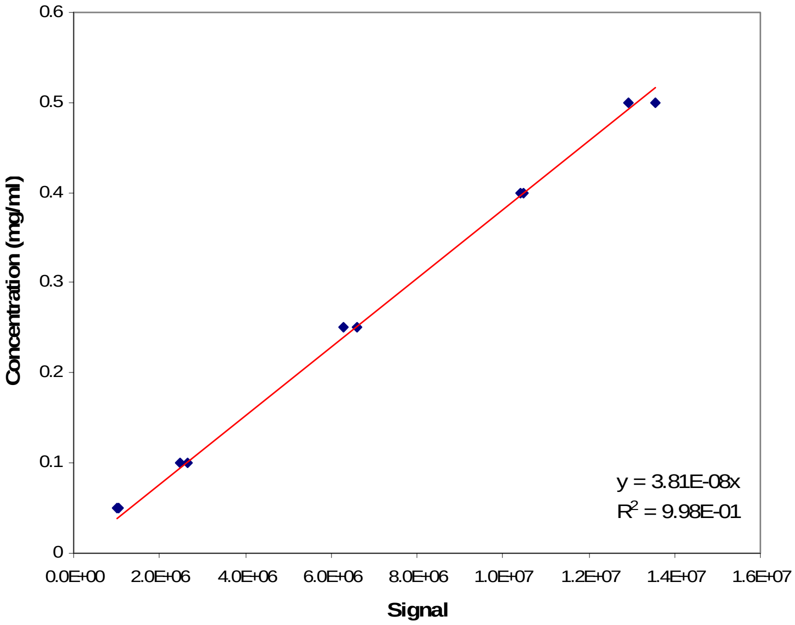


Figure 3.3.10: Calibration curve of 3-nitrobenzaldehyde for GC tests.

Figure 3.3.11 plots the results for the thermal effect with the conversion of 3-nitrobenzaldehyde. Although data scattering is appreciable, due to the random errors introduced by the experimental technique used, a linear correlation can be identified among the points. The slope of the interpolation line (1057 J/g) is a good evaluation of the heat of decomposition for the 3-nitrobenzaldehyde, within the experimental errors of the technique. At values of conversion higher than 70% the cell opens, yielding higher apparent conversions, due to material loss. The interpolation line does not show zero conversion for zero thermal effect. This bias was interpreted as a systematic error introduced by the experimental setup.

Once a correlation is known among total thermal effects and conversion, an apparent kinetic model can be proposed for DSC data. Figure 3.3.12 reports an Arrenius plot for the 3-nitrobenzaldehyde. A 0-order apparent kinetic model is assumed:

$$\frac{d\chi}{dt} = -A\, e^{-\frac{E}{RT}} \qquad (3.3.1)$$

The regression of the Arrenius plot yield an activation energy of 557 kJ/mol. This is a rather high value, but it is consistent with a relatively high onset temperature as 242°C and a quick decomposition.

Table 3.3.4 summarize the thermal and kinetic data identified by DSC-GC tests.

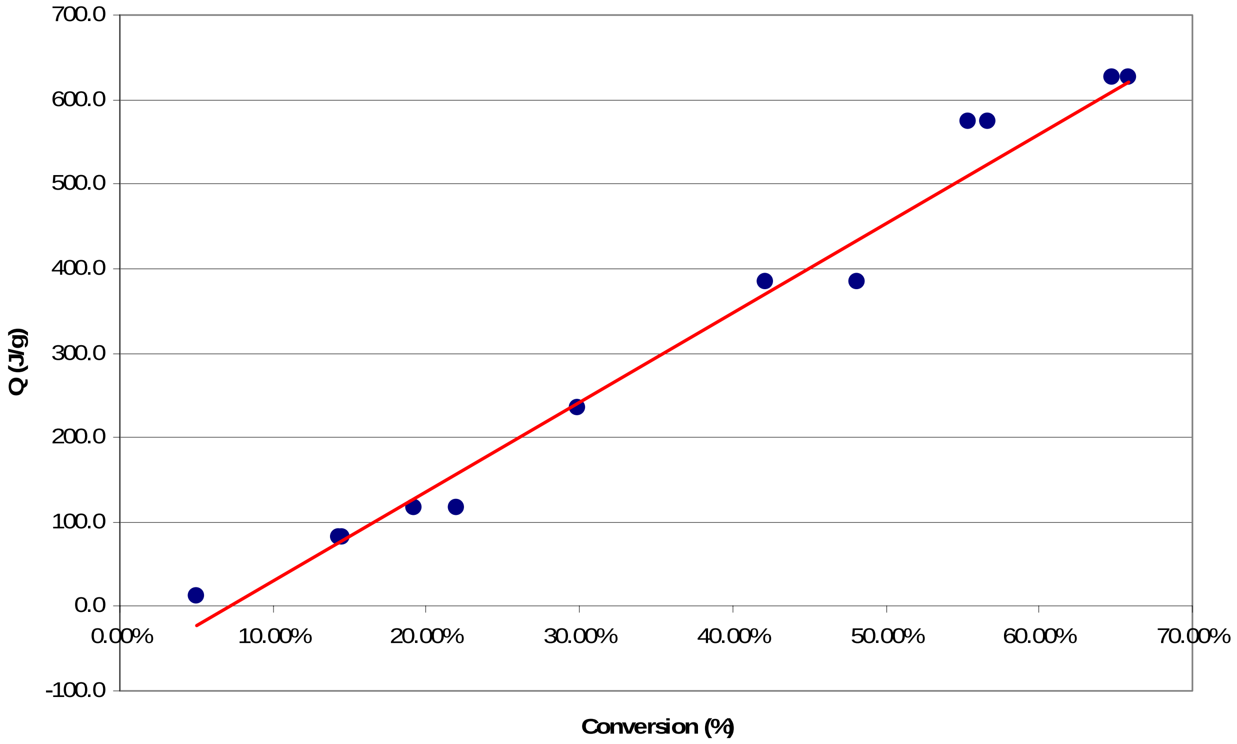


Figure 3.3.11: Heat release as function of conversion of the initial material in DSC-GC of 3-nitrobenzaldehyde for GC tests.

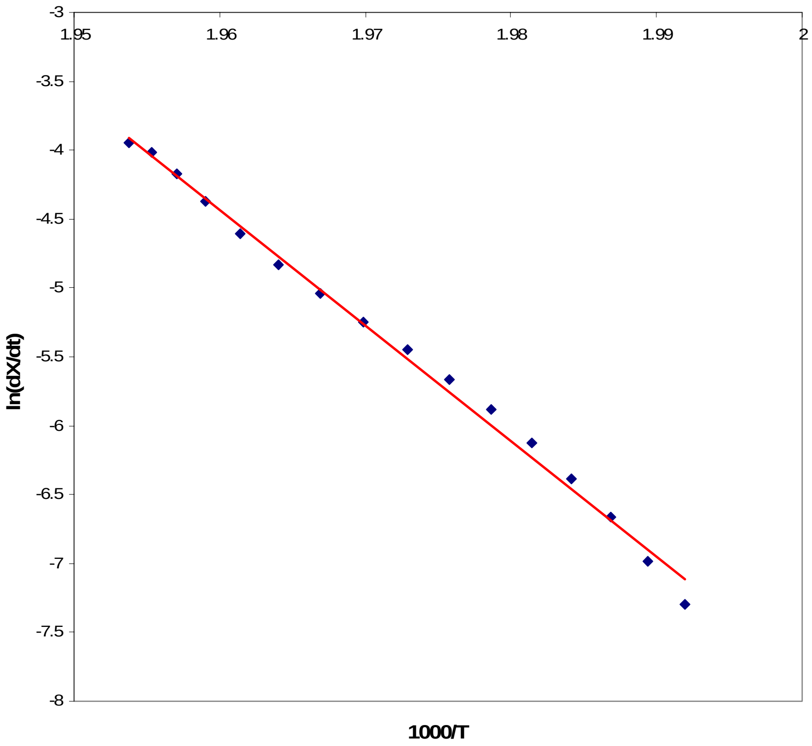


Figure 3.3.12: Arrenius plot for DSC test on 3-nitrobenzaldehyde.

A similar procedure was followed for the 4-nitrobenzaldehyde. Figure 3.3.13 plots the results from the DSC-CG tests. The general comments on the figure are the same earlier presented for 3-nitrobenzaldehyde. However here the data bias at low conversions appears higher. In this case the presence of initial reactions with small thermal effects may not completely excluded, as suggested by the low conversion data presented in the figure. The heat of decomposition obtained by the regression of the line is 1386 J/g.

Also in this case a kinetic model was evaluated from DSC data. The Arrenius plot is reported in Figure 3.3.14. The activation energy for an first order apparent kinetic results 562 J/kmol. Again the values is quite high. Table 3.3.4 summarize the thermal and kinetic data identified by DSC-GC tests.

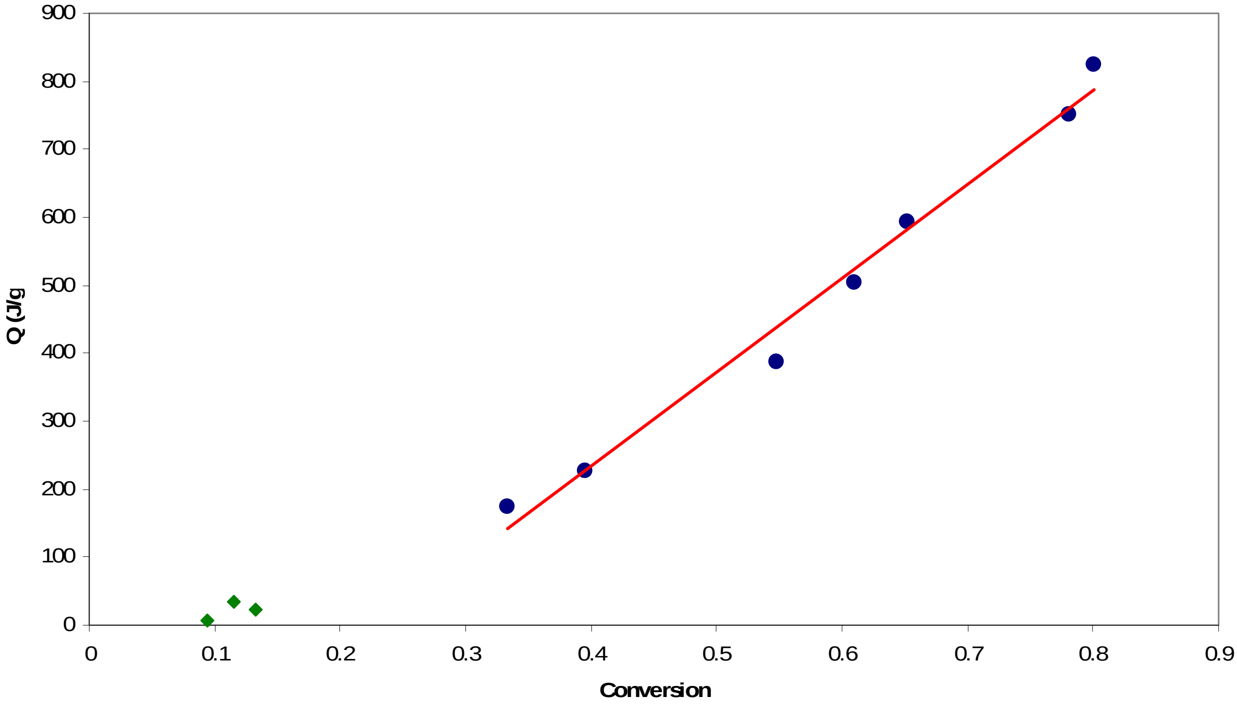


Figure 3.3.13: Heat release as function of conversion of the initial material in DSC-GC of 4-nitrobenzaldehyde for GC tests.

	3-Nitrobenzaldehyde	*4-Nitrobenzaldehyde*
Heat of decomposition (J/g)	1057	1386
Activation energy (kJ/mol)	557	562
Pre-exponential factor (s^{-1})	$7.80 \cdot 10^{54}$	$2.00 \cdot 10^{55}$

Table 3.3.4: Summary the thermal and kinetic data identified by DSC-GC tests

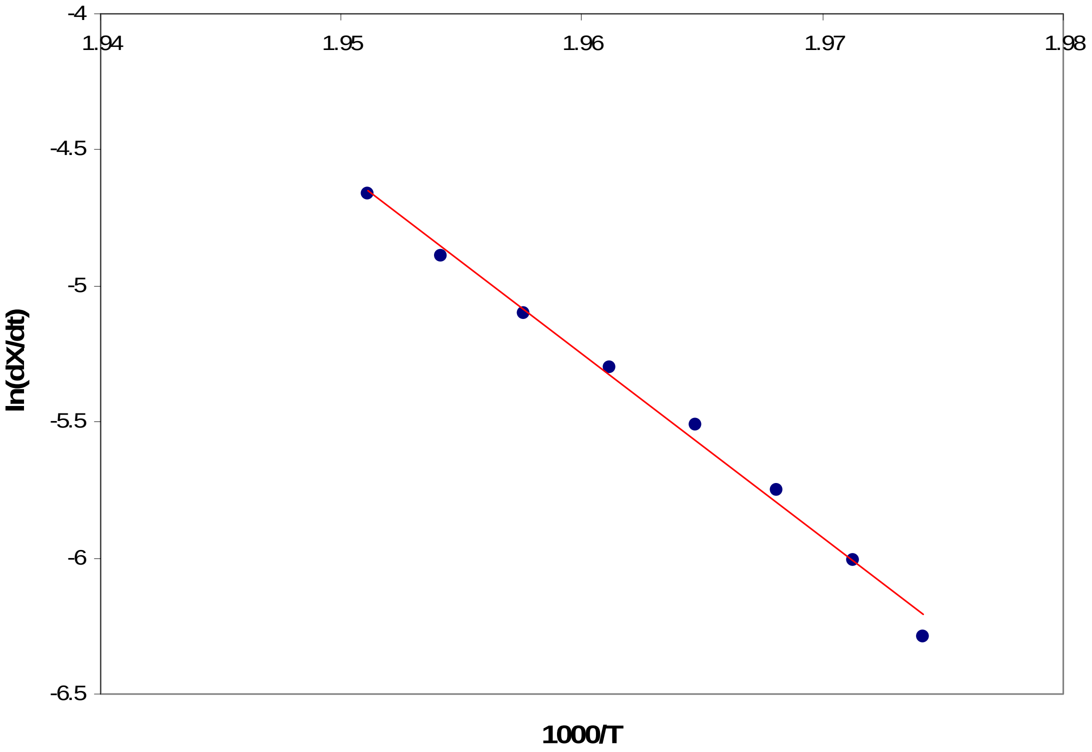


Figure 3.3.14: Arrenius plot for DSC test on 4-nitrobenzaldehyde.

3.4 – Results from experimental studies: DTA

3.4.0 – Overview

The current section presents the results obtained within the DTA experimental protocol (Figure 3.1.2) for the group of materials identified in §3.2.
The application of this protocol provides useful data for the design of the adiabatic calorimetry tests (§3.5).

3.4.1 – DTA tests

The DTA tests were performed by the Radex oven. The DTA tests overcome some of the limits of DSC tests. In fact, the test cell is able to withstand pressures up to 100bar. Tests aimed at the following objectives:

i. Study of the decomposition behaviour
ii. Study of the gaseous product release as a function of the temperature
iii. Study of the formation of non-volatile residue (char)

The principal limit of the DTA technique, as it was applied in present study, concerns the non availability of data on heat fluxes.
Typical sample sizes used in these study were of about 250mg. The sample size was chosen at the lower side of the possible range to avoid excessive pressure build-up. The cell material is stainless steel. The sample in the cell is not stirred, but lays in the bottom surrounding the cell temperature thermocouple. Cells are sealed in air.
The temperature profile of the oven is a constant slope ramp of 1°C/min till the maximum temperature of 380°C. Test runs on the same material showed good reproducibility.

Figure 3.4.1 shows an example of typical result of the test for a 2-nitrobenzaldehyde sample.
The red line reports the pressure increase with respect to oven temperature or time (that is the same because of the constant heating rate). The initial drift of the line upward is partially due to expansion of the gasses trapped in the cell. In data elaboration pressure data were corrected subtracting the contribution by assuming the perfect gas model. The same gas model allows defining the quantity (moles) of gas present in the cell. This can be corrected by the number of moles initially present in the vapour space to yield the moles released during the tests. Summing up:

$$\varepsilon(t) = \frac{n_r(t)}{n_0} = \left(\frac{P(t)}{T(t)} - \frac{P(t=t_0)}{T(t=t_0)} \right) \frac{V}{R} \frac{1}{n_0} \qquad (3.4.1)$$

where ε is the release ratio, $n_r(t)$ is the number of moles released at time t, n_0 the sample molar quantity, $P(t)$ and $T(t)$ the cell pressure and temperature at time t, V the cell volume, R the perfect gas constant and t_0 a reference time.

The blue line of Figure 3.4.1 shows the temperature difference of the sample cell (reactor) and the oven. The oven is heating the reactor, so in normal conditions there is a constant temperature difference that is the driving force of the heat exchange. When exothermic phenomena occur in the sample, the temperature difference decreases due to heat generation. The temperature difference data were elaborated subtracting a polynomial baseline obtained interpolating the sections of the curve where no decomposition occurs. The heat transfer among the oven and the rector is not fully reproducible and blank runs are not suitable to obtain reliable baselines.

The parameter obtained by the subtraction of the baseline (named Δ) can be plotted as a function of the reactor temperature. The resulting curve is qualitatively comparable with DSC curves in terms of number and temperatures of the peaks. Of course the effects of peak drifting because of different temperature profiles in the test should be considered, as earlier discussed with respect to Figure 3.3.4.
In the plots of Δ as function of the temperature of the reactor, a peculiar graphic effect may appear: peaks "bend" with segments of the curve that are back-moving on the reactor temperature axis. This is a consequence of the plotted parameter Δ being a temperature difference. The effect is graphically explained in Figure 3.4.2.

Figure 3.4.3 reports the profiles of Δ and ε as a function of the temperature of the reactor for 2-nitrobenzhaldehyde. The figure reports the DSC results for the same material. It can be observed that the two partially overlapped stages of decomposition, identified by DSC runs, are detected also by DTA. As expected for the slower temperature rise in DTA (1°C/min vs. 10°C/min of DSC tests) the peaks are shifted at lower temperatures. The first exothermic effects related to decomposition (i.e. onset) can be identified at about 195°C. A secondary peak, not present in DSC tests, is detected for temperatures higher than 320°C. This can be interpreted as a further decomposition of the materials generated by the two main decomposition stages. The volatilization of the materials after lid opening is probably the cause of the absence of this peak in DSC runs.

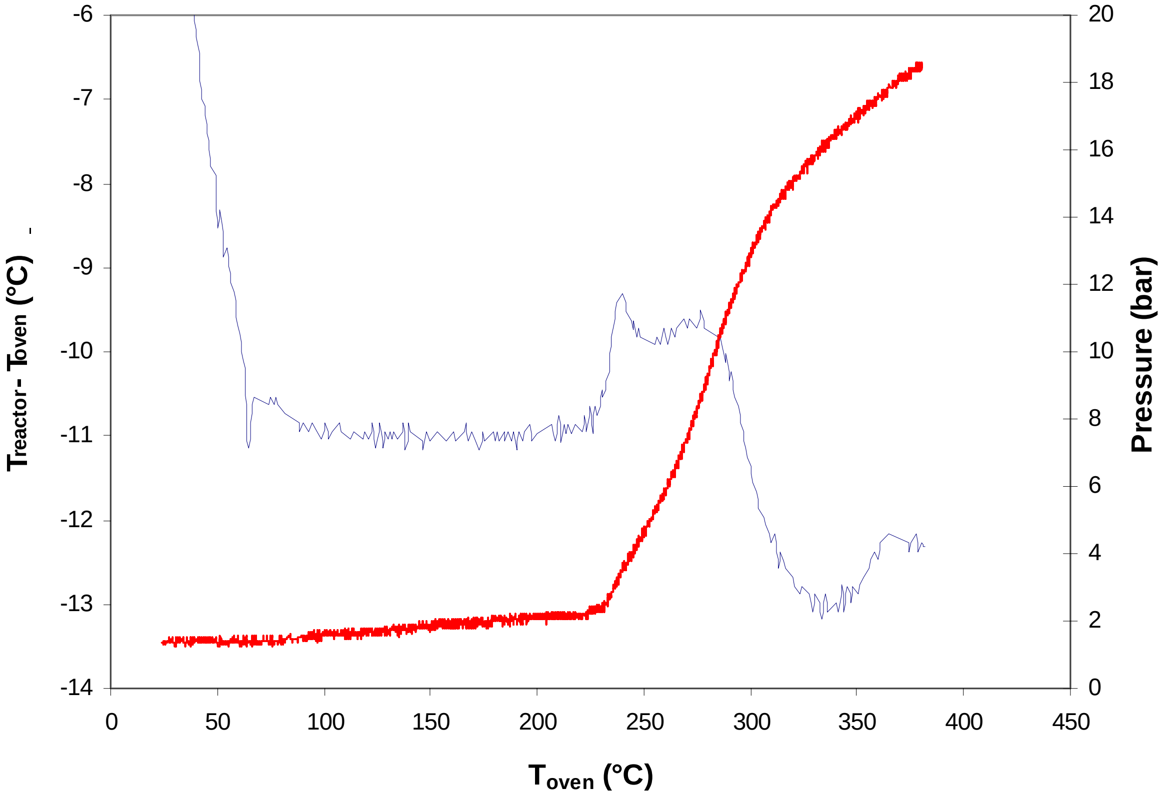


Figure 3.4.1 Example of typical output from DTA tests on 2-nitrobenzhaldehyde.

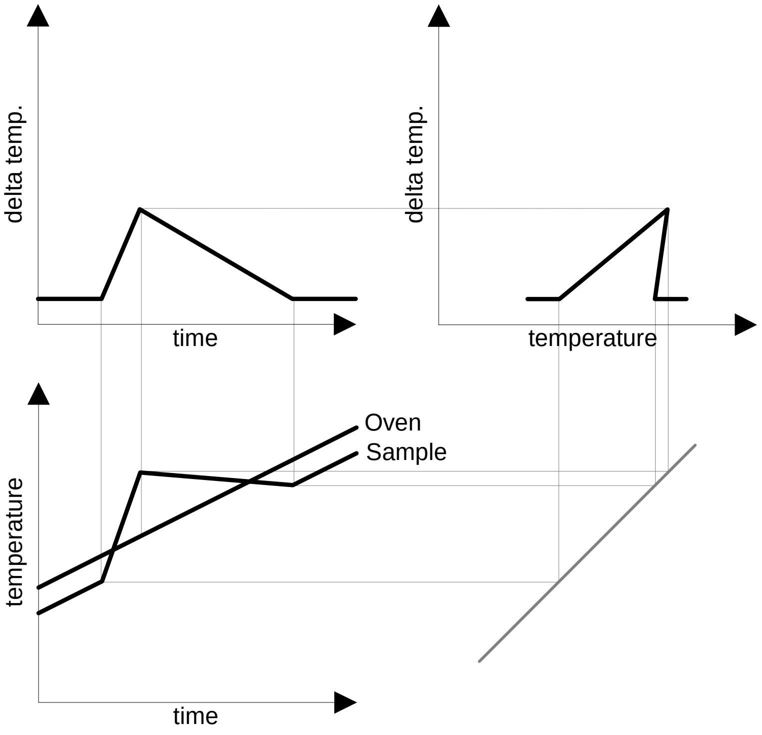


Figure 3.4.2 Graphical example of "peak bending" in "Δ – $T_{reactor}$" plots. From low right, moving clockwise: temperature-time plot showing $T_{reactor}$ and T_{oven} profiles; Δ-time plot; Δ – $T_{reactor}$ plot, showing a back-moving segment.

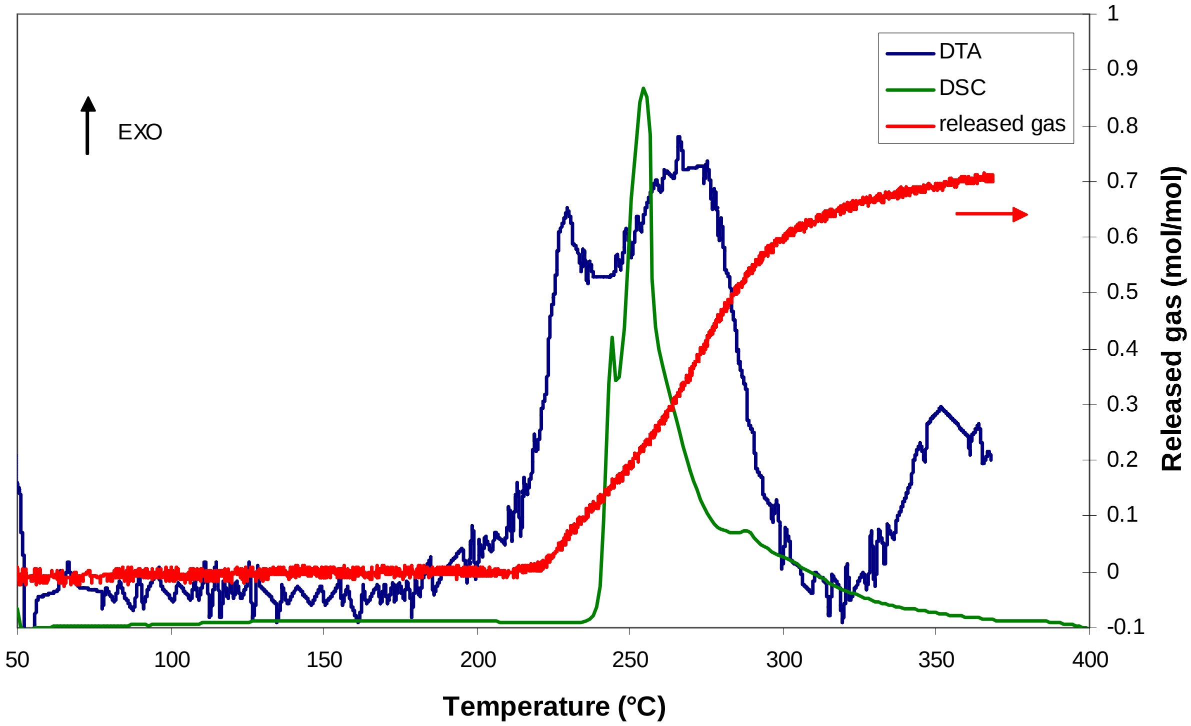


Figure 3.4.3 Results from the DTA test on 2-nitrobenzaldehyde. A heat flux curve from DSC tests is reported in the graph; scales on y-axis of DTA and DSC were altered to allow qualitative comparison.

With respect to the quantity of gases in the vapour space of the cell, it has been evaluated by equation (3.4.1). At temperatures below onset temperature no appreciable drift from the horizontal baseline is appreciated: thus evaporative phenomena, if present, are below the detection limit. The release of gases appears to be slightly delayed compared to the onset. The release is significant during the two main decomposition steps. Above 310°C, that is the upper limit of the second decomposition peak, the rate of gas release decreases, but does not appear to stop completely. This is interpreted as a gas release from the slow decomposition of the primary residue. However no clear correspondence is found among the variation in gas release rate and the peak above 320°C.

Figure 3.4.4 shows the results a of DTA test on 3-nitrobenzaldehyde. Also in this case the behaviour detected with DSC is confirmed. A single decomposition stage is identified with an onset temperature of 218°C. Above 275°C further exothermic effects are identified (two low peaks can be identified, one starting at 275°C and the other at 320°C). This may correspond to the low peak observed in DSC runs above the main decomposition peak.
The release of gases shows a sharp step at thermal onset temperature. The release ratio (ε) of this step is about 0.13, meaning that 13 mol of gases are released for 100 mol of 3-nitrobenzaldeide in this phase. Above the temperatures of the main decomposition, the gas release continues, as previously discussed for 2-nitrobenzaldheyde. However, in this case, a change of release rate is experienced for the temperatures corresponding to the decomposition of the primary residue. As a matter of fact, the majority of the released gas is produced in this phase.

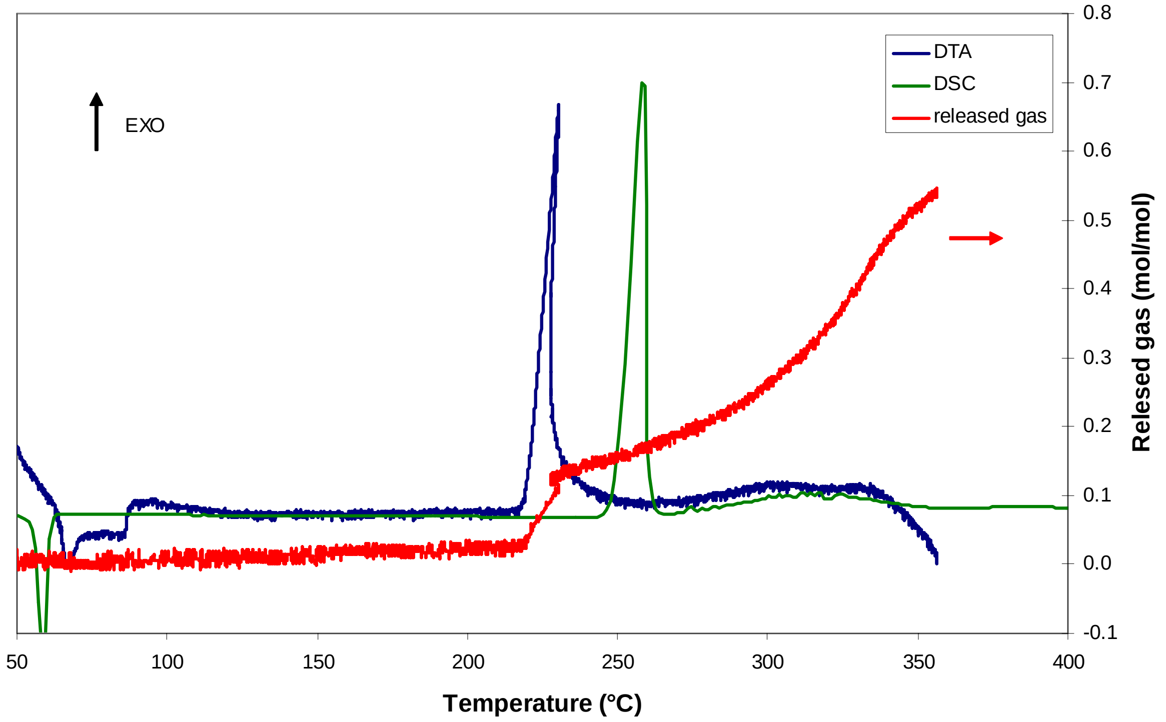


Figure 3.4.4 Results from the DTA test on 3-nitrobenzaldehyde. A heat flux curve from DSC tests is reported in the graph; scales on y-axis of DTA and DSC were altered for allow qualitative comparison. (Note: the values of Δ for temperatures above 250°C are influenced by the choice of the baseline, that is admittedly difficult because of the change of heat transfer coefficients of the system due to char formation)

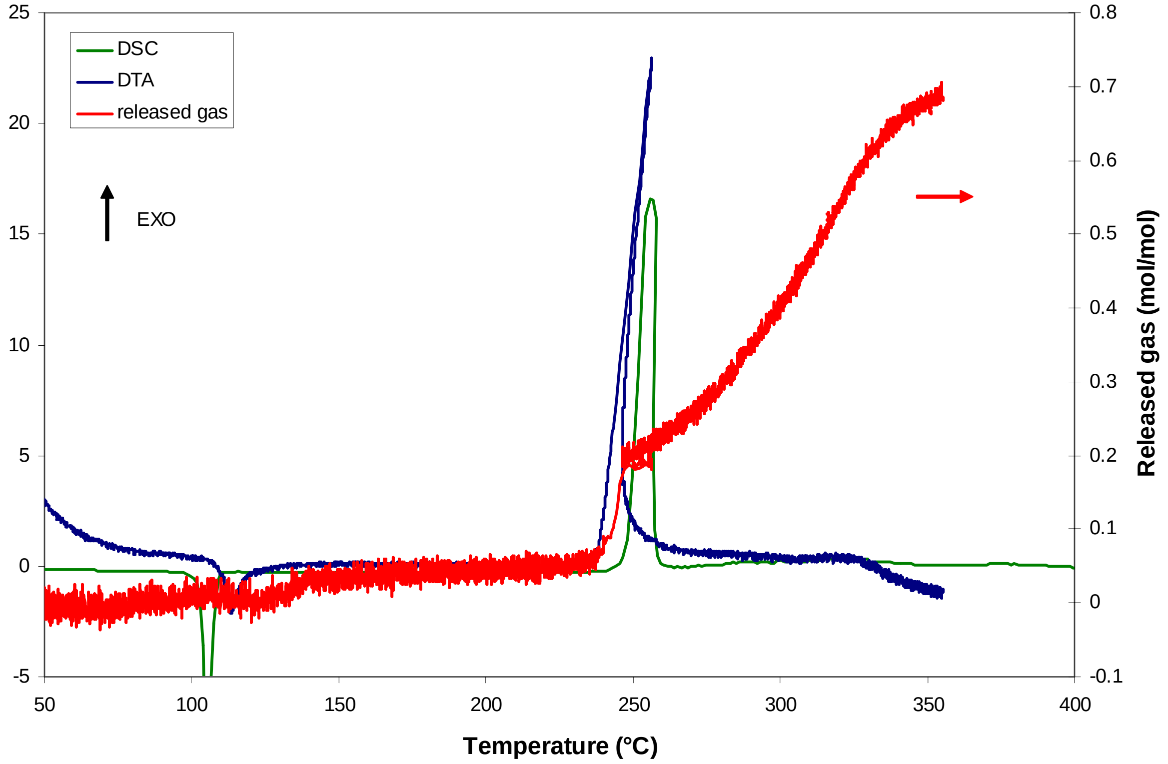


Figure 3.4.5 Results from the DTA test on 4-nitrobenzaldehyde. A heat flux curve from DSC tests is reported in the graph; scales on y-axis of DTA and DSC were altered for allow qualitative comparison.

With respect to 4-nitrobenzaldehyde (Figure 3.4.5), the results of the DTA tests shows a behaviour qualitatively similar to 3-nitrobenzaldehyde. Thus similar considerations on the decomposition apply in this case. The decomposition takes place in one stage (onset at about 237°C) and a sharp step in gas release is experienced during the phenomenon ($\varepsilon \approx 0.2$). The main fraction of released gas is formed at higher temperatures, when the decomposition of the primary residue occurs. The change in the steep of the gas release ratio and of the value of Δ above 330°C suggests that the phenomenon slows down above that temperature, probably due to the formation of a more stable solid char.

Figure 3.4.6 reports some results from DTA tests on 2-chloro-6-nitrobenzaldehyde. The decomposition takes place in a single stage (onset 185°C). The decomposition peak is quite broad, similarly to what happened in DSC tests. Gas are mainly released during the decomposition, but no sharp step is identified for the emission. Gases release from the primary residue is low, in particular at temperatures above 300°C. No appreciable thermal effects are detected in this range. It is worth noticing that in this stages the pressure in the cell is between 16 and 18 bar.

At least for the main decomposition stage, the behaviour of 2-chloro-6-nitrobenzaldehyde shows interesting similarities with 2-nitrobenzaldhyde: broad peaks, large difference between the onset temperature of DTA and DSC, gas release spread uniformly over the decomposition temperature range.

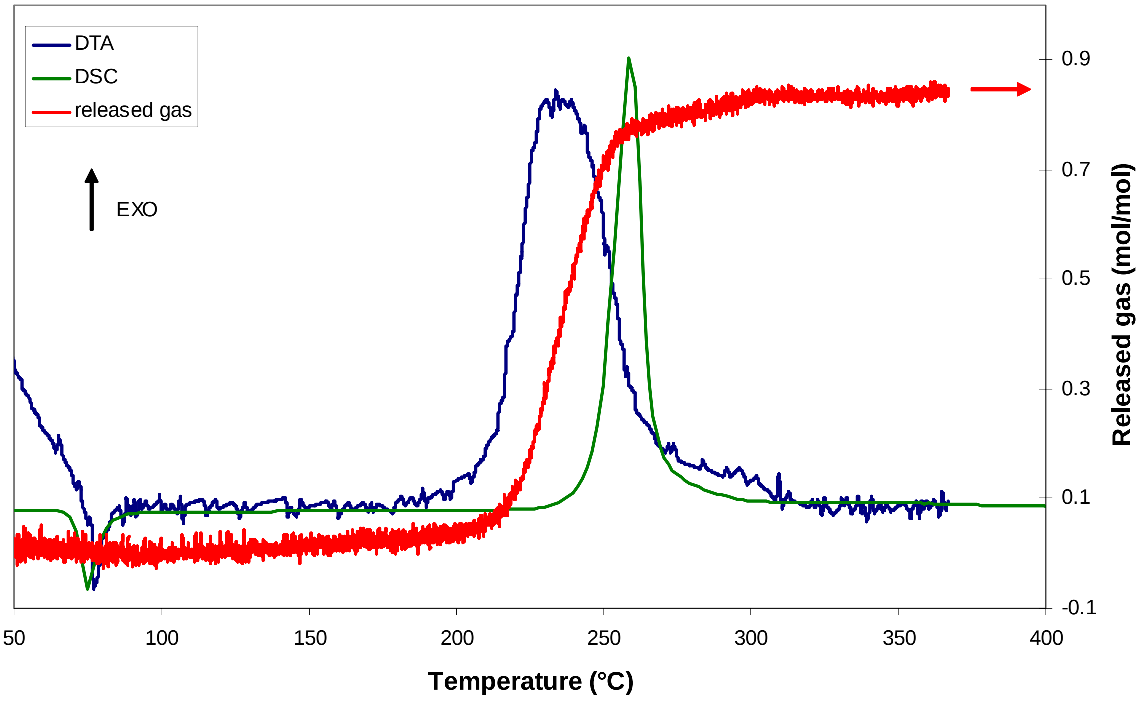


Figure 3.4.6 Results from the DTA test on 2-chloro-6-nitrobenzaldehyde. A heat flux curve from DSC tests is reported in the graph; scales on y-axis of DTA and DSC were altered for allow qualitative comparison.

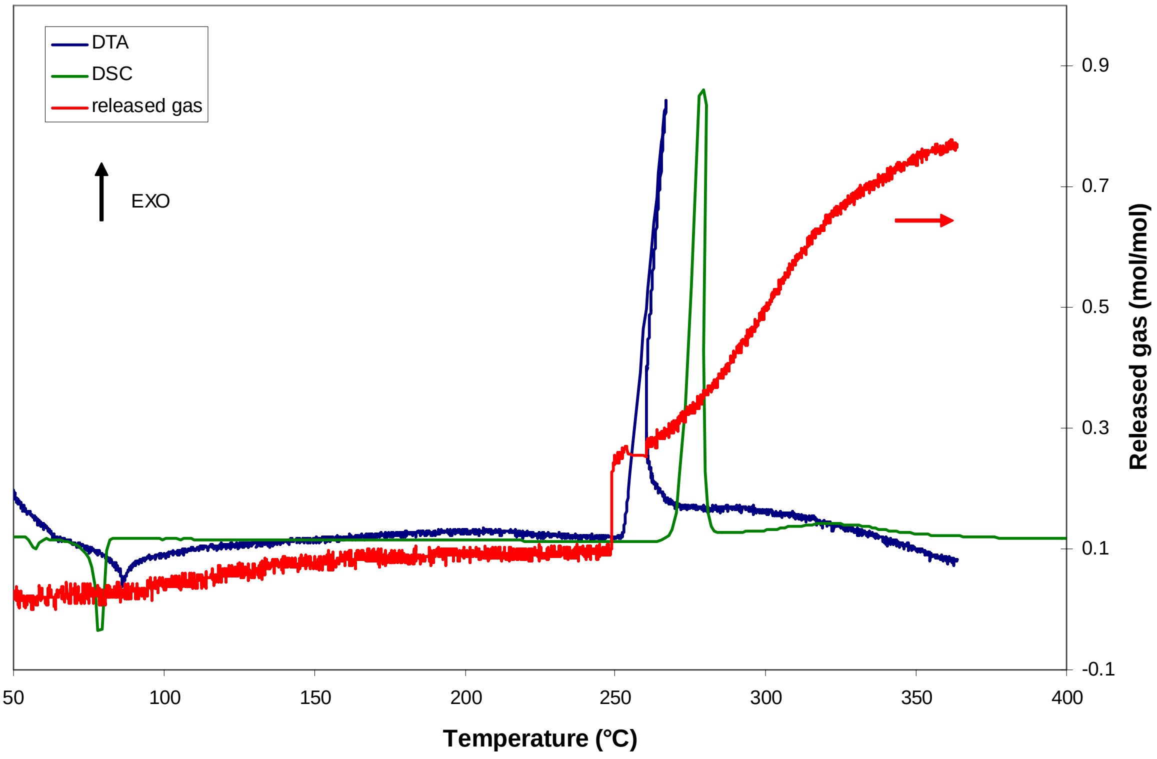


Figure 3.4.7 Results from the DTA test on 2-chloro-5-nitrobenzaldehyde. A heat flux curve from DSC tests is reported in the graph; scales on y-axis of DTA and DSC were altered for allow qualitative comparison.

The results of the a DTA test on 2-chloro-5-nitrobenzaldehyde are presented on Figure 3.4.7. The decomposition shows a narrow peak having an onset temperature of about 252°C. The rate of energy release and thus of reactor temperature increase is very high in the peak. Also the gas release is intense in this phase (0.26 mol of gas are released per mole of sample), as the sharp step in Figure 3.4.7 shows.

At temperatures above the main decomposition step, the gas release continues. The thermal effects corresponding to that release are anyway modest, though a low broad peak can be identified.

The overall behaviour is qualitatively similar to 3- and 4- nitrobenzaldehyde.

The 4-chloro-3-nitobenzaldehyde shows, also at DTA a peculiar behaviour if compared with the other materials (Figure 3.4.8). A low and broad peak (the scale of Δ was enlarged in Figure 3.4.8 compared to other figures in order to better show the trend) shows the onset at 138°C, a temperature well below that of DSC tests. The gas release at the temperatures of this first peak is very modest (release ratio around 0.07). This is confirmed by TG-DSC tests, where the lid was nit opening during first decomposition stage (see §3.3.1). A large quantity of gases is released, instead, at temperatures above 250°C. Exothermic phenomena are identified above 270°C by 2 partially overlapped peaks. These may correspond to the two peaks above 280°C in the DSC. The gas release slope decrease at temperatures above these peaks.

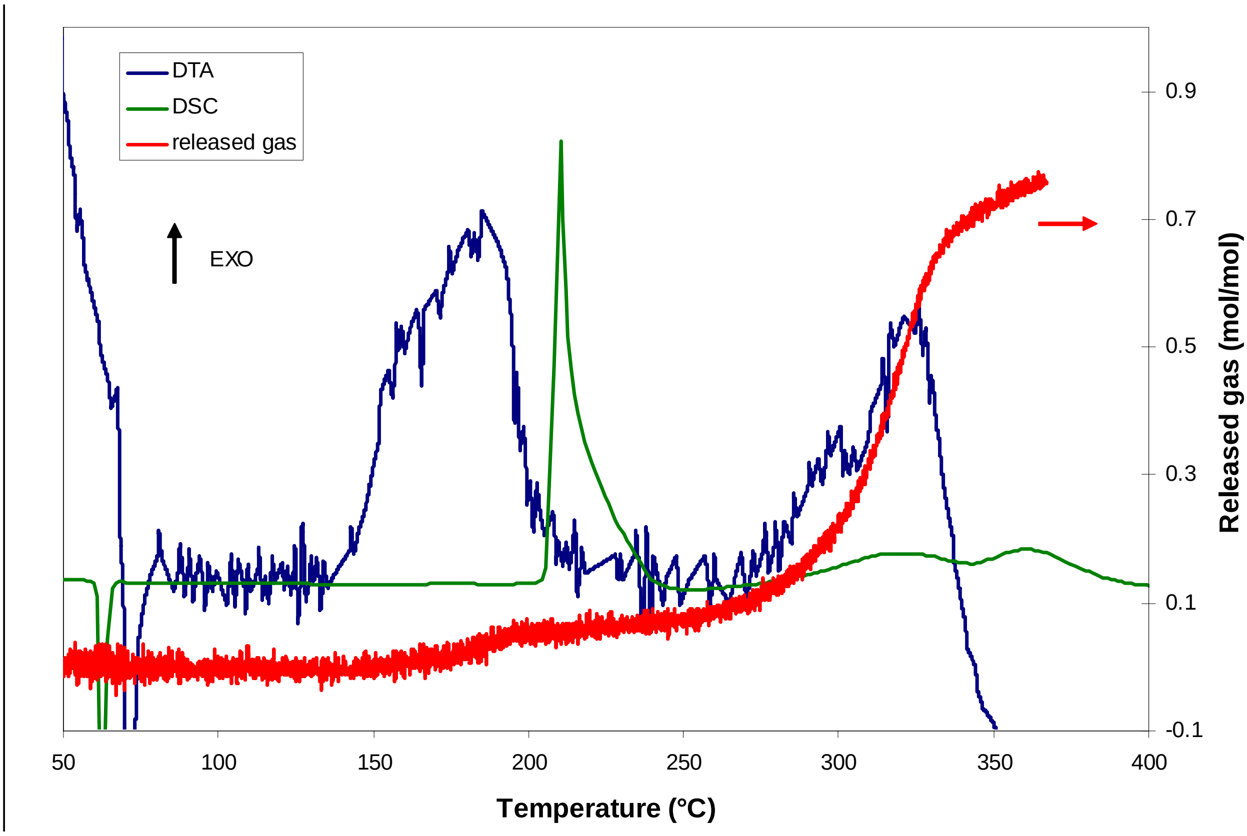


Figure 3.4.8 Results from the DTA test on 4-chloro-3-nitrobenzaldehyde. A heat flux curve from DSC tests is reported in the graph; scales on y-axis of DTA and DSC were altered for allow qualitative comparison.

Table 3.4.1 summarises the main quantitative results of the DTA tests. The fraction of the residue was determined weighting the test cell after cooling. The reference temperature is the maximum temperature reached by the sample in the test.
The release ratio ε was calculated by equation (3.4.1) in the final conditions of the test, considering as reference condition the onset.

Table 3.4.2 introduces a comparison among the values of residue fraction in DTA tests and the outcome from TG tests at the same reference temperature. It is apparent from the table that TG data result systematically lower than DTA tests performed in a closed cell. This proves one more time the significance of material evaporation in TG and DSC tests on the materials studied.

	Onset temp. (°C)	**Residue at [T]**	**ε at maximum temperature**
2-Nitrobenzaldehyde	195	61% [368°C]	0.70
3-Nitrobenzaldehyde	218	67% [356°C]	0.53
4-Nitrobenzaldehyde	237	63% [355°C]	0.75
2-Chloro-6-nitrobenzaldehyde	185	73% [349°C]	0.86
2-Chloro-5-nitrobenzaldehyde	252	67% [363°C]	0.70
4-Chloro-3-nitrobenzaldehyde	139	88% [367°C]	0.80

Table 3.4.1 Summary of the quantitative experimental results of DTA tests.

	Reference temperature (°C)	**Residue DTA at [T]**	**Residue DSC at [T]**
2-Nitrobenzaldehyde	368	61%	35%
3-Nitrobenzaldehyde	356	67%	52%
4-Nitrobenzaldehyde	355	63%	49%
2-Chloro-6-nitrobenzaldehyde	349	73%	52%
2-Chloro-5-nitrobenzaldehyde	363	67%	49%
4-Chloro-3-nitrobenzaldehyde	367	88%	51%

Table 3.4.2 Comparison of residue fractions at the same reference temperature in DTA and TG tests.

3.5 – Results from experimental studies: Adiabatic Calorimetry

3.5.0 – Overview

Current section presents the results obtained within the Adiabatic Calorimetry experimental protocols (Figure 3.1.3) for some of the materials identified in §3.2.
The application of these protocols allows the simulation of the behaviour of a adiabatic decomposition of the materials of interest. This is a particularly interesting accident condition for the assessment of the inherent safety of materials that may undergo decomposition.
In the following the results of the Adiabatic Calorimetry tests are presented and discussed. In the first part (§3.5.1) the thermal results of the tests are of concern. The second part (§3.5.2) deals with the identification of the products of decomposition formed in the tests.

3.5.1 – Thermal results in Adiabatic Calorimetry tests

The adiabatic calorimetric tests were performed in the Phi-tec II calorimeter. The experimental setup will allow testing:

i. The onset temperature of the materials in adiabatic conditions
ii. The temperature increase for adiabatic decomposition and, thus, the heat of decomposition
iii. The pressure increase for adiabatic decomposition and, thus, the gas release
iv. The formation of a non-volatile residue (char) during the adiabatic decomposition

Moreover the integration with off-line analytic techniques yields:

v. The identification of the decomposition products present in the gas phase of the test cell
vi. The identification of the decomposition products present in the condensable and solid fraction in the test cell

High pressure test cells were used (maximum pressure 140 bar, volume 10ml) since the pressure compensation system of the equipment is not able to compensate the pressure increase rate experienced in the DTA tests. Moreover the limits of the equipment as maximum operative temperature (400°C) force to use small samples (0.5÷1g), so to limit temperature increases acting on the phi-factor. The cell is flushed by nitrogen to yield an inert environment. The sample in the test cell is stirred by a magnetic bar coupling during the test.

Different temperature profiles can be used in the test to reach the conditions where the adiabatic decomposition occurs. The “Heat-Wait-Search” mode is a temperature program particularly suitable for the identification of the onset temperature. In this operational mode, temperature of the test cell is increased in steps of fixed pace (“heat”). After a time gap, to allow the system to reach thermal equilibrium (“wait”), adiabatic condition is maintained for a fixed amount of time by a system of guard heaters that compensate dispersions. During the adiabatic phase, possible temperature variations related to exothermic reactions are monitored (“search”). If an exothermic behaviour is detected, adiabatic conditions will be maintained; else a new step “heat” step will start.

Figure 3.5.1 shows the results of an Heat-Wait-Search test on 3-nirobenzaldehyde. In the figure, after sample heating up to 190°C, some steps are required to reach the onset temperature. The temperature increase after onset results very steep, showing a nearly explosive behaviour. After the run-away the cell is cooled down and the gas present in the vapour space can be sampled for analysis. The figure reports also the curve of the absolute pressure in the test cell. A steep increase in the pressure, due to gas release, is recorded during the run-away. After the cooling the pressure decrease due to of gas sampling can be observed.

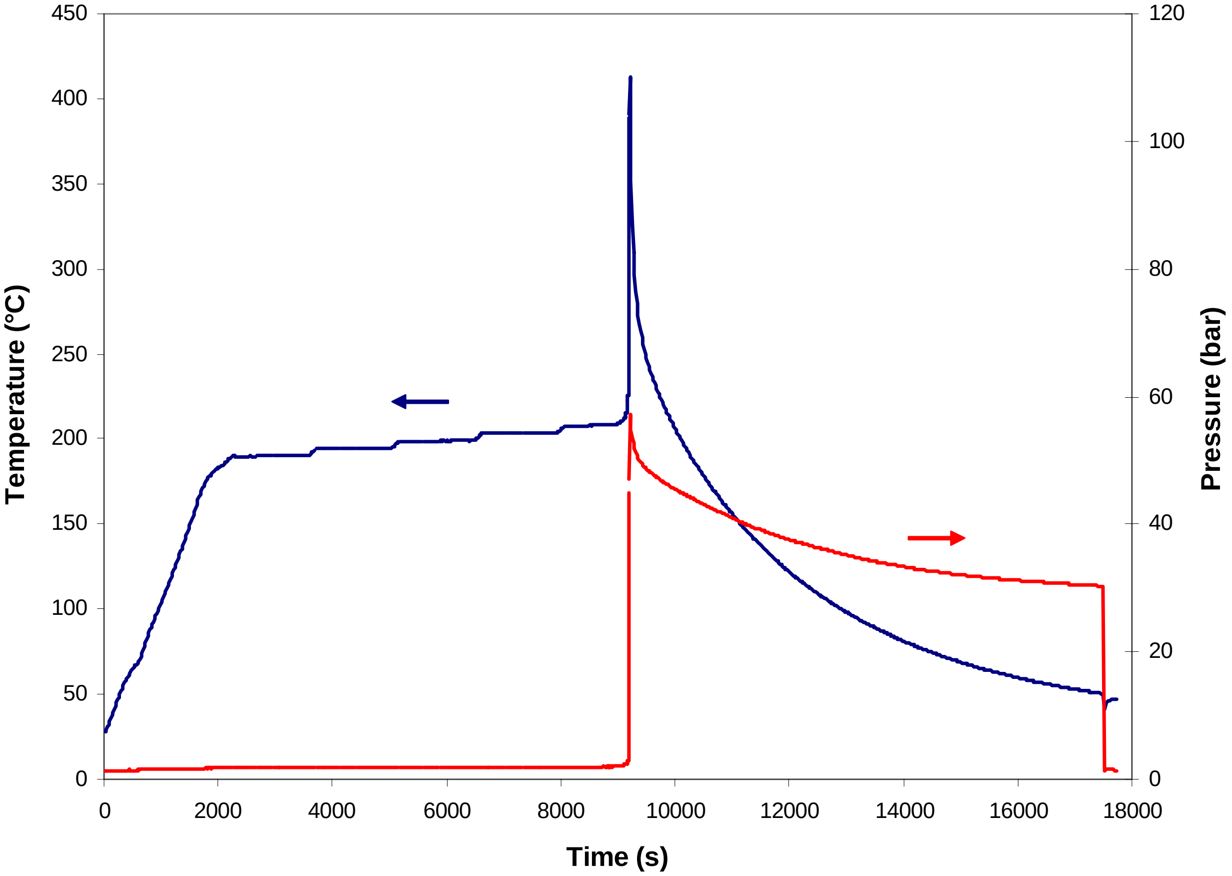


Figure 3.5.1: Temperature and pressure profiles of 3-nitrobenzaldehyde in an Adiabatic Calorimetry test using Heat-Wait-Search mode.

The main goal of Heat-Wait-Search tests is to identify the onset temperature. The identification of this temperature required some test runs, since small differences in the experimental setup may affect the onset for a few °C. However it was possible to identify a run-away onset temperature for all the chemical systems studied.

The typical sample size in the tests was between 0.6 and 1 grams. This yields a phi-factor between 8 and 13 for the cells used. It is worth recalling that the phi-factor is defied as:

$$\phi = 1 + \frac{m_{cell}\ \hat{C}p_{cell}}{m_{sample}\ \hat{C}p_{sample}} \tag{3.5.1}$$

where *m* is the mass and *Cp* the specific heat. In the current study the specific heat of the analysed material was considered constant in the test and equal to the initial value of the liquid phase. Since no data were available in the literature for the substances of interest, this was predicted by structure-propriety correlations *[Perry, 1998]*. Values of 2.15 J/(g K) and 1.94 J/(g K) were respectively adopted for non-chlorinated and chlorinated isomers.

Table 3.5.1 reports the onset temperatures identified for the materials studied. The same table shows the onset temperatures identified in DTA tests, for the sake of comparison. The 2-nitrobenzaldeyde is identified also in this case as the less stable among the 3 isomers. The data show a good agreement with DTA data, provided that in adiabatic conditions it was expected that onset temperatures were lower.

	Onset temperature AC (°C)	**Onset temperature DTA (°C)**
2-Nitrobenzaldehyde	190	195
3-Nitrobenzaldehyde	200	218
4-Nitrobenzaldehyde	210	237
2-Chloro-6-nitrobenzaldehyde	183	185

Table 3.5.1 Onset temperatures from Adiabatic Calorimetry (AC) and DTA tests.

Adiabatic calorimetry test allow the estimation of an adiabatic temperature rise, that can be related to the heat of decomposition by the equation:

$$\Delta H_{decomposition} = \phi \, \hat{C}p_{sample} \left(T_{final} - T_{onset}\right) \tag{3.5.2}$$

where T_{final} is the final temperature reached in the runaway.

The experimental setup used in the tests has safety limits on the maximum temperature that can be reached (around 400°C). Since the process is intensely exothermic (see. §3.3.5) high phi-factors (Φ) are used (i.e. small sample mass) in the tests. For instance, in the case of 3-nitrobenzaldehyde if an ideal test with $\Phi = 1$ is performed and the final temperature of the test is 400°C, the maximum heat of reaction that can be measured is:

$$\Delta H_{decomposition} = \phi \, \hat{C}p_{sample} \left(T_{final} - T_{onset}\right) = 1 \cdot 2.15 \cdot (400 - 200) = 430 \;\; J/g \tag{3.5.3}$$

that is too low compared to the predicted values from DSC tests (see §3.3.5).

By converse, the sample weight and, consequently, the phi-factor influence the final temperature that is reached by the adiabatic test. This, in turn, influences the decomposition, since higher temperatures activate further decomposition stages of the residue. Thus, by a changing of the sample mass, the reaction will stop at different maximum temperatures, depending on the decomposition stages activated. This is particularly interesting for the analysis of the decomposition residues at different stages.

Several tests were performed on the materials of concern in the study, using different sample mass (0.4÷0.9 g) and high phi factors (9÷18.5). Tests were performed in “closed can” mode. In this experimental setup, the test cell is heated at a given temperature few degrees above the onset by a defined ramp. Then the guard heaters start to compensate heat losses in order to achieve adiabatic conditions. In that phase the runaway will occur. A cool down follow the end of runaway.

This test mode is preferred to the heat-wait-search for the determination of the heat of decomposition, since the sample is not left at high temperature for a long time before of the runaway, preventing the alteration of the material and the start of slow non-detectable decomposition reactions.

Figure 3.5.2 shows an example of the whole cycle of a "closed can" test on 3-nitrobenzaldehyde.

Table 3.5.2 reports an overview of the principal results obtained by Adiabatic Calorimetry tests in "closed can" mode. For each material, the average data is reported among different tests resulting in the same final temperature range. The final pressure is the maximum pressure reached in the test and is reported in order to better define the final test conditions. The heat of decomposition is calculated by equation 3.5.2. The factor ε is the molar ratio of gas produced per unit of sample. It is calculated similarly to DTA tests by equation (3.4.1) from final temperature and pressure data, assuming an ideal gas behaviour. The weight of final residue is obtained by cell weighting after the cooling down and gas discharge.
The table clearly shows as the heat of decomposition is influenced by the maximum temperatures reached in the test. This is pretty evident in the case of 3-nitrobenzadehyde, that had a more extensive coverage of final temperatures. The reaction involving the compounds in the primary residue at high temperatures (see DSC and DTA tests for diagrams of reactions steps with temperature, §3.3.2 and §3.4.1) yield higher release of gas and reduce the percentage of residue at the end of the test.

Table 3.5.3 compares the results from Adiabatic Calorimetry tests with the DTA tests at comparable final temperatures. It can be observed as the results for the residue fraction and the gas release ratio are generally in line among the two kind of test at comparable final temperatures.

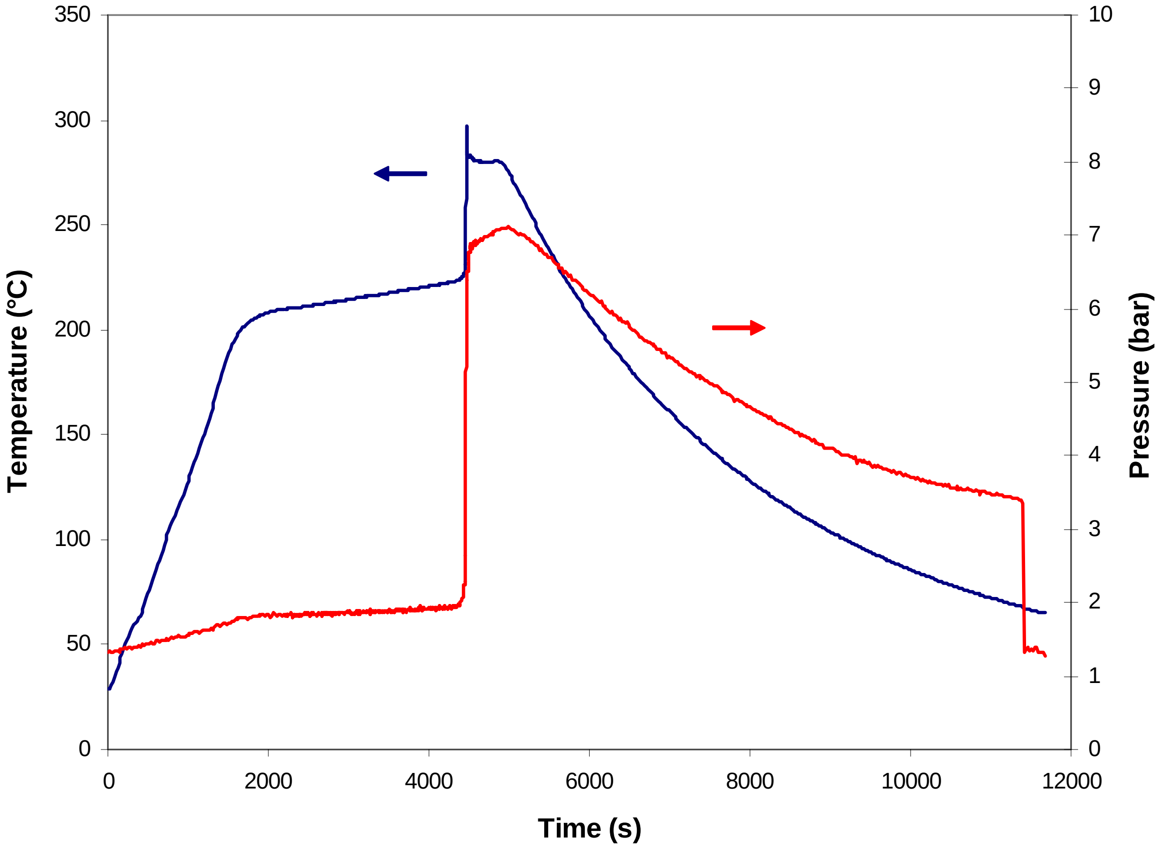


Figure 3.5.2: Temperature and pressure profiles of 3-nitrobenzaldehyde in an Adiabatic Calorimetry test with Closed Can mode.

Table 3.5.4 compares the heat of decomposition obtained by Adiabatic Calorimetry tests and the DSC-GC tests. The DSC-GC data refer to the main step of decomposition of the product, in particular to a conversion of the final product < 80%. The results have a very good match for 3-nitrobanzaldehyde. For 4-nitrobenzaldehyde it was not possible in AC tests to reproduce a comparable final temperature within the experimental survey (DSC and DTA tests show that secondary reactions are active at the final temperature of 290°C, see Figure 3.4.5).

	Final temp. range (°C)	**Final pressure (bar)**	**Heat of decomposition (J/g)**	**ε at final conditions**	**Residue**
2-Nitrobenzaldehyde	Up to 390	18.8	4510	0.70	54 %
3-Nitrobenzaldehyde	Up to 260	4.4	1085	0.15	96 %
	Up to 300	6.8	1846	0.25	89 %
	Up to 400	38.0	3616	1.10	42 %
4-Nitrobenzaldehyde	Up to 290	9.8	2448	0.52	44 %
	Up to 390	43.5	3509	1.33	37 %
2-Chloro-6-nitrobenzaldehyde	Up to 245	6.0	1876	0.37	74 %

Table 3.5.2: Selected quantitative results from Adiabatic Calorimetry (AC) tests.

	AC	**DTA**	**AC**	**DTA**
	Residue at [T]		**ε at [T]**	
2-Nitrobenzaldehyde	54 % [390°C]	61% [368°C]	0.70 [390°C]	0.70 [368°C]
3-Nitrobenzaldehyde	89 % [300°C] 42 % [400°C]	67% [356°C]	0.25 [300°C] 1.10 [400°C]	0.53 [356°C]
4-Nitrobenzaldehyde	44 % [290°C] 37 % [390°C]	63% [355°C]	0.52 [290°C] 1.33 [390°C]	0.75 [355°C]
2-Chloro-6-nitrobenzaldehyde	74 % [245°C]	73% [349°C]	0.37 [245°C]	0.86 [349°C]

Table 3.5.3: Comparison of results from Adiabatic Calorimetry (AC) and DTA tests.

	AC	**DSC**
	Heat of decomposition up to [T] (J/g)	
3-Nitrobenzaldehyde	1085 [260°C]	1057 [241°C]
4-Nitrobenzaldehyde	2448 [290°C]	1386 [240°C]

Table 3.5.4: Comparison of results from Adiabatic Calorimetry (AC) and DSC-GC tests.

3.5.2 – Identification of the decomposition products in Adiabatic Calorimetry tests

Following the Adiabatic Calorimetry protocol, the contents of the cell after the decomposition test were analysed in order to identify the substances present. Two main fractions were recovered from test cells and analysed:

- The gas fraction: this fraction was sampled at the and of the test, after cool down, as described in §3.1.2.3. The gas was expanded in the gas cell and analysed by FTIR. Usually a single sampling was possible because of the small size of the AC test cell.
- The condensable fraction: this fraction was recovered from the test cell by a solvent (acetone, HPLC grade) and analysed by GC-MS analyser.

The FTIR analysis of the gas fraction yield an absorbance spectrum. The IR-opaque substances present in the gas cell can be identified by the analyses of the bands in that spectrum. The wavenumbers used for the identification of the compounds of interest in current analysis are reported in Table 3.5.5. Water is not considered, since traces are always present in the spectrum due to the experimental setup.

Compound	**Wavenumber (cm^{-1})**
CO_2	669
HCN	713
CH_4	729
NH_3	800-1200
C_2H_4	949
N_2O	1225-1335
CH_4	1306
NO_2	1560-1650
NO	1830-1930
CO	2010-2220
N_2O	2140-2270
CO_2	2250-2400
N_2O	2420-2500
N_2O	2520-2605
CH_4	2850-3190
HCN	3225-3385
NH_3	3334
N_2O	3420-3510
CO_2	3525-3765

Table 3.5.5: Wavenumbers used in the interpretation of FTIR spectra.

Figure 3.5.3 provides an example of infrared spectrum for the gases collected from a Adiabatic Calorimetry test on 3-nirobenzadehyde. It can be seen as the different compounds can be identified according to the wavenumbers. The spectra have good reproducibility.

Figure 3.5.3, in particular, refers to a test in witch the final temperature belong to the class “up to 400°C” of Table 3.5.2. For the purpose of comparison, Figure 3.5.4 shows a spectrum from a test in the class “up to 300°C”. The differences among the products in gas phase of severe and milder conditions are plain. The analysis of these results suggest that, for

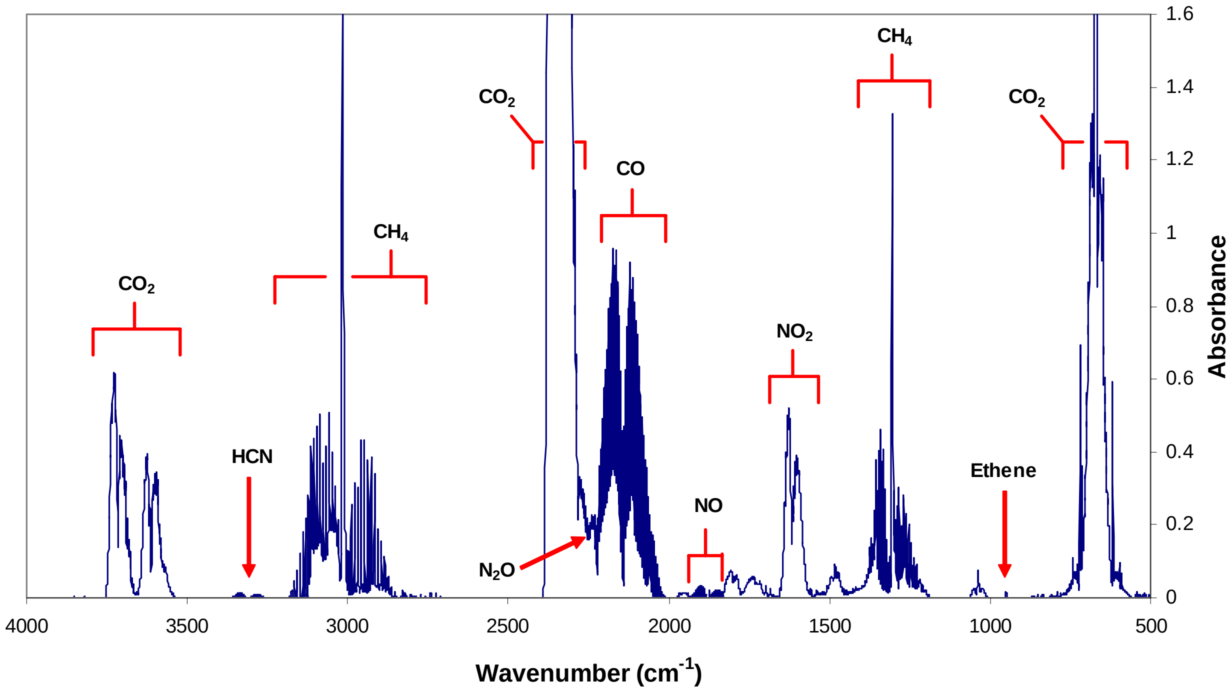


Figure 3.5.3: FTIR spectrum of the gas phase in an AC test in severe conditions on 3-nitrobanzaldehyde.

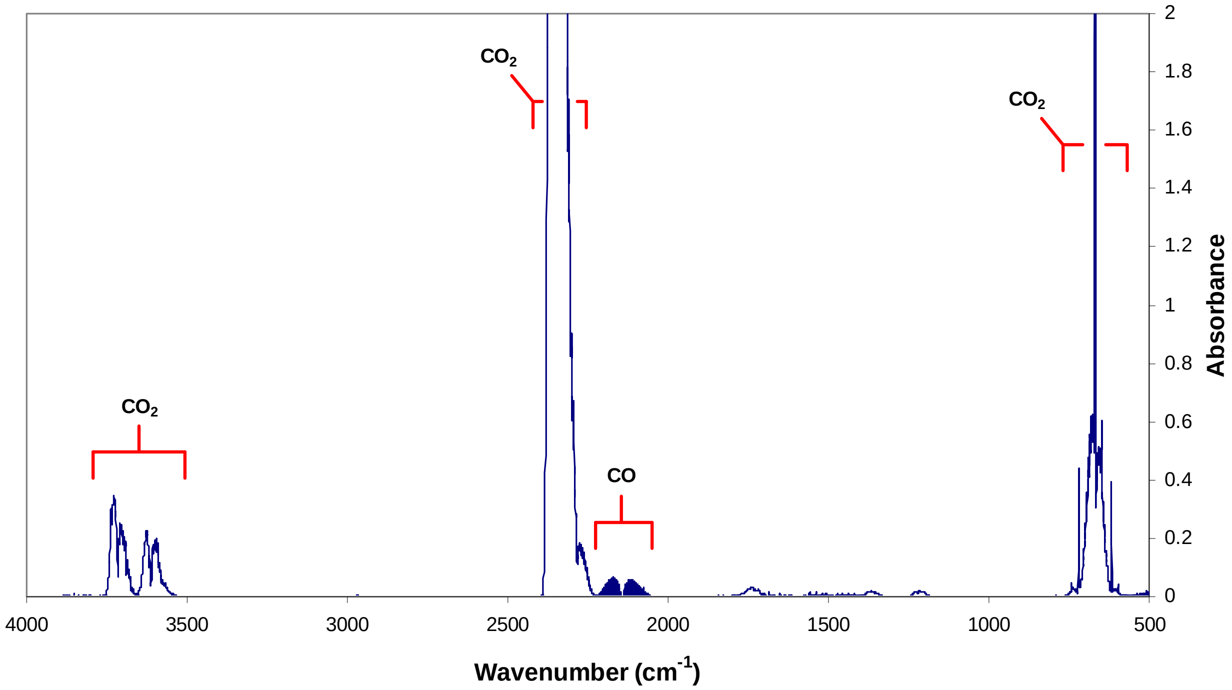


Figure 3.5.4: FTIR spectrum of the gas phase in an AC test in mild conditions on 3-nitrobanzaldehyde.

3-nitrobenzaldehyde, only carbon oxides are released to gas phase in detectable quantities in the main decomposition (probably along with nitrogen, that is however non-detectable by FTIR). The other compounds of Figure 3.5.3 should be formed at higher temperatures and pressure from primary residue decomposition or gas phase reactions.

Table 3.5.6 reports a summary of the FTIR analysis, classified according with the groups of tests similarly to Table 3.5.2. It can be observed as, in all the cases, the AC tests reaching more severe conditions yield a higher number of gaseous compounds. The reason of this behaviour should be the same earlier argued for 3-nitrobenzaldehyde: successive reactions occur at higher temperatures.

In all the cases methane and nitrogen oxides are formed in the most severe conditions. In several cases also hydrogen cyanide is detected. For the chlorinated isomers, at least at the temperatures of the test considered no hydrogen chloride is detected. Probably chlorine is bound in residue as was earlier suggested by TG-DSC-FTIR tests (see §3.3.4).

The FTIR spectra can be analysed in order to obtain quantitative information as described in §3.1.2.1. Although this require calibration on a reference. Reference calibration data were obtained for carbon dioxide, carbon monoxide, methane and ethene, as by the gas concentration method (see §3.1.2.1).

Table 3.5.6 reports average release ratios of the substances for which the calibration was available. It is apparent from the table as the release of the gases increases with the increase of the final temperature. Moreover the molar ratio identified for single compounds, if compared with the ε factors of Table 3.5.2, clearly shows that the quantified gases do not represent the major fraction of the actual gas phase. At least for the tests in milder conditions, where carbon oxides are the only substances identified at FTIR, the more likely candidate for the missing fraction is nitrogen, since it can not be identified in FTIR analysis and its molar mass can justify the weight loss of the residue.

	Final temp. (°C)	**Final pressure (bar)**	**CO_2**	**CO**	**CH_4**	**C_2H_4**	**HCN**	**N_2O**	**NO**	**NO_2**
2-Nitrobenzaldehyde	Up to 280	8.3	✓	✓						
	Up to 390	18.8	✓	✓	✓	✓		✓	✓	✓
3-Nitrobenzaldehyde	Up to 260	4.4	✓	✓						
	Up to 300	6.8	✓	✓						
	Up to 400	38.0	✓	✓	✓	✓	✓	✓	✓	✓
4-Nitrobenzaldehyde	Up to 250	4.9	✓	✓						
	Up to 290	9.8	✓	✓				✓	✓	✓
	Up to 390	43.5	✓	✓	✓	✓	✓	✓	✓	✓
2-Chloro-6-nitrobenzaldehyde	Up to 245	6.0	✓	✓						

Table 3.5.6: Selected quantitative results from FTIR analysis on gas phases sampled from Adiabatic Calorimetry (AC) tests.

	Final temp.	Final pressure	CO_2	CO	CH_4	C_2H_4	Ratio CO/CO_2	Ratio CH_4/CO_2
	(°C)	(bar)			(mmol/mol)			
2-Nitrobenzaldehyde	Up to 280	8.3	0.033	0.008			0.33	
	Up to 390	18.8	135	27	2.43	0.18	0.20	0.001
3-Nitrobenzaldehyde	Up to 260	4.4	15.7	0.2			0.014	
	Up to 300	6.8	48.8	1.5			0.031	
	Up to 400	38.0	184	124	75.6	-	0.673	0.411
4-Nitrobenzaldehyde	Up to 250	4.9	43.0	2.0			0.046	
	Up to 290	9.8	122	10.5			0.086	
	Up to 390	43.5	197	108	69.4	-	0.546	0.352
2-Chloro-6-nitrobenzaldehyde	Up to 245	6.0	153	14			0.065	

Table 3.5.6: Selected quantitative results from FTIR analysis on gas phases sampled from Adiabatic Calorimetry (AC) tests.

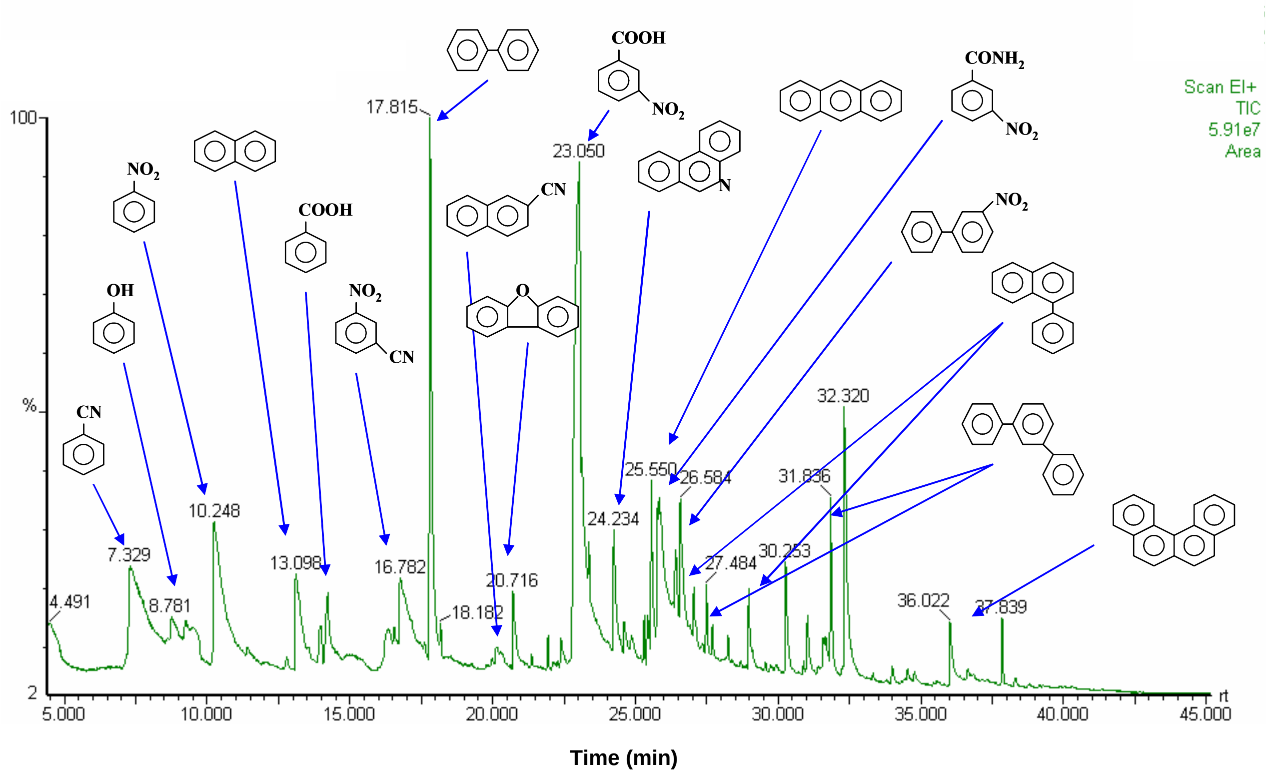


Figure 3.5.5: example of chromatogram from GC-MS analysis of condensable fraction in an AC test in severe conditions on 3-nitrobanzaldehyde. Some of the identified compounds are reported in the figure.

The condensable fraction recovered by acetone from the test cells was analysed by GC-MS (§3.1.2.5). Figure 3.3.5 reports and example of chromatogram that is obtained from the analysis: the total ion current is reported as function of the retention time in the chromatographic column. The single compounds release were identified from the mass spectra, using the internal database of the software for reference spectra. In the following tables, when the identification yields various options for the compounds, all the plausible possibilities are reported.

Tables from 3.5.7 to 3.5.10 report the results of GC-MS analysis on the samples collected from the AC tests on 3-nitrobenzaldehyde. It can be observed as, also in this case, the profile changes a lot among the tests that reached different final temperatures.
At milder conditions, the presence of compound containing nitrogen is dominant, in particular for the nitro group. The 3-nitrobenzaldehyde is identified among the compounds, meaning the conversion is not complete. Few aromatic and poly-aromatic hydrocarbons and no heterocyclic aromatics are found, suggesting that the primary residue it is far away from being a stable char.
In more severe conditions (tests up to 400°C) a wider variety of aromatic and poly-aromatic hydrocarbons is formed. On the other side less compounds containing nitro- groups are found. This suggests that they tend to react forming e.g. heterocyclic compounds or being expulsed to gas phase compounds (molecular nitrogen, nitrogen oxides, hydrogen cyanide). Substances containing cyano- group are detected in the severe condition tests. This matches well with the identification of hydrogen cyanide in FTIR spectra for the gas phase.

Class of compounds	**AC test up to 300°C**	**AC test up to 400°C**
Aromatic and poly-cyclic aromatic hydrocarbons	1	14
Oxygenated aromatic compounds without N	3	6
Aromatic compounds with nitrogen		
➢ *nitro- group*	8	5
➢ *azo- group*	1	1
➢ *cyano- group*	---	2
➢ *amide*	---	1
➢ *imide*	1	---
➢ *poly-functional compounds*	3	3
➢ *heterocyclic-aromatic compounds*	---	3

Table 3.5.7: summary of the classes of compounds identified by GC-MS analysis in samples from AC tests on 3-nitrobenzaldehyde. The values refer to the number of compounds (or of group of compounds impossible to differentiate by GC-MS analysis).

	MM	**AC test up to 300°C**	**AC test up to 400°C**
Naphthalene	128		✓
Biphenyl / Acenaphthene	154	✓	✓
Acenaphthylene / biphenylene	152		✓
Fluorene	166		✓
Methyl-biphenyl	168		✓
Anthracene / phenanthrene	178		✓
Pyrene / fluoranthene	202		✓
Phenyl naphthalene / dihydropyrene	204		✓
Benzo[a]anthracene / Benzo[c]phenanthrene / Naphthacene / Triphenylene / Chrysene /….	228		✓
Terphenyl	230		✓
Benzo[j]fluoranthene / Benzo[b]fluoranthene / Benzo[e]pyrene / Benzo[k]fluoranthene / Perylene / Benzo[a]pyrene	252		✓
Binaphthalene / 4,5-dihydrobenzo[a]pyrene / phenylanthracene	254		✓
Benzo[b]triphenylene / benzo[b]chrysene / dibenzo[a,h]anthracene / dibenzo[a,j]anthracene / benzo[a]naphthacene	278		✓
Quarterphenyl	306		✓

Table 3.5.8: aromatic and poly-aromatic hydrocarbons identified by GC-MS analysis in samples from AC tests on 3-nitrobenzaldehyde.

	MM	**AC test up to 300°C**	**AC test up to 400°C**
Phenol	94		✓
Benzaldehyde	106	✓	
Benzoic acid	122	✓	✓
Hydroxybenzaldehyde	122	✓	
Dibenzofuran	168		✓
Diphenyl ether	170		✓
Hydroxybiphenyl	170		✓
Fluoren-9-one	180		✓

Table 3.5.9: oxygenated aromatic compounds without nitrogen identified by GC-MS analysis in samples from AC tests on 3-nitrobenzaldehyde.

	MM	AC test up to 300°C	AC test up to 400°C
Nitro- group			
Nitrobenzene	123	✓	✓
m-nitrophenol	139	✓	✓
m-nitrobenzaldehyde	151	✓	
m-nitrobenzoic acid	167	✓	✓
m-nitrobiphenyl/ nitro-acenaphthene	199	✓	✓
2-nitro-9-fluorenone	225	✓	
m-nitrobenzophenone	227	✓	✓
Dinitrobiphenyl	244	✓	
Azo- group			
2-Phenylbenzoxazole	195		✓
Azobenzene	182	✓	
Cyano- group			
Benzonitrile	103		✓
Isocyanonaphthalene / naphthalene carbonitrile	153		✓
Amide			
N-phenylbenzamide	197		✓
Imide			
Phthalimide	147	✓	
Poly-functional compounds			
m-nitrobenzamide	166	✓	✓
Amino benzonitrile	118		✓
Nitro benzonitrile	148		✓
N-(4-nitrophenyl)methylene-benzamine	226	✓	
Diphenylcarbadiazone	238	✓	
Heterocyclic-aromatic compounds			
Phenylpyridine	155		✓
Phenyl benzonitrile / phenantridine / acridine / Benzoquinoline	179		✓
Dibenzo(B,DEF)carbazole	241		✓

Table 3.5.10: aromatic compounds with nitrogen identified by GC-MS analysis in samples from AC tests on 3-nitrobenzaldehyde.

For sake of comparison with 3-nitrobenzaldehyde, the results of the analysis of the condensable fraction of AD tests on 2-nitrobenzaldehyde is reported in the Tables from 3.5.11 to 2.5.14.

The same considerations as for 3-nitrobenzaldehyde may be repeated on the formation of poly-cyclic and hetero aromatic compounds. Also in this case the cyano group is identified only at severe test conditions, as well as the number of nitro compounds reduces in these conditions.

In this case, however, amino- groups were identified in the condensable fraction, no matter the severity of the test. These groups may derive from the reduction of the nitro group.

Class of compounds	**AC test up to 280°C**	**AC test up to 390°C**
Aromatic and poly-cyclic aromatic hydrocarbons	2	23
Oxygenated aromatic compounds without N	5	7
Aromatic compounds with nitrogen		
➢ *nitro- group*	3	2
➢ *amino- group*	2	2
➢ *azo- group*	1	1
➢ *cyano- group*	---	8
➢ *poly-functional compounds*	6	4
➢ *heterocyclic-aromatic compounds*	---	12

Table 3.5.11: summary of the classes of compounds identified by GC-MS analysis in samples from AC tests on 2-nitrobenzaldehyde. The values refer to the number of compounds (or of group of compounds impossible to differentiate by GC-MS analysis).

	MM	**AC test up to 280°C**	**AC test up to 390°C**
Naphthalene	128	✓	✓
Methylnaphthalene (2)	142		✓
Acenaphthylene / biphenylene	152		✓
Ethenylnaphthalene / 1,4-diidro-1,4-ethenonaphthalene / biphenyl / acenaphthene	154		✓
Fluorene	166		✓
Methylbiphenyl / diphenylmethane (2) / ethenylnaphthalene	168		✓
Anthracene / phenanthrene	178	✓	✓
Fluoranthene / pyrene	202		✓
Phenylnaphthalene / ethenylanthracene / 1-(phenylmethylen)-1H-indene / 1,4-diidro-1,4-ethenoanthracene / dihydropyrene / dihydrofluoranthene	204		✓
Benzo[a]anthracene / naphthacene / benzo[c]phenanthrene / triphenylene / chrysene	228		✓
Terphenyl / dihydronaphthacene / dihydrochrysene	230		✓
Benzo[j]fluoranthene / benzo[e]acephenanthrylene / benzo[k]fluoranthene / perylene / benzo[e]pyrene	252		✓
Dihydrobenzo[a]pyrene / dihydrobenzo[e]pyrene / binaphthalene	254		✓
Quaterphenyl	306		✓

Table 3.5.12: aromatic and poly-cyclic aromatic hydrocarbons identified by GC-MS analysis in samples from AC tests on 2-nitrobenzaldehyde.

	MM	AC test up to 280°C	AC test up to 390°C
nitro- group			
nitrobenzene	123	✓	✓
2-nitrobenzaldehyde	151	✓	
2-nitrobiphenyl	199	✓	✓
3-nitrobiphenyl	199	✓	
amino- group			
Aniline	93	✓	✓
Biphenylamine	169	✓	✓
azo- group			
Azobenzene	182	✓	✓
cyano- group			
Benzonitrile	103		✓
Methylbenzonitrile / benzenacetonitrile	117		✓
Methylen-benzenacetonitrile / 3-phenyl-2-propen-nitrile / isoquinoline	129		✓
Naphthalencarbonitrile (2)	153		✓
Phenylbenzonitrile / phenanthridine / acridine (3) / benzo[h]quinoline / benzo[f]quinoline	179		✓
poly-functional compounds			
Aminobenzonitrile / 1H-benzoimidazole / 1H-pyrrole 2,3-[b]pyridine / 1H-indazole	118		✓
Phenylbenzoxazole	195	✓	
N-phenylbenzamide	197	✓	
N-(aminophenyl)-benzamide / amino-N-phenylbenzamide	212	✓	
N-phenylphthalimmide	223	✓	✓
N-(o-nitrobenzyliden)aniline	226	✓	✓
6H,12H-indazole 2,1-A indazol-6,12-dione	236	✓	✓
heterocyclic-aromatic compounds			
Isoquinoline / methylen-benzenacetonitrile / 3-phenyl-2-propen-nitrile	129		✓
1H-benzimidazole / 1H-pyrrol 2,3-B pyridine / 1H-indazole / aminobenzonitrile	118		✓
Phenylpyridine	155		✓
4-azofluorene	167		✓
Phenanthridine / acridine / benzo[h]quinoline (3) / benzo[f]quinoline / phenylbenzonitrile	179		✓
Phenazine / 2-(2- pyridinyl)benzonitrile / o-phenanthroline / 1,7-phenanthroline	180		✓
4-azapyrene / indeno(1,2,3-IJ) isoquinoline / acenaphtho(1,2-B)pyridine	203		✓
dibenzo(B,DEF)carbazole	241		✓
9-phenyl-9H-carbazole / methylbenzo[c]acridine / methylbenzo[a]acridine	243		✓

Table 3.5.13: aromatic compounds with nitrogen identified by GC-MS analysis in samples from AC tests on 2-nitrobenzaldehyde.

	MM	AC test up to 280°C	AC test up to 390°C
Phenol	94	✓	✓
2H-1-benzopyran-2-one	146	✓	
Dibenzofuran	168	✓	✓
Hydroxybiphenyl	170		✓
9H-xanten-9-one	196	✓	✓
4-hydroxy-9-fluorenone	196	✓	✓
benzoic acid phenyl ester	198		✓
9,10- anthracendione	208		✓

Table 3.5.14: oxygenated aromatic compounds without nitrogen identified by GC-MS analysis in samples from AC tests on 2-nitrobenzaldehyde.

	PM	AC test up to 245°C
Aromatic hydrocarbons		**1**
Anthracene / phenanthrene	178	✓
Aromatic compounds with Cl, without N, O		**6**
Dichlorobenzene (2)	146	✓
Trichlorobenzene	180	✓
Tetrachlorobenzene (2)	214	✓
Dichlorobiphenyl (2)	222	✓
Trichlorobiphenyl (3)	256	✓
Tetrachlorobiphenyl (4)	290	✓
Aromatic compounds with O and Cl, without N		**7**
Chlorophenol	128	✓
Chlorohydroxybenzaldehyde	156	✓
Chlorobenzoic acid	156	✓
Dichloro benzaldehyde	174	✓
Dichlorobenzoic acid	190	✓
Dichlorobenzophenone	250	✓
Trichlorobenzophenone	284	✓
Aromatic compound with N		
Nitro- group		**5**
Chloronitrobenzene	157	✓
2-chloro-6-nitrobenzaldehyde	186	✓
Dichloronitrobenzene	191	✓
4-chloro-1-chloromethyil-2-nitrobenzene	205	✓
Dichloronitroaniline	206	✓
Amino- group		**6**
Dichloroaniline	161	✓
Dichlorobenzamide	189	✓
Dichoronitroaniline	206	✓
Tetrachloroaniline	229	✓
N-phenyl-dichloroaniline	237	✓
4, 4’-dichlorobenzaniline	265	✓
Cyano- group		**1**
Dichlorobenzonitrile	171	✓
Azo- group		**1**
Tetrachloroazobenzene	318	✓

Table 3.5.15: compounds identified by GC-MS analysis in samples from AC tests on 2-chloro-6-nitrobenzaldehyde.

# of chlorine atoms	MM	# of compounds
0	178	1
1	128, 139 (2), 156, 157, 180, 185, 233	8
2	146 (2), 161, 171, 174, 189, 190, 191, 196, 206, 222, 237, 247, 250 (2), 262, 263, 265, 267 (2), 279, 290, 291, 310, 316, 319, 336	27
3	180 (2), 195 (2), 242, 256 (4), 271 (3), 272 (2), 283, 284, 285, 290, 296 (2), 297 (2), 298, 299, 304, 308, 313, 323, 324 (2), 325, 338, 344, 373, 400, 414, 444, 445	38
4	214 (2), 229, 288, 290 (4), 305 (2), 318, 331 (3), 333, 348 (2), 433 (2), 434, 479	21
5	365, 467, 468 (2)	4

Table 3.5.16: partition of chlorine atoms in the compounds identified by GC-MS analysis in samples from AC tests of the group “final temperature up to 245°C” on 2-chloro-6-nitrobenzaldehyde.

Finally a set of GC-MS results for a specific group of AC tests on the 2-chloro-3-nitrobenzaldehyde is reported in Table 3.5.15. In this case it is of particular interest to analyse the fate of chlorine. Table 3.5.16 summarizes the number of compounds identified as a function of the number of chlorine atoms present in the molecule.

The results show that poly-chlorinated compounds of medium-high molecular mass are formed in the decomposition. This fact, together with the absence of hydrogen chloride in gas phase at FTIR analysis, suggests that chlorine, at least in the first main stage of decomposition, remains principally in the residue. It is worth noticing that among the chlorinated products, well-known hazardous compounds (e.g. chlorophenol, polychloro-benzene, polychloro-biphenyl) are formed.

As regard compounds containing nitrogen, the 2-chloro-3-nitrobenzaldehyde shows a behaviour similar to the tests in milder conditions on the non chlorinated samples above discussed. As in other tests at similar final temperature, few species of non-substituted hydrocarbons were detected. Similarly to 2-nitrobenzaldehyde, also in this case compounds with amino groups were identified.

A brief review of the results presented above shows that a variety of compounds are formed in the decomposition of the materials studied. Though some of them were mentioned in the some of the corresponding Material Safety Data Sheets, a large number was unspecified. Nevertheless many of them are well known to be hazardous compounds.

The analysis of the hazard of these materials through the procedure identified in §2.2 will be the subject of a specific example in §4.5.

3.6 – Summary and Conclusions

An experimental survey aimed at the characterization of a group of thermally unstable materials was presented in this section. The study principally concerned the thermal effects and the chemical compound release occurring during the degradation of the initial material.
Experimental protocols were defined for the tests. This allowed performing the tests on different materials by a coherent methodological basis.

The group of materials studied included different isomers of non-chlorinated and chlorinated nitrobenzaldehyde. The main outcomes are summarized in the following:

- **2-nitrobenzaldehyde**: this compound shows an onset temperature of 190°C in AC tests. The first decomposition stage involves two thermal steps. In this phase gases are released (about 0.65 mol/mol of initial material); CO_2 and CO are the principal gaeous compounds identified by FTIR analysis. The residue contains various species with functional groups containing oxygen and nitrogen (nitro-, amino-, hydroxyl-, etc.). The primary residue undergoes further degradation reactions that, though not increasing the released quantity of gases, greatly affects the nature of the gases (nitrogen oxides, CH_4, HCN are formed). In the residue several poly-aromatic and hetero-cyclic hydrocarbons and cyano- groups were identified. The heat release for the whole decomposition up to 390°C, calculated by AC data, is of 4510 J/g of the initial material.
- **3-nitrobenzaldehyde**: this compound shows an onset temperature of 200°C in AC tests. The first decomposition stage takes place in a single thermal step. Gas is quickly released in this phase (0.13 mol/mol of initial material); CO_2 and CO are the main gaseous compounds identified by FTIR analysis. The residue contains several species with functional groups containing oxygen and nitrogen (nitro-, carbonyl-, etc.). The heat release in this phase is estimated around 1085 J/g of the initial material. The primary residue undergoes further degradation reactions that may further release gases (0.53 mol/mol of initial material total at 356°C, 1.1 mol/mol above 400°C). The nature of the gas phase (nitrogen oxides, CH_4, HCN) and of the residue (poly-aromatic and hetero-cyclic hydrocarbons, cyano-, hydroxyl- groups are identified) changes in the more severe conditions. The heat release in this phase appears significant. The heat release for the whole decomposition up to 400°C is of 3616 J/g of initial material, calculated by AC data.
- **4-nitrobenzaldehyde**: this compound shows a behaviour qualitatively similar to 3-nitrobenzaldehyde. The onset temperature is of 210°C in AC tests. The first decomposition stage takes place in a single thermal step. Gas is quickly released in this phase (0.2 mol/mol of initial material); CO_2 and CO are the principal compounds identified by FTIR analysis. The heat release is estimated around 1386 J/g of the initial material. The primary residue undergoes further degradation reactions that may release further gaseous compounds (0.75 mol/mol of initial material at 355°C, 1.3 mol/mol at 390°C). The nature of the gases changes in these further stages: nitrogen oxides are detected at 290°C, CH_4 and HCN appear in the mixture at 390°C. The heat release for the whole decomposition process up to 390°C, calculated by AC data, is of 3509 J/g of the initial material
- **2-chloro-6-nitrobenzaldehyde**: this compound shows an onset temperature of 183°C in AC tests. The first decomposition stage involves a single thermal step. All along this stage gases are released (about 0.8 mol/mol of initial material); CO_2 and CO are the main compounds identified by FTIR analysis in AC tests concerning the early

phases of this decomposition. In TG-DSC-FTIR tests also HCl is detected. The residue contains several species having functional groups containing oxygen and nitrogen (nitro-, amino-, hydroxyl-, carbonyl-, etc.). Chlorine is fixed in the residue, where ploy-chlorinated compounds are formed. The heat release up to the temperature of 245°C, calculated by AC data, is 1876 J/g of initial material. The primary residue does not show significant thermal degradation effects above 300°C, though a minor increase in the released quantity of gas is detected above that temperature.

- **2-chloro-5-nitrobenzaldehyde**: this compound shows a narrow decomposition peak above 252°C in DTA tests. The result is confirmed in DSC tests. Together with the thermal peak, gas is quickly released (about 0.26 mol/mol of initial material). The residue undergoes further decomposition at higher temperatures, releasing heat and significant quantities of gases. The whole gas released up to the temperature of 363°C in DTA test is about 0.7 mol/mol of initial material. The qualitative behaviour of the decomposition is similar to 3- and 4-nitrobenzaldehyde. The material was not tested by AC.
- **4-chloro-3-nitrobenzaldehyde**: this compound shows a decomposition peak characterized by a steep increase in temperature. The onset of the peak varies among 139 and 203°C in DTA and DSC tests. However, a heat release of 839 J/g of initial material was estimated from DSC runs. The heat of decomposition was almost constant, no matter the onset of the stage. The heat release is related to a very modest release of gases (about 0.07 mol/mol of initial material). The residue undergoes further decomposition at higher temperatures (above 250°C) releasing heat and significant quantities of gases. The whole gas released up to the temperature of 367°C in DTA test is about 0.8 mol/mol of initial material. The material was not tested by AC.

The described results of the experimental survey were used as input data in case-studies of Section 4. In fact, some applications of the inherent safety assessment tools described in Section 2 require data on the decomposition behaviour of processed materials (e.g. thermal effects, formation of secondary substances). For instance, §4.5.1 demonstrates the application of the procedure defined for hazard assessment of materials (§2.2) to nitrobenzaldehyde. In the case-study, the information on the substances that may be released in the decomposition of nitrobenzaldehyde are used to identify the hazard footprint of the material.

Section 4: Case Studies

4.0 - Introduction

In the current section the assessment methods presented in sections 1 and 2 are applied to several cases studies. Some of the case-studies were defined in collaboration with industries, that provided the necessary data on alternative processes, procedures and facilities.

The development and analysis of the case studies aims at two main goals:

- **Demonstration:** the cases studies presented in the following extensively report several applications of the proposed methodologies, demonstrating the use of the developed procedures. Moreover, the case studies analyze a wide range of design problems, encompassing two different dimensions: type of facility and stage in the design activities (Table 4.0.1). The applicability of the tools at any of these case studies demonstrates the flexibility and the simple use of the developed portfolio of approaches.

- **Validation**: in the analysis of the cases studies constant attention is paid at the ability of the final and intermediate results to match the expected impact profiles. The expected profiles are identified “a priori” from expert judgment and process experience, that was possible to collect for the analyzed processes. On the reverse, whenever the application of the method identified a given aspect as significant, a check was made in order to verify the plausibility of the result.
  When possible (e.g. inherent safety assessment), a comparison with existing methods was made. However, as discussed in sections 1 and 2, literature approaches show several limits in the applicability for design support, preventing the results to be compared.

Table 4.0.1 lists the cases studies described in the current section with respect to the type of facility and the stage of the design activities. Table 4.0.2 matches the cases-studies with the assessment methods that were applied.

		Type of facility		
		Chemical processing	**Storages**	**Waste disposal**
Stage of the design activities	**Material selection**	Nitrobenzaldehyde and other materials (§4.5)		
	Process design	Cyclohexanone production (§4.3) Hydrogen production (§4.4)		Disposal electronic boards (§4.1) Disposal used solvent (§4.2)
	Plant design	Storage and mixing of a reactant (§4.6) Finishing of an oligomer (§4.6)	Hydrogen storage (§4.4) Storage and mixing of a reactant (§4.6)	
	Layout design	Acrylic acid plant layout (§4.7) Gas & oil separation layout (§4.7)	Acrylic acid plant layout (§4.7) Fuel storage section layout (§4.7)	

Table 4.0.1: List of the cases studies described in Section 4 with respect to the type of facility and the stage of design activities considered.

		Assessment method			
	Case study	**Sustainability (§1.2)**	**Inherent safety of materials (§2.2)**	**Inherent safety of process (§2.3)**	**Inherent safety of layout (§2.4)**
(§4.1)	Disposal electronic boards	✓			
(§4.2)	Disposal used solvent	✓			
(§4.3)	Cyclohexanone production	✓		✓	
(§4.4)	Hydrogen production	✓		✓	
(§4.4)	Hydrogen storage			✓	✓
(§4.5)	Nitrobenzaldehyde and other materials		✓		
(§4.6)	Storage and mixing of a reactant	✓		✓	
(§4.6)	Finishing of an oligomer	✓		✓	
(§4.7)	Acrylic acid plant layout				✓
(§4.7)	Gas & oil separation section layout				✓
(§4.7)	Fuel storage section layout				✓

Table 4.0.2: Proposed assessment methods used in the case studies of Section 4.

4.1 – Electronic Waste

4.1.1 Case study description

The following case study concerns the analysis of available alternative processes for the disposal of waste printed wiring boards (PWB). Printed wiring boards are part of many widely used electronic devices (e.g. computers, mobile phones, TV sets and toys). The annual world production of PWB was estimated to be of 265 Mm^2 in the year 2000 and is constantly increasing. Due to the rapid obsolescence of the electronic devices and to the presence of hazardous components in PWB *[Cui & Forssberg, 2003; Jang & Townsend, 2003; Menad et al., 1998]*, the management of electronic waste is becoming an important problem, as recognized also by sector regulations *[Directive 2002/95/EC; Directive 2002/96/EC]*. On the other hand, the recovery of valuable materials present in PWB (gold, silver, tantalum, etc.) is economically attractive. Waste PWB usually contain three material fractions: a plastic fraction (epoxy cross-linked resin), a metallic fraction (copper, lead, etc.) and an inert fraction (usually glass fibers). Brominated organic compounds are frequently employed to improve the flame resistance of the plastic fraction in the boards. In some disposal processes, the thermal degradation of this plastic fraction is likely to result in the formation of hazardous high-molecular-weight organobrominated compounds, such as bromophenols, bromodioxins and furans *[Barontini & Cozzani, 2006; Barontini et al., 2005; Drohmann & Tange, 2002; Sakai et al., 2001]*.

Electronic scrap is usually disassembled to different waste streams for the disposal. The operations of grinding and mechanical separation produce a waste stream which mainly contains the material of the support board (average composition of the stream: 35%w plastic, 50% of inert and 15% metal). Present study compares four different process alternatives for the disposal of this waste stream from printed boards scrap: A) pyrolysis-gasification; B) dedicated incineration without energy recovery; C) incineration in a non-dedicated facility with energy recovery; and D) landfilling. The landfill disposal option was introduced to test the capability of the developed procedure to assess such a solution.

The potentiality of 400 kg/h of ground PWB waste was assumed as a common reference basis. The impacts deriving from the waste transport and from the previous treatments of the waste stream were not considered in the present analysis, because they are common to all the cases.

The alternative disposal processes assumed for the analysis were defined from the literature data available for existing or pilot plants *[Boerrigter, 2001; Vehlow et al., 2002]*. The level of detail of the alternative definition reflects the typical situation of early stages of process design. The features of each disposal alternative are briefly reported in the following.

A) Pyrolysis-gasification plant

The considered process (Figure 4.1.1-A) consists in a thermal degradation of the plastic fraction of the waste in non oxidative conditions (pyrolysis) at about 550°C. The volatiles formed are fed to a catalytic reforming to yield syn-gas. This gas stream is quenched with an alkaline solution to remove hydrogen bromide and bromine (if present). The exhaust bromide solution, after filtration and neutralization, is not of environmental concern and may be disposed or used in other activities (e.g. as biocide, in drilling addictives, for de-icing). The purified syn-gas, after scrubbing and activated carbon absorption, is suitable for combustion. The gas is thus used in part to heat the pyrolysis oven (around 20%) and in part to generate electricity by a gas engine. Energy recovery is actually one of the main advantages of this process. The pyrolysis residue (char) is available to be fed to a secondary copper smelter, in order to separate the inorganic part and to recycle copper. However in the present study landfilling was considered for this stream as a conservative working hypothesis.

B) Dedicated incineration facility

This process alternative (Figure 4.1.1-B) aims at waste volume reduction by a thermal oxidative destruction of the waste plastic fraction. Due to the high content of flame retardants, combustion must be assisted by a pilot flame, fired by natural gas. The flue gases are scrubbed as in the previous process, but it is worth to notice that oxidative conditions enhance the formation of bromodioxins *[Barontini & Cozzani, 2006; Barontini et al., 2005; Sakai et al., 2001]*. In order to limit this reaction, a quench must be applied and energy recovery from flue gases is not feasible. Also in this case the solid residual was considered to be disposed by landfilling.

C) Non dedicated incineration facility

As in the previous alternative, this process (Figure 4.1.1-C) aims to volume reduction of the waste: in this case combustion is carried out in a waste-to-energy plant, in which the electronic scrap (about 3%w) is fed with other wastes that provide the necessary conditions for combustion. A combustion efficiency is introduced to account for the possibility of incomplete combustion. The plant has a proper flue gas treatment to control dioxins emission via activated carbon adsorption. Energy recovery is in place and the quantity of electric energy generated allocable to the contribution of the PWB waste stream was calculated. Also in this case the combustion residue is landfilled.

D) Landfill

A landfill for the disposal of hazardous waste was considered. Proper devices were supposed to be present in order to avoid waste dispersion in the surrounding environment. Thus, leaching and gas releases are prevented or, if present, are drained and properly disposed, at least in a short term perspective. However occupation of land for a very long time (virtually infinite) occurs, and is accounted for by a land use environmental indicator.

4.1.2 Results from sustainability assessment

4.1.2.1 – Calculation of Level 1indicators

The input data required for the application of the proposed methodology to this case study were derived from the available literature on existing or pilot plants *[Boerrigter, 2001; Vehlow et al., 2002]*. This allowed specifying the process diagram and the main process streams. Flow rates and compositions were calculated by material and energy balances. The fugitive emissions were assessed by average emission factors for the expected leak points within the process diagram (e.g. seals, joints, valves, etc.) *[Allen & Shonnard, 2002]*. The emission of micro-pollutant from the utilities (e.g. power generation, furnaces, etc.) were evaluated by emission factors from available databases *[EPA, WPa]*. The main material and energy flows across the system boundaries are reported in Table 4.1.2. The main sources of emissions are the off-gases from combustion in the pyrolysis oven and in the syn-gas fired engine for power generation.

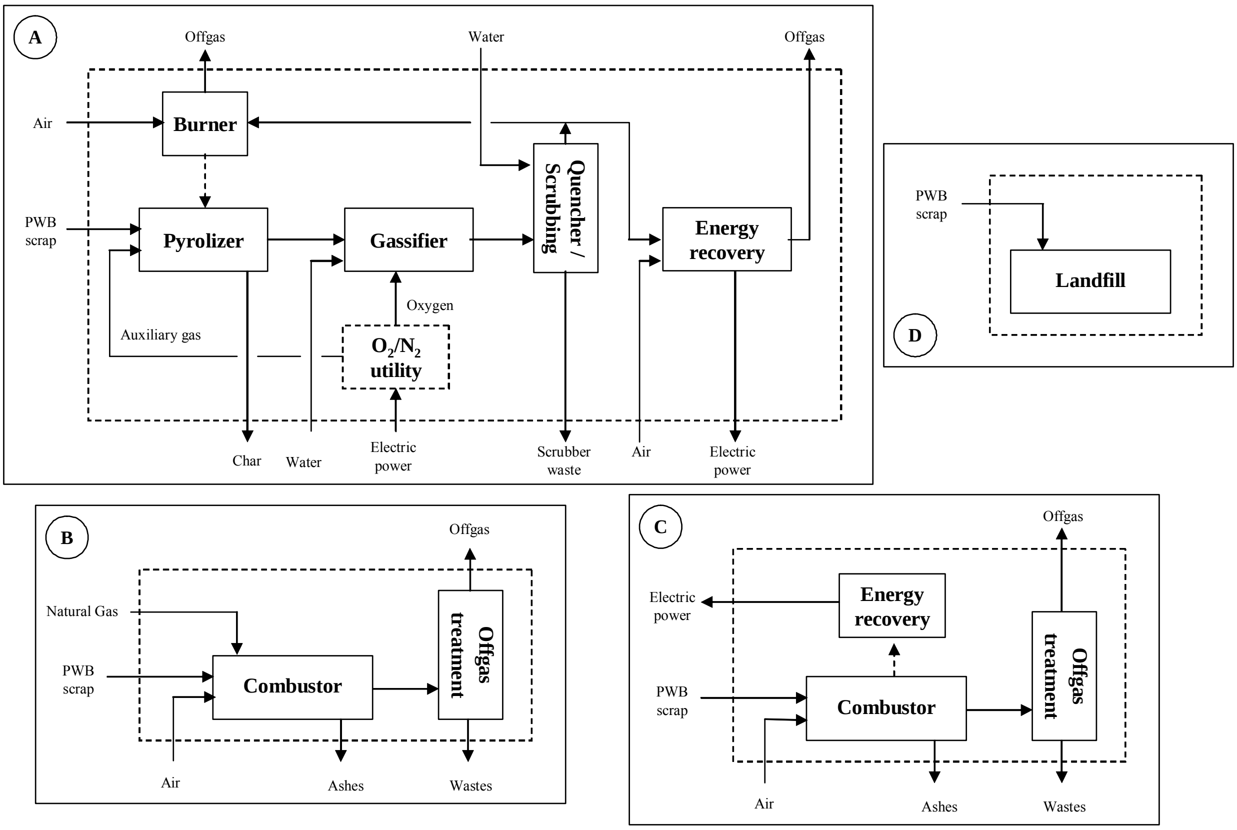


Figure 4.1.1: Diagrams of the alternative processes analysed for the disposal of waste from electronic scrap: boundary definition and main flows. A) Pyrolysis-gasification plant, B) Dedicated incineration facility, C) Incineration in a non-dedicated facility, D) Landfill.

Air emissions	*Stack*	*Fugitive*	*Total*	*Unit*
CO_2	$2.10 \cdot 10^6$		$2.10 \cdot 10^6$	kg/y
NO_x	$7.35 \cdot 10^3$		$7.35 \cdot 10^3$	kg/y
CO	$4.82 \cdot 10^3$	$1.88 \cdot 10^3$	$6.70 \cdot 10^3$	kg/y
HBr	$1.85 \cdot 10^3$	$3.52 \cdot 10^2$	$2.20 \cdot 10^3$	kg/y
Br_2	$1.82 \cdot 10^3$		$1.82 \cdot 10^3$	kg/y
Volatile organic mix	$1.02 \cdot 10^3$	$6.16 \cdot 10^2$	$1.64 \cdot 10^3$	kg/y
Dioxins and furans	$7.08 \cdot 10^{-8}$		$7.08 \cdot 10^{-8}$	kg/y
Waste	*To disposal*			
Char	$2.24 \cdot 10^6$		$2.24 \cdot 10^6$	kg/y
Resources	*Consumed*	*Produced*		
Electric power	$3.50 \cdot 10^1$	$1.80 \cdot 10^2$	$1.45 \cdot 10^2$	kW

Table 4.1.2: Material and energetic flows relevant to pyrolysis-gasification alternative of disposal of waste from electronic scrap.

The more important pieces of equipment were preliminary sized, allowing the estimation of the plant capital cost *[Matche; WP; Perry & Green, 1997]* necessary for economic evaluations and of the hold-ups required for inherent safety analysis. Material, energy and operative costs were evaluated multiplying the calculated flow rates by average unitary costs from various sources *[IChemE, 2002; Perry & Green, 1997]*. The specific equivalent number of employees necessary for process activities was estimated by expert judgment based on similar activities. The estimation of the number of employees is necessary for the assessment of both occupational and economic indices.

The level 1 indicators may be directly obtained from the input data by the application of specific rules for each category of impact. In the following these rules are detailed and a calculation example of the procedure is provided for the “pyrolysis-gasification” alternative for electronic scrap waste disposal (alternative process A in Figure 4.1.1). Since the general procedure is common to all the applications, the detailed assessment of the indicators for the other process alternatives is not reported here for sake of brevity.

All the *environmental indicators* considered in this case study are assessed following the principle of *potential impact benchmarking [Allen & Shonnard, 2002; Chen et al., 2002; Pennington et al., 2000]*. Thus they are expressed as a quantity of an equivalent reference material by an equivalence factor named *potential impact factor* (see 1.2.3). The values of the potential impact factors applied in the assessment of option A are shown in Table 4.1.3.
For some impact categories consolidated values from the literature (e.g. *Allen & Shonnard, [2002]*) are suitable for the discussed method. For *toxic* and *carcinogenic air emissions* and for *solid waste disposal* specific approaches described in 1.2.3 were followed to define the impact factor. The data on toxicity and carcinogenicity of the substances of concern are collected from suitable databases *[CDC,WP; EPA, WPc]*.

For example, the nitrogen dioxide is reported to be a greenhouse, acidifying and toxic compound. The *global warming* and *acidification potential* for this compound is evaluated by the standard approach described by *Pennington et al., [2000]*. In particular the values tabulated by *Allen & Shonnard, [2002]* were used in current case study (Table 4.1.3). For as

	GWP	RAP	SFP	TAP	CAP	WDP
CO_2	$1.0 \cdot 10^0$					
NO_2	$4.0 \cdot 10^1$	$7.0 \cdot 10^{-1}$		$3.0 \cdot 10^2$		
CO				$2.4 \cdot 10^1$		
HBr		$4.0 \cdot 10^{-1}$		$7.4 \cdot 10^3$		
Br_2		$4.0 \cdot 10^{-1}$		$3.8 \cdot 10^3$		
Volatile organic mix			$8.7 \cdot 10^{-1}$	$1.6 \cdot 10^2$		
Dioxins and furans				$1.2 \cdot 10^5$	$1.3 \cdot 10^6$	
Hazardous waste						$9.0 \cdot 10^0$
Reference	*[Allen & Shonnard, 2002]*	*[Allen & Shonnard, 2002]*	*[Allen & Shonnard, 2002]*	*C.f [CDC,WP]*	*C.f. [EPA, WPc]*	*C.f. [Saling et al., 2002]*

Table 4.1.3: Example of potential impact factors applied in Level 1 impact indicators assessment of pyrolysis-gasification alternative for disposal of waste from electronic scrap. GWP: global warming potential, RAP: rain acidification potential, SFP: smog formation potential, TAP: acute toxicity in air potential, CAP: carcinogenicity in air potential, WDP: solid waste disposal hazard potential, C.f. : calculated from data in the reference.

concerns the *air toxicity potential*, data on LC_{50} to be used in Equation (1.2.2) for rats are derived from NIOSH database *[CDC, WP]* for both nitrogen dioxide (88ppm/4h) and the benchmark reference toluene (49g/m^3 /4h). The straightforward application of Equation (1.2.2) leads to the value reported in Table 4.1.3:

$$TAP_{NO_2} = \frac{\dfrac{1}{0.17\ [g/m^3]}}{\dfrac{1}{49\ [g/m^3]}} = 300 \qquad (4.1.1)$$

The *solid waste disposals* are assessed within the category of landfilled wastes, since landfill is assumed to be the worst disposal option. As a working hypothesis, the ratio of the average disposal cost of the waste of concern to that of municipal waste is used as potential impact factor. The disposal cost is in general representative of the hazard due to the different standards necessary for landfilling a type of waste *[Saling et al., 2002]*.
The *land use* indicator is related to the occupation of land. In particular, in the present case study, the impact is assessed for process alternative D, where the landfill facility occupies a significant land area for a long time span (virtually infinite). In that case, the occupied area per unit of disposed waste is evaluated by data of similar facilities.

The impact category of *resource consumption* is related to the material and energy flows entering the process. In particular, in current case study, the use of *fossil fuels* and of *electrical power* is of concern. Fuel consumption is assessed with respect to the energy released corrected by a penalty factor that is related to the emission of toxic combustion products. The electrical power is straightforward evaluated as an energy consumption rate.

Capital cost	$1.11\cdot10^6$	€
Annual income	$1.44\cdot10^6$	€/y
Annual costs	$7.23\cdot10^5$	€/y
Net Present Value	$3.43\cdot10^6$	€

Table 4.1.4: Example of economic data used the assessment of pyrolysis-gasification alternative for disposal of waste from electronic scrap.

The flow data presented in Table 4.1.2 are combined with the pertinent potential impact factors (Table 4.1.3) by Equation (1.2.1) according to the rules defined in §1.2.3. The calculation yields the Level 1 environmental indicators for the various impact categories. The values obtained are reported in Table 4.1.4. For example, the global warming indicator for process option A is calculated as in the following:

$$I_{GW,A} = PIF_{A,CO_2}\ m_{CO_2,A} + PIF_{A,NO_x}\ m_{NO_x,A} =$$

$$= 1.0\cdot2.10\cdot10^6 + 40\cdot7.35\cdot10^3 = 2.39\cdot10^6\,kg_{CO_2eq}/y \qquad (4.1.2)$$

The input data on operative (raw material, sales, labor, etc.) and capital costs allow calculating parameters relevant to the assessment of the *economic impact*. Some of the intermediate values are reported in Table 4.1.4. The Net Present Value (NPV_i) over the plant life (n) is calculated from estimated annual cash flows ($C_{t,i}$) and discount rate (r) by equation (4.2.3):

$$NPV_i = \sum_{t=0}^{n} \frac{C_{t,i}}{(1+r)^t} \tag{4.2.3}$$

The net present value is multiplied by -1 to yield the *net potential economic impact* index (NPEI), that is the economic indicator used in the assessment framework. The change of sign is introduced since impact indices must have a higher value in the worst case.

The data on process scheme, operative conditions, material flow rates and inventories are the input for the assessment of the *inherent safety* index. In current case study the Mond Fire, Explosion and Toxicity Index *[ICI Mond, 1985; Tyler, 1985]* is used as *inherent safety index*. In particular the Overall Risk Factor of the Mond index approach is calculated for the principal units of the process by the procedure described in the Mond Guide *[ICI Mond, 1985]*. Table 4.1.5 reports an example of intermediate results in the application of the Mond procedure to the gas reformer in process alternative A (pyrolysis-gasification plant). The higher index value among the units is assumed as hazard index for the process alternative.

	Value
Material factor	21
Hazard factors	
Special material hazards	30
General process hazards	50
Special process hazards	265
Layout hazards	50
Overall risk factor	428

Table 4.1.5: Example of intermediate values in the assessment of Mond Index for the gas reformer in the pyrolysis-gasification alternative for disposal of waste from electronic scrap.

The *occupational index* is calculated multiplying the previously evaluated number of employees by -1. As in the case of NPEI, the change of sign is necessary since impact indices must have a higher value in the worst case.

The resulting values of the considered set of Level 1 indicators for all the options are reported in Table 4.1.6. The table clearly shows that the first result obtained by the application of the proposed procedure was to point out the major differences among the impact of the different alternatives considered for the disposal of the PWB waste stream. The data in Table 2 evidence that, as expected, relevant differences are present among the values of the *environmental impact* indicator for landfilling with respect to those of the other processes. The main impact of landfilling is in land-use, while all the other processes result in impacts related to emission of greenhouse-gases and of airborne micropollutants. Among the thermal disposal processes, dedicated incineration is that showing the worst performances with respect to global warming and natural gas consumption (since the process is not autothermal), although it has the best performances with respect to the emission of acidifying and toxic compounds.

The *inherent safety index* also shows relevant differences among the processes. Landfilling is the process showing the worst performance, due to the possibility of accidental combustion of wastes, while the pyrolysis-gasification alternative is also penalized due to the formation and the treatment of a flammable gas in the process.

	Impact indicator	**Pyrolysis – gasification**	**Dedicated incineration**	**Non-dedicated incineration**	**Landfill**	**Unit**	**Norm. Factor (unit/km^2)**
Level 1							
Environment	Global warming	$2.39\cdot10^{6}$	$2.47\cdot10^{6}$	$2.32\cdot10^{6}$	0.00	kg/y	$1.16\cdot10^{6}$
	Rain Acidification	$6.75\cdot10^{3}$	$3.00\cdot10^{3}$	$3.61\cdot10^{3}$	0.00	kg/y	$4.83\cdot10^{3}$
	Smog Formation	$1.43\cdot10^{3}$	$1.53\cdot10^{1}$	$1.53\cdot10^{1}$	0.00	kg/y	$5.63\cdot10^{3}$
	Air toxicity	$2.57\cdot10^{7}$	$2.13\cdot10^{7}$	$3.06\cdot10^{7}$	0.00	kg/y	$3.79\cdot10^{5}$
	Air carcinogenicity	$9.20\cdot10^{-2}$	1.29	$3.32\cdot10^{1}$	0.00	kg/y	$2.06\cdot10^{1}$
	Solid waste disposal	$2.02\cdot10^{7}$	$1.89\cdot10^{7}$	$1.95\cdot10^{7}$	0.00	kg/y	$2.32\cdot10^{5}$
	Land use	0.00	0.00	0.00	$3.17\cdot10^{-3}$	km^2/y	$2.34\cdot10^{-5}$
	Natural Gas	0.00	1.50	0.00	0.00	TJ/y	$4.02\cdot10^{1}$
	Electric Power	$-1.16\cdot10^{6}$	0.00	$-1.94\cdot10^{6}$	0.00	kWh/y	$1.10\cdot10^{6}$
Economy	NPEI	$-3.43\cdot10^{6}$	$-3.00\cdot10^{6}$	$-3.78\cdot10^{6}$	$-5.04\cdot10^{6}$	Euro$_{05}$	$2.83\cdot10^{6}$
Society	Occupational index	$-1.50\cdot10^{1}$	$-1.50\cdot10^{1}$	$-1.50\cdot10^{1}$	-9.00	People	$7.92\cdot10^{1}$
	Inherent Safety	$4.28\cdot10^{2}$	$1.90\cdot10^{1}$	$1.90\cdot10^{1}$	$1.43\cdot10^{4}$	Score	$1.06\cdot10^{3}$

Table 4.1.6: Values of Level 1 impact indicators calculated for disposal of waste from electronic scrap.

4.1.2.2 – Normalization and aggregation

Table 4.1.6 also reports the *normalization factors* used in the procedure. The normalization factors assumed were calculated from the reference background data available for a site in the North of Italy. Table 4.1.7 reports the corresponding *normalized values* of the indicators, as obtained by Equation 1.2.7.

The normalized values of the *environmental indicators* allow the comparative assessment of the main impacts of the alternative processes based on external references. As shown in the table, two main criticalities are present: i) waste stream disposal for all the alternative processes; and ii) emission of hazardous airborne toxic compounds from the thermal processes. In the case of landfilling, waste stream disposal concerns the entire waste stream, while in the thermal processes the impact is related to the disposal of the residual solid fraction obtained from the thermal treatment. The criticality of these aspects is clearly related to the characteristics of the waste streams. As a matter of fact, the thermally degradable fraction is only a part of the overall waste stream (about 30% by weight *[Barontini & Cozzani, 2006]*). On the other hand, the potential formation of highly hazardous compounds in the thermal processing of PWB was demonstrated in several previous studies *[Barontini & Cozzani, 2006; Barontini et al., 2005; Sakai et al., 2001]*. The identification of critical elements at this level of the analysis is a key issue for driving improvements in further steps of the design process (e.g. research for technologies/operative conditions for reducing toxic compound emissions).

Impact index		Pyrolysis – gasification	Dedicated incineration	Non-dedicated incineration	Landfill	Weight Factor
Level 1 (normalized)						
Environment	Global warming	2.05	2.12	1.99	0.00	0.051
	Rain Acidification	1.40	0.62	0.75	0.00	0.066
	Smog Formation	0.25	0.003	0.003	0.00	0.049
	Air toxicity	67.95	56.21	80.75	0.00	0.095
	Air carcinogenicity	0.004	0.06	1.61	0.00	0.168
	Solid waste disposal	87.09	81.35	83.86	0.00	0.030
	Land use	0.00	0.00	0.00	135.30	0.081
	Natural Gas	0.00	0.037	0.00	0.00	0.044
	Electric Power	-1.05	0.00	-1.76	0.00	0.064
Economy	NPEI	-1.21	-1.06	-1.34	-1.78	
Society	Occupational index	-0.19	-0.19	-0.19	-0.11	0.200
	Inherent Safety	0.40	0.018	0.018	13.42	0.800

Table 4.1.7: Normalized values of Level 1 indicators for disposal of waste from electronic scrap.

Impact index	Pyrolysis – gasification	Dedicated incineration	Non-dedicated incineration	Landfill	Weight Factor
Level 2					
Environment	9.18	7.92	10.47	10.90	0.300
Economy	-1.21	-1.06	-1.34	-1.78	0.300
Society	0.29	-0.02	-0.02	10.71	0.400
Level 3					
Overall Index	2.51	2.05	2.73	7.02	
Overall Index *(normalized)*	0.36	0.29	0.39	1.00	

Table 4.1.8: Normalized values of Level 1 indicators and values of Level 2 and 3 indices calculated for case-study 1 (waste PWB disposal).

The *weight factors* used in the first step of aggregation are also reported in the Table 4.1.7. Table 4.1.8 reports the values calculated for Level 2 (*aggregated*) and Level 3 (*overall*) indices and the other weight factors used.

As discussed in §1.2.5, the choice of weight factors is based on decisions concerning the local sustainability policy. In the present case-study, weight factors were chosen on the basis of the relative importance given in the Italian national policy to the reduction of emissions, economic growth and societal problems, provided the historical data and the compliance to international agreements (e.g. Kyoto Protocol, Goteborg Protocol, etc.). However, it must be remarked that the general approach developed in the present study may be applied as well using alternative weight factors, although selected on the basis of the criteria discussed.

The fingerprint of the impacts of the different process alternatives on the three main aspects of sustainability (*environmental, economic, societal*) are reported in Figure 4.1.2. The figure evidences that landfilling is the alternative that shows the highest environmental and societal impact, although is the more advantageous with respect to the economic aspects. Pyrolysis-gasification also shows a relevant societal impact, having a wider impact fingerprint with respect to the other thermal processes. A more detailed comparison among the Level 2 indices is reported in Table 4.1.8. The table confirms that the societal index is that showing the wider differences (up to three orders of magnitude) among the proposed alternatives. More limited variations (less than a factor 2) are present in the values of the environmental and economic indices. The table also reports the value of the overall sustainability index for the proposed alternatives. As shown in the table, the *overall index* calculated by the weight factors reported in the table is mainly influenced by the differences in the inherent safety and environmental impact of the different processes. Thus, landfilling results, as expected, the less sustainable process, having an overall impact more than three times higher with respect to the other processes. Lower differences (less than a factor 1.5) are present among the other alternatives. Thermal methods are found to have almost equivalent overall impacts, although non-dedicated incineration is penalized as well by safety and environmental impact factors, and dedicated incineration emerges as the more sustainable process. The analysis of the results obtained for the indices at the different levels of the hierarchy is the basis of the decision making process among the alternatives. The defined performance indices allow outlining the impact fingerprint of the alternative options both in terms of difference between alternatives and as impact significance respect to the external reference.

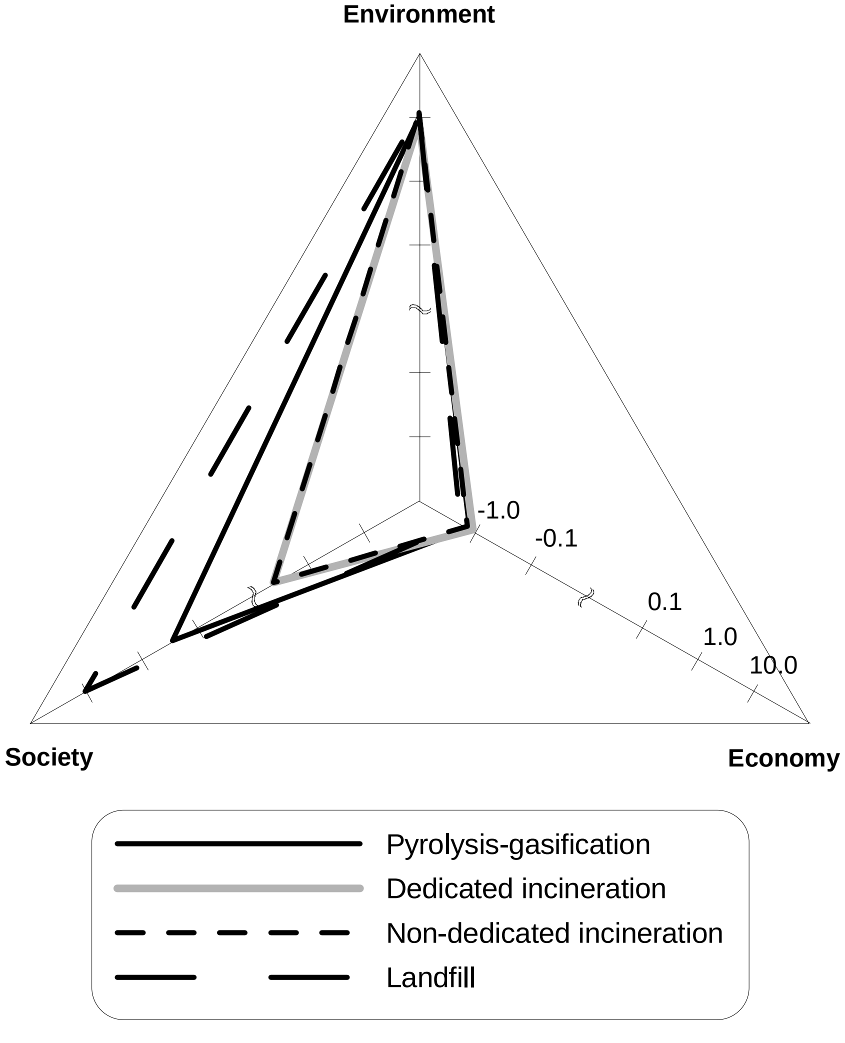


Figure 4.1.2: Radar diagram representing the impact footprint of the disposal processes analysed in the present study.

4.1.2.3 – Sensitivity analysis

The results obtained for the overall index are obviously influenced by the weight factors used in the procedure. As remarked in §1.2.6, uncertainties may be present in the value attributed to these parameters. A sensitivity analysis was performed to assess the influence of these uncertainties on the results of the method. A Monte Carlo method was used to calculate the resulting distribution of the aggregated indices (the overall index and the Level 2 indices) and the contribution of the different weight factors to the variance of the results. A beta distribution of probability is arbitrary associated to each weight factor ($\alpha=\beta=4$ and a 20% maximum variation of the values in Table 4.1.7 and 4.1.8 are assumed).

Table 4.1.9 shows the contribution to the variance of the overall index in the current case study. Only two weight factors showed a relevant contribution to variance. Moreover, these are the same for all the processes involving thermal treatments, confirming that the critical impacts of these processes are the same (environmental aspects and, mainly, air toxicity).
The probability distribution of the difference between overall sustainability indexes for selected couples of process alternatives was calculated by Monte Carlo runs. The analysis of the cumulative distributions allows identifying the likelihood of changes in the impact ranking of the alternatives. Figure 4.1.3 shows the cumulative probability of the values calculated for the difference between the overall sustainability impact indices for the different processes. As shown in the figure, a change of sign of the difference (that implies a change in the impact ranking among the alternatives) is extremely unlikely to take place. Thus, the analysis evidenced that a limited uncertainty in the selection of the weight factors seems not critical for the identification of the process alternative that has the lowest impact on sustainability. It may be concluded that the use of the overall sustainability index provided in Table 4.1.8 and of the impact fingerprint provided in Figure 4.1.2 allow at least a preliminary screening of the expected impact on sustainability of the different process alternatives. Moreover, the case-study evidenced that the preliminary data available during early process design are sufficient to carry out a sustainability assessment by the developed procedure.

Pyrolysis – gasification		**Dedicated incineration**		**Non-dedicated incineration**		**Landfill**	
Environment	$6.2\cdot10^{-1}$	Environment	6.5E-01	Environment	$6.3\cdot10^{-1}$	Inherent Safety	$4.4\cdot10^{-1}$
Air toxicity	$3.1\cdot10^{-1}$	Air toxicity	2.8E-01	Air toxicity	$3.2\cdot10^{-1}$	Economy	$3.2\cdot10^{-1}$
Waste disposal	$5.0\cdot10^{-2}$	Waste disposal	5.7E-02	Waste disposal	$3.4\cdot10^{-2}$	Land use	$2.4\cdot10^{-1}$
Economy	$1.5\cdot10^{-2}$	Economy	9.2E-03	Economy	$8.1\cdot10^{-3}$	Environment	$3.3\cdot10^{-5}$
Inherent Safety	$2.8\cdot10^{-3}$	Inherent Safety	4.3E-04	Air carcinog.	$5.1\cdot10^{-4}$	Global warming	$1.8\cdot10^{-5}$
Global warming	$1.3\cdot10^{-4}$	Global warming	1.7E-04	Inherent Safety	$2.3\cdot10^{-4}$	Air toxicity	$1.6\cdot10^{-5}$
Rain acidification	$2.1\cdot10^{-5}$	Air carcinog.	1.5E-05	Global warming	$9.4\cdot10^{-5}$	Ozone depletion	$1.1\cdot10^{-5}$
Electrical Power	$1.2\cdot10^{-5}$	Electrical Power	6.9E-06	Electrical Power	$3.3\cdot10^{-5}$	Air carcinog.	$1.0\cdot10^{-5}$
Air carcinog.	$9.7\cdot10^{-6}$	Natural gas	6.1E-06	Natural gas	$6.5\cdot10^{-6}$	Rain acidificatio.	$4.0\cdot10^{-6}$
Natural gas	$6.0\cdot10^{-6}$	Ozone depletion	4.2E-06	Ozone depletion	$3.4\cdot10^{-6}$	Natural gas	$3.1\cdot10^{-6}$
Ozone depletion	$2.9\cdot10^{-6}$	Land use	2.1E-06	Land use	$1.7\cdot10^{-6}$	Electrical Power	$1.5\cdot10^{-6}$
Land use	$2.0\cdot10^{-6}$	Rain acidificatio.	1.1E-06	Rain acidificatio.	$6.0\cdot10^{-7}$	Smog formation	$1.4\cdot10^{-6}$
Smog formation	$1.1\cdot10^{-6}$	Smog formation	1.2E-07	Smog formation	$6.8\cdot10^{-9}$	Waste disposal	$1.8\cdot10^{-8}$

Table 4.1.9: Contribution to the variance of the overall indexes calculated for the weighing factors. A beta distribution of each weight assumed with $\alpha = \beta = 4$ and a maximum range of ±20% of initial values were assumed.

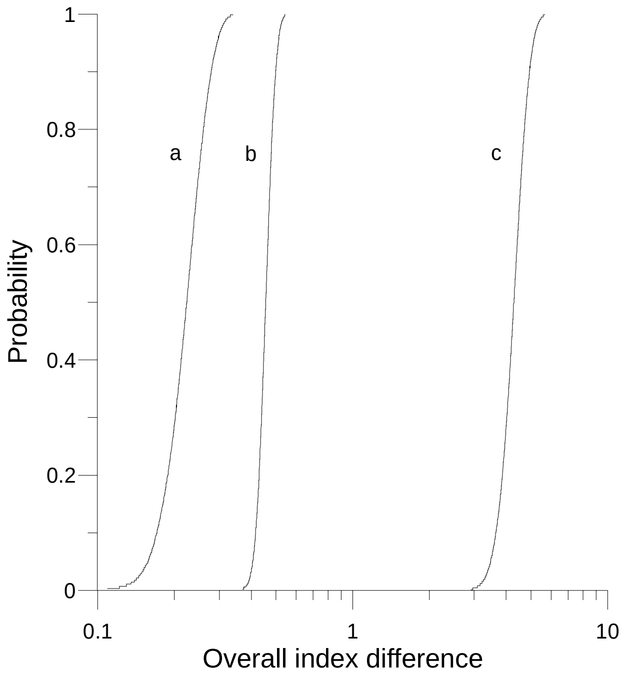


Figure 4.1.3: Distribution of cumulative probabilities for the difference between the overall sustainability indexes for selected couples of alternative options. a) Non-dedicated incineration - Pyrolysis–gasification; b) Pyrolysis–gasification - Dedicated incineration; c) Landfill - Non-dedicated incineration

4.2 – Solvent Recovery

4.2.1 – Case study description

This case-study concerns the analysis of the disposal alternatives for waste liquid organic solvents. Organic solvents are commonly used in many industrial activities and in year 2002 the world demand of solvents was around 17.5 Gg. Several industrial activities result in the production of waste streams of exhaust solvents. These waste solvents may have a wide range of possible compositions, depending on the specific industrial activity and on the specific process operation that results in the production of the waste. In the present case study, a model composition is assumed for a solvent waste from a paint production plant. The disposal of a stream of medium-low boiling solvent contaminated by 1%w of chromate salt (i.e. strontium chromate) is considered. Disposal of this waste is a critical issue due to the many threats present: liquid phase, volatile components, toxicological relevance of some chemicals used as solvents or pigments, formation of unstable compounds (e.g. peroxides).

The design of disposal alternatives for waste must take into account that both energy recovery and the recovery of solvent for reuse may be economically attractive. However, process safety may play an important role in the selection among alternatives, since the waste stream is a flammable liquid in which peroxides or other unstable substances may be present *[Cozzani et al., 1999]*. Moreover, the chromium (VI) of the stream is toxic and carcinogen.

Three process alternatives derived from industrial practice were assessed for the treatment of this waste stream: A) incineration in a dedicated facility with energy recovery; B) solvent recovery for reuse; and C) landfilling. The disposal of a 1000 kg/h stream was considered. Also in this case, the level of information is comparable to typical early stages of process design.

A) Dedicated incineration

This process aims at elimination of the waste stream by combustion in controlled and safe conditions. The process (Figure 4.2.1-A) is designed in order to assure the typical emission values of an hazardous waste incinerator, equipped with a proper flue-gas treatment (scrubbing, filtering, etc.). The main fraction of chromium is found in the combustion ashes and, after proper treatment, is delivered to an hazardous waste landfill. Due to solvent flammability, the combustion is supposed to be almost complete. Provided that the waste is halogen-free, no formation of halogenated dioxins is considered. The process greatly reduces the volume of the waste and destroys all the flammable and thermally unstable components. Besides, the energy recovery on the flue gas generates electric power that is accounted in the assessment.

B) Solvent recovery

This process consists in the distillation of the waste stream to recover a commercial solvent mixture. The process is attractive both from an environmental (reuse) and from an economic (valuable product) point of view. A batch distillation process is considered (Figure 4.2.1-B). The distillation residue in the evaporation vessel contains almost all the chromium salt and is disposed off by landfilling. In the present analysis it is conservatively estimated that around 5% of the waste solvent is present in the residual.

Safety is the major problem concerning this process alternative: thermally unstable compounds may be present (e.g. peroxides), that may lead to explosive decomposition when heated. In order to limit this hazard, samples of each batch of processed solvent must be thermally tested *[Cozzani et al., 1999]*. Safety limits should also be introduced for the maximum process temperatures.

The process requires heat for the distillation and nitrogen for equipment blanketing. The heat is generated in a proper device by natural gas combustion, and the emissions of this utility are included in the assessment. The nitrogen is separated from air off-site. However, the electrical power consumption required for nitrogen production is considered in present analysis.

C) Landfill

A landfill for the disposal of barrels of the hazardous waste was considered. Proper devices were supposed to be present in order to avoid waste dispersion in the surrounding environment. Thus, emissions are prevented or, if present, are drained or captured and properly disposed, at least in a short term perspective. However occupation of land for a very long time (virtually infinite) occurs, and is accounted for by a land use environmental indicator.

It is worth to notice that on the very long term there are two main possible release events: release of volatile organic compounds and release of chromium salts. The first one is expected to occur at a very slow time rates: thus no significant effects derive from it. The second, even if at slow rate can be hazardous. Nevertheless, it has to be considered that, in a long term perspective, this release is common to all the disposal options under analysis, since most of the chromium salt is landfilled in any case. Although the elimination of chromium from paints is the inherent approach to this problem, this issues was not considered in the current assessment, since it falls out of the scopes of the present study (i.e. comparison of disposal options for an already existing stream).

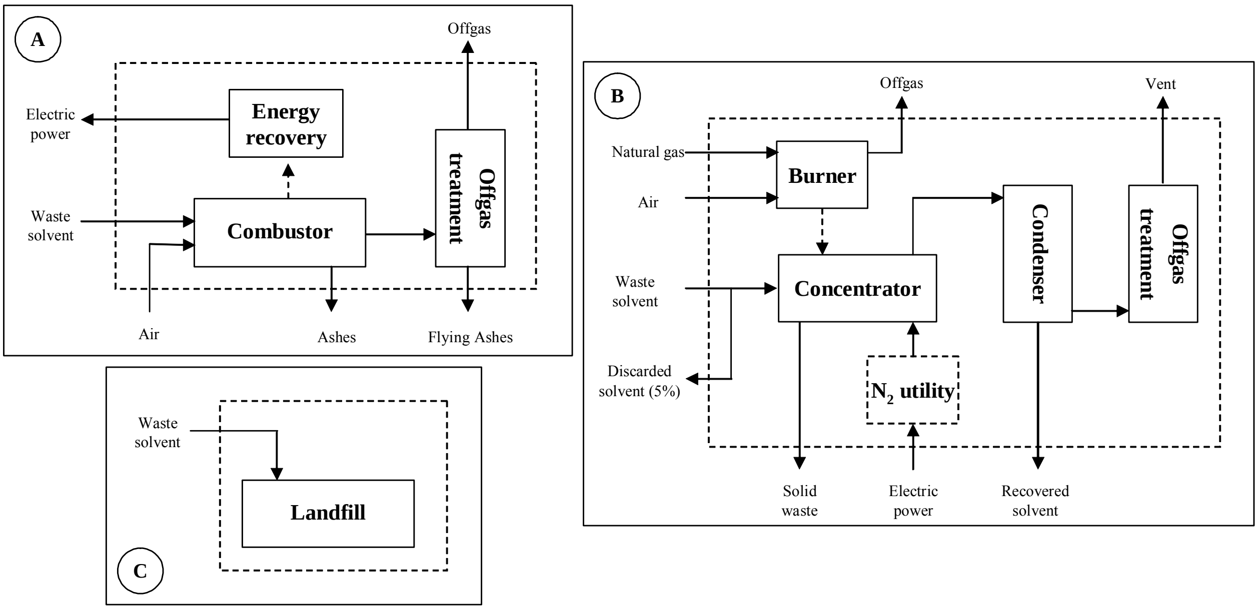


Figure 4.2.1: Alternative processes analysed for the disposal of waste solvents: boundary definition and main flows. A) Dedicated incinerator, B) Solvent recovery, C) Landfill.

4.2.2 – Results from sustainability assessment

The assessment procedure described in §1.2 and demonstrated in detail for the case-study of electronic waste disposal (§4.1), applies similarly also to this one. Hence, for sake of brevity, only the final results of the indices will be presented and discussed.

Tables 4.2.1 and 4.2.2 summarize the results obtained from the analysis of the waste solvent disposal options. As shown in the tables, quite different results were obtained for the *impact indices* of the different processes. This is shown by Figure 4.2.2, that reports the impact fingerprint of the process alternatives. As evident from the figure, the three alternatives have the main impact in different sectors: combustion and landfilling have a main impact on environment, solvent recovery on societal aspects (due to the higher safety problems associated with the process).

Also in this case landfilling resulted the process having a higher impact on sustainability. Moreover, the results obtained for the *overall index* evidence again the importance of introducing inherent safety and economic factors in the assessment. As a matter of fact, the overall impact on sustainability may be high for processes as solvent recovery, that have a low environmental impact with respect to combustion, but that seem to "shift" the impact to other compartments (in the specific case, to societal aspects).

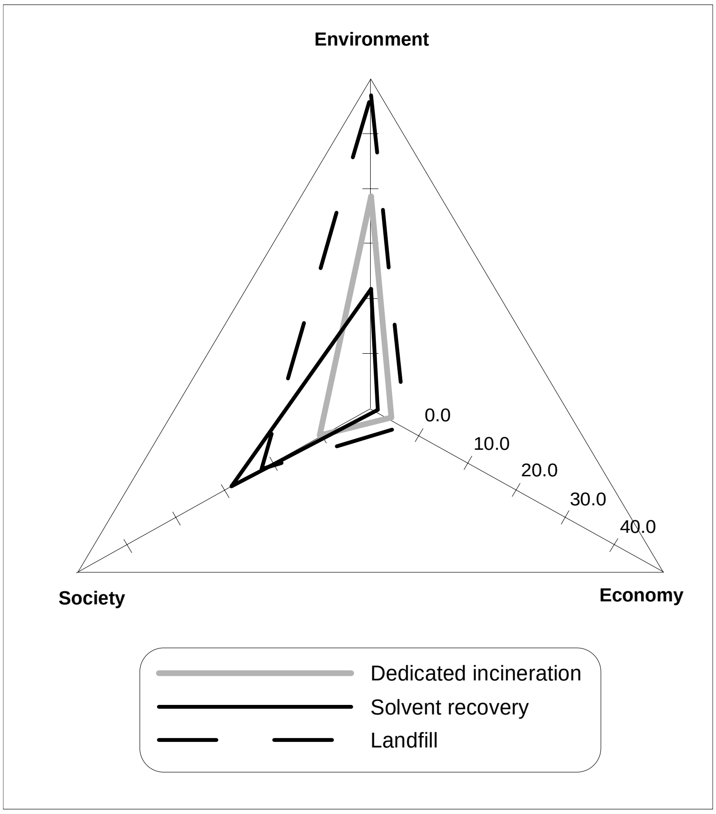


Figure 4.2.2: Radar diagram representing the impact footprint of the disposal processes analysed in the present study.

	Impact indicator	Dedicated incineration	Solvent recovery	Landfill	Unit	Norm. Factor (unit/km^2)
Level 1						
Environment	Global warming	$2.02\cdot10^{7}$	$3.53\cdot10^{5}$	0.00	kg/y	$1.16\cdot10^{6}$
	Rain Acidification	$1.43\cdot10^{4}$	$9.20\cdot10^{1}$	0.00	kg/y	$4.83\cdot10^{3}$
	Smog Formation	$2.06\cdot10^{3}$	$4.26\cdot10^{3}$	0.00	kg/y	$5.63\cdot10^{3}$
	Air toxicity	$6.18\cdot10^{6}$	$5.02\cdot10^{4}$	0.00	kg/y	$3.79\cdot10^{5}$
	Air carcinogenicity	$3.26\cdot10^{5}$	$1.36\cdot10^{5}$	0.00	kg/y	$2.10\cdot10^{3}$
	Solid waste disposal	$6.10\cdot10^{5}$	$4.18\cdot10^{6}$	0.00	kg/y	$2.32\cdot10^{5}$
	Land use	0.00	0.00	$1.32\cdot10^{-2}$	km^2/y	$2.34\cdot10^{-5}$
	Natural Gas	0.00	5.41	0.00	TJ/y	$4.02\cdot10^{1}$
	Electric Power	$-2.43\cdot10^{7}$	$2.19\cdot10^{4}$	0.00	kWh/y	$1.10\cdot10^{6}$
	Solvent	0.00	$-7.52\cdot10^{6}$	0.00	kg/y	$3.66\cdot10^{5}$
Economy	NPEI	$-1.64\cdot10^{7}$	$-2.44\cdot10^{7}$	$-8.40\cdot10^{6}$	Euro$_{05}$	$2.83\cdot10^{6}$
Society	Occupational index	$-1.50\cdot10^{1}$	$-1.50\cdot10^{1}$	-9.00	People	$7.92\cdot10^{1}$
	Inherent Safety	$8.01\cdot10^{2}$	$2.49\cdot10^{4}$	$1.67\cdot10^{4}$	Score	$1.06\cdot10^{3}$

Table 4.2.1: Values of Level 1 impact indicators calculated for case-study on waste solvent disposal.

Impact index		Dedicated incineration	Solvent recovery	Landfill	Weight Factor
Level 1 (normalized)					
Environment	Global warming	17.33	0.30	0.00	0.051
	Rain Acidification	2.96	0.02	0.00	0.066
	Smog Formation	0.37	0.76	0.00	0.049
	Air toxicity	16.32	0.13	0.00	0.095
	Air carcinogenicity	154.89	64.82	0.00	0.168
	Solid waste disposal	2.63	18.02	0.00	0.030
	Land use	0.00	0.00	563.77	0.081
	Natural Gas	0.00	0.13	0.00	0.044
	Electric Power	-22.04	0.02	0.00	0.064
	Solvent	0.00	-20.52	0.00	0.031
Economy	NPEI	-5.80	-8.61	-2.97	
Society	Occupational index	-0.19	-0.19	-0.11	0.2
	Inherent Safety	0.75	23.43	15.74	0.8
Level 2					
Environment		27.36	10.87	45.42	0.3
Economy		-5.80	-8.61	-2.97	0.3
Society		0.56	18.71	12.57	0.4
Level 3					
Overall Index		6.69	8.16	17.76	
Overall Index *(normalized)*		0.38	0.46	1.00	

Table 4.2.2: Normalized values of Level 1 indicators and values of Level 2 and 3 indices calculated for the case-study.

The results obtained for the overall index are obviously influenced by the weight factors used in the procedure. A sensitivity analysis was performed by the Monte Carlo approach described in §1.2.6. A beta distribution of probability is arbitrary associated to each weight factor (α=β=4 and a 20% maximum variation of the values in Table 4.2.1 and 4.2.2 are assumed).

In particular it was possible to calculate the distribution of the differences of overall indices. As discussed in §1.2.6, the options were ranked according to the value of the overall index in Table 4.2.2: i) Landfill; ii) Solvent recovery; iii) Dedicated incineration. Then the cumulative distribution is calculated by random runs for the differences of consecutive ranks: a) (Landfill-Solvent recovery) and b) (Solvent recovery-Dedicated incineration). The result is shown in Figure 4.2.3. As shown in the figure, a change of sign of the difference (that implies a change in the impact ranking among the alternatives) is extremely unlikely to take place (e.g. it is lower than 6%, under the assumed hypothesis, for the difference "b)").

Thus, the sensitivity analysis evidenced that the final values of the impact factors are not critically affected by limited uncertainties in the values selected for the weight factors. Therefore, as shown in Figure 4.2.2 and in Table 4.2.2, the application of the developed methodology allows the preliminary assessment of the main expected impacts of process alternatives, based on a limited set of preliminary data available in early process design.

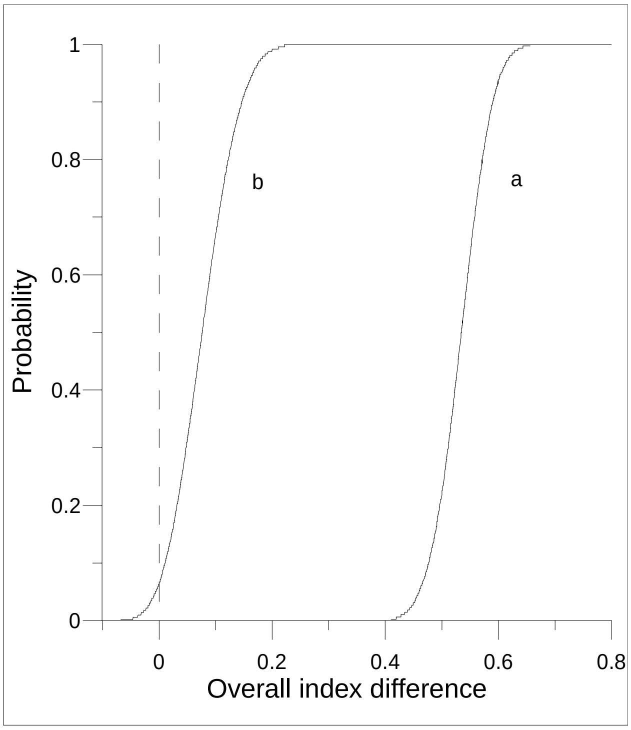


Figure 4.2.3: Distribution of cumulative probabilities for the difference between the overall sustainability indexes for selected couples of alternative options. a) Landfill-Solvent recovery; b) Solvent recovery-Dedicated incineration.

4.3 – Cyclohexanone

This chapter reports a case study concerning the comparison of alternative options for the industrial production of cyclohexanone, in the early stages of process design. Both sustainability (§4.3.2) and inherent safety assessment methods (§4.3.3) are applied in the following.

4.3.1 – Case study description

Cyclohexanone is an important intermediate in chemical industry. It is principally used as feedstock in the production of nylon 6,6 (via cyclohexanone-oxime) and of adipic acid (via oxidation by nitric acid). Other application include use as solvent and as feedstock for fine chemicals (pharmaceutics and agrochemicals). The world production was 3 billions of kg in 1990, about 97% was converted to ε-caprolactam or adipic acid *[Kirk-Othmer, 1992]*.

In the following five alternative processes are compared for the production of cyclohexanone. They are based on alternative chemical routes and represent the evolution, over the time, of the production technologies. The information required for the definition of the alternative process schemes was obtained from the scientific literature, patents, informal contacts with producers and engineering experience. Common boundaries were chosen for the options: the analysis extends from the same initial raw material (i.e. benzene) to the final product cyclohexanone. The boundaries include the allocable fraction of the utilities (e.g. boilers, wastewater treatment) that are necessary for the process. Storage of the raw materials, products and intermediates is not considered. A production potential of cyclohexanone in the final step of 98Gg/year was assumed as reference basis for all the cases.

4.3.1.1 – Process A: synthesis via oxidation of cyclohexane

The first industrial application of this process date back to the 40s. The process is notorious for the Flixborough accident *[Lees, 1996]*, where a vapour cloud explosion took place following the loss of containment in the reactor of an oxidation plant. The whole process (Figure 4.3.1) can be divided in two main steps *[Ullmann,1987; Kirk-Othmer, 1992; Crouch, 1960]*:

i) synthesis of cyclohexane (hydrogenation of benzene)
ii) synthesis of cyclohexanone (oxidation of cyclohexane)

The first step follows the reaction:

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} \tag{4.3.1}$$

The reaction is exothermic and temperature must be kept below 300°C (thermodynamic equilibrium favourites benzene at higher temperatures). Pressure is usually between 20 and 30 MPa. Methylcyclopentane may be formed as side-product, but catalytic systems based on nickel, palladium and platinum on alumina are selective toward the desired product. The reactor is operated in vapour phase with inter-cooled stages. Benzene conversion is almost complete. The hydrogen in the reactor output (hydrogen is fed to the reactor in stoichiometric excess) is separated from the condensable fraction and recycled back to the reactor feed. A fraction of the cyclohexane is recycled to the reactor as thermal inert.

The second step of the process is based on cyclohexane oxidation. The reaction system can be divided in two stages:

$$C_6H_{12} + O_2 \rightarrow C_6H_{11}OOH \qquad (4.3.2)$$

$$\begin{aligned} &C_6H_{11}OOH \rightarrow C_6H_{10}O + H_2O \\ &C_6H_{11}OOH \rightarrow \frac{16}{17}C_6H_{12}O + \frac{6}{17}H_2O + \frac{6}{17}CO_2 \\ &C_6H_{11}OOH \rightarrow sideproducts \end{aligned} \qquad (4.3.3)$$

In the first stage, the cyclohexane is oxidized by air, yielding cyclohexyl-hydroperoxide. The peroxide may undergo decomposition to the desired products (cyclohexanone and cyclohexanol) as well as to other undesired side-products. The decomposition of the hydroperoxide should be avoided in the oxidation reactor, since the oxidation of the decomposition products is easier than oxidation of cyclohexane, resulting in the formation of a large number of side-products. Thus, the two stages of reaction (cyclohexane oxidation and hydroperoxide decomposition) are segregated in different units, in order to enhance the yield in the desired products.

In the oxidation reactors (1.5÷4.0 MPa, 175÷220 °C, residence times 2÷10 minutes), the conversion of cyclohexanone is maintained low (2÷5%). The principal side-products of oxidation are minor fractions of low and high-boiling acids and aliphatic alcohols. Due to the low conversion, separation and recycle of the unreacted cyclohexane is fundamental for the process. The operative and capital costs of the plant are consequently affected by the large recycle. The amount of air fed to the reactor is dosed and diluted with inert gas so to limit the unreacted oxygen in the gaseous mixture leaving the reactor (below 0,2%vol). This enhances selectivity to cyclohexyl hydroperoxide and improves safety. The cyclohexane in the exhaust gas stream is condensed and recycled back to the reactor. The liquid output of the reactor is sent to a column in order to separate the bulk of unreacted cyclohexane that, after decanting to remove water and soluble low-boiling acids, is recycled to the reactor. The bottoms of the column are sent to the decomposition reactor.

The decomposition of the hydroperoxide is carried on in a dedicated reactor, in alkaline environment, free of oxygen. A water solution of sodium hydroxide is used for the decomposition. The aqueous fraction of the reactor output is separated in a decanter. This aqueous stream removes the sodium salts of the high-boiling acids presents in the side-reaction products and need to be treated in order to be disposed. In the analysed process scheme, the steam is neutralized by mixing with a waste acid steams from other processes, and the organic fraction is removed by electro-oxidation. The resulting salt solution is a marketable product (e.g. de-icing applications). The oily-phase from the decanter is distilled and the fraction of cyclohexane sill present is separated and recycled back to the oxidation reactor. Cyclohexanone is vacuum distilled from the bottoms of the former column. A further distillation step removes high boiling products from cyclohexanol. Cyclohexanol is processed in a dehydrogenation section. Here it is vaporized and converted to cyclohexanone by catalytic de-hydrogenation in gas phase (250÷450°C, 0.1÷0.15 MPa). The reaction is endothermic and reaches yields of about 80%. The stream leaving the reactor is cooled, hydrogen is separated and the condensate is vacuum distilled to separate cyclohexanone.

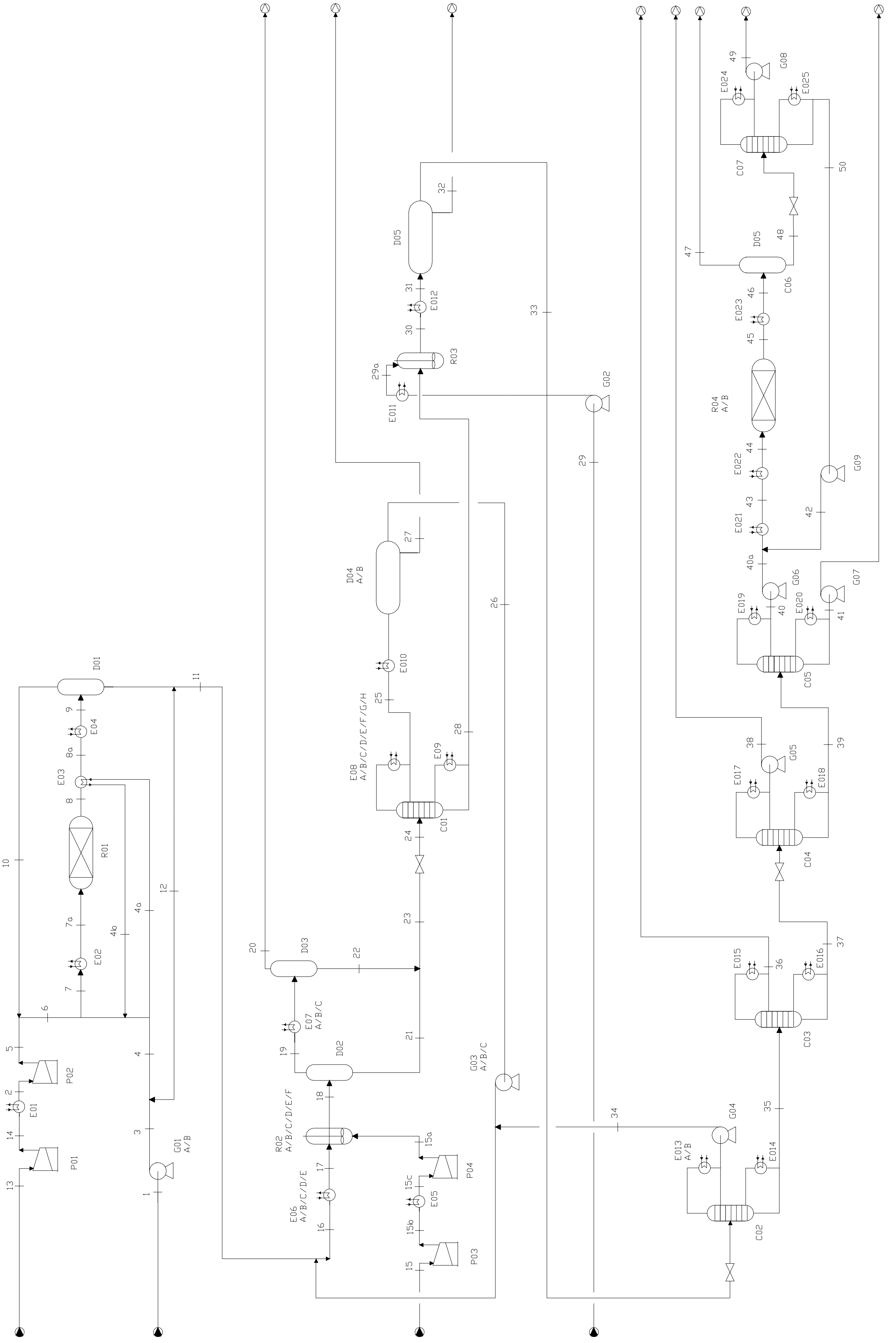


Figure 4.3.1: Simplified PFD for process scheme A (synthesis via oxidation of cyclohexane)

4.3.1.2 – Process B: synthesis via hydration of cyclohexene

This option is an innovative process, first proposed in the 90s by Asahi. The whole process can be divided in three main steps:

1. synthesis of cyclohexene (hydrogenation of benzene)
2. synthesis of cyclohexanol (hydration of cyclohexene)
3. synthesis of cyclohexanone (de-hydrogenation of cyclohexanol)

The first step (hydrogenation of benzene) is based on the following reaction:

$$C_6H_6 + 2H_2 \rightarrow C_6H_{10} \qquad (4.3.4)$$

The reaction is occurs in liquid phase (40atm, 140°C, slurry of Ru-Ti-Zn catalyst). The heat of reaction is removed by external exchangers. Non reacted hydrogen is recycled. Conversion is not complete (about 50%) and selectivity is limited (35% yield), the main byproducts being cyclohexane (about 0.5% of methyl-cyclopentane is also produced). The liquid mixture leaving the reactor is filtered, in order to remove the catalyst.
The mixture is sent to a two step hydration process where it occurs the overall reaction:

$$C_6H_{10} + H_2O \leftrightarrow C_6H_{11}OH \qquad (4.3.5)$$

In the first reactor (80°C, 0.1÷0.15 MPa) the double bond is attacked by sulphuric acid (60% water solution). In a second reactor (110°C) water is added and the cyclohexyl-hydrogen sulphate is decomposed. The overall conversion of cyclohexene is about 55% and the selectivity toward cyclohexanol is about 95% (cyclohexanone is the main side-product). The mixture is sent to a separation section (distillation columns and decanters). The following streams are obtained in this section: cyclohexanol (to be fed to the dehydrogenation section), sulphuric acid and water (to be recycled back to the corresponding phases of hydration reactors), a mixture of benzene, cyclohexane and cyclohexene (to be sent to the de-hydrogenation section) and streams of other impurities (e.g. phenol). As a matter of fact, benzene, cyclohexane and cyclohexene give low-boiling azeotropes that make separation practically unfeasible. The principal advantage of the described process is to produce cyclohexanol avoiding the separation of that mixture. On the other side, the dehydrogenation of that mixture back to benzene is required to make the recycle feasible. The dehydrogenation to benzene is endothermic and requires a multiple stage reactor (average temperature 370°C).
The dehydrogenation of cyclohexanol is similar to the process step described above in option A (vapour phase reaction and vacuum distillation).

4.3.1.3 – Process C: synthesis via hydrogenation of phenol (pressurized liquid phase)

The hydrogenation of phenol was actually one of the first industrial processes for cyclohexanone production. The hydrogenation of phenol is currently the process option more common for cyclohexanone production (the vapour phase hydrogenation, process E, is actually the option more frequently applied nowadays). The whole process can be divided in three main steps:

1. synthesis of cumene (alkylation of benzene)
2. synthesis of phenol (oxidation of cumene)
3. synthesis of cyclohexanone (hydrogenation of phenol)

In current analysis three alternative options are compared for the last step (hydrogenation of phenol), while the former two are the same for option C, D and E.
In the following the common steps and the pressurized liquid phase hydrogenation (option C) is presented.

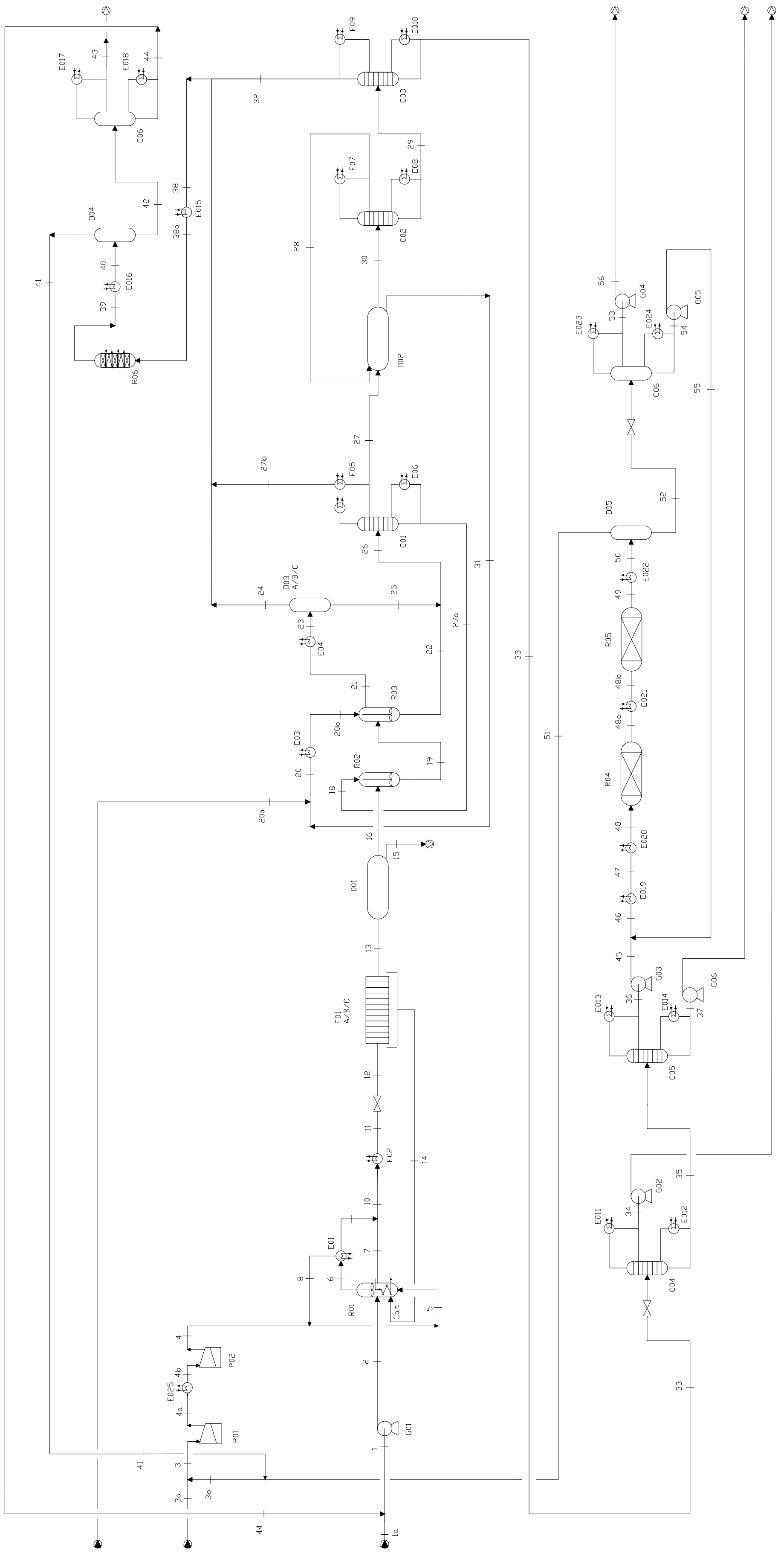


Figure 4.3.2: Simplified PFD for process scheme B (synthesis via hydration of cyclohexene)

Cumene is produced by alkylation of benzene with propene *[Ulman, 1996; Kirk-Othmer, 1992]*:

$$C_6H_6 + C_3H_6 \leftrightarrow C_9H_{12} \qquad (4.3.6)$$

The reaction is exothermic and is operated in gas phase and excess of benzene (250°C, 1.5 MPa, supported polyphosphoric acids as catalyst). Average conversion of propene is about 94%. The stream leaving the reactor is condensed and separated by various distillation stages. Streams of benzene and propylene are recovered and recycled back to the reactor. A stream of cumene at desired grade is obtained. Side-products (dipropylbenzene isomers, methylpentene, etc.) are separated.

Phenol is obtained by oxidation of cumene with air. It is a two-stage process: in the first step cumene is oxidized to cumyl-hydroperoxide in liquid phase and, in the second step, the hydroperoxide is decomposed to phenol and acetone. The oxidation steps yields phenyl-dimethylcarbinol, acetophenon and dicumyl-hydroperoxide as side-products (selectivity toward cumyl-hydroperoxide is about 89.5%). The operation is performed in a series of reactors operating at 0.6÷0.65 MPa and 105÷115°C, where the temperature is controlled by external coils. The air feed is dosed in order to prevent the formation of explosive mixtures in the top of the reactor. The product stream contains about 32% of cyclohexanone. This stream is concentrated in a vacuum column and the major part of cumene is separated and recycled back to the reactors. The concentrated solution of cyclohexyl-hydroperoxide is sent to the decomposition reactor (0.1÷0.15 MPa, 115°C, catalyzed by sulphuric acid in water solution). The reaction is exothermic and the heat of reaction is removed by evaporation and condensation of acetone. The output stream of the reaction is washed and decanted, to remove sulphuric acid. The oily-phase is separated in a train of distillation columns to yield pure phenol (99.96% in weight). In particular the separation of some compounds, like α-methylstyrene, requires an extractive distillation with ethylene glycol. Acetone is also purified from water in a dedicated column.

Phenol is hydrogenated, in current option, in liquid phase, in a slurry pressurized reactor (1MPa, 135°C, slurry of supported palladium catalyst) *[Joris et al., 1956]*. Heat of reaction is removed by external heat exchangers. Conversion is about 95%. The yield to cyclohexanone is about 90%. The excess of hydrogen collected in the top of the reactor is recycled back to the feed. The liquid output of the reactor is filtered to separate the slurry catalyst and vacuum distilled to separate cyclohexanone at desired grade. The side-product with high-boiling point are separated from the bottoms of the column by flash of the recycle stream of unreacted phenol to the reactor.

4.3.1.4 – Process D: synthesis via hydrogenation of phenol (liquid phase with product stripping)

As mentioned above the steps of cumene and phenol synthesis of this process option are similar to option D.

The hydrogenation of phenol is in liquid phase (0.1÷0.2 MPa, 100÷150°C, slurry palladium catalyst), but in current option products are continuously stripped from the liquid by a gas flow (unreacted hydrogen plus inert gas) *[Phielix, 1959]*. This eliminates the problem of solid st separation. The separation of high-boiling side-products that may accumulate into the reactor is performed by a filtration and flash circuit, that treats only minor amounts of the material. The reaction products are recovered from the gaseous stream by cooling, quenching

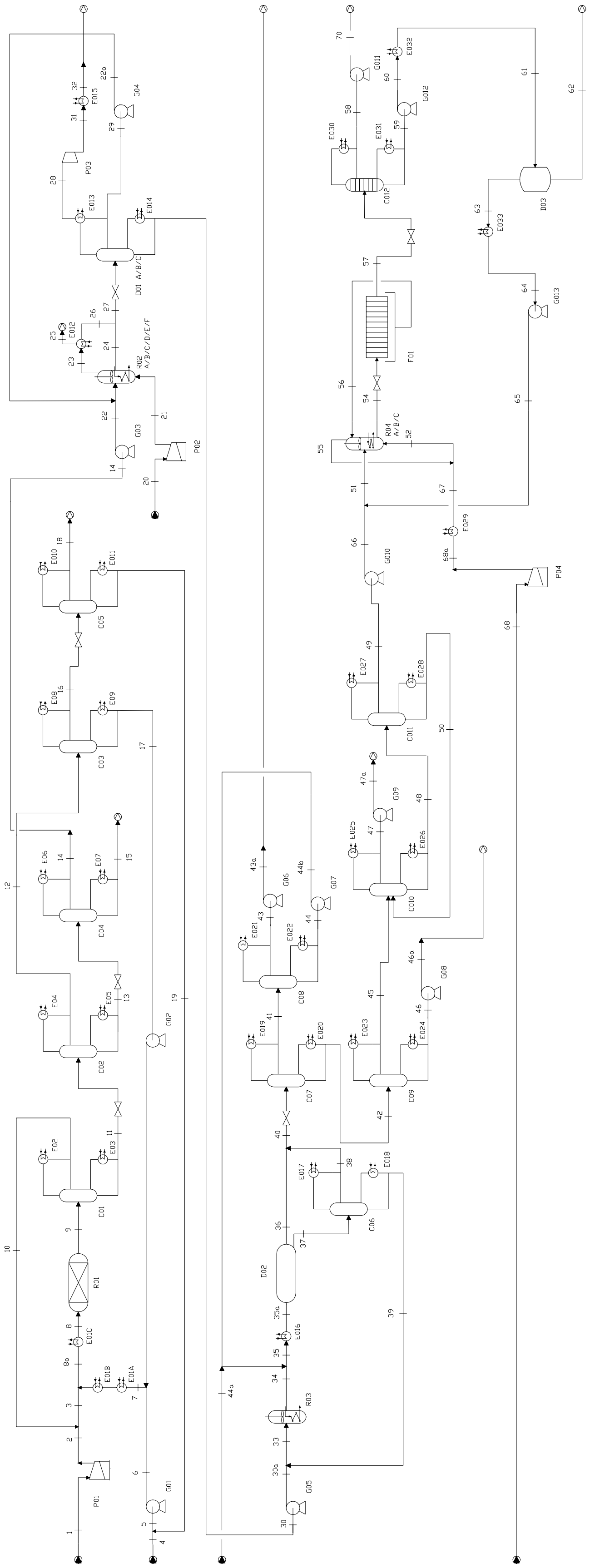


Figure 4.3.3: Simplified PFD for process scheme C (synthesis via hydrogenation of phenol - pressurized liquid phase)

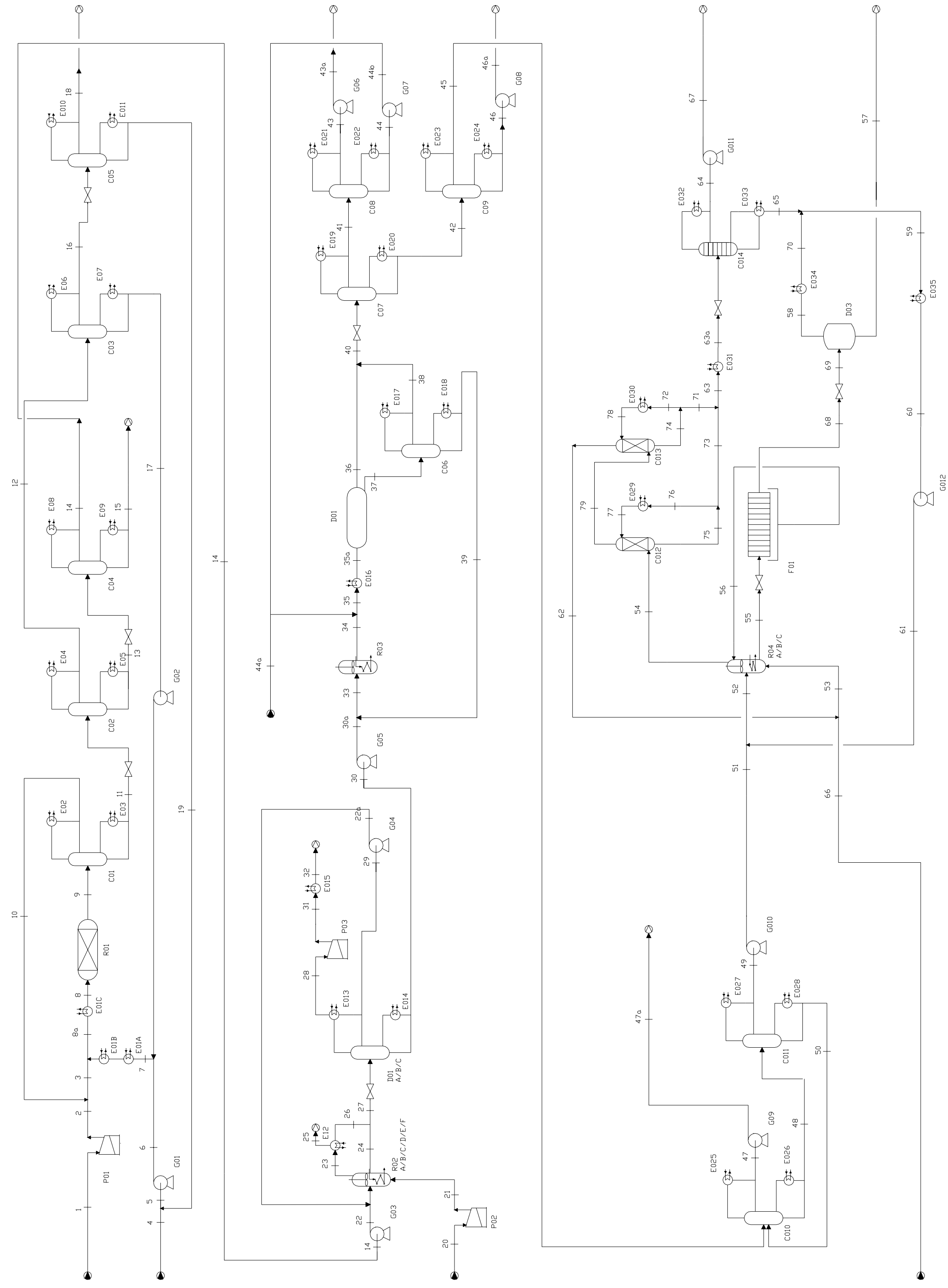


Figure 4.3.4: Simplified PFD for process scheme D (synthesis via hydrogenation of phenol - liquid phase with product stripping)

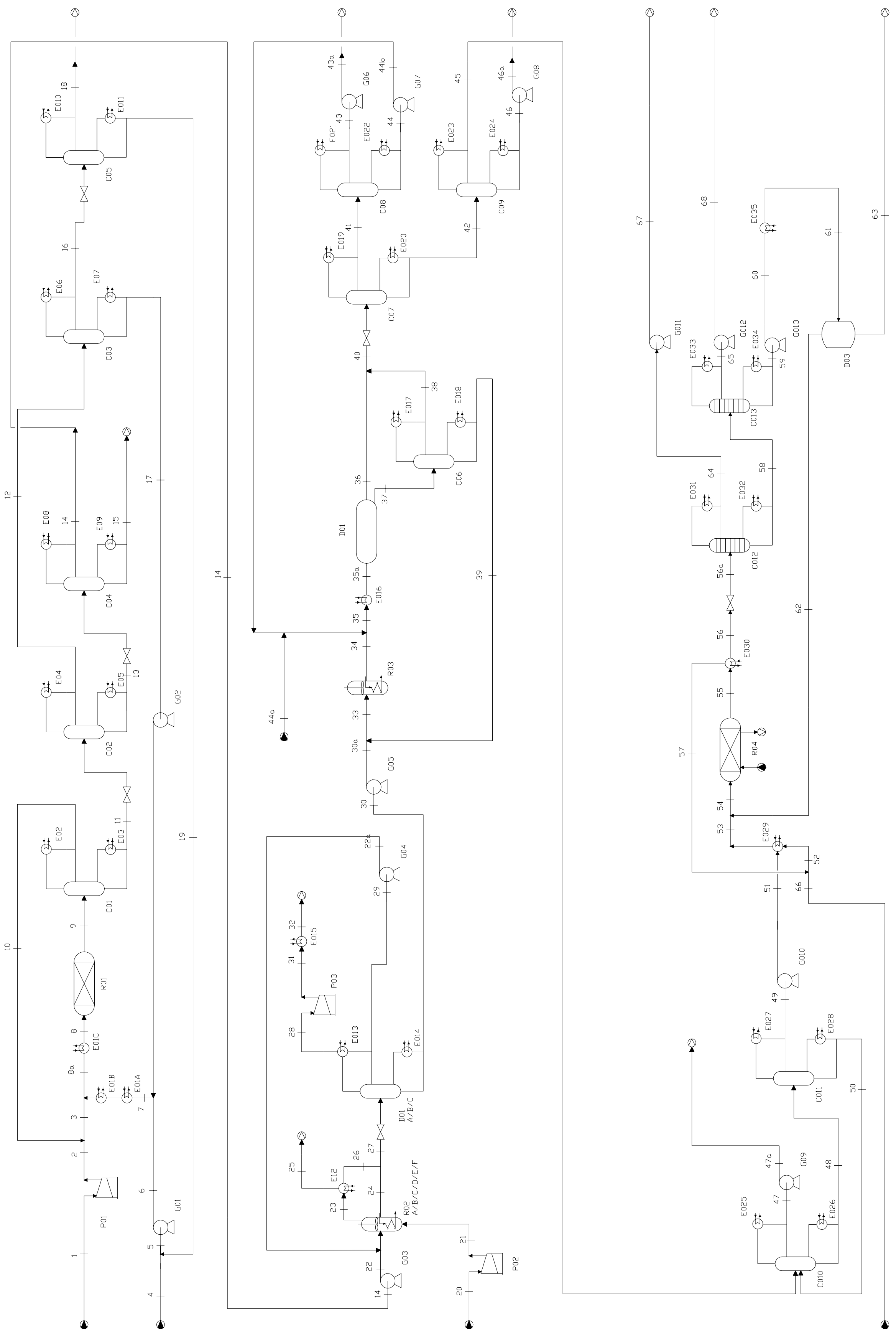


Figure 4.3.5: Simplified PFD for process scheme E (synthesis via hydrogenation of phenol - vapour phase)

and washing with the very same cooled condensate. The condensate is vacuum distilled in order to recycle unreacted phenol and separate pure cyclohexanone at acceptable grade (traces of cyclohexanol are present).

4.3.1.5 – Process E: synthesis via hydrogenation of phenol (vapour phase)

As mentioned above the steps of cumene and phenol synthesis of this process option are similar to option D. In current process, the step of hydrogenation is in gas phase (0.1÷0.2 MPa, 145°C, palladium catalyst) *[Ullman, 1987; Dodgson et al., 1989]*. This requires vaporization of the feed mixture and condensation of the product stream. The non condensed gas is recycled back to the reactor. The condensate is vacuum distilled to remove cyclohexanol (the selectivity to cyclohexanol is about 4% in the reactor), which can be sold at the market. Cyclohexanone is distilled in a second vacuum column. The bottoms of the column are flashed to remove high-boiling compounds and are recycled to the reactor.

4.3.2 – Sustainability assessment

The assessment method proposed in §1.2 was applied to the described process options. The required input data about the processes were obtained integrating the information in the literature with material and energy balances and basic engineering rules. The fugitive emissions were assessed by average emission factors for the expected leak points in the process diagram (e.g. seals, joints, valves, etc.) *[Allen & Shonnard, 2002]*. The emission of micro-pollutant from the utilities (e.g. power generation, wastewater treatment, etc.) were evaluated by emission factors from available databases *[EPA, WPa, WPf]*. Economic parameters (e.g. material, energy and operative costs, capital costs) were evaluated by average costs from various sources *[IChemE, 2002; Matche; WP; Perry & Green, 1997]*. The more important pieces of equipment were preliminary sized.

Table 4.3.1 lists the impact categories considered in the analysis. It can be observed that the assessed environmental impacts include several aspects: air emissions, water emission, resource use. Emissions to air are expected to derive from: i) emissions from stack at boiler section; ii) fugitive losses from the possible leak points of the plant (valves, flanges, etc.) and from the waste water treatment section.
Table 4.3.1 reports the non-normalized values of the indices calculated for the single options. The analysis of the environmental indicators reveals that the impacts regarding single impact categories have generally comparable values among the options. However, option A (cyclohexane oxidation) shows higher impacts on smog formation and electrical power consumption than the other options. This is mainly due to the wastewater treatment section, where fugitive emissions are significant and an electro-oxidation process is operated.

The proposed method allow the analysis of the contribute of single sections of the plant on the overall impact performance. Table 4.3.2 reports an example for the carcinogenicity indicator. It can be observed as the majority of the impact can be related to emissions of micro-pollutants from energy production. As a matter of facts traces of organic compounds and metals are continuously emitted by natural gas fired boilers *[EPA, WPa]*. Some of these compounds are potentially toxic and carcinogen. The analysis identifies a minor contribution on carcinogenicity related to fugitive emissions. This contribution mainly depend on the sections that handle large quantities of benzene.

A similar scheme in partition of sources can be identified in the analysis of the contribution to the emissions for the toxic and smog-promoting compounds.

With regard to the economic impact, the impact indicator (NPEI, i.e. NPV multiplied by -1) largely varies among the alternatives. Process A is not economically profitable with the assumed cost values. On the other side process B appears to be the more economically profitable. The indicator shows limited changes among the 3 options based on phenol hydrogenation, since the main part of the process is actually similar. Table 4.3.3 shows the evaluated capital costs: process B is the one requiring lower investments, since the total

	Unit	**(A)**	**(B)**	**(C)**	**(D)**	**(E)**	**Norm. Factor**
Environmental impact							
Emissions to air							
Global worming	kg_{eq}/y	2.58E+08	1.76E+08	1.85E+08	1.82E+08	1.97E+08	1.16E+06
ARP	kg_{eq}/y	8.60E+04	5.48E+04	6.14E+04	5.84E+04	6.23E+04	4.83E+03
MIR	kg_{eq}/y	1.11E+06	2.85E+04	9.43E+04	9.27E+04	9.61E+04	5.63E+03
Air Toxicity	kg_{eq}/y	2.99E+07	2.11E+07	2.42E+07	2.29E+07	2.44E+07	3.77E+05
Air Carcinogenicity	kg_{eq}/y	1.61E+04	2.17E+04	1.69E+04	1.66E+04	1.77E+04	1.01E+02
Emissions to water							
Organic load	kg_{eq}/y	2.48E+03	1.33E+00	-	-	-	1.79E+02
Water toxicity	kg_{eq}/y	2.17E+04	1.65E+03	-	-	-	2.80E+02
Water Carcinogenicity	kg_{eq}/y	0.00E+00	1.10E+00	-	-	-	1.09E+03
Eco-toxicity	kg_{eq}/y	0.00E+00	3.33E-01	-	-	-	3.41E+04
Resources							
Raw materials	kg_{eq}/y	3.81E+08	2.65E+08	2.68E+08	2.64E+08	2.59E+08	3.51E+05
Electrical power	kWh/y	1.21E+08	2.91E+07	1.82E+07	1.59E+07	1.63E+07	1.10E+06
Economic impact							
NPEI	€	1.69E+07	-1.28E+08	-3.74E+07	-4.38E+07	-4.99E+07	3.40E+07
Societal impact							
Inherent safety	km^2/y	1.71E-03	2.90E-04	1.87E-03	1.87E-03	1.87E-03	6.00E-06
Occupation	People	3.40E+01	2.40E+01	5.40E+01	5.40E+01	4.90E+01	7.92E+01

Table 4.3.1: Non normalized values of the level 1 indicators and normalization factors used in the assessment.

C.S.		**Fugitive**	**Energy production**	***Total***
A)	Benzene hydrogenation	1010	200	*1210*
	Cyclohexane oxidation		11360	*11360*
	Alkaline wastewater treatment		3570	*3570*
	Total	*1010*	*15130*	*16140*
B)	Cyclohexene process	6440	13360	*19800*
	Wastewater treatment	1900		*1900*
	Total	*8340*	*13360*	*21700*
E)	Cumene production	2830	5340	*8170*
	Phenol production	1150	7770	*8920*
	Phenol hydrogenation		610	*610*
	Total	*3970*	*13720*	*17700*

Table 4.3.2: Non normalized values of the level 1 indicator for carcinogenicity: analysis of single contributions.

process has a size comparable with single sections of the other alternatives. This element is one of the keys toward higher NPV for this option. Another element is a favourable annual savings/costs ratio (Table 4.3.4). This performance is due to the lower total annual costs, since the production potential is the same of other processes (annual savings are dominated by sells of cyclohexanone) and the composition of costs (Table 4.3.4) is similar among the processes. The same table outlines the role of raw materials on the pattern of operative costs: they show a contribution spanning from 64% to 70% of the overall costs, as expected in a production process of commodities.

With regard to the societal impacts, inherent safety will be more extensively discussed in a dedicated section (§4.3.3). The occupation index relies on the evaluation of the number of employees necessary to operate the plant. The value results affected by the complexity of the plant and somehow reflects the pattern of the capital investments.

Table 4.3.5 reports the normalized values of the environmental indicators. It can be observed that a few impact categories show significant emission to air. In particular emissions of greenhouse gases and potentially carcinogen compounds are one order of magnitude higher than the others impacts for all options. This reflects the fact that, in such a type of processes, an important issue for environmental impacts is energy production. In fact, the greenhouse

		Capital cost	**NPV**
A)	Cyclohexane oxidation (w. p.)	46’820’000	-16’898’000
B)	Cyclohexene process (w. p.)	29’337’000	128’251’000
C)	Phenol hydrogenation process (w. p.)	57’325’000	37’409’000
D)	Phenol hydrogenation process (w. p.)	53’025’000	43’839’000
E)	Phenol hydrogenation process (w. p.)	47’225’000	49’898’000

Figure 4.3.3: Capital costs and net present values (NPV) for the options considered.

		Savings / Total costs	**Raw material costs / Total costs**	**Combustible cost / Total costs**	**Electrical power / Total costs**
A)	Whole process	1.02	0.64	0.124	0.021
B)	Whole process	1.42	0.70	0.099	0.018
C)	*Cumene production*	*1.02*	*0.86*	*0.038*	*0.002*
	Phenol production	*1.09*	*0.85*	*0.033*	*0.005*
	Hydrogenation	*1.05*	*0.90*	*0.001*	*0.001*
	Whole process	1.12	0.69	0.057	0.007
D)	*Cumene production*	*1.02*	*0.86*	*0.038*	*0.002*
	Phenol production	*1.09*	*0.85*	*0.033*	*0.005*
	Hydrogenation	*0.94*	*0.85*	*0.002*	*0.000*
	Whole process	1.02	0.66	0.056	0.006
E)	*Cumene production*	*1.02*	*0.86*	*0.038*	*0.002*
	Phenol production	*1.09*	*0.85*	*0.033*	*0.005*
	Hydrogenation	*1.06*	*0.90*	*0.008*	*0.000*
	Whole process	1.13	0.69	0.063	0.006

Figure 4.3.4: Selected ratios for annual costs and savings for the options considered.

gases, principally carbon dioxide, are emitted due to the combustion of natural gas in the boilers and the carcinogens are related to micro-pollutants released in the same conditions (see Table 4.3.2.and related comments). The use of resources is the other significant category of impact for the processes. Again this was expected, since material consumption depends on both the flows of feedstock materials (benzene, propene, etc.) and of fuel for energy production (natural gas). The former is inevitably significant for a material transformation process as the current one, where benzene is converted into the desired product (the use of propene in processes C, D and E is partially compensated by the sold by-product acetone). The latter is related to the air emissions.
Some of the process schemes require disposal of water streams. However the impact potential is not particularly critical, provided the compliance to law limits. On the other side, the wastewater treatment is a significant source of fugitive emissions to air and of resource consumption (e.g. electrical power in electro-oxidation).

The normalized economic indicator have a potential impact that is a couple of orders of magnitude lower than the other indices. This is expected, since in commodities production processes the margins are modest compared to the investments, yielding low NPVs.

Inherent safety is identified as the dominant issue in this kind of processes. This is a consequence of both the actually high value of the index and the relatively low value of other impact categories. The high value of the index is due to the amount of flammable and toxic materials processed and to the large number of units in the process – that reflects complexity.
The occupational index is at least two orders of magnitude lower than the inherent safety index. This reflects the high automation level typical of chemical industry.

	(A)	**(B)**	**(C)**	**(D)**	**(E)**	**Weight factors**
Environmental impact						
Emissions to air						
Global worming	2.21E+02	1.51E+02	1.59E+02	1.56E+02	1.69E+02	0.051
ARP	1.78E+01	1.13E+01	1.27E+01	1.21E+01	1.29E+01	0.066
MIR	1.98E+02	5.06E+00	1.67E+01	1.65E+01	1.71E+01	0.049
Air Toxicity	7.93E+01	5.59E+01	6.43E+01	6.07E+01	6.48E+01	0.095
Air Carcinogenicity	1.59E+02	2.14E+02	1.67E+02	1.65E+02	1.75E+02	0.168
Emissions to water						
Organic load	1.38E+01	7.43E-03	-	-	-	0.020
Water toxicity	7.75E+01	5.91E+00	-	-	-	0.095
Water Carcinogenicity	-	1.00E-03	-	-	-	0.168
Eco-toxicity	-	9.76E-06	-	-	-	0.033
Resources						
Raw materials	1.08E+03	7.53E+02	7.62E+02	7.51E+02	7.38E+02	0.044
Electrical power	1.10E+02	2.64E+01	1.65E+01	1.44E+01	1.47E+01	0.064
Economic impact						
NPEI	4.97E-01	-3.77E+00	-1.10E+00	-1.29E+00	-1.47E+00	-
Societal impact						
Inherent safety	2.86E+02	4.83E+01	3.12E+02	3.12E+02	3.12E+02	0.5
Occupation	-4.29E-01	-3.03E-01	-6.82E-01	-6.82E-01	-6.19E-01	0.5

Table 4.3.5: Normalized values of the level 1 indicators and weighting factors used in the assessment.

The weight factors listed in Table 4.3.5 are assumed for the aggregation of the level 1 indices. Table 4.5.6 reports the aggregated values, also represented in figure 4.3.6.
Figure 4.3.7 reports another representation of the environmental impact index. The histogram shows the contribution of the single steps of the process to the final values. It can be observed that the feedstock benzene (i.e. material resource use) accounts for about one quarter of the environmental impact. The contribution obviously depends on the overall yield of the process. The wastewater treatment for process A gives a significant contribution to the environmental impact. However option A results to have the higher environmental impact independently of the wastewater treatment score and, thus, of the technology considered for the aqueous stream disposal.
It is worth noticing that in alternatives from C to E cumene production impact appears to be larger than phenol. However this effect is partially do to the accounting of the material flows: in cumene production the consumption of propene raises the impact value, while in phenol production the by-production of acetone (accounted as a material consumption multiplied by -1) lowers the value. Hydrogenation of phenol plays a minor role on the environmental impact of these alternatives, since it is actually a small section compared to the whole process.

Environmental and societal indices result to be the dominating ones also at level 2 (Table 4.3.5). This confirms the aforementioned comments on economic index. Option B clearly results the preferable one from societal and economic point of views. As regard environmental impact the performance is slightly worse than for the options based on phenol hydrogenation. It is worth noticing that environmental indices are quite close among the options, while the societal and economic performance show larger variations. As a consequence, option B results preferable from the point of view of the integrated impact on sustainability.

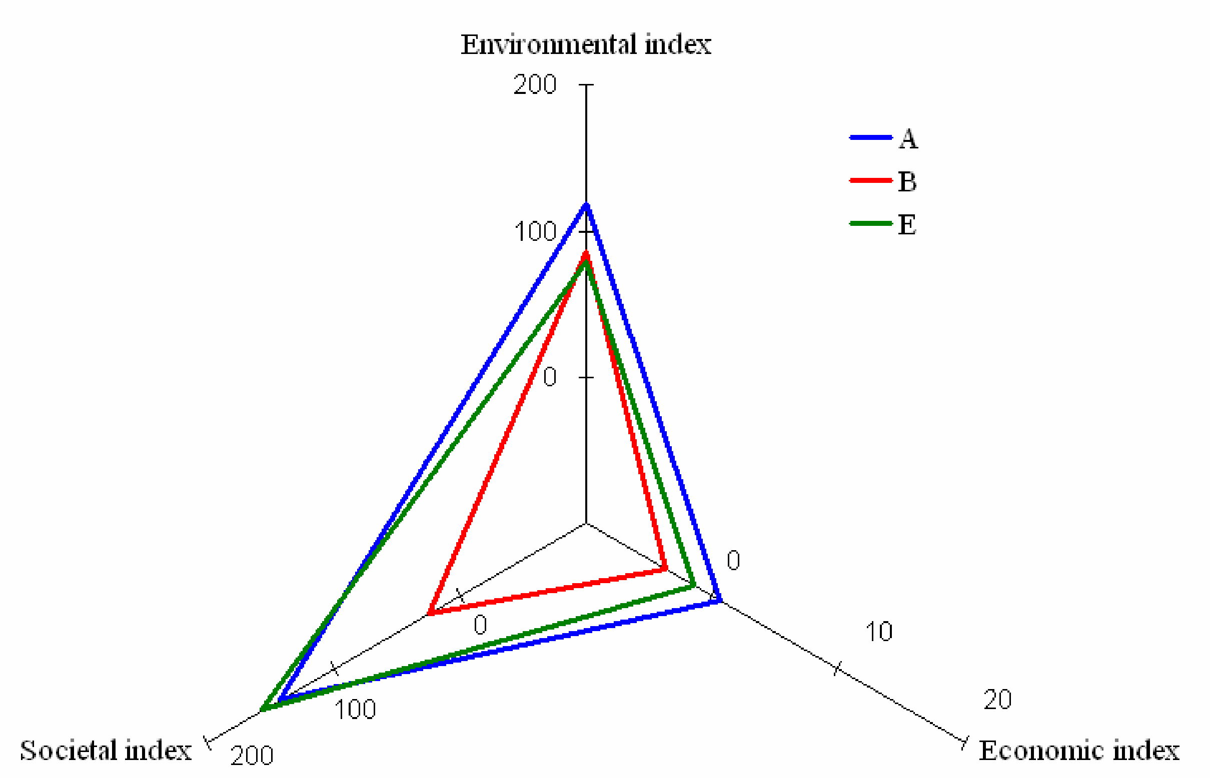


Figure 4.3.6: Level 2 indices for the options considered in the case study. The profile of option C and D practically collapses on E in this representation.

The Monte-Carlo method proposed for sensitivity analysis (§1.2.6) was applied in order to explore the effects of the chosen weight factors. The analysis confirms all the observations drawn in the discussion above even for moderate variations of the value of the weight factors. For example Figure 4.3.8 reports the cumulative probability of the difference of the overall index for option B and D. It refers to variations in all the weight factors of 20% of their value. The graph shows that no change in the sign of the difference is possible, confirming the identified rank of preference for the options.

Further examples of the application of the sensitivity analysis are discussed in detail for other cases studies (§4.1, §4.2, §4.4).

Level 2	**A**	**B**	**C**	**D**	**E**	**Weight factors**
Environmental index	1.19E+02	8.55E+01	7.85E+01	7.71E+01	7.94E+01	0.3
Economic index	4.97E-01	-3.77E+00	-1.10E+00	-1.29E+00	-1.47E+00	0.5
Societal index	1.43E+02	2.40E+01	1.56E+02	1.56E+02	1.55E+02	0.2
Level 3						
Overall impact index	6.45E+01	2.86E+01	5.42E+01	5.36E+01	5.42E+01	
Normalized	*0.82*	*0.36*	*0.69*	*0.68*	*0.69*	

Table 4.3.6: Values of the level 2 and 3 indices and weighting factors used in the aggregation.

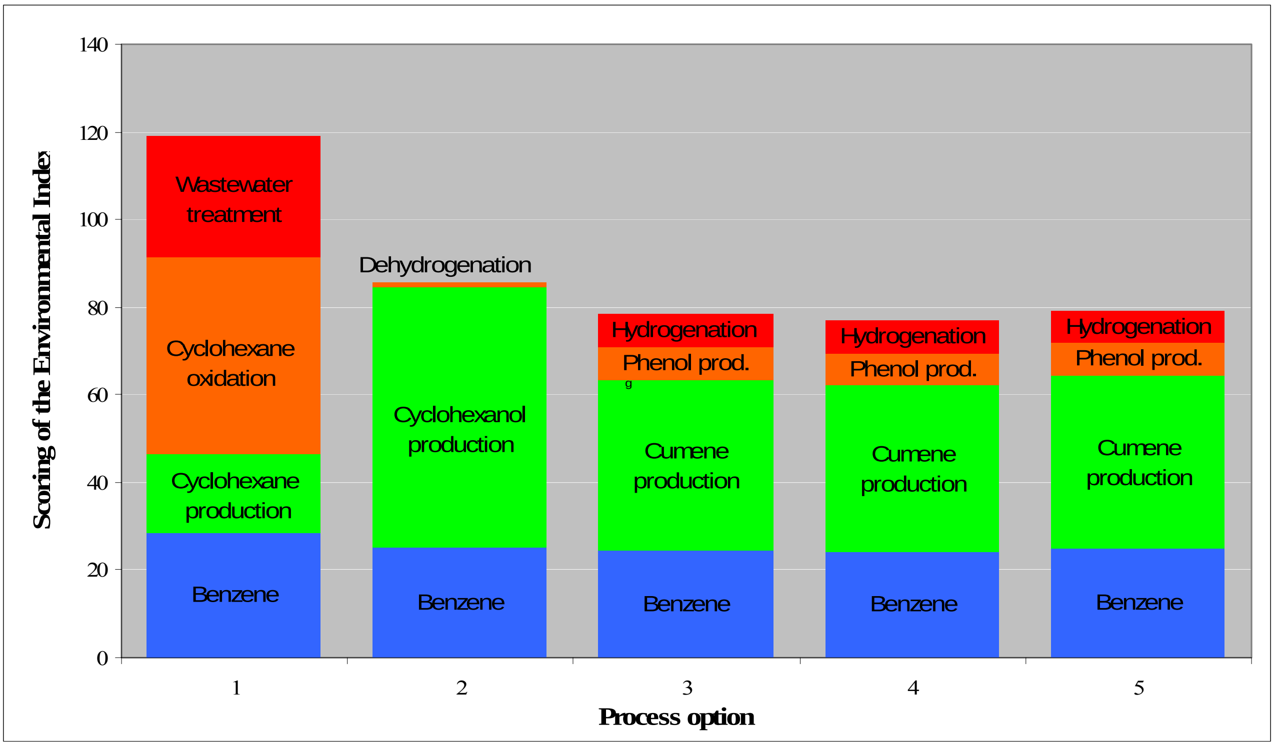


Figure 4.3.7: Environmental impact index, contribution of the single steps of the process.

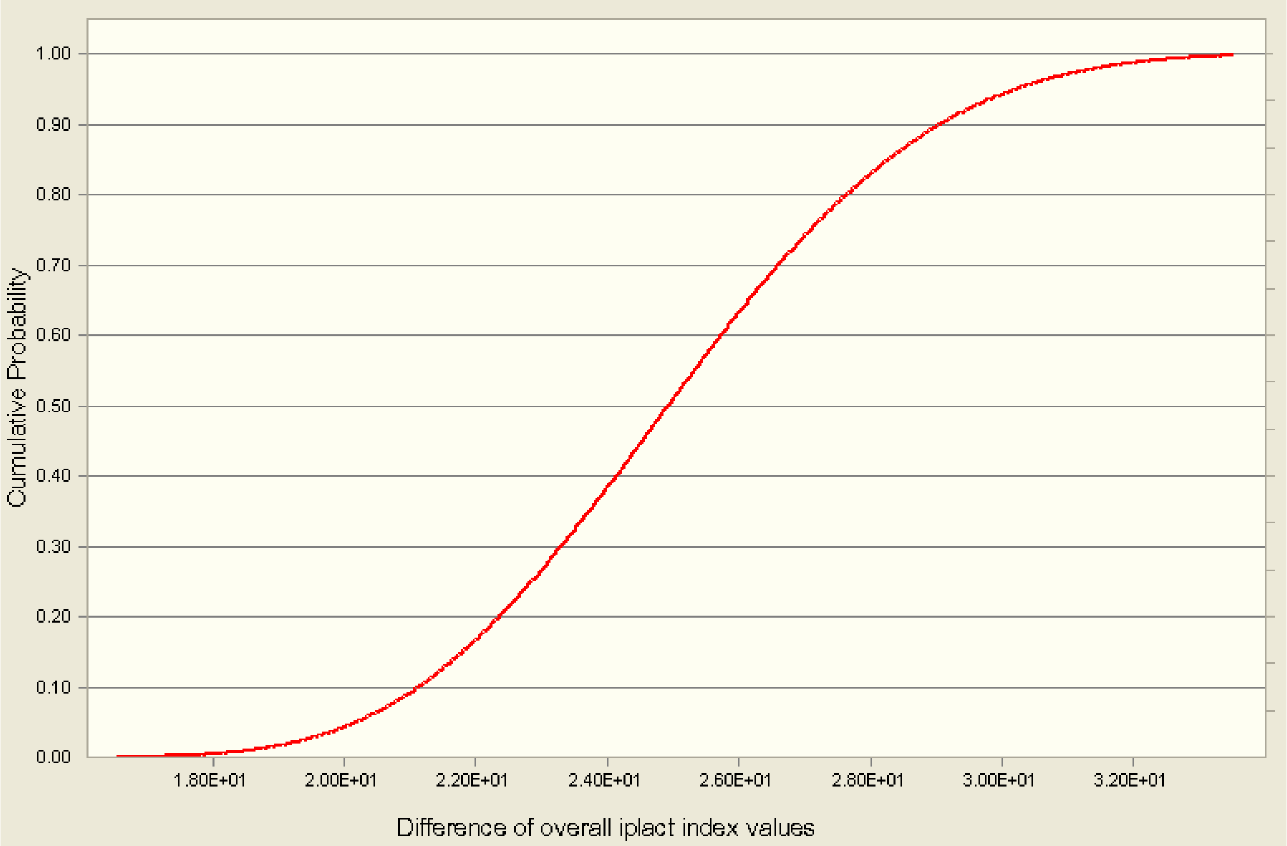


Figure 4.3.8: Example of result from sensitivity analysis: difference of the values of overall impact index for options D and B.

<u>4.3.3 – Inherent safety assessment</u>

The developed method for inherently assessment (§2.3) was applied to the alternative options for cyclohexanone production. The input data required for the application actually match the information collected for sustainability assessment.

The process is divided in single units, as reported in Table 4.3.7. The failure modes were identified and event trees associated to each units. This allow the calculation of the damage distances by proper consequence models. Table 4.3.7 reports an example of LOC events, accidental scenarios, damage distances and credit factors for the section of phenol hydrogenation in option C. The table shows that important differences (up to some orders of magnitude) may be present both in the damage distances and in the credit factors for different LOCs concerning the same piece of equipment. As expected, scenarios involving toxic dispersions are those resulting in higher damage distances. On the other hand, higher credit factors are obtained for units that are more likely to cause loss of containment (e.g. heat exchangers, compressors and pumps etc.).

Tables from 4.3.8 to 4.3.12 shows the results obtained in the calculation of the equipment potential and of the inherent hazard indexes. The potential hazard index only gives information on the equipment that may potentially trigger the most severe scenario, while the inherent hazard index also includes information concerning the credibility of the possible scenarios. Thus, the inherent hazard index yields a more realistic description of the credible

	Unit	Eq. Class	LOC	Scenario	$cf_{i,k}$ (1/a)	$d_{i,j,k}$ (m)
R01	Single slurry reactor	EQ1.2	R1	JF	1x10^{-4}	7.6
				VE	1x10^{-4}	12
				FF	1x10^{-4}	7.4
				TD	1x10^{-4}	58
				PF	1x10^{-4}	14
			R2	TD	5x10^{-6}	66
				PF	5x10^{-6}	14
			R3	JF	5x10^{-6}	23
				VE	5x10^{-6}	19
				PF	5x10^{-6}	13
C01	Vacuum distillation column	EQ1.2	R3	VE	1x10^{-5}	30
				TD	1x10^{-5}	61
				PF	1x10^{-5}	17
				EX	1x10^{-4}	36
D01	Flash drum	EQ1.2	R3	JF	1x10^{-7}	20
				VE	1x10^{-7}	9.6
				FF	1x10^{-7}	6.4
				TD	1x10^{-7}	16
F01	Filter	EQ3.1	R4	TD	6x10^{-4}	8
				PF	6x10^{-4}	15
			R5	TD	1x10^{-5}	61
				PF	1x10^{-5}	17
E01	Hydrogen cooler	EQ2.1	R1	JF	1x10^{-3}	8.2
				VE	1x10^{-3}	13
				FF	1x10^{-3}	7.5
			R3	JF	1x10^{-5}	22
				VE	1x10^{-5}	14
E02	Condenser	EQ2.1	R3	TD	2x10^{-5}	16
				PF	2x10^{-5}	17
				EX	1x10^{-3}	6.3
E03	Reboiler	EQ2.1	R3	VE	2x10^{-5}	14
				TD	2x10^{-5}	8.2
				PF	2x10^{-5}	16
				EX	1x10^{-3}	7.7
E04	Evaporator	EQ2.1	R1	PF	1x10^{-3}	8.5
			R3	TD	5x10^{-5}	17
				PF	5x10^{-5}	8.5
E05	Condenser	EQ2.1	R1	PF	1x10^{-3}	7.7
			R2	TD	1x10^{-5}	6.2
				PF	1x10^{-5}	7.7
			R3	JF	1x10^{-5}	20
				VE	1x10^{-5}	9.6
				FF	1x10^{-5}	19
				TD	1x10^{-5}	16
				PF	1x10^{-5}	7.7
G01	Phenol feed pump	EQ5.1	R4	PF	5x10^{-4}	8.1
			R5	PF	1x10^{-4}	13
G02	Cyclohexanone pump	EQ5.1	R5	TD	1x10^{-4}	16
				PF	1x10^{-4}	17
P01	Hydrogen compressor	EQ5.2	R4	JF	1x10^{-3}	13
				VE	1x10^{-3}	18
				FF	1x10^{-3}	10
			R5	JF	1x10^{-4}	22
				VE	1x10^{-4}	14

Table 4.3.7: Example of damage distances and credit factors: phenol hydrogenation section of option C.

Unit	Number of units	UHI		UPI	
		Synthesis of cyclohexane	Synthesis of cyclohexanone	Synthesis of cyclohexane	Synthesis of cyclohexanone
R01 – Reactor	1	1.6E+01		1.6E+04	
R02 - Reactor	6		1.1E+01		1.2E+06
R03 - Reactor	1		2.3E+00		3.1E+05
R04 - Reactor	2		1.6E-01		3.2E+03
C01 – Distillation column	1		2.9E+00		4.8E+05
C02 - Distillation column	1		1.6E+00		3.1E+05
C03 - Distillation column	1		3.1E-01		5.0E+04
C04 - Distillation column	1		6.3E-03		8.9E+02
C05 - Distillation column	1		3.8E-03		4.3E+02
C07 - Distillation column	1		8.7E-03		3.2E+03
D01 – Flash drum	1	4.7E-01		3.7E+04	
D02 - Flash drum	1		5.4E+00		6.1E+05
D03 - Flash drum	1		9.0E-01		1.5E+05
D06 - Flash drum	1		4.3E-03		8.1E+02
D04 - Decanter	2		1.6E-01		2.5E+04
D05 - Decanter	1		2.7E-02		2.5E+02
E01 – Heat exchanger	1	2.7E-01		8.6E+02	
E02 – Vaporizer	1	2.1E+02		2.1E+05	
E03 - Heat exchanger	1	2.2E+01		4.7E+04	
E04 - Condenser	1	5.6E+00		8.5E+03	
E06 - Heat exchanger	5		1.0E+01		7.6E+04
E07 - Condenser	4		4.1E+00		3.1E+04
E08 - Condenser	8		9.7E+00		1.1E+05
E09 - Reboiler	1		1.7E+01		1.8E+05
E10 - Heat exchanger	1		2.5E+01		4.1E+05
E12 - Heat exchanger	1		7.7E+00		7.6E+03
E13 - Condenser	2		9.9E-01		7.6E+04
E14 - Reboiler	1		2.6E+00		2.2E+05
E15 - Condenser	1		1.1E+00		1.1E+05
E16 - Reboiler	1		6.2E-01		4.1E+04
E17 - Condenser	1		2.7E-01		1.3E+04
E18 - Reboiler	1		1.5E-02		3.0E+02
E19 - Condenser	1		1.0E-02		1.7E+02
E20 - Reboiler	1		1.1E-02		9.2E+01
E21 – Vaporiser	1		1.8E-01		2.1E+03
E22 - Heat exchanger	1		3.2E-02		3.2E+03
E23 - Condenser	1		1.1E-01		3.3E+03
E24 - Condenser	1		2.0E-02		6.1E+02
E25 - Reboiler	1		1.6E-02		3.0E+02
P01 - Compressor	1	1.3E+00		1.2E+03	
P02 - Compressor	1	4.8E-01		8.6E+02	
G01 - Pump	1	1.1E+00		2.2E+03	
G03 - Pump	1		3.2E-01		5.3E+02
G04 - Pump	1		1.2E+00		2.2E+03
G05 - Pump	1		1.6E-02		3.1E+01
G06 - Pump	1		2.0E-02		4.1E+01
G08 - Pump	1		1.6E-01		3.1E+02
G09 - Pump	1		6.5E-02		1.3E+02
Total		2.6E+02	2.9E+02	3.2E+05	1.2E+07
Overall process		**HI**	5.5E+02	**PI**	1.2E+07

Table 4.3.8: Unit and overall KPIs for option A.

Unit	Number of units	**UHI**	**UPI**
R01 – Reactor	2	8.1E+00	2.4E+05
R02 - Reactor	1	8.0E-01	1.3E+05
R03 - Reactor	1	6.2E-01	1.2E+05
R04 - Reactor	1	4.3E-02	4.2E+03
R05 - Reactor	1	4.4E-02	4.3E+03
R06 - Reactor	6	1.2E-01	1.1E+04
D03 - flash drum	3	2.9E-01	5.7E+04
D04 - flash drum	1	1.9E+00	3.4E+05
D05 - flash drum	1	1.2E-03	2.5E+02
C01 - Distillation column	1	8.3E-04	1.3E+02
C02 - Distillation column	1	0.0E+00	6.4E+04
C03- Distillation column	1	0.0E+00	4.0E+04
C04- Distillation column	1	3.2E-01	3.2E+03
C05- Distillation column	1	1.1E-01	1.1E+03
C06- Distillation column	1	5.4E-01	9.1E+04
C07- Distillation column	1	3.3E-01	3.2E+03
D01 – Decanter	1	3.8E-01	6.9E+04
D02 - Decanter	1	2.3E-01	3.8E+04
E01 - Condenser	1	1.5E+00	1.4E+03
E02 – Heat exchanger	1	4.4E+01	1.4E+05
E04 - Condenser	3	5.7E-01	5.7E+04
E05 - Condenser	2	1.1E-01	6.2E+02
E07 - Condenser	1	5.2E-01	4.3E+04
E08- Reboiler	1	1.0E+00	5.8E+04
E09- Condenser	1	2.8E-01	2.3E+04
E10- Reboiler	1	6.2E-01	4.4E+04
E11- Condenser	1	6.6E-02	3.2E+02
E12- Reboiler	1	8.9E-02	2.9E+02
E13- Condenser	1	5.0E-02	2.1E+02
E14- Reboiler	1	8.7E-02	2.3E+02
E15 - Heat exchanger	1	7.1E+00	1.4E+05
E16- Condenser	1	2.5E-01	1.1E+04
E17- Condenser	1	1.2E+00	9.0E+04
E18- Reboiler	1	8.9E-01	4.5E+04
E19 – Vaporizer	1	3.7E-02	7.2E+01
E20 - Heat exchanger	1	6.1E-01	1.2E+04
E21 - Heat exchanger	1	2.1E-01	4.2E+03
E22- Condenser	1	1.3E-01	4.3E+03
E23- Condenser	1	7.2E-02	3.3E+02
E24- Reboiler	1	1.3E-01	3.1E+02
E25 - Heat exchanger	1	3.1E-01	3.2E+03
G01 - Pump	1	4.4E+00	8.4E+03
G02 - Pump	1	8.2E-03	8.2E+01
G03 - Pump	1	2.1E-02	2.1E+02
G04 - Pump	1	2.3E-02	2.3E+02
G05 - Pump	1	2.1E-02	2.1E+02
G06 - Pump	1	5.3E-03	5.3E+01
P01 - Compressor	1	1.7E+00	3.2E+03
P02 – Compressor	1	1.6E+00	3.2E+03
F01 – Filter	1	1.2E-01	1.9E+02
		HI	**PI**
Total		9.2E+01	2.4E+06

Table 4.3.9: Unit and overall KPIs for option B.

Unit	**UHI**	**UPI**
R01 – Reactor	6.6E+00	1.9E+04
C01 – Distillation column	9.1E+00	4.3E+05
C02 - Distillation column	3.6E+00	3.6E+05
C03 - Distillation column	5.0E+00	3.5E+05
C04 - Distillation column	8.5E-01	1.7E+05
C05 - Distillation column	5.3E-01	8.7E+04
E02 – Condenser	2.9E+01	1.9E+05
E03 – Reboiler	9.0E+01	4.2E+05
E04 - Condenser	2.9E+01	3.4E+05
E05 - Reboiler	2.7E+01	1.7E+05
E06 - Condenser	9.4E-01	9.4E+04
E07 - Reboiler	3.6E-01	3.2E+04
E08 - Condenser	2.0E+01	2.1E+05
E09 - Reboiler	4.5E+01	3.7E+05
E10 - Condenser	6.1E-02	6.1E+03
E11 - Reboiler	3.1E-01	2.4E+04
E01a – Heat exchanger	6.2E+01	2.6E+05
E01b - Vaporizer	6.1E+01	2.7E+05
E01c - Heat exchanger	1.9E+01	1.5E+05
P01 – Compressor	9.1E-03	9.1E+01
G01 – Pump	6.4E-02	1.1E+02
G02 – Pump	1.2E+02	2.4E+05
Total	5.3E+02	4.2E+06

Table 4.3.10: Unit and overall KPIs for synthesis of cumene in options C, D and E.

accidental events that may be associated to plant operation. In particular, this index points out the importance of the safety performance of small pieces of equipment (e.g. heat exchangers, pumps, compressors, etc.) on the inherent safety of the plant, since these components may have per se relatively small damage distances but are more vulnerable to undergo loss of containment events. As shown in the tables, these units have inherent hazard indexes that are often comparable or higher than those of major process units (e.g. columns or reactors), that have potentially more severe scenarios but higher safety scores and thus lower credit factors.

The analysis of the results in the Tables allows the addressing of some important features of the different alternatives for cyclohexanone production. The unit potential hazard indexes show that, as expected, LOCs in reactors and distillation columns may cause high damage areas due to the quantities of toxic material that may be released. Units directly connected to that critical units may similarly show high damage distances since a significant part of the inventory of the principal unit may be released from LOCs in the minor units.

The analysis of the unit inherent safety index outline the role of the credit factor. For instance, high values of UHI are obtained for units, like heat exchangers and pumps, operated at medium and high pressure (e.g. benzene alkylation section of processes C, D, E). In fact, relatively large damage distances are calculated for these units due to the potential of pressurized equipment to release large amounts of materials – especially liquids – even through small leaks. Though this characteristic is common with all the units in the same process section, higher credibility is given to the small leaks occurring for these types of equipment compared to LOCs from reactors and columns.

If the overall indexes are considered (Table 4.3.13), the ranking among the alternatives given by potential indexes (PI) results as a direct consequence of the number of units that may trigger long distance scenarios. Process A is the more penalized. It can be observed as the oxidation reactors play a major role in the value of PI for options A, C, D and E. On the other side option B appears to have quite low PI, due to reduced number of units and the moderate values of single UPIs. When credit factors are considered, the hazard related to small leaks from pressurized units is magnified and the pressurized sections of the plant gain larger weight over the other ones. Options A and C, D, E invert their relative rank, because of the number of units with critical values of UHIs. The difference among performance of the options C, D and E is minor, since the section of concern (phenol hydrogenation) contains few units and operated at low pressures.

Unit	Number of units	**UHI**	**UPI**
R02 - Reactor	6	5.1E+00	9.5E+05
R03 - Reactor	1	6.3E-01	6.1E+04
D02 - Decanter	1	3.6E-01	6.7E+04
D01 – Distillation column	3	3.1E-01	3.1E+03
C06 - Distillation column	1	1.6E-02	1.0E+03
C07 - Distillation column	1	2.4E-01	7.2E+03
C08 - Distillation column	1	1.7E-01	1.6E+03
C09 - Distillation column	1	3.6E-01	3.3E+03
C10 - Distillation column	1	1.9E-01	1.8E+03
C11 - Distillation column	1	1.4E-01	1.3E+03
E12 – Condenser	1	2.1E+01	2.0E+05
E13 – Condenser	3	2.0E-01	8.4E+03
E14 – Reboiler	3	3.9E-01	4.8E+02
E15 – Condenser	1	1.2E-01	8.2E+03
E16 – Heat exchanger	1	1.3E+00	1.1E+05
E17 – Condenser	1	4.3E-02	3.5E+03
E18 – Reboiler	1	1.1E-02	8.6E+02
E19 – Condenser	1	2.1E-01	7.2E+03
E20 – Reboiler	1	3.8E-01	3.8E+02
E21 – Condenser	1	1.0E-01	9.8E+02
E22 – Reboiler	1	8.8E-02	3.2E+02
E23 – Condenser	1	6.8E-02	3.1E+02
E24 – Reboiler	1	3.1E-01	4.7E+02
E25 – Condenser	1	6.5E-02	3.5E+02
E26 – Reboiler	1	2.2E-01	4.4E+02
E27 – Condenser	1	5.1E-02	2.6E+02
E28 – Reboiler	1	4.9E-01	1.1E+03
P03 – Compressor	1	8.2E-01	8.2E+03
G03 - Pump	1	1.2E-02	1.2E+02
G04 - Pump	1	1.5E-02	1.5E+02
G05 - Pump	1	7.5E-03	7.5E+01
G06 - Pump	1	3.4E-03	3.4E+01
G07 - Pump	1	5.9E-03	5.9E+01
G08 - Pump	1	2.5E-03	2.5E+01
G09 - Pump	1	3.8E-03	3.8E+01
G10 - Pump	1	4.0E-03	4.0E+01
Total		6.1E+01	6.2E+06

Table 4.3.11: Unit and overall KPIs for synthesis of phenol in options C, D and E.

Option B is identified as the preferable process scheme by both inherent safety performance indicators, PI and HI. This is a direct consequence of the low UPI and UHI values of the single units. In particular, the use of few pressurized units with large liquid inventories results to be the key factor to achieve this performance, in comparison with other options. In fact, the hydrogenation section alone, that is the pressurized one, accounts for about two thirds of the HI and half of the PI.

Phenol hydrogenation section of option C	**UHI**	**UPI**	**Phenol hydrogenation section of option D**	**UHI**	**UPI**	**Phenol hydrogenation section of option E**	**UHI**	**UPI**
R01A Slurry reactor	$3.7x10^{-1}$	$4.3x10^{3}$	R01A Slurry reactor	$2.2x10^{-1}$	$7.9x10^{3}$	R01A Fixed bed reactor	$2.6x10^{-2}$	$2.5x10^{3}$
R01B Slurry reactor	$3.7x10^{-1}$	$4.3x10^{3}$	R01B Slurry reactor	$2.2x10^{-1}$	$7.9x10^{3}$	R01B Fixed bed reactor	$2.6x10^{-2}$	$2.5x10^{3}$
R01C Slurry reactor	$3.7x10^{-1}$	$4.3x10^{3}$	R01C Slurry reactor	$2.2x10^{-1}$	$7.9x10^{3}$	C01 Vacuum distillation of cyclohexanone	$2.2x10^{-1}$	$2.1x10^{3}$
C01 Vacuum distillation column	$1.7x10^{-1}$	$3.7x10^{3}$	C01 Quenching column	$3.0x10^{-1}$	$5.2x10^{4}$	C02 Vacuum distillation of cyclohexanol	$2.8x10^{-2}$	$2.7x10^{2}$
D01 Flash drum	$4.2x10^{-5}$	$4.2x10^{2}$	C02 Quenching column	$7.2x10^{-2}$	$8.6\ x10^{3}$	D01 Flash drum	$5.2x10^{-5}$	$5.2x10^{2}$
F01 Filter	$1.8x10^{-1}$	$3.7x10^{3}$	C03 Vacuum distillation column	$1.5x10^{-1}$	$1.4x10^{3}$	E01 Feed evaporator	$9.2x10^{-2}$	$1.8x10^{3}$
E01 Hydrogen cooler	$1.7x10^{-1}$	$4.8x10^{2}$	D01 Flash drum	$8.6x10^{-4}$	$8.5x10^{1}$	E02 Product condenser	$1.2x10^{-1}$	$4.6x10^{3}$
E02 Condenser of C01	$4.5x10^{-2}$	$2.9x10^{2}$	F01 Filter	$7.6x10^{-4}$	$7.6x10^{1}$	E03 Condenser of C01	$4.6x10^{-2}$	$3.6\ x10^{2}$
E03 Reboiler of C01	$6.4x10^{-2}$	$2.6x10^{2}$	E01 Quencher C01 cooler	$2.5x10^{-1}$	$4.2x10^{3}$	E04 Reboiler of C01	$8.2x10^{-2}$	$2.8\ x10^{2}$
E04 Evaporator of D01	$1.4x10^{-2}$	$2.8x10^{2}$	E02 Quencher C02 cooler	$2.3x10^{-1}$	$2.4x10^{3}$	E05 Condenser of C02	$1.4x10^{-3}$	$1.4x10^{2}$
E05 Condenser of D01	$6.4x10^{-2}$	$4.2x10^{2}$	E03 Condensate cooler	$1.6x10^{-1}$	$2.7x10^{3}$	E06 Reboiler of C02	$1.4x10^{-3}$	$1.4\ x10^{2}$
G01 Phenol feed pump	$4.9x10^{-2}$	$1.6x10^{2}$	E04 Condenser of C03	$4.5x10^{-2}$	$2.9x10^{2}$	E07 Evaporator of D01	$6.1x10^{-2}$	$2.1x10^{2}$
G02 Cyclohexanone pump	$2.9x10^{-2}$	$2.9x10^{2}$	E05 Reboiler of C03	$8.8x10^{-2}$	$8.0x10^{2}$	G01 Cyclohexanone pump	$3.1x10^{-2}$	$3.1x10^{2}$
G03 Bottom pump	$5.9x10^{-3}$	$5.9x10^{1}$	E06 Condenser of D01	$1.5x10^{-3}$	$7.6x10^{1}$	G02 Cyclohexanol pump	$5.9x10^{-3}$	$5.9x10^{1}$
G04 Recycle pump	$3.8x10^{-2}$	$8.5x10^{1}$	E07 Recycle cooler	$1.5x10^{-3}$	$7.6x10^{1}$	G03 Recycle pump	$5.9x10^{-3}$	$5.9x10^{1}$
P01 Hydrogen compressor	$3.9x10^{-1}$	$4.8x10^{2}$	G01 Cyclohexanone pump	$2.9x10^{-2}$	$2.9x10^{2}$			
			G02 Recycle pump	$8.8x10^{-3}$	$8.8x10^{1}$			
	HI	**PI**		**HI**	**PI**		**HI**	**PI**
	$2.3x10^{0}$	$2.3x10^{4}$		$2.0x10^{0}$	$9.7x10^{4}$		$7.4x10^{-1}$	$1.6x10^{4}$

Table 4.3.12: Unit and overall KPIs for synthesis of cyclohexanone in options C, D and E.

HI

	A	B		C	D	E
Synthesis cyclohexane	2.6E+02	9.2E+01	Synthesis cumene	5.3E+02	5.3E+02	5.3E+02
Synthesis cyclohexanone	2.9E+02		Synthesis phenol	6.1E+01	6.1E+01	6.1E+01
			Synthesis cyclohexanone	2.3E+00	2.0E+00	7.5E-01
Total	5.5E+02	9.2E+01		6.0E+02	6.0E+02	6.0E+02

PI

	A	B		C	D	E
Synthesis cyclohexane	3.2E+05	2.4E+06	Synthesis cumene	4.2E+06	4.2E+06	4.2E+06
Synthesis cyclohexanone	1.2E+07		Synthesis phenol	6.2E+06	6.2E+06	6.2E+06
			Synthesis cyclohexanone	2.4E+04	9.7E+04	1.6E+04
Total	1.2E+07	2.4E+06		1.0E+07	1.1E+07	1.0E+07

Table 4.3.13: Summary of overall KPIs for the current case study.

4.3.3.1 – Comparison with literature approaches

The case study was also analysed using literature methodologies for inherent safety index assessment. In particular, the following methods were considered:

- Prototype Index of Inherent Safety (PIIS) proposed by *Edwards & Lawrence, [1993]*;
- Inherent Safety Index (ISI) proposed by *Heikkilä et al., [1996, 1998, 1999]*;
- Potentials Danger for safety in Environmental Safety and Health (ESH) by *Koller et al., [2000]*.
- Tools I and J of INSET Toolkit (INSET) *[INSIDE, 2001]*;
- Safety Weighted Hazard Index (SWeHI) by *Khan at al., [2001]*;
- Integrated Inherent Safety Index (I2SI) by *Khan & Amyotte, [2004,2005]*;
- Dow Fire and Explosion Index (F&EI) *[Dow, 1994]*;
- Dow Chemical Exposure Index (CEI) *[Dow, 1993]*.

The comparison of the results obtained by the methods listed above required some further assumptions. In particular, some methods (e.g. ESH, INSET) yield a cluster of indexes for specific types of unit hazards. Thus, additional assumptions were necessary to obtain overall combined indexes: in accordance with the literature, the maximum expected values and an equal weight of the indexes were considered in normalization and aggregation *[INSIDE, 2001; Koller et al., 2001]*. Whenever single indexes are expressed in terms of damage distance (Dow F&EI, Dow CEI) the use of the higher distance was preferred, in accordance with the approach suggested by the SWeHI method *[Khan at al., 2001]* and by the methodology developed in the present paper. Furthermore, several methods do not define clear and homogeneous procedures to calculate the material quantities to be considered in the unit assessment, requiring specific assumptions to limit potential biases in the results.

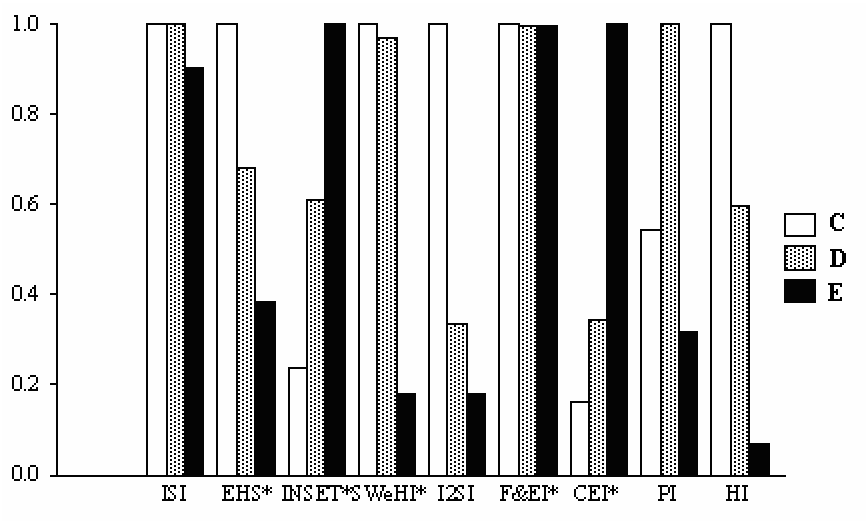


Figure 4.3.9: Inherent safety indexes calculated by different methods for the hydrogenation reactor present in options C, D and E.

Figure 4.3.9 shows an example of comparison of the results obtained for the inherent safety assessment of a single unit. The phenol hydrogenation reactor of options C, D and E was selected, since the assessment of a reaction unit is considered in most of the literature methods. Moreover this reactor actually accomplish the same type operation in the three different operative conditions. Since the indexes calculated by the different methods have different scales, the index values reported in Figure 4.3.9 were normalized dividing them by the higher value obtained for each methodology. In the case of I2SI, that has a higher value for an inherently safer option, the inverse of the index was considered for normalization.

A first remark that comes from the analysis of the figure is that there is no agreement in the results obtained by the different methods, both from a qualitative and a quantitative point of view. The differences are likely to arise both from the different level of detail required by the application of the method and by the different penalization factors considered. For instance, the reversed behaviour of INSET method compared to EHS is mainly due to the penalization parameters used in the former, that do not consider the high operating pressure of the units. As a consequence, the inventory of phenol, which is linked to the conversion, becomes determinant in the ranking by the INSET method, since it has a prevailing role among the toxic material hazard.

Moreover, the results in Figure 4.3.9 show that the less information demanding indexes yield poor evaluation of single units. PIIS is not at all suitable for the analysis of a single reaction unit, being designed to address the process as a whole. On the other hand, the scoring of ISI, that can be applied to the sole reaction section, seems not sensitive to differences in unit operating conditions. Even the more detailed approaches are not able to take into account all the hazards evaluated by the UPI: the SWeHI is strongly influenced in the results by the data on inventory value and, on the other hand, the F&EI is quite unable to take into account the specific unit characteristics. Both these indexes base the assessment of the reactor only on the flammable proprieties of materials, respectively identifying as secondary issues or neglecting the toxic dispersions. On the other hand, the CEI index is limited to considered toxic effects, thus it only takes into account phenol releases, since this is the only substance that has available ERPG data. Finally, I2SI seems to have a behaviour similar to UHI, but it shall be recalled that the results of this index partially reflect the expertise of the analyst, being thus "tailored" on the specific cases.

Figure 4.3.10 extends the analysis to the whole plant section of phenol hydrogenation. This is actually the section that is different among options C, D and E. The figure shows the comparison of the overall inherent safety indexes calculated by different methods. The values of the overall indexes largely differ among the different methods. In quite all the overall indexes represented in Figure 4.3.10, the reactors play a dominating role in determining the index values, as evident from the comparison with Figure 4.3.9. In spite of the large differences shown by the different methods, most of them indicate that option E is preferable, in accordance with the results of PI and HI.

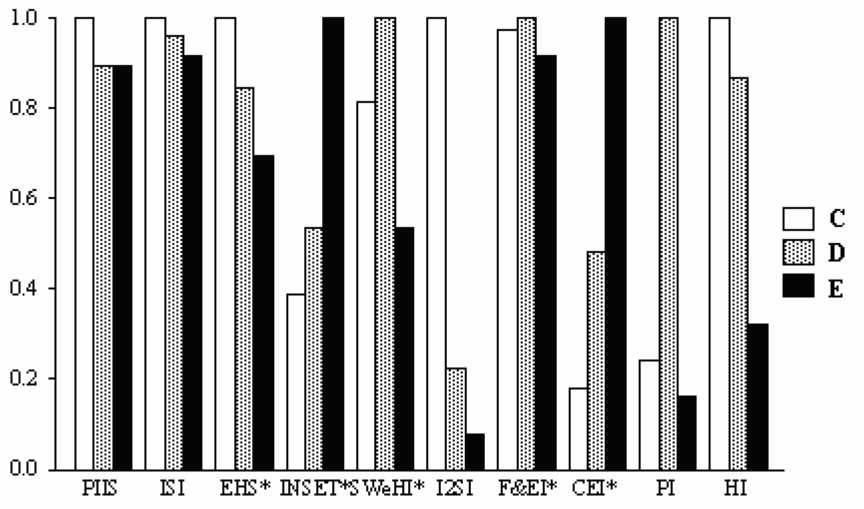


Figure 4.3.10: Comparison of the overall inherent safety indexes calculated by different methods for the hydrogenation section of options C, D and E.

The results reported above can be confirmed extending the application to the whole processes of the considered options. Thus some general conclusions can be drawn. No coherence exists among the available methods for the quantitative assessment of inherent safety. Several factors are responsible of the disagreement in the results, evidenced by Figures 4.3.9 and 4.3.10. In particular, the detail of information required for the application of each method influences the results. Thus, procedures based on general data do not allow a detailed hazard identification. Moreover, subjective assumptions on material quantities resulted a significant issue for the reliability of some literature methods. Furthermore, not all the tools attribute the same importance to different potential hazard factors. These elements, if added to built-in assumption and to some degree of freedom left to the experience of the analyst, may well justify the differences in the results obtained.

The Potential hazard index (PI) and the detailed methods proposed in the literature (e.g. EHS, SWeHI) are frequently in disagreement, even if consider the potential severity of the scenarios as the prevailing factor in the analysis. On the other hand, the inherent safety hazard index (HI) introduced in the present study adds further details to the results, accounting for the recorded safety scores of the different units, thus assessing the hazards coming from auxiliary equipment, as compressors, filters, and heat exchangers, that are often overlooked in conventional severity-based inherent safety assessment methods.

4.3.4 - Conclusions

In this chapter, some of the developed assessment tools (§1.2 and §2.3) were applied to case studies concerning the design of a process for industrial production of the chemical intermediate cyclohexanone. Several design options were compared, considering three different chemical routes for the production as well as different technological solutions for the plant. The applied methodologies allowed the analysis of the options, identifying the impact profile expected from experience/expert judgement. The comparison with conventional inherent safety assessment methodologies from the literature evidences the ability of the proposed approach to override several problems that used to hinder the implementation of inherent safety in design.

The principal outcomes identified in the analysis of the cyclohexanone case-study are:

- The innovative route proposed for the production (process B, synthesis via cyclohexene hydration), is the preferable option form the point of view of impact on sustainability. This results from the combined effect of inherent safety and economic performance, since the process is simpler (lower capital and operative costs) and requires milder operative conditions. However some specific impacts pertaining to the environmental sphere (e.g. release of carcinogen compounds) are identified as critical for this option compared to the others.
- The aggregate environmental impacts of the processes are mainly depending on the thermal energy requirements. In option A (synthesis via oxidation of cyclohexane) the wastewater treatment shows a significant contribution to the impact. On the other side, the economic index has a minor role on the performance of all the options, as expected in a process for production of commodities, that typically has low annual margins.
- Inherent safety performance is principally influenced by the presence of two elements in the option: sections operated at medium/high pressures and units having large inventories of flammable and/or toxic liquid. The developed inherent safety approach allows to effectively capture this hazard profile, since it accounts by one hand the maximum expected consequences of an accident and, by the other, the role of minor but more credible releases. This is evident from the comparison with the literature approaches that lack these assessment features.

4.4 – Hydrogen

4.4.0 – Overview

The challenge for a widespread hydrogen utilization as an energy vector requires the adoption of proper strategies to manage the issues related to safety, environment and process efficiency. The identification of sustainable industrial processes for hydrogen production thus arises as a key element in this challenge. Thus, the introduction of sustainability drivers in process design is a key issue to orient the further development and the selection among industrial alternatives.
On the other side, the increase in the number and in the potentialities of hydrogen production plants will require a strong increase of hydrogen storage capacities *[Sarkar & Banerjee, 2005; Venter & Pucher, 1997; Zhou, 2005]*. Moreover, it is expected that use of hydrogen as an energy carrier may cause a spread of hydrogen storage installations also in vulnerable contexts, such as residential and commercial areas.

In the following, alternative processes proposed for industrial high purity hydrogen (99.5-99.9%) production by steam reforming of natural gas are compared with regard to their sustainability and inherent safety performance (§4.4.1). Then the problem of storage is faced by an analysis of the inherent safety of alternative options for hydrogen storage (§4.4.4).
The case studies in both the afforded themes represent a demonstration of the applicability of the methods described in sections 1 and 2. Moreover, the discussion of the results will allow to evidence how the approaches yield interesting and effective results, overcoming the limitations of former literature methods.

4.4.1 – Production case-study description

The present case-study focuses on the comparison of five different processes proposed for industrial high purity hydrogen (99.5-99.9%) production by steam reforming of natural gas. Even if in a long time period hydrogen industrial production needs to be based on the use of renewable resources, in a short time perspective the shift toward the widespread utilization of hydrogen requires to manage the transitory period of change by the optimization and improvement of current technologies for hydrogen production *[Mueller-Langer et al., 2007; Häussinger et al., 2003; Fu & Wu, 2007; Adhikari et al., 2007]*. This is confirmed by the active research in this field, that resulted in the development of several innovative processes based on steam reforming *[Aasberg-Petersen et al., 2001; Reyes et al., 2003; Song & Guo, 2006; Biesheuvel & Kramer, 2003]*.

The steam reforming process is presently the most common and well known method for large scale hydrogen production. The process is based on the catalytic conversion of a mixture of methane and steam to yield hydrogen and carbon monoxide, following the endothermic “conversion reaction”:

$$CH_4 + H_2O \xrightarrow[1.4\text{–}2\ MPa]{700\text{–}1000K} CO + 3H_2 \qquad (4.4.1)$$

Carbon monoxide is then converted to carbon dioxide following the slightly exothermic “shift reaction”:

$$CO + H_2O \xrightarrow[1.4\text{–}1.8\ MPa]{650K} CO_2 + H_2 \qquad (4.4.2)$$

Finally hydrogen is purified by separation.

The key-issues to enhance the process yields are the reaction and separation design. Alternative processes, characterized by different levels of development, are nowadays available. In particular, high temperature membrane separation was proposed and several processes based on membrane separation are currently under development. In the following, five reference processes will be analyzed (Figure 4.4.1), namely:

1. traditional with pressure swing adsorption (PSA) – reference process #1
2. auto-thermal with pressure swing adsorption (PSA) – reference process #2
3. internal membrane separator – reference process #3
4. external membrane separator – reference process #4
5. integrated reactor – reference process #5

The processes mainly differ in the arrangement of the reaction and separation sections as well as in the adoption of different separation technologies (adsorption or membranes). *Traditional* and *auto-thermal processes with PSA (#1 and #2)* are those currently used in industrial hydrogen production *[Häussinger et al., 2003; Ahmed & Krumpelt 2001; Seo et al., 2002; Hagh, 2003]*. In these conventional process arrangements, hydrogen is separated by selective adsorption at mild temperature. In the *internal membrane separation process (#3),* a novel approach to the reaction section is introduced: the shift reactor is eliminated and hydrogen production only occurs in a single adiabatic reactor, where semi-permeable membranes allow the direct high-temperature separation of hydrogen, enhancing the conversion. The *external* high-temperature *membrane separation (#4)* was also proposed, although lower conversions are obtained by this process. The *integrated reactor (#5)* process presents a novel design for both heat transfer and hydrogen separation. In particular, the reaction heat is not provided by an external heat exchanger, but by hot gases in an integrated tubular exchanger. Hydrogen separation is obtained by a high-temperature internal membrane.
A brief description of each process is reported in the following.

i) Reference process scheme #1: Traditional with Pressure Swing Adsorption

The most common and available technique for hydrogen production is presently the so called *Traditional process with PSA [Häussinger et al., 2003; Ahmed & Krumpelt 2001; Seo et al., 2002]*, in which hydrogen purification is realized in zeolite bed batteries. The process may be divided in three sections. In the first section, the hydrodesulphurization of natural gas occurs by hydrogen addition. A pre-heater of natural gas and a H_2S adsorber on zinc oxides are present in this section. In the second section, the purified natural gas is mixed with hot steam and fed to the catalytic bed in the reforming side of the reactor. A further not purified stream of natural gas is burned into the furnace side, together with the off gas (a flammable mixture containing 42% of hydrogen) from the purification section. The combustion is carried out with atmospheric air and provides the heat for the endothermic reforming reaction. The reacted stream is then cooled in a spray quencher with water and fed to another catalytic reactor, in which a further hydrogen production is realized via shift reaction. In the last section, hydrogen is purified and a thermal recovery is performed cooling the hydrogen stream and producing hot steam. The water obtained in the conversion and shift reaction is removed from the hydrogen stream via condensation and recycled to the reaction section. Hydrogen is purified in the PSA unit and sent to the storage. The exhausted beds of PSA are regenerated by hydrogen washing. Hence, even if a high purity hydrogen is obtained, almost the 25% of the final product is consumed in this operation. The purged gas from the regeneration, which is called off gas, is fed to the furnace side of the reactor. The PFD shown in figure 4.4.2 was used as the reference schemes for the assessment carried out in the present study.

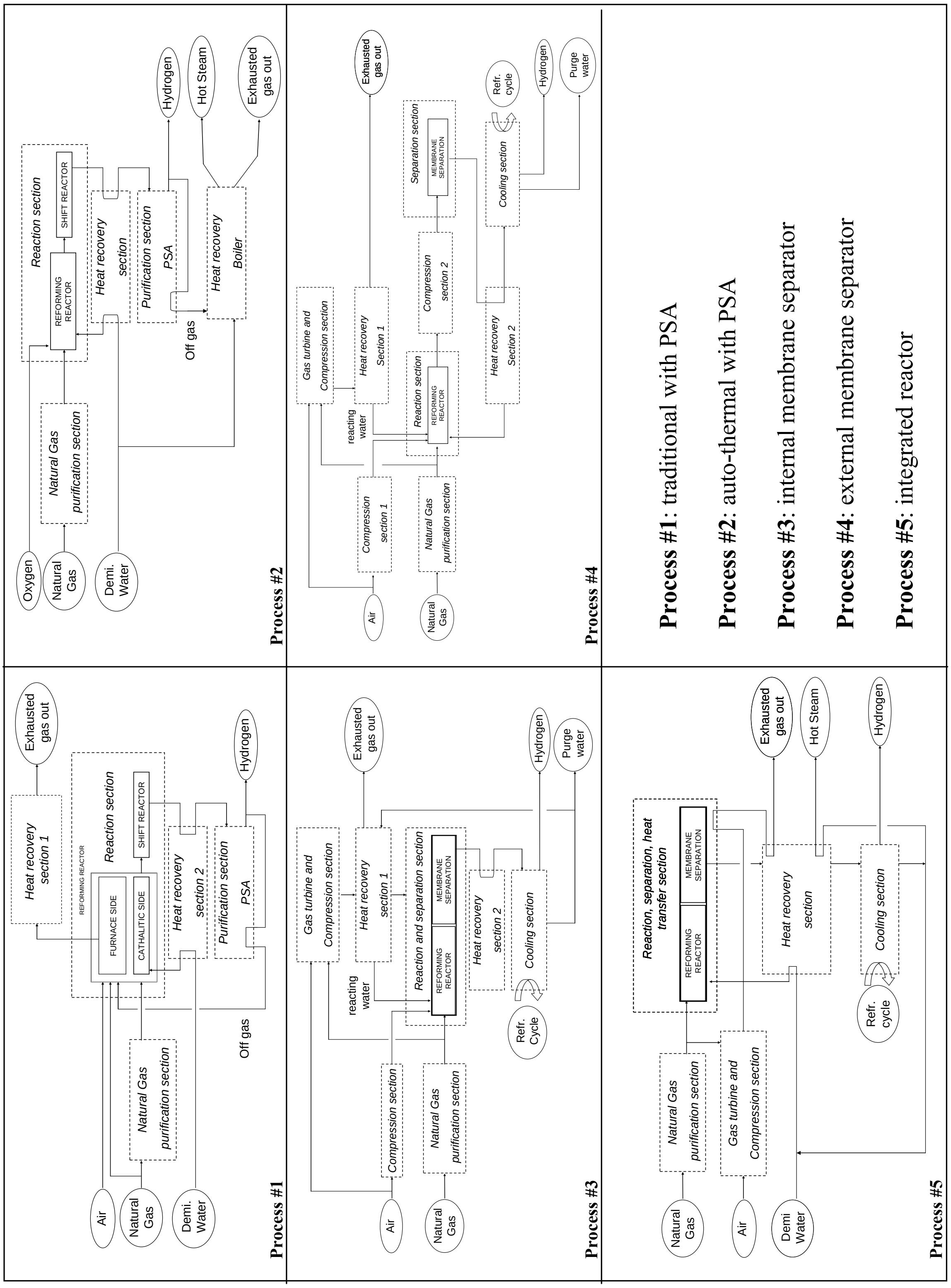


Figure 4.4.1: Block diagram of the five reference processes for hydrogen production by natural gas steam reforming considered in the present study

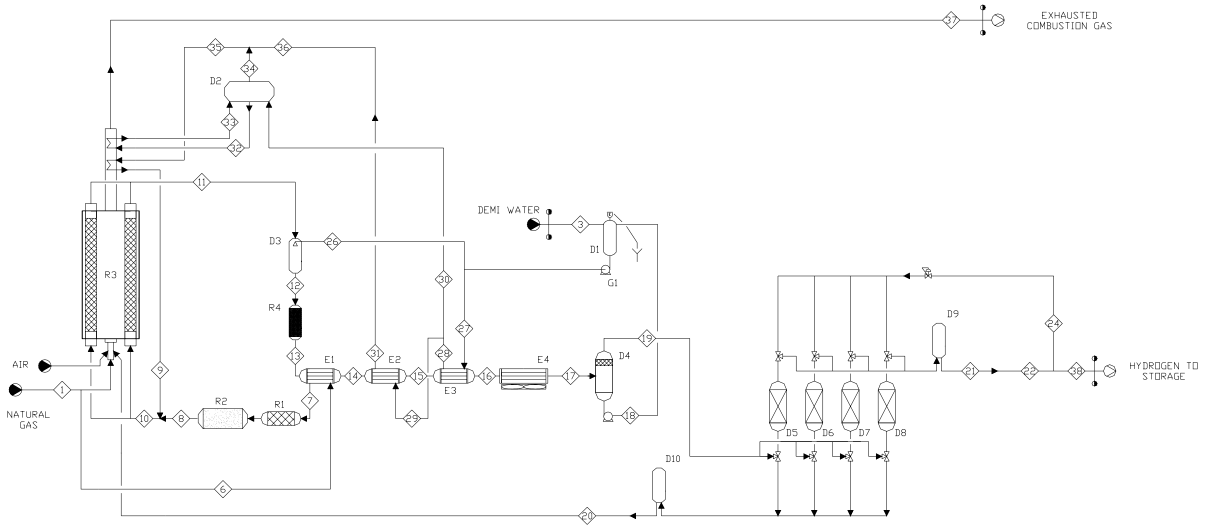


Figure 4.4.2: Reference process flow diagram (PFD) defined for the traditional process with PSA (*#1*). R1: hydrodesulphurization reactor; R2: H_2S adsorption; R3: reforming reactor and furnace; D5-D6-D7-D8: adsorption beds; E1, E2, E3: heat recovery system; E4: air cooler; D9-D10: pressure buffers.

ii) Reference process scheme #2: Auto-thermal with Pressure Swing Adsorption

The second process considered in the present study for hydrogen production is the *auto-thermal process with PSA [Häussinger et al., 2003; Ahmed & Krumpelt 2001; Seo et al., 2002; Hagh, 2003]*, which is as well widely adopted in the current industrial practice, although being more complex than the *traditional PSA process*. The main difference with respect to the *traditional PSA* is in the reaction section. All the natural gas fed to the reactor is purified, since hydrogen is produced in two parallel streams, by endothermic catalytic reforming and by exothermic partial oxidation with pure oxygen (instead of air). The exothermic partial oxidation reaction provides the energy contribution necessary for the conversion reaction.

In this scheme, pure oxygen is used instead of air and larger quantities of natural gas are processed, since less heat is produced in the furnace, where only a partial oxidation is carried out. Moreover, the off-gas from the regeneration of the adsorbers can not be recycled to the furnace, thus increasing the natural gas consumption. On the other hand, the off-gas may be used for hot steam generation, in particular if thermal energy users are present (e.g. as in integrated eco-parks).

iii) Reference process scheme #3: Internal membrane separator

The third process considered is indicated as *internal membrane separation process* and is characterized by a novel approach to the reaction section *[Gallucci et al., 2004; Lattner & Harold, 2004]*. The shift reactor is eliminated and hydrogen production only occurs in a single adiabatic reactor. All the reforming reactions (i.e. conversion, water gas shifting and partial oxidation) are integrated in the reactor and the separation is carried out via semi-permeable membranes in the reactor. The continuous removal of hydrogen from the reaction zone influences the equilibrium, enhancing reactant conversion. In the process analyzed, the generation of hot gases, which provides the thermal energy required for the reforming reaction, is coupled to mechanical energy production with a gas turbine. Hot steam is fed to the permeate side of the reactor in order to easily sweep the hydrogen through the membrane.

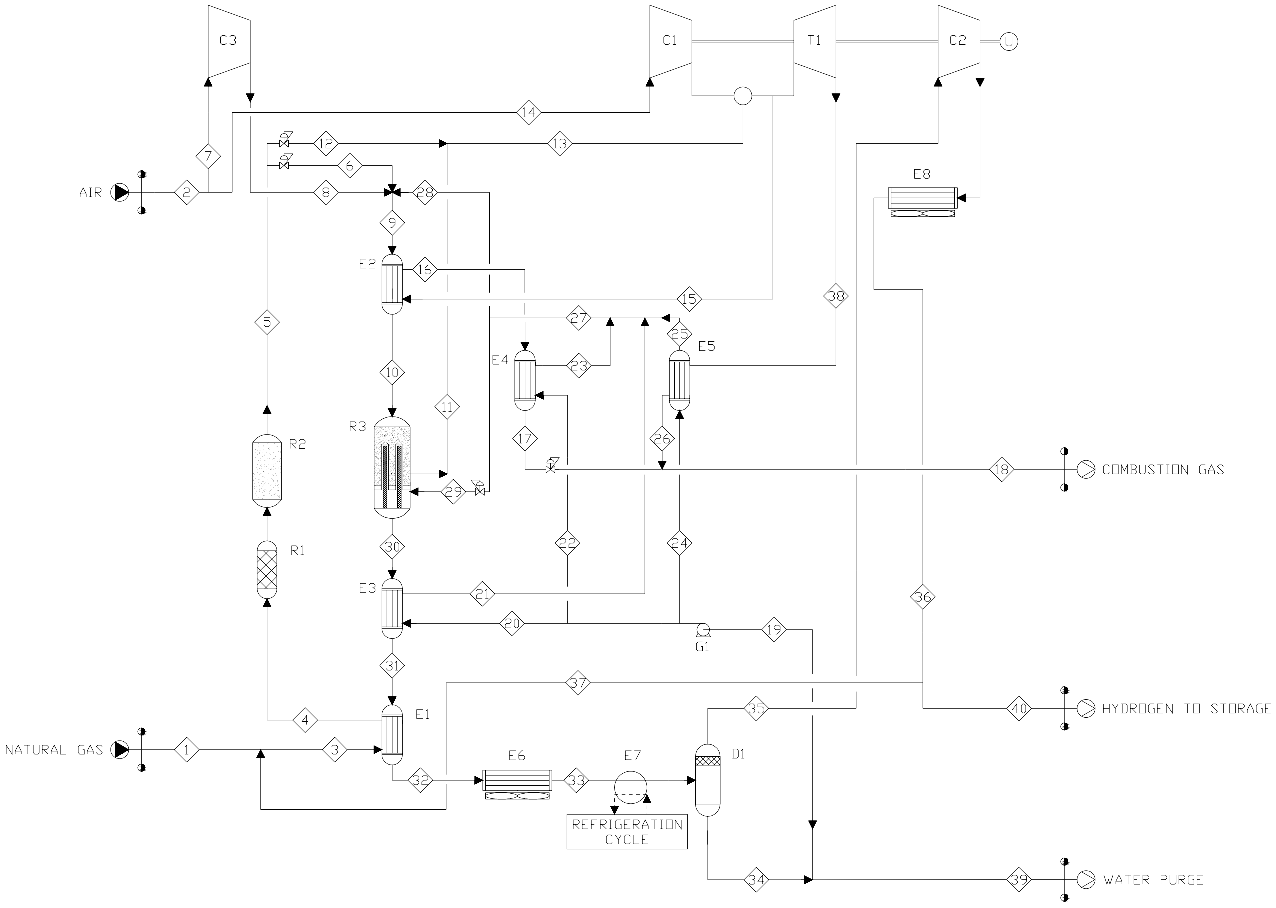


Figure 4.4.3: Reference process flow diagram (PFD) defined for the integrated membrane separation process (*#3*). R1: hydrodesulphurization reactor; R2: H_2S adsorption; R3: membrane reforming reactor; T1: gas turbine group; C1: compressor; C2: process air compressor; E1-6: heat recovery system, E7: steam condenser with refrigeration cycle; E8; air cooler; D1: flash drum.

The condensation of this steam requires a refrigeration cycle, that is the main disadvantage of this scheme, due to the related power consumption. The condensed demineralized water may be recycled to the process without external integration, while in the first two schemes a water make-up was required. A final compression and cooling unit is needed to provide a hydrogen output at the same operating conditions of the previous processes. The mechanical energy for this compression is provided by the gas turbine. Figure 4.4.3 reports the reference scheme assumed in the present study for the sustainability assessment of the process.

iv) Reference process scheme #4: External membrane separator

An alternative type of membrane separation process was considered in the comparison. Although many elements are similar to *internal membrane separation process*, this process presents an *external membrane* apparatus to remove hydrogen from the reforming gases, after the cooling for thermal recovery *[Simpson & Lutz, 2007]*. Thus, operating conditions in the separation section are less severe. In particular, temperatures are lower, so the membrane is exposed to a less severe environment and the selectivity is higher. However a compression is required before of the membrane separator to increase the partial pressure of hydrogen. On the other hand, hydrogen is not continuously removed from the reaction side as in the *internal membrane separation process*, so the conversion is lower. Moreover, also in this process the non permeated gas, containing a high percentage of unreacted methane, is fed to a gas turbine in order to exploit the heating value of the stream, and to provide the reaction heat to the process.

v) Reference process scheme #5: Integrated reactor

Also the last process considered is similar to the *internal membrane separation process,* but the reactor presents an alternative design *[Iaquaniello & Mangiapane, 2006]*. In particular, the reaction heat is not provided by an external heat exchanger, but by an *integrated* tubular exchanger. The heat is provided by a hot stream obtained from methane combustion, thus composed only of exhaust burned gases. A further equipment integration is thus realized in this scheme. The reactor is compact and efficient, carrying out reaction, separation and heat transfer. Moreover, there is no need to feed compressed air to the reactor as in the previous processes. Thus, the air compression section (C3 in figure 4.4.3) is not present. The critical point of the scheme concerns the membrane in the reactor, that is characterized by severe operative conditions, in particular during process start-up, when temperature gradients between the two sides of the membrane are higher. Heat recovery is possible from many streams of the process, leading to the production of excess steam suitable for external uses.

4.4.2 – Sustainability assessment of the production case study

In the following the case study is assessed according to the procedure described in §1.2. The application of the procedure will require the definition of an index pro inherent safety assessment. The more derailed discussion on inherent safety assessment trough the method described in §2.3 will be the topic of §4.4.3.

4.4.2.1 - Definition of reference basis, boundary limits and data collection

The starting point of the analysis was the definition of reference process schemes at a sufficient level of detail, and the collection of the quantitative data necessary for the analysis. For each reference process considered in the analysis, a simplified block diagram is presented in figure 4.4.1. It must be remarked that the process schemes defined in the following have the only purpose to show the results of the sustainability assessment performed and to provide

Process	**Thermal/reaction use rate (ψ)**	**Reactor conversion (χ)**	**Separation efficiency (ζ)**	**Overall reaction yield (η)**
Traditional PSA	0.56	0.95	0.75	2.6
Auto-thermal PSA	-	0.90	0.75	1.6
Internal membrane	1.22	0.85	0.90	2.1
External membrane	0.86	0.80	0.95	2.2
Integrated reactor	10.57	0.90	0.90	3.2

ψ = (natural gas for thermal use) / (natural gas fed to the reactor)
χ = (converted methane [mol]) / (methane feed to the reactor [mol])
ζ = (hydrogen entering the separation device) / (hydrogen production potential)
η = (hydrogen production potential [mol]) / (methane feed to the reactor [mol])

Table 4.4.1: Selected key parameters calculated for the alternative process options.

data useful for the identification of critical issues in the main alternative routes for hydrogen production. Obviously other processes or different arrangements may be proposed or are actually used for hydrogen production.

On the basis of the average size of several existing plants, a hydrogen production potential of 7100 t/y was considered. A reference process flow diagram (PFD) was defined for each reference process. The reference PFD was derived from those of existing plants for available industrial scale processes, or was based on data available in the technical literature for processes that are still under development. Figures 4.4.2 and 4.4.3, reporting the PFDs of the *traditional with PSA (#1)* and of the *internal membrane separator (#3)* processes, show the typical level of detail of the reference process schemes required for the application of the assessment procedure.

The boundaries of the analysis should include all the stages of the process as well as the utilities, even if outside process or design battery limits. However, in the analysis of the required utilities (e.g. oxygen feedstock, refrigeration cycle), only the impacts directly allocable to the process of interest were considered. Therefore the environmental impacts related to oxygen production were considered for *auto-thermal process with PSA (#2)*. Similarly, a portion of the overall impacts of *auto-thermal with PSA (#2)* and *integrated reactor (#5)* processes should be allocated to a co-product (a medium pressure steam stream) obtained in these processes. The storage and the distribution of hydrogen was not considered in the present analysis.

Besides the full definition of material and energy flows, the analysis of each reference process scheme requires data on equipment and operating conditions. For each alternative these were gathered from literature data *[Ahmed & Krumpelt 2001; Gallucci et al., 2004; Hagh, 2003; Häussinger et al., 2003; Iaquaniello & Mangiapane, 2006; Lattner & Harold, 2004; Seo et al., 2002; Simpson & Lutz, 2007]* and from design calculations. Material and energy flow balances yield flow rates and compositions of the main streams. Table 4.4.1 summarizes selected key parameters calculated for the alternative options. The fugitive emissions were assessed by average emission factors for the expected leak points within the process diagram (e.g. seals, joints, valves, etc.) *[Allen & Shonnard, 2002]*. The emission of micro-pollutant (primarily NO_x and CO) from the utilities (e.g. gas turbines, furnaces, etc.) were evaluated by emission factors from available databases *[EPA, WPa, WPe]*. The main pieces of equipment were preliminary sized, allowing the estimation of the unit inventories required for inherent safety analysis.

Economic data were also retrieved or assessed. Material, energy and operative costs were evaluated multiplying the calculated flow rates by average unitary costs *[IChemE, 2002; ICIS, WP]*. The specific equivalent number of employees necessary for process activities was the result of an expert judgment based on similar activities.

The adoption of a site specific approach in the normalization procedure required to select a reference site for the analysis (see §1.3 for details about). This was arbitrarily chosen in the outskirts of an industrial city in northern Italy. The resulting normalization factors are reported in the last column of table 4.4.2. Nevertheless, in the discussion of the results the influence of the site on the results of the analysis will be examined.

4.4.2.2 - Results from sustainability assessment and discussion

Table 4.4.2 shows the non normalized values of the Level 1 indicators calculated for the five reference schemes defined. The upper part of table 4.4.3 reports the normalized values of the indices for each impact category. The values were obtained from the indicators and normalization factors in table 4.4.2 applying Equation (1.2.7). The table also reports the values calculated for Level 2 (aggregated) and Level 3 (overall) indices. All of them were obtained introducing in Equation (1.2.9) the proper values of indices and weight factors from table 4.4.3.

	# 1	**# 2**	**# 3**	**# 4**	**# 5**	**Unit**	**Normalz. Factor**
Environment							
Global Warming	$8.81 \cdot 10^{7}$	$6.43 \cdot 10^{7}$	$1.85 \cdot 10^{8}$	$1.51 \cdot 10^{8}$	$6.44 \cdot 10^{7}$	kg_{eq}/y	$1.16 \cdot 10^{6}$
Rain Acidification	$5.23 \cdot 10^{4}$	$7.83 \cdot 10^{2}$	$9.78 \cdot 10^{4}$	$7.15 \cdot 10^{4}$	$-2.28 \cdot 10^{4}$	kg_{eq}/y	$4.83 \cdot 10^{3}$
Air Toxicity	$2.32 \cdot 10^{7}$	$3.47 \cdot 10^{5}$	$4.21 \cdot 10^{7}$	$3.08 \cdot 10^{7}$	$-1.45 \cdot 10^{7}$	kg_{eq}/y	$3.79 \cdot 10^{5}$
Solid waste disposal	$1.55 \cdot 10^{4}$	$2.46 \cdot 10^{4}$	$3.35 \cdot 10^{4}$	$2.76 \cdot 10^{4}$	$9.08 \cdot 10^{4}$	kg_{eq}/y	$2.32 \cdot 10^{5}$
Natural gas	$4.06 \cdot 10^{7}$	$3.18 \cdot 10^{7}$	$7.39 \cdot 10^{7}$	$6.07 \cdot 10^{7}$	$2.73 \cdot 10^{7}$	kg_{eq}/y	$1.19 \cdot 10^{5}$
Electric power	0.00	$1.76 \cdot 10^{7}$	$3.74 \cdot 10^{5}$	$3.25 \cdot 10^{6}$	$3.74 \cdot 10^{5}$	kWh/y	$1.10 \cdot 10^{6}$
Economy							
Economic impact index	$-7.14 \cdot 10^{6}$	$-8.99 \cdot 10^{6}$	$4.25 \cdot 10^{6}$	$-1.52 \cdot 10^{5}$	$-1.42 \cdot 10^{7}$	€/y	$2.83 \cdot 10^{6}$
Society							
Occupational index	$-2.10 \cdot 10^{1}$	$-2.10 \cdot 10^{1}$	$-1.50 \cdot 10^{1}$	$-1.50 \cdot 10^{1}$	$-1.80 \cdot 10^{1}$	people	$7.92 \cdot 10^{1}$
Inherent Safety	$4.38 \cdot 10^{-6}$	$3.73 \cdot 10^{-6}$	$5.61 \cdot 10^{-6}$	$1.06 \cdot 10^{-5}$	$4.86 \cdot 10^{-6}$	km^2/y	$6.00 \cdot 10^{-6}$

Table 4.4.2: Non normalized values of Level 1 impact indicators calculated for the five reference processes assessed.

	# 1	**# 2**	**# 3**	**# 4**	**# 5**	**Weight factor**
Level 1						
Global Warming	$7.57 \cdot 10^{1}$	$5.52 \cdot 10^{1}$	$1.59 \cdot 10^{2}$	$1.30 \cdot 10^{2}$	$5.53 \cdot 10^{1}$	0.051
Rain Acidification	$1.08 \cdot 10^{1}$	$1.62 \cdot 10^{-1}$	$2.02 \cdot 10^{1}$	$1.48 \cdot 10^{1}$	$-4.72 \cdot 10^{0}$	0.066
Air Toxicity	$6.12 \cdot 10^{1}$	$9.17 \cdot 10^{-1}$	$1.11 \cdot 10^{2}$	$8.13 \cdot 10^{1}$	$-3.84 \cdot 10^{1}$	0.095
Solid waste disposal	$6.69 \cdot 10^{-2}$	$1.06 \cdot 10^{-1}$	$1.45 \cdot 10^{-1}$	$1.19 \cdot 10^{-1}$	$3.91 \cdot 10^{-1}$	0.030
Natural gas	$3.42 \cdot 10^{2}$	$2.67 \cdot 10^{2}$	$6.22 \cdot 10^{2}$	$5.11 \cdot 10^{2}$	$2.29 \cdot 10^{2}$	0.044
Electric power	$0.00 \cdot 10^{0}$	$1.60 \cdot 10^{1}$	$3.39 \cdot 10^{-1}$	$2.95 \cdot 10^{0}$	$3.39 \cdot 10^{-1}$	0.064
Economic impact index	$-2.52 \cdot 10^{0}$	$-3.18 \cdot 10^{0}$	$1.50 \cdot 10^{0}$	$-5.36 \cdot 10^{-2}$	$-5.02 \cdot 10^{0}$	
Occupational index	$-2.65 \cdot 10^{-1}$	$-2.65 \cdot 10^{-1}$	$-1.89 \cdot 10^{-1}$	$-1.89 \cdot 10^{-1}$	$-2.27 \cdot 10^{-1}$	0.200
Inherent Safety	$7.30 \cdot 10^{-1}$	$6.22 \cdot 10^{-1}$	$9.35 \cdot 10^{-1}$	$1.77 \cdot 10^{0}$	$8.10 \cdot 10^{-1}$	0.800
Level 2						
Environmental impact	$2.54 \cdot 10^{1}$	$1.57 \cdot 10^{1}$	$4.74 \cdot 10^{1}$	$3.80 \cdot 10^{1}$	$9.03 \cdot 10^{0}$	0.300
Economic impact	$-2.52 \cdot 10^{0}$	$-3.18 \cdot 10^{0}$	$1.50 \cdot 10^{0}$	$-5.36 \cdot 10^{-2}$	$-5.02 \cdot 10^{0}$	0.300
Societal impact	$5.31 \cdot 10^{-1}$	$4.45 \cdot 10^{-1}$	$7.10 \cdot 10^{-1}$	$1.38 \cdot 10^{0}$	$6.03 \cdot 10^{-1}$	0.400
Level 3						
Overall index	$7.09 \cdot 10^{0}$	$3.94 \cdot 10^{0}$	$1.50 \cdot 10^{1}$	$1.19 \cdot 10^{1}$	$1.44 \cdot 10^{0}$	
Normalized	0.47	0.26	1.00	0.80	0.10	

Table 4.4.3: Normalized values of Level 1 indicators and values of Level 2 and 3 indices calculated for the five reference processes assessed.

It is evident from table 4.4.2 that the alternative processes differ significantly in the amount of raw material (i.e. natural gas) required for the fixed annual production of hydrogen. This is a straightforward consequence of both the different overall yield of the processes and the different requirement of methane for thermal use (table 4.4.1). Though the co-production of medium-pressure steam has to be considered in some schemes. In particular, in *auto-thermal with PSA (#2)* and *integrated reactor (#5)* processes a large fraction of the raw material consumption (respectively 26% and 86% of the actual natural gas feed) and of the consequent emissions were allocated to the steam production and, thus, not accounted for the environmental impact in table 4.4.2.

The emission of greenhouse gases (mainly due to CO_2 emission from combustion) and the solid waste disposal (i.e. the exhausted H_2S adsorbent) follow the same pattern of natural gas consumption.

The emission of toxic and acidifying compounds is mainly related to the emission of nitrogen oxides (NO_x). Also NO_x and CO formation may be roughly correlated to the amount of natural gas consumed for thermal uses, although emission factors slightly differ among technologies *[EPA, WPa, WPe]*. However, for *reference processes #2 and #5* the allocation of emissions to steam production gives an important contribution in reducing the values of the impact index due to micro-pollutant emissions. Furthermore, the allocation leads to negative values of the toxicity and acidification indices for the *integrated reactor process (#5)*, since the NO_x formation is lower in the assessed process than in the average industrial boilers which were considered in the allocation procedure as the source of the emissions avoided.

Electric power consumption is mainly due to the drive engines of the compressors that are required in some schemes. In *reference process #2,* the electric power required for the production of the pure oxygen yields an index that is at least an order of magnitude higher than in the other reference schemes.

The economic impact index shows a wide range of values among the alternatives. Negative cash flows (and thus positive index values) were calculated for the *internal membrane separation process (#3)* on the basis of the prices considered for hydrogen and raw materials. *External membrane separation process (#4)* is found economically profitable, but is at least one order of magnitude less convenient than other alternatives. Both the processes are affected by the large costs of natural gas, correlated to the low hydrogen yield and the high thermal energy requirement (table 4.4.1), with no profitable steam co-production. On the other hand, *reference processes #2 and #5* benefit of the selling of the co-product medium pressure steam that partially compensates the natural gas purchase.

The analysis of the inherent safety index evidences that a higher level of hazard is present in the reference processes which require compressors or heat exchangers treating an hydrogen rich stream. A high hazard index results for the compression, due both to the high flammability of the processed stream and to the significant credit of compressor failure scenarios. Similarly, heat exchangers treating hydrogen streams play a significant role in the overall plant hazard, due to their operating conditions. In *process #4*, the compressor used before of the membrane separator, that has no corresponding unit in the other membrane alternatives, is mainly responsible of the lower inherent safety performance of the reference process.

The normalized values of the environmental indicators, reported in table 4.4.3, allow the comparative analysis of the main impacts of the alternative process schemes and the analysis of their importance with respect to the external references. As shown in the table, in all the processes the critical impact results the consumption of natural gas as raw material. This was expected, due to the non renewable nature of this feedstock. Global warming and toxicity impact indexes also have significant values, about one order of magnitude higher than the normalized values of the others indices. Again, this is related to natural gas consumption. In *reference scheme #2* it is worth noting that the impact of electrical power requirement contributes to balance the lower natural gas request.

With respect to societal impacts, non-critical values are obtained for both the inherent safety and occupational normalized indexes. In the case of the occupational index, this result may be expected, due to the high automation of chemical plants. On the other hand, the quite low value of the normalized inherent safety is due to the boundaries chosen for the analysis of the reference schemes, that excluded the storage and distribution facilities. Thus, only limited quantities of gas-phase hazardous substances are present in the reference process schemes assessed.

Level 2 key performance indicators (KPIs) are reported in the impact fingerprint plot shown in figure 4.4.4. The diagram evidences that environmental impacts prevail on all the other issues in all the reference schemes considered. On the other hand, in general societal aspects do not result critical. *Process scheme #4* is an exception, due to the higher value of the inherent safety index caused by the aforementioned presence of two compressors in the process, that are both likely to give releases of hydrogen-rich streams.

A more detailed comparison of the Level 2 KPIs is possible in table 4.4.3. The table confirms that the environmental impact is dominant, while the economic impact is lower of about an order of magnitude. The table also evidences the poor sustainability performance of reference *process schemes #3 and #4.* This is a consequence of both the low overall yield and the high use of methane for energy production, with no compensation by heat recovery as co-product medium pressure steam (table 4.4.1). This is due to the low conversion in the adiabatic reactor assumed in the reference process scheme. Even if the membrane allows higher hydrogen

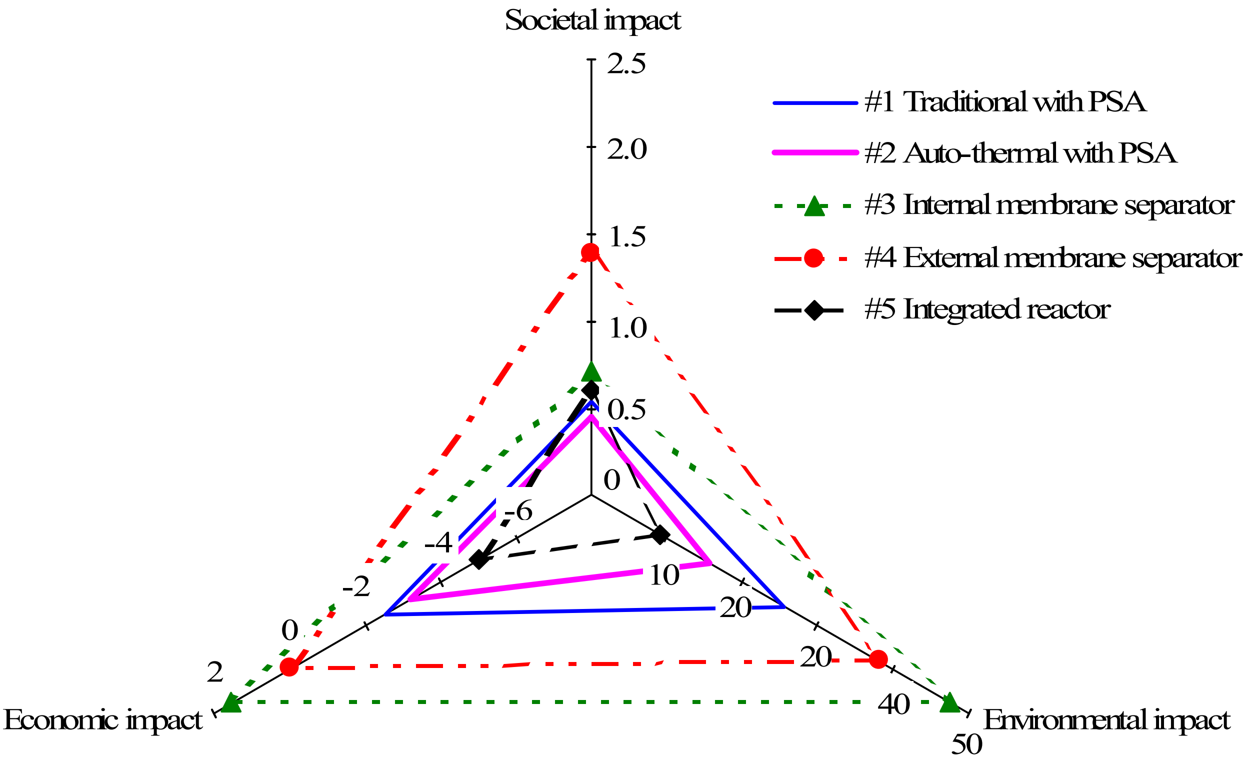


Figure 4.4.4: Radar plot reporting the impact fingerprint of the alternative processes analyzed in the present study.

recoveries than, for instance, a *traditional process with PSA*, the overall yield remains lower (table 4.4.1). A lower yield requires a larger consumption of natural gas in the reactor and larger requirement for thermal energy to preheat the reactor feed and to produce process steam. The higher consumption of natural gas consequently affects emissions, raw material costs, gas desulphurization and scale of possible releases of flammable materials.

On the other hand, the sustainability performance of *reference processes #2 (auto-thermal with PSA) and #5 (integrated reactor)*, that is promising from the point of view of sustainability, is strongly influenced by the assumptions concerning co-product allocation (the medium pressure steam stream). Thus, the valorization of this product stream is critical for the sustainability performance of the process. Non considering the allocation to the co-product stream (i.e. steam is not exploited by other facilities/users) would yield important modifications in the final results. For instance, the environmental index of process #5 would increase of about 15 times.

The value of the overall sustainability performance indicator shown in table 4.4.3 confirms the conclusions drawn on the basis of Level 2 KPIs. The comparison of the index values evidences that in the present assessment, the reference scheme considered for the *integrated reactor process (#5)* results that having the best expected sustainability performances, mainly due to the high reaction yield and the sharing of impacts with a co-product stream. The internal membrane separation and integrated heat transfer has similar expected performances, although the valorization of the steam co-production is crucial. Membrane technologies present clear advantages like high selectivity and possibility of shifting the reforming reactions by product removal. However they have to be properly integrated with the reaction in order to result in high product recovery, high process yield, and efficient use of the thermal energy. The fully integrated reactor of process scheme #5 seems to be effective in this sense. Other promising options may concern the use of multi-stage configurations, that should improve the low conversion performances of the single stage adiabatic reactor considered for reference schemes #3 and #4 *[Feng & Ji, 2007]*. However, if such processes require compression stages, the compression units may result critical from the point of view of inherent safety, as earlier identified in option #4.
A final note on reference process #2 (*auto-thermal with PSA*) should be added. This process results profitable and more sustainable compared to the *traditional PSA*. However the results, also in this case, can be affected by assumption on the allocation of the co-product medium pressure steam. Moreover this option requires the availability of a industrial oxygen production plant for the feedstock.

The results obtained for the overall and Level 2 KPIs are obviously influenced by the weight factors used in the procedure. As remarked above, uncertainties may be present in the values attributed to these parameters. A sensitivity analysis was performed in order to identify the influence of the weight factors on the results. The uncertainty of the weight factors was described by an arbitrary probability distribution of values (a Beta distribution with $\alpha=\beta=4$ and a 50% maximum variation of the values reported in table 4.4.3 were assumed in current study). A Monte Carlo method was applied to calculate the resulting probability distribution of the aggregated KPIs (the overall index and the Level 2 indices) and the contribution of the different weight factors to the variance of the results. As shown in table 4.4.4, only two weight factors showed a relevant contribution to the variance of the overall index: those attributed to natural gas consumption and to environmental impact (see table 4.4.4). In *reference scheme #2,* also the contribution of weight factor attributed to electric power consumption was significant. These results confirm that natural gas consumption, which in turn greatly influences the environmental performance, is the key element for the comparison of the overall sustainability performance of the alternative processes considered.

The ranking among the expected sustainability performance of the alternative processes analyzed, as expressed by the overall sustainability index, is only slightly affected by the uncertainty in the weight factors. Figure 4.4.5 reports the cumulative probability of the values of the differences among the overall sustainability indexes of different couples of processes, calculated by Monte Carlo runs. As shown in the figure, a change of sign of the difference among the overall sustainability index has a negligible probability within the range of uncertainty assumed for the weight factors. Hence, although the absolute values of the results are obviously influenced by the values of the weight factors selected, the sensitivity analysis evidenced that the ranking obtained in the former analysis is sufficiently robust. A limited uncertainty in the selection of the weight factors thus seems not critical for the identification of the process alternative that has the lowest impact on sustainability. Similar conclusions may be drawn for the normalization factors, that are expected to change if the site considered in the analysis is changed. Thus, even if the reported values are site specific, the general trends evidenced in the results reported are expected to have a sufficiently general validity, at least if sites in industrialized districts are considered.

4.4.3 – Inherent safety assessment of the production case study

The same five process options described in §4.4.1 were assessed for inherent safety by the approach defined in §2.2.3. The application of the procedure yields the values reported in table 4.4.2 that were briefly commented in the discussion of results for sustainability. In the following a few further details on the application of the procedure are reported. However, the attention is focused on only 2 options, for sake of brevity: option #1 (traditional with PSA) and #5 (integrated reactor).

The indices obtained from the assessment of the two options considered are reported in Table 4.4.6, that shows the equipment potential and inherent hazard indexes calculated for the alternative processes considered in the analysis. The table also reports the overall indexes calculated for the two alternatives.

	# 1	# 2	# 3	# 4	# 5
Global Warming	1.3 %	1.5 %	2.0 %	2.0 %	2.1 %
Rain Acidification	< 0.1 %	< 0.1 %	< 0.1 %	< 0.1 %	< 0.1 %
Air Toxicity	2.9 %	< 0.1 %	3.4 %	2.7 %	3.2 %
Solid waste disposal	< 0.1 %	< 0.1 %	< 0.1 %	< 0.1 %	< 0.1 %
Natural gas	19.8 %	24.9 %	23.4 %	23.2 %	26.4 %
Electric power	< 0.1 %	0.2 %	< 0.1 %	< 0.1 %	< 0.1 %
Inherent Safety	< 0.1 %	0.1 %	< 0.1 %	0.1 %	0.2 %
Environmental impact	74.4 %	69.2 %	71.0 %	71.7 %	53.5 %
Societal impact	1.5 %	4.2 %	< 0.1 %	0.2 %	14.5 %

Table 4.4.5: Contribution (%) of the weight factors to the variance of the overall index.

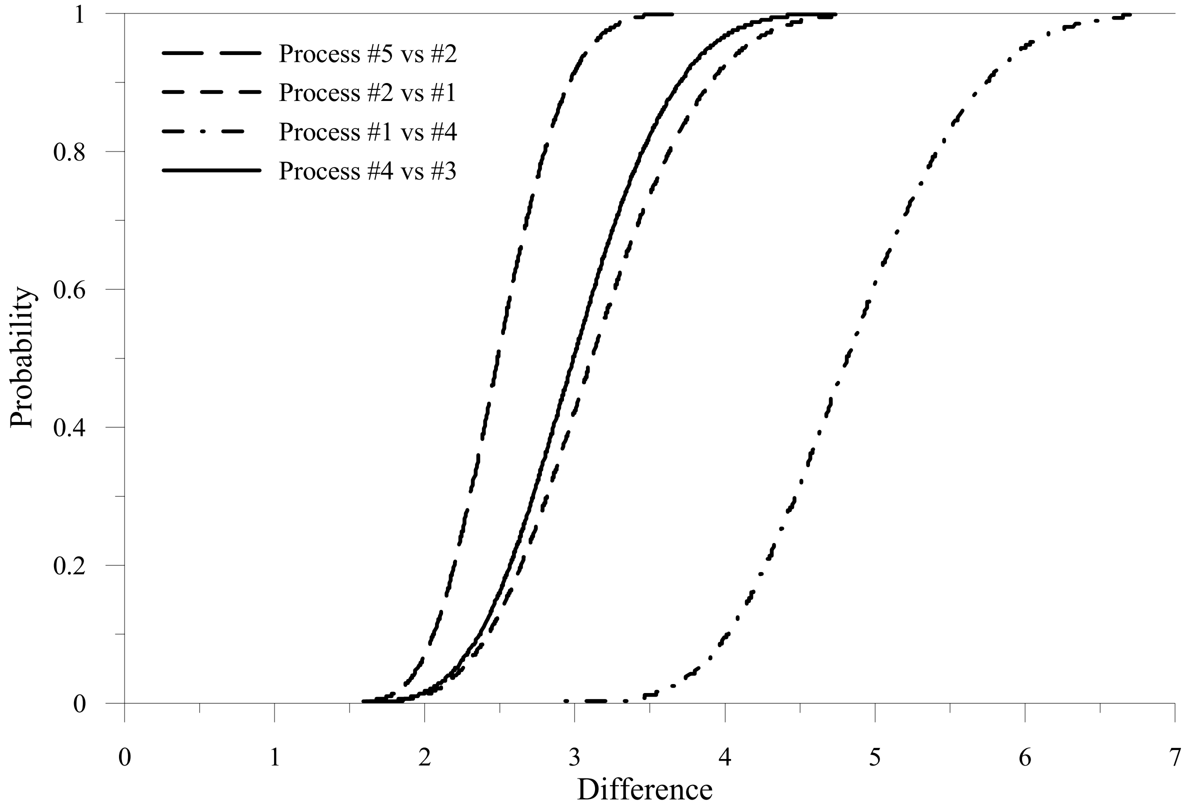


Figure 4.4.5: Distribution of cumulative probabilities for the difference between the overall sustainability indices of selected couples of alternative processes.

#1 – traditional with PSA				#5 - integrated reactor			
		UHI$_k$ (m^2/y)	**UPI$_k$ (m^2)**			**UHI$_k$ (m^2/y)**	**UPI$_k$ (m^2)**
R1	hydrodesulfuration	3.1x10^{-2}	4.6x10^{3}	R1	hydrodesulfuration	2.3x10^{-2}	2.5x10^{3}
R2	H_2S adsorption	3.1x10^{-2}	4.6x10^{3}	R2	H_2S adsorption	2.2x10^{-2}	2.5x10^{3}
R3	reforming reactor	1.7x10^{-1}	9.6x10^{3}	R3	membrane reactor	1.0x10^{-2}	2.0x10^{3}
R4	water-shift reactor	3.7x10^{-2}	6.0x10^{3}	C2	hydrogen compressor	1.8 x10^{0}	7.5x10^{2}
D3	spray quencher / water mixer	3.2x10^{-2}	4.9x10^{3}	D1	water separator	1.0x10^{-2}	1.9x10^{3}
D4	water separator	5.3x10^{-2}	8.4x10^{3}	E1	methane heater	3.4x10^{-1}	4.3x10^{3}
D5-8	PSA beds battery	1.4x10^{-2}	7.0x10^{2}	E2	hydrogen cooling	3.9x10^{-1}	7.5x10^{2}
D9	hydrogen buffer	3.6x10^{-3}	4.9x10^{3}	E3	syn-gas cooler	9.6x10^{-2}	1.9x10^{3}
D10	off-gas buffer	2.0x10^{-3}	3.8x10^{3}	E6	syn-gas cooler	9.4x10^{-2}	7.5x10^{2}
E1	methane heater	4.7x10^{-1}	7.0x10^{3}	C1	turbogas	5.0x10^{-2}	2.8x10^{3}
E2	syn-gas cooler	4.0x10^{-1}	6.2x10^{3}				
E3	syn-gas cooler	4.4x10^{-1}	7.1x10^{3}				
E4	syn-gas cooler	1.6x10^{-1}	6.2x10^{3}				
		HI	**PI**			**HI**	**PI**
		1.9x10^{0}	7.4x10^{4}			2.8x10^{0}	2.0x10^{4}

Table 4.4.6: Values of unit and overall inherent safety key performance indicators for the alternative processes considered in the analysis.

The reforming reactor is outlined as the most potentially dangerous unit. On the other hand, the adoption of the membrane technology in option #5 proved to be effective in limiting the maximum possible consequences of release scenarios. Due to the unconventional nature of this piece of equipment, a FMEA was performed, indicating that the unit is extremely unlikely to cause LOC events resulting in high damage areas. Focusing on UHIs, the heat exchangers generally resulted among the more inherently hazardous units, having severe scenarios associated to rather high credit factors. However, the hydrogen compressor of option #5 is the unit that has the higher value for UHI, despite of the low UPI value, due to the effect of credit factors.

If the overall indexes are considered, option #1 results the worst with respect to the potential hazard index. If credit factors are considered, the high equipment inherent hazard index of the compressor in option #5 causes the overall inherent hazard index (PI) to be higher. Thus, the application of the method yields two important pieces of information for the further development and/or the selection among alternatives: on one hand, the potential hazards of alternative #1 are higher; on the other, a safety critical unit is present in alternative #5.

4.4.3.1 – Comparison of the results with inherent safety assessment methods from the literature

The case studies were also analysed using literature methodologies for inherent safety assessment. In particular, the following methods were considered:

- Prototype Index of Inherent Safety (PIIS) proposed by *Edwards & Lawrence, [1993]*;
- Inherent Safety Index (ISI) proposed by *Heikkilä et al., [1996, 1998, 1999]*;
- Potentials Danger for safety in Environmental Safety and Health (ESH) by *Koller et al., [2000]*.
- Tools I and J of INSET Toolkit (INSET) *[INSIDE, 2001]*;
- Safety Weighted Hazard Index (SWeHI) by *Khan at al., [2001]*;
- Integrated Inherent Safety Index (I2SI) by *Khan & Amyotte, [2004,2005]*;
- Dow Fire and Explosion Index (F&EI) *[Dow, 1994]*;
- Dow Chemical Exposure Index (CEI) *[Dow, 1993]*.

The comparison of the results obtained by the methods listed above required some further assumptions. In particular, some methods (e.g. ESH, INSET) yield unaggregated indexes for specific types of unit hazards. Thus, additional assumptions were necessary to obtain overall aggregated indexes: in accordance with the literature, the maximum expected values and an equal weight of the indexes were considered in normalization and aggregation *[INSIDE, 2001; Koller et al., 2001]*. Whenever unaggregated indexes are expressed in terms of damage distance (Dow F&EI, Dow CEI) the use of the higher distance was preferred, in accordance with the approach suggested by the SWeHI method *[Khan at al., 2001]* and by the methodology developed in the present paper. Furthermore, several methods do not define clear and homogeneous procedures to calculate the material quantities to be considered in the unit assessment, requiring specific assumptions to limit potential biases in results. Since the indexes calculated by the different methods have different scales, the index values reported in Figure 4.4.6 were normalized dividing them by the higher value obtained for each methodology. In the case of I2SI, that has a higher value for an inherently safer option, the inverse of the index was considered for normalization.

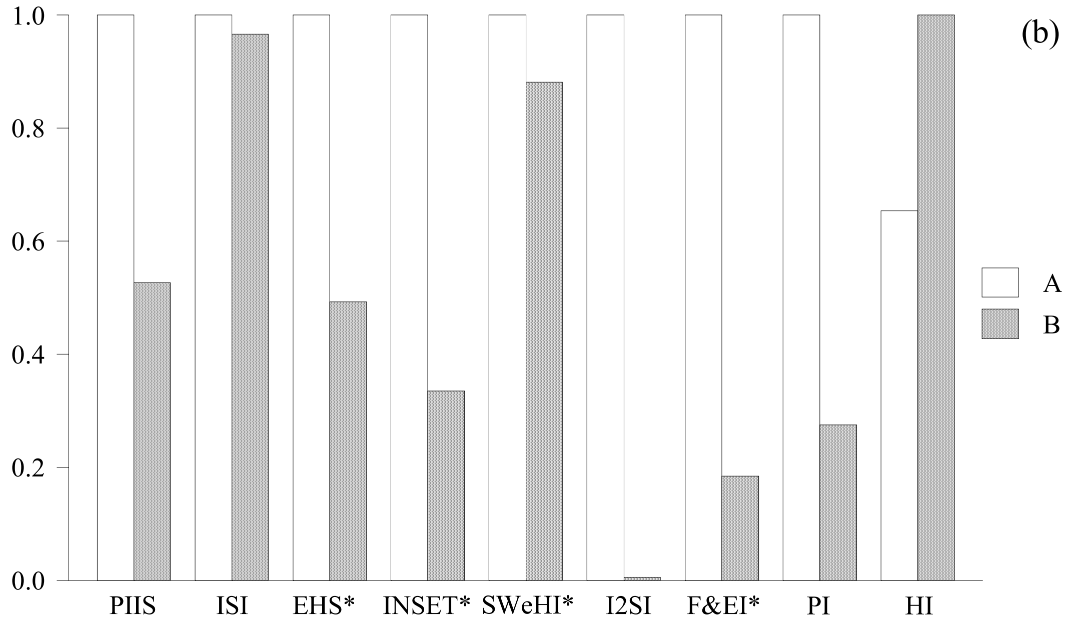


Figure 4.4.6: Comparison of the overall inherent safety indexes calculated by different methods (see text) for two of the processes considered for hydrogen production: A: #1 - traditional with PSA, B: #2 - integrated reactor. (*) Aggregation was obtained by the assumptions discussed in the text.

Figure 4.4.6 shows the comparison of the overall inherent safety indexes calculated by different methods for all the case studies considered. The results evidence that also the values of the overall indexes largely differ among the different methods. The differences are likely to arise both from the different level of detail required by the application of the method (see Table 2.1.1) and by the different penalization factors considered in the methods.

The application of PIIS, that requires to consider reforming and shift reaction as two independent steps, results in the penalization of option #1. The application of the more detailed indexes (EHS, INSET, SWeHI and F&EI) is influenced by the absence of explicit rules for the definition of material quantities to be considered in the analysis, since all the process are based on gas phase streams and the unit inventories are generally low. However, almost all the approaches identify as more hazardous the process alternatives having the higher material inventories. The values of the PI index obtained by the proposed approach show a similar behaviour with respect to most of the other indexes. However, the analysis of each single unit allows the identification of important differences related to the ability of the proposed method to take into account specific features and release modes of the units. Moreover, credit factors derived from equipment safety scores are not considered by the majority of the other tools.

The results reported above allow some general conclusions to be drawn. No coherence exists among the available methods for the quantitative assessment of inherent safety. Several factors are responsible of the disagreement in the results, evidenced in Figure 4.4.6. In particular, the detail of information required for the application of each method influences the results: thus procedures based on general data do not allow a detailed hazard identification. Moreover, subjective assumptions on material quantities resulted a significant issue for the reliability of some literature methods. Furthermore, not all the tools attribute the same importance to different potential hazard factors. These elements, if added to built-in assumption and to some degree of freedom left to the experience of the analyst, may well justify the differences in the results obtained.

As expected, the results obtained for the overall potential hazard index (PI) are in line with those obtained using the more detailed methods proposed in the literature (e.g. EHS, SWeHI), since in the methodologies considered the potential severity of the scenarios as the prevailing factor in the analysis. On the other hand, the inherent safety hazard index (HI) introduced in the present study, adds further details to the results, accounting for the recorded safety scores of the different equipment items, thus taking into account the hazards coming from auxiliary equipment, as compressors, filters, and heat exchangers, that are often overlooked in conventional severity-based inherent safety assessment methods.

4.4.4 – Storage case-study description

Hydrogen storage represents a well-known and widely investigated technological problem. Due to the physical and chemical properties of this substance, conventional storage processes have to manage critical operating conditions: high pressures are required by pressurized storages (tens of MPa), while liquefied storage needs lower temperatures than other cryogenic processes (a few tens of Kelvin) *[Conte et al., 2004; Zhou, 2005; Takeichi et al., 2003; Domashenko et al., 2002. Mitlitsky et al., 2001]*. Moreover the flammability limits are wider and the ignition energy is much lower than that of other flammable substances *[Cadwallader et al., 1999]*. Thus, several innovative technologies were proposed for hydrogen storage. Examples are the adsorption on metals or the storage as a complex hydride *[Conte et al., 2004; Zhou, 2005; Takeichi et al., 2003; Hagstrom et al., 1995]*.

Since different technologies are suitable for different potentialities of storage, three different “sizes” were explored in the study, namely “small”, “medium” and “large” scale applications. These were defined on the basis of the analysis of technical literature *[Conte et al., 2004; Zhou, 2005; Takeichi et al., 2003; Domashenko et al., 2002. Mitlitsky et al., 2001; Hagstrom et al., 1995]* and of available commercial datasheets.

- **“Small scale”** storages are needed in innovative automotive applications. A 5 kg storage was considered, supplying gaseous hydrogen at a fuel cell engine operating at low pressure (e.g. 0.3 MPa).
- **“Medium scale”** storages will be required in hydrogen refuelling stations. In several preliminary and demonstrative plants the storage unit contains about 500kg of hydrogen. In these applications, hydrogen is supplied to the user at 35 MPa. Thus, a compression unit is also required.
- **“Large scale”** applications are used in current industrial application, including hydrogen production and supply in oil refineries. On the basis of literature data, a bulk storage of 27t of hydrogen was considered in the analysis. In order to have a correct overview of the hazards related to the alternative technologies, the storage facilities were considered coupled with the necessary “upstream” operations (e.g. the liquefaction unit for liquefied storage).

Four alternative storage techniques were considered in the case-studies:

i) storage of hydrogen gas under pressure;

ii) storage of liquefied hydrogen;

iii) storage as a metal hydride;

iv) storage as a complex hydride.

These were indicated in the literature as the more effective and competitive technologies for the future development of hydrogen storage processes *[Browning et al., 1997; Aiello et al., 1999; Mahmut & Kaplan, 2001]*. The present stage of development of these four technologies is quite different *[Conte et al., 2004; Zhou, 2005; Takeichi et al., 2003; Browning et al., 1997; Aiello et al., 1999; Mahmut & Kaplan, 2001]*. In particular, technologies based on compressed gas and liquefied cryogenic storage are currently used worldwide for large scale applications, such as refineries or chemical plants *[Browning et al., 1997; Aiello et al., 1999]*. On the other hand, technologies based on metal and complex hydrides are still under development but are indicated as possible safer alternatives *[Browning et al., 1997; Mahmut & Kaplan, 2001]*.

Table 4.4.7 reports the main features and the stage of technology development for the different scale hydrogen storage processes considered. In the case of storage based on metal or complex hydrides, some data in the table were estimated on the basis of the characteristics of the available pilot applications.

Scheme	**Features**	**Small scale**	**Medium scale**	**Large scale**
Compressed	Technology	Commercial	Commercial	-
	Pressure (MPa)	40	25	-
	Temperature (K)	300	300	-
	H_2 mass stored per unit (kg)	2.5	35.7	-
	Number of units	2	2 tube trailers (7 units each)	-
Cryogenic	Technology	Research	Commercial	Commercial
	Pressure (MPa)	0.6	0.6	1.7
	Temperature (K)	20/25	20/25	20/25
	H_2 mass stored per unit (kg)	5	500	13500
	Number of units	1	1	2
Metal Hydride	Technology	Commercial	Research	-
	Pressure (MPa)	1.1	1.1	-
	Temperature (K)	300	300	-
	H_2 mass stored per unit (kg)	1	105	-
	Number of units	5	5	-
Complex Hydride	Technology	-	Research	Research
	Pressure (MPa)	-	0.1	0.1
	Temperature (K)	-	300	300
	H_2 mass stored per unit (kg)	-	500	13500
	Number of units	-	1	2

Table 4.4.7: Stage of development and main features of different scale hydrogen storage systems.

Reference schemes were defined for the storage technologies considered in the present study. Figures 4.4.7 to 4.4.9 report the reference schemes defined for the different technologies and the different scales considered in the assessment on the basis of literature data and of available information on existing hydrogen storage plants. The symbols used to identify the units in the figures are explained in table 4.4.10.

"Small scale" storages are devoted to automotive applications. The PFDs for the proposed technologies are reported in figure 4.4.7. A 5 kg storage on board was considered for all the alternative technologies, supplying gaseous hydrogen at a fuel cell engine on the vehicle. The fuel cell operating pressure was supposed to be 0.3 MPa, which is a typical operating condition for these equipment items. In the case of the gaseous storage (figure 4.4.7-(a)), the high pressure hydrogen is delivered from the cylinders D1 and D2 by pressure gradient. In the case of the liquefied storage at 25 K (figure 4.4.7-(b)), an electric vaporizer E1 provides low pressure gaseous hydrogen. Finally, in the case of the metal hydrides storage, a battery of 5 reactors (D1-D5) is used, each containing up to 1kg hydrogen via adsorption on a specific metal support (figure 4.4.7-(c)). An organic oil is used as a thermal vector, both to provide and subtract heat from the bulk storage unit in the different operating conditions. In the loading phase, the adsorption heat is removed and the oil is cooled in the E2 heat exchanger. In the discharging phase, the oil heated in E1 heat exchanger, provides the desorption heat to the storage unit. The released hydrogen is stored in a pressurized buffer D6.

"Medium scale" storages are mainly developed in the perspective of application to hydrogen refuelling stations. In most applications, the storage unit is supposed to contain about 500 kg of hydrogen, stored using different alternative technologies. In the case of the gaseous storage technology, the bulk storage was considered at on operating pressure of 25 MPa (figure 4.4.8-

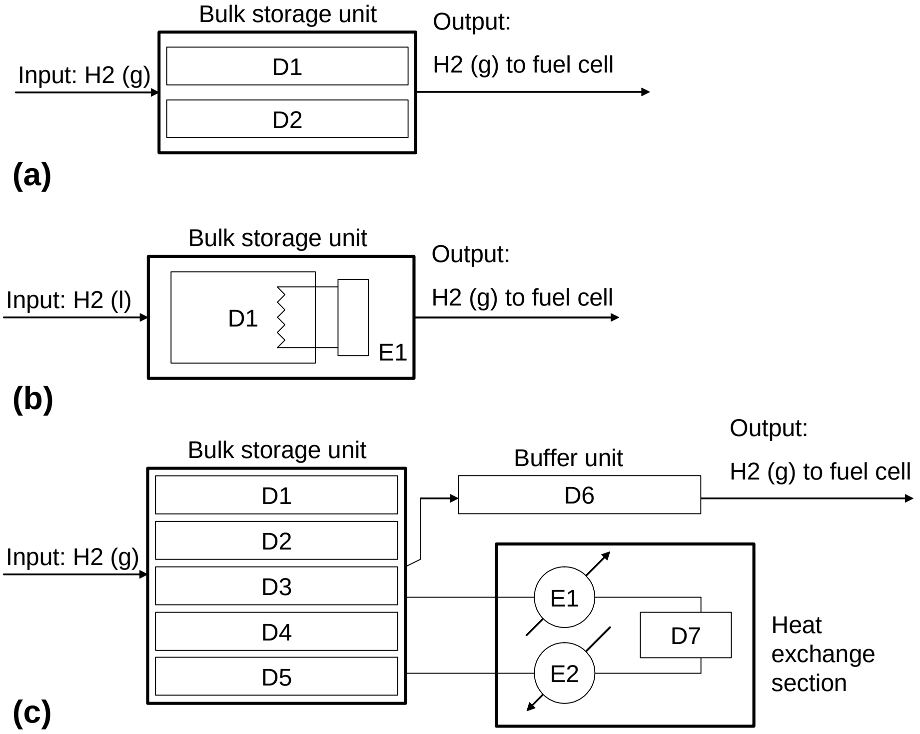


Figure 4.4.7: Small scale hydrogen storage processes: reference schemes considered in the analysis. (a) Compressed, (b) cryogenic and (c) metal hydrides storage technologies.

(a)) with 2 commercial tube trailers (D1 and D2). Each trailer was considered as composed of 6 pressurized cylinders, each containing about 40kg of hydrogen. Since for the refuelling of the next generation hydrogen vehicles high pressures will be required, a compressor (K1) coupled with a buffer storage unit (D3-D13) is needed, providing gaseous hydrogen at 35 MPa.

In the case of the cryogenic storage (figure 4.4.8-(b)), hydrogen is stored at 20-25 K at moderate pressure (0.6 MPa). An external finned tubes heat exchanger (E1) is needed to provide gaseous hydrogen. Also in this case, the coupled compression (K1) - high pressure buffer (D2-D12) units are needed.

The medium scale reference scheme for metal hydrides storage technology (figure 4.4.8-(c)) was based on the same principle of the small scale scheme. Each unit was supposed to store up to 100 kg hydrogen by adsorption on metal hydrides. In the discharge phase, hydrogen is released at low pressure (about 1.1 MPa) and compressed as in previous cases.

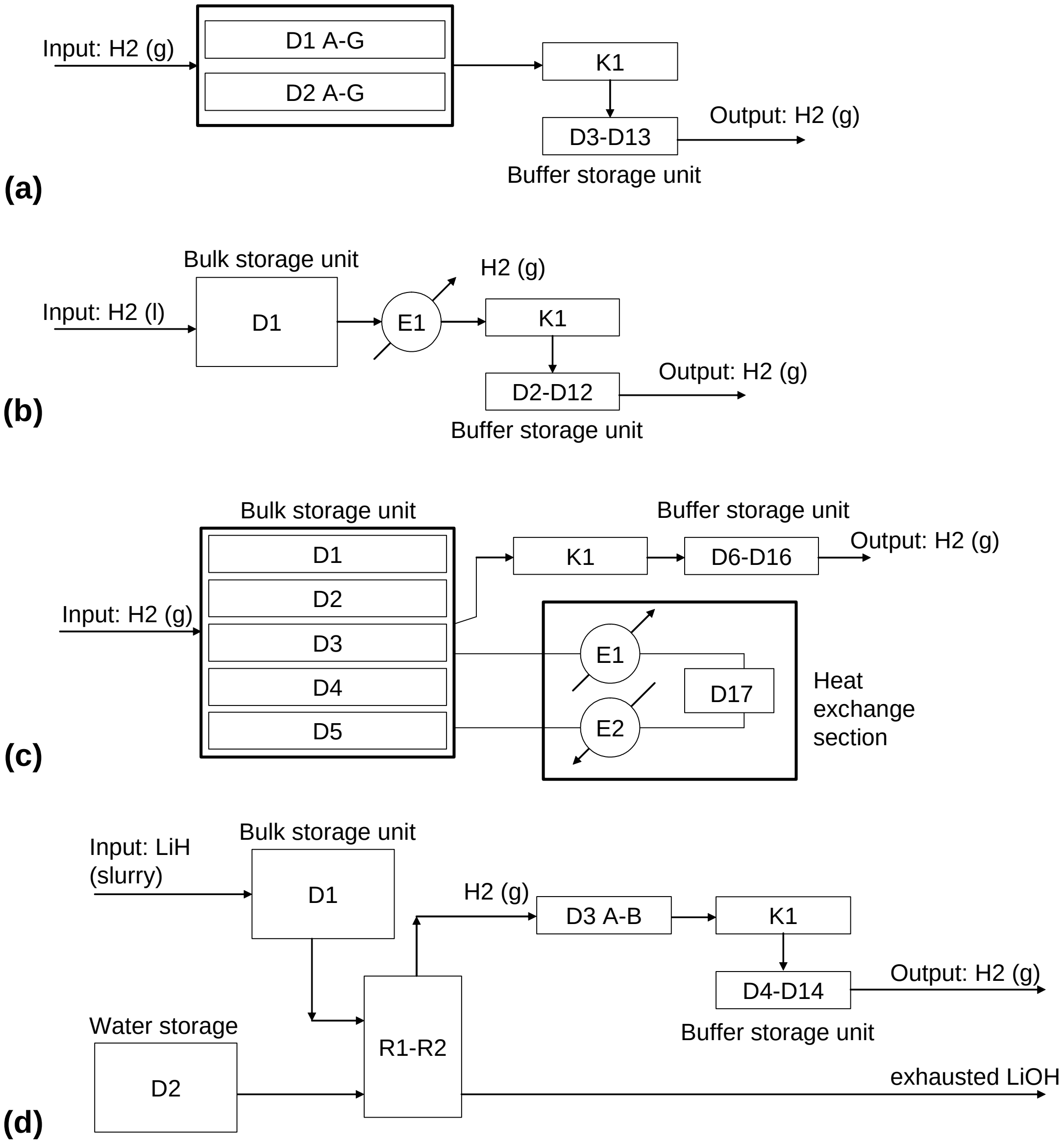


Figure 4.4.8: Medium scale hydrogen storage processes: reference schemes considered in the analysis. (a) Compressed, (b) cryogenic, (c) metal hydrides and (d) complex hydrides storage technologies.

The medium scale reference scheme for hydrogen storage on complex hydrides (figure 4.4.8-(d)) consists in three main sections: i) a bulk storage unit for the hydride, at atmospheric pressure and ambient temperature; ii) a reaction section, in which the gaseous hydrogen is produced; and iii) a compression and buffer storage unit. The hydride is dispersed in a mineral oil in order to prevent the contact with moisture, which may cause unwanted hydrogen release. In the reaction section, the slurry is mixed with water and gaseous hydrogen is released via hydrolysis. Gaseous hydrogen is then compressed (K1) and sent to the high pressure buffer (D4-D14). Two semi-batch reactors are supposed to work alternatively, in order to allow continuous supply of hydrogen to the compression unit.

In "large scale" reference schemes, also auxiliary sections were considered in order to obtain a correct representation of the expected safety performance of the process. Thus, a

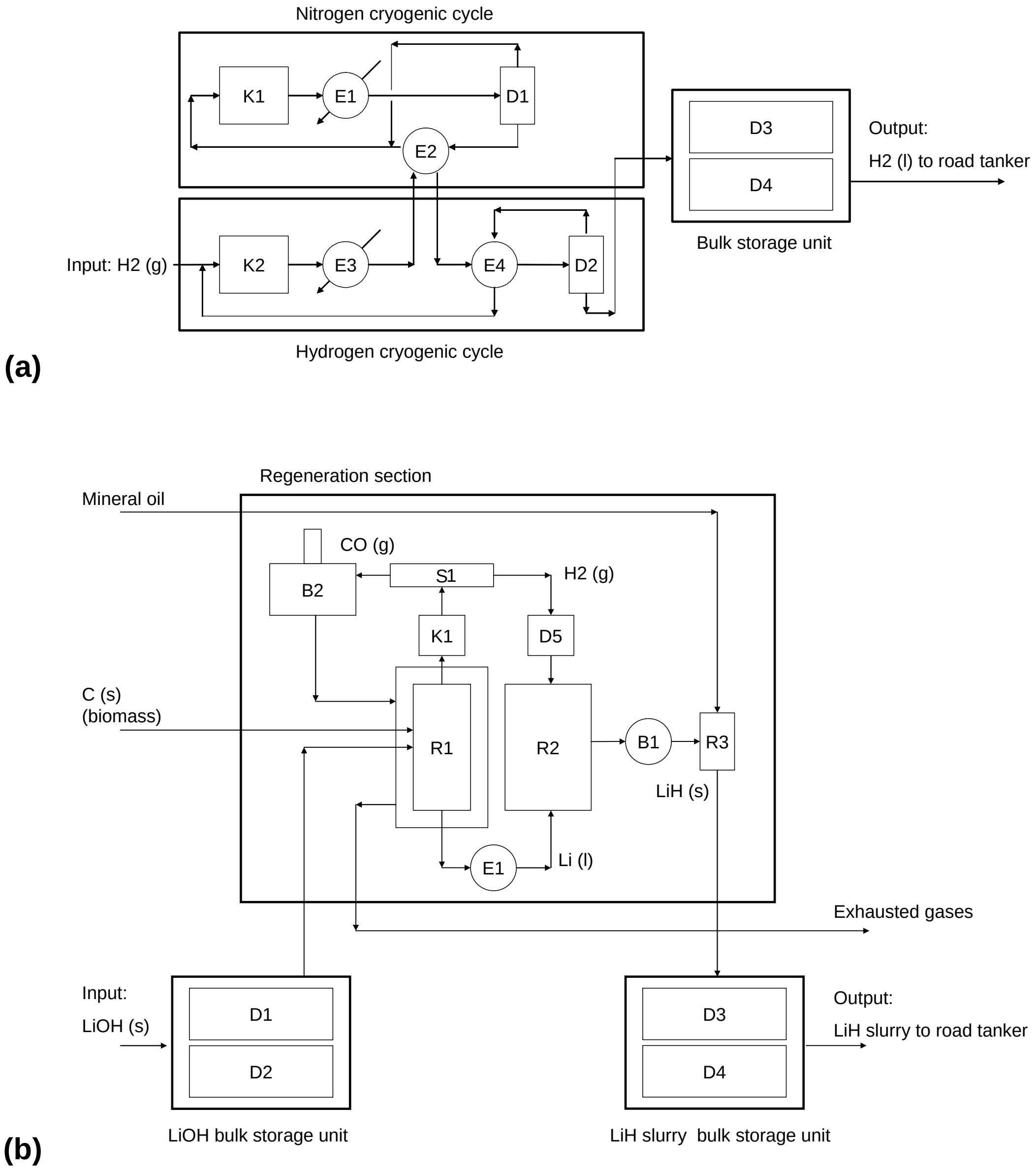


Figure 4.4.9: Large scale hydrogen storage processes: reference schemes considered in the analysis. (a) Liquefied and (b) complex hydrides storage technologies.

liquefaction section was considered together with cryogenic storage, and a hydroxide regeneration section was associated to the complex hydrides storage.

In large scale cryogenic storage reference scheme (figure 4.4.9-(a)), a double tank bulk storage unit (D3 and D4) was considered, containing 27 t of liquid hydrogen at 1.7 MPa and 20-25 K. The liquefaction process is characterized by the coupling of two cycles, respectively for nitrogen and hydrogen liquefaction. In each cycle, the gas is compressed (compressors K1 and K2 respectively), then cooled (heat exchangers E1-E4) and finally expanded and liquefied. The liquid is separated from the vapour in a buffer flash chamber (respectively D1 and D2), and the vapour is recycled to the compressor.

Also in the case of the complex hydrides reference scheme (figure 4.4.9-(b)), two large tanks (D3 and D4) were considered for the bulk storage, containing 90t of hydride slurry, equivalent to 27 t of hydrogen. A LiH slurry with mineral oil was considered as a support for hydrogen storage. The hydrogen release section is the same illustrated for the medium scale storage. In the regeneration section, carbon based material (e.g. biomass) is mixed with the exhaust hydroxide supplied from the exhaust storage (D1 and D2 tanks). In a decomposition reactor (R1), the reduction of the hydroxide was considered. The gases formed are extracted and compressed (K1). Hydrogen is separated via membrane separation (S1) and coupled in the mixer R2 with the liquid lithium coming from R1 to give the regenerated hydride, which is separated (B1) and mixed with the mineral oil (R3). The heat necessary is provided by the combustion of auxiliary fuel and waste carbon monoxide gas coming from S1 in burner B2.

4.4.5 – Inherent safety assessment of the storage case-study

4.4.5.1 – Small scale

Table 4.4.8 reports the damage distances, the escalation distances and the credit factors assessed for the “small scale” reference schemes.

The unit potential index was directly obtained from the data in table Table 4.4.8 selecting the maximum damage distance for each unit, while the unit hazard index was calculated applying equations(2.3.3) and (2.3.4) to the same data. The results obtained are reported in table 4.4.10. As shown in the table, in all the alternative schemes considered the hydrogen bulk storage is the unit that shows the higher value of the unit potential index, UPI. On the other hand, the introduction of credit factors in the analysis penalizes the presence of equipment items that may origin more easily LOC events. Thus, as shown in table 4.4.10, in the case of metal hydrides the higher values of the unit hazard index, UHI, were obtained for the shell&tube heat exchangers.

Table 4.4.9 shows the values calculated for the overall potential and hazard indexes, PI and HI. The table evidences that the highest potential hazard index PI was obtained for the compressed gas storage, while the introduction of credit factors results in a penalization of the cryogenic technology, that results associated to the highest value of the hazard index, HI.

Figure 4.4.11-(a) reports a comparison among the normalized values of the potential and hazard indexes calculated for the alternative technologies. The radar plot allows an effective comparison among the expected safety performance of the alternative technologies. As shown in the plot, metal hydride technology shows the best expected safety performances. Compressed storage is the technology associated to the higher potential hazards. On the other hand, if credit factors are considered, liquefied storage is penalized, while compressed storage and metal hydrides are expected to have similar performances. This result is caused by the high credit factors associated to LOC events from auxiliary units, in particular heat exchangers, present in the metal hydrides scheme. These factors increase the overall hazard

index associated to the technology, that results comparable to that of compressed storage, even if the UPI and UHI values of the bulk storage are much lower for metal hydrides than for compressed storage, as shown in figure 4.4.11-(a).

It must be remarked that the values of the credit factors used in the present study are derived from available literature data based on the analysis of standard equipment performances. Thus, in particular in the case of technologies still under development, as metal hydrides, the actual values of these factors in a future industrial application may be different, since specific equipment with improved safety performances may be used. Nevertheless, the results obtained evidence that in the perspective of an industrial implementation of this technology, the reliability of the auxiliary equipment will be an important issue to be addressed.

Scheme	**Unit**	**LOC**	**Scenario**	$cf_{i,k}$	$d_{i,j,k}$ **(m)**
Compressed	D1-D2: Bulk storage tanks	R1	JF	$1x10^{-5}$	40.1
			VE	$1x10^{-5}$	18.2
			FF	$1x10^{-5}$	18.3
		R2	JF	$5x10^{-7}$	<5.0
		R3	FB	$5x10^{-7}$	21.0
			VE	$5x10^{-7}$	41.0
			FF	$5x10^{-7}$	7.5
Cryogenic	D1: Bulk storage tank	R1	JF	$1x10^{-4}$	24.4
			VE	$1x10^{-4}$	29.4
			FF	$1x10^{-4}$	22.4
		R2	JF	$5x10^{-6}$	<5.0
			FF	$5x10^{-6}$	<5.0
		R3	FB	$5x10^{-6}$	20.1
			VE	$5x10^{-6}$	23.4
	E1: electric vaporizer	-	-	-	
Metal hydrides	D1-D5: Bulk storage tanks	R1	JF	$1x10^{-3}$	5.9
			FF	$1x10^{-3}$	5.6
		R2	JF	$5x10^{-5}$	<5.0
			FF	$5x10^{-5}$	<5.0
		R3	FB	$5x10^{-5}$	6.5
			VE	$5x10^{-5}$	18.6
	D6: gas dispenser	R1	JF	$1x10^{-5}$	7.6
			FF	$1x10^{-5}$	<5.0
		R2	JF	$5x10^{-7}$	<5.0
		R3	FB	$5x10^{-7}$	12.4
			VE	$5x10^{-7}$	9.2
			FF	$5x10^{-7}$	<5.0
	D7: Oil buffer tank	R1	PF	$1x10^{-5}$	5.9
			FF	$1x10^{-5}$	6.1
		R2	FF	$5x10^{-7}$	5.8
		R3	FF	$5x10^{-7}$	5.9
	E1: heat exchanger	R4	PF	$1x10^{-3}$	7.3
			JF	$1x10^{-3}$	8.5
		R5	PF	$1x10^{-4}$	6.5
	E2: heat exchanger	R4	PF	$1x10^{-3}$	7.1
			JF	$1x10^{-3}$	8.1
		R5	PF	$5x10^{-4}$	5.9

Table 4.4.8: Small scale hydrogen storage schemes: calculated damage distances ($d_{i,j,k}$) and credit factors ($cf_{i,k}$) for each scenario (i) of each LOC (j) considered for each process unit (k). For LOC and scenario definition, see table §2.3.

4.4.5.2 – Medium scale

The values calculated for the unit potential and hazard indexes of "medium scale" reference schemes are shown in table 4.4.10. The results evidence that, as in the previous case, the hydrogen bulk storage is the unit associated to the higher values of the potential index in all reference schemes, with the exception of that based on metal hydrides. In this case, the buffer tanks containing pressurized hydrogen show higher potential indexes than the bulk storage, due to the higher expected safety performance of bulk storage based on metal hydrides.

If the unit hazard indexes are compared, the hydrogen compressor always results the more hazardous unit. The credit factors related to this equipment item are particularly high, even if the damage distances are rather low with respect to those obtained for the bulk storage units. Thus, the compression units result the more critical with respect to inherent safety. Again, this is due to the importance given to the credit of LOC events in the unit hazard index (credit factors).

Table 4.4.9 reports the values of the overall indexes. The table evidences that the overall potential hazard index PI results higher for commercial technologies (compressed and liquefied storages) than for the innovative ones based on metal and complex hydrides. This is mostly due to the contribution of the bulk storage unit, and is caused by the more severe operating conditions of this unit, that may result in worst consequences of the possible LOC events. From the point of view of inherent safety principles, these outcomes were expected, since the innovative technologies are examples of application of the principles underlying the "substitution" and "moderation" guidewords. On the other hand, the higher values of the overall inherent hazard index HI were obtained for metal hydride and liquefied storage systems, while the HI value for compressed storage resulted lower and comparable to that obtained for the chemical hydride system. A key issue that influences the values of the overall hazard index is the plant complexity, in terms of auxiliary equipments and secondary units. The innovative technologies, such as hydride storages, need heat transfer utilities, while the process diagram of commercial compressed storage technologies is much simpler and a more limited number of units is present. The contribution of auxiliary equipment to the overall KPIs may be important, in particular if high credit factors are associated to LOC events from these units. As a matter of fact, the introduction of credit factors in the analysis penalizes more complex designs, or the use of equipment items that more easily may origin LOC events. In particular, high values of the credit factor associated to the LOC events considered were obtained for the shell&tube unit present in the metal hydride reference scheme and for the multilayer coated vessel considered for cryogenic storage.

The radar plot reporting the normalized values of the more significant hazard and potential indexes is shown in figure 4.4.11-(b). The figure evidences that chemical and metal hydrides are expected to have better safety performances than the more conventional technologies for hydrogen storage. Again, the similar values of the hazard indexes obtained for the compressed storage and of metal and complex hydrides technologies evidence the problem of the reliability of auxiliary equipment as a key factor in the development of alternative technologies for hydrogen storage.

In medium scale installations, escalation events may give an important contribution to the overall hazard. Figure 4.4.12 reports the values calculated for the domino potential and hazard indexes.

As shown in figure 4.4.12, cryogenic liquefied storage has very high values of both potential and hazard indexes, mainly due to the contribution of the hydrogen bulk storage. On the other hand, compressed storage has associated the higher potential index for domino effect, although credit factors are low, as shown in figure 4.4.12-(b). Besides, alternative technologies present also in this case lower potential indexes (figure 4.4.12-(a)) but, at the same time, the hazard indexes result influenced by the compression unit. As a matter of fact, the maximum domino unit hazard index, UHD, is connected to this piece of equipment in all the assessed technologies.

4.4.5.3 – Comparison with other literature methods at medium scale

Similarly to §4.4.3.1, the proposed method can be compared with the literature. For sake of brevity, an example concerning only two options for the medium scale storage is reported in the following (compressed and cryogenic storage). The literature methods considered and the assumptions in the analysis are the same as §4.4.3.1.

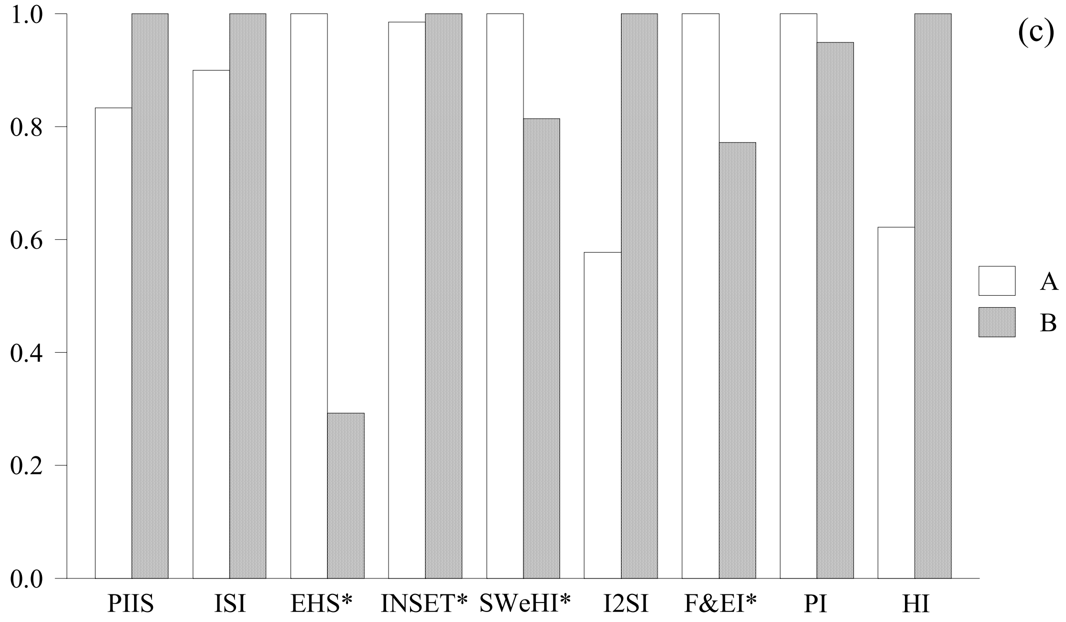


Figure 4.4.10: Comparison of the overall inherent safety indexes calculated by different methods for the medium scale storage: A, pressurized gas storage; B: liquid storage. (*) Aggregation was obtained by the assumptions discussed in the text.

Scheme	Small scale		Medium scale		Large scale	
	PI	HI	PI	HI	PI	HI
Compressed	1.3×10^{3}	1.7×10^{-2}	9.8×10^{3}	3.1×10^{-1}		
Cryogenic	6.0×10^{2}	1.3×10^{-1}	9.4×10^{3}	5.0×10^{-1}	1.7×10^{6}	1.4×10^{2}
Metal hydride	2.4×10^{2}	3.5×10^{-2}	3.2×10^{3}	4.9×10^{-1}		
Complex hydride			4.6×10^{3}	3.3×10^{-1}	1.8×10^{4}	6.8×10^{0}

Table 4.4.9: Overall inherent safety KPIs calculated for the for the four reference process schemes considered

Figure 4.4.10 shows the comparison of the overall inherent safety indexes calculated by different methods for all the options considered. A first remark that comes from the analysis of the figure is that there is no agreement in the results obtained by the different methods, both from a qualitative and a quantitative point of view. Again, the differences are likely to arise both from the different level of detail required by the application of the method and by the different penalization factors considered in the methods.

Scheme	**Small scale**			
	Unit	**Description**	**UPI**	**UHI**
Compressed	D1-D2	Bulk storage tanks	1.3×10^{3}	1.7×10^{-2}
Cryogenic	D1	Bulk storage tank	6.0×10^{2}	1.3×10^{-1}
	E1	Electric vaporizer	-	-
Metal Hydride	D1-D5	Bulk storage tanks	1.8×10^{2}	3.0×10^{-3}
	D6	Gas dispenser	5.5×10^{1}	1.0×10^{-4}
	D7	Oil buffer tank	1.1×10^{0}	2.0×10^{-5}
	E1	Heat exchanger	3.7×10^{0}	1.8×10^{-2}
	E2	Heat exchanger	3.4×10^{0}	1.4×10^{-2}
Scheme	**Medium scale**			
	Unit	**Description**	**UPI**	**UHI**
Compressed	D1-D2 (A-G)	Bulk storage tanks	7.3×10^{3}	1.8×10^{-2}
	D3-D13	Buffer storage tanks	1.4×10^{3}	1.9×10^{-2}
	K1	Compressor	1.1×10^{3}	2.7×10^{-1}
Cryogenic	D1	Bulk storage tank	6.8×10^{3}	2.0×10^{-1}
	D2-D12	Buffer storage tanks	1.4×10^{3}	1.9×10^{-2}
	E1	Vaporizer	9.4×10^{1}	1.5×10^{-2}
	K1	Compressor	1.1×10^{3}	2.7×10^{-1}
Metal Hydride	D1-D5	Bulk storage tanks	6.9×10^{2}	1.7×10^{-1}
	D7	Oil buffer tank	1.1×10^{1}	1.8×10^{-3}
	D6-D16	Buffer storage tanks	1.4×10^{3}	1.9×10^{-2}
	E1	Heat exchanger	5.5×10^{0}	1.8×10^{-2}
	E2	Heat exchanger	6.5×10^{0}	1.4×10^{-2}
	K1	Compressor	1.1×10^{3}	2.7×10^{-1}
Complex Hydride	D1	Bulk storage tank	1.5×10^{3}	3.5×10^{-2}
	D2	Water storage tank	-	-
	D3 (A-B)	Collector tank unit	5.5×10^{1}	5.0×10^{-5}
	D4-D14	Buffer storage tanks	1.4×10^{3}	1.9×10^{-2}
	R1-R2	Hydrolysis reactors	5.3×10^{2}	4.0×10^{-3}
	K1	Compressor	1.1×10^{3}	2.7×10^{-1}

Table 4.4.10 (Part1): Values of the unit KPIs calculated for the alternative storage technologies considered (small and medium scale)

Scheme	Large scale			
	Unit	**Description**	**UPI**	**UHI**
Cryogenic	D1	N_2 Buffer storage tank	-	-
	D2	Buffer storage tank	1.6×10^4	2.9×10^{-2}
	D3-D4	Bulk storage tanks	1.1×10^6	1.2×10^1
	K1	N_2 Compressor	-	-
	K2	Compressor	5.9×10^5	1.3×10^2
	E1	Heat exchanger	-	-
	E2	Heat exchanger	7.8×10^2	1.1×10^0
	E3	Heat exchanger	6.8×10^2	8.8×10^{-3}
	E4	Heat exchanger	7.3×10^2	5.6×10^{-2}
Complex Hydride	D1-D2	Hydroxide storage tank	-	-
	D3-D4	Bulk storage tanks	3.6×10^3	7.3×10^{-2}
	D5	Buffer storage tank	3.5×10^2	2.7×10^{-4}
	R1	Reactor for regeneration	3.1×10^3	1.8×10^{-2}
	R2	Reactor for hydride production	1.7×10^3	2.1×10^{-2}
	R3	Mixer	1.7×10^3	1.4×10^{-2}
	E1	Lithium cooler	-	-
	K1	Compressor	4.2×10^3	6.4×10^0
	B1	Rotating furnace	1.0×10^3	8.2×10^{-2}
	B2	Furnace	-	-
	S1	Membrane separator	2.0×10^3	2.1×10^{-1}

Table 4.4.10 (Part2): Values of the unit KPIs calculated for the alternative storage technologies considered (large scale)

The analysis with literature tools has to face the particular features of the process considered. Only a partial application of PIIS and ISI was possible, since no reactions are present in the case study. However, both methods penalize the option “cryogenic storage” due to the low temperatures. The other methods identify the storage as the critical unit, but the ranking varies among them. The results from EHS, SWeHI and F&EI, consider alternative cryogenic storage more inherently safe, due to the low hazard factors used for liquids, in agreement with the results obtained for the PI index, that takes into account the lower severity of cryogenic scenarios with respect to those deriving from the release of compressed hydrogen. The INSET method, that does not consider temperature and pressure differences, is not effective in the assessment. I2SI and HI agree in attributing a higher hazard score to cryogenic storage, since both these methods account for the lower safety performance expected from equipment handling liquid hydrogen. Nevertheless, it is worth to recall that this aspect is introduced in I2SI by an arbitrary scoring derivate by expertise.

The general conclusions that can be drawn from this example match the ones previously obtained: no coherence exists among the available methods, the detail of information required for the application of each method influences the results; subjective assumptions on material quantities are a significant issue for the reliability of the results; built-in assumption make assessment hard for non conventional units.

4.4.5.4 – Large Scale

Table 4.4.10 reports the values calculated for the two large scale hydrogen storage reference schemes considered in the present study. Table 4.4.10 evidences that in both processes the hydrogen bulk storage unit does not result the more critical item. Nevertheless, both the unit potential and unit hazard indexes are much lower for the chemical hydride bulk storage, as evidenced also in the radar plot reported in figure 4.4.11-(c). This is due to the inherently safer storage of hydrogen as stable hydride in solid phase in this technology. Thus, the results obtained for the bulk storage indexes are a concrete example of the effectiveness of the application of the "substitution" and "moderation" inherent safety guidewords for hazard reduction.

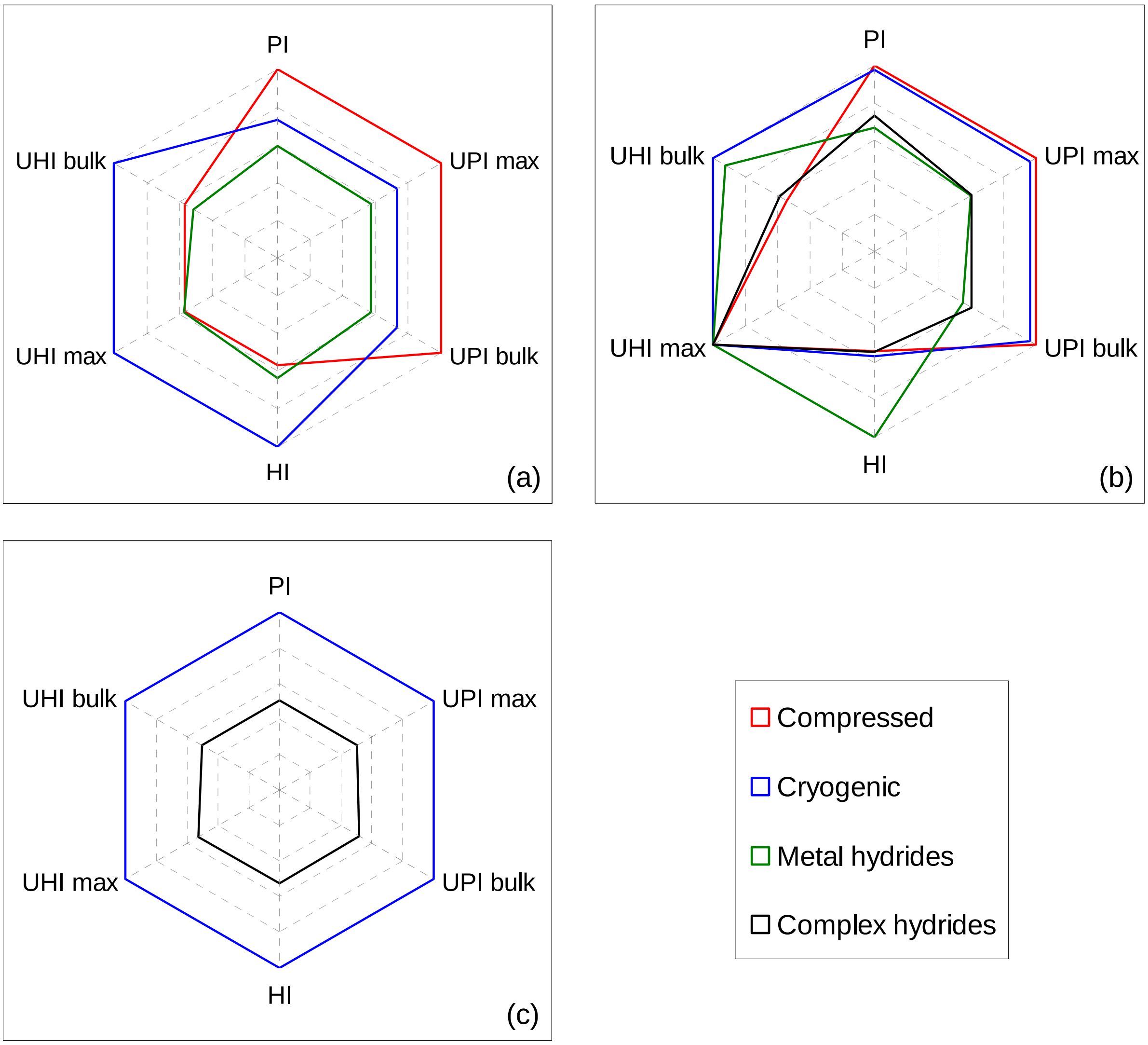
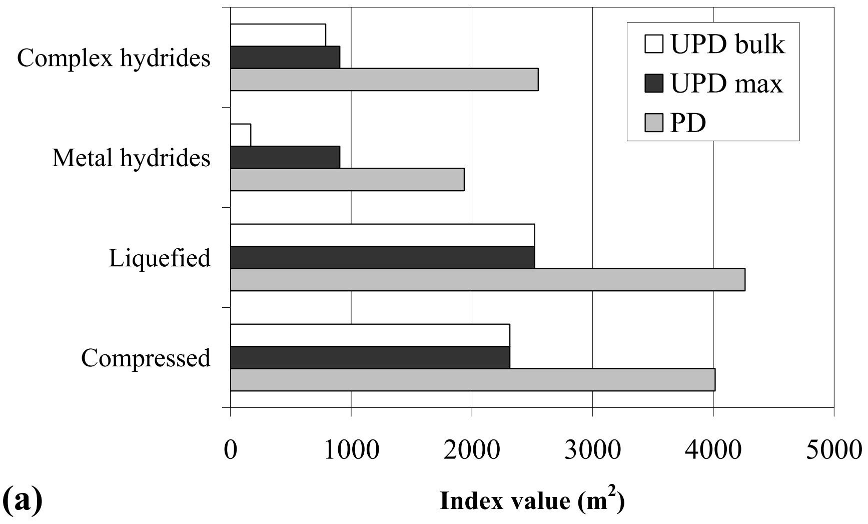


Figure 4.4.11: Normalized values of: overall potential hazard and inherent hazard indexes; unit potential hazard and inherent hazard indexes for the bulk storage unit; maximum unit potential hazard and inherent hazard indexes. (a) Small scale, (b) medium scale, and (c) large scale.

Also in this case, the most critical unit resulted the compression system for both alternatives. This unit is needed in the conventional process for hydrogen liquefaction and in complex hydrides storage for hydrogen gas delivery. As shown in table 4.4.10, in both alternatives the compression unit gives the more important contribution to both the potential and the hazard indexes.

The overall potential and hazard indexes reported in table 4.4.9 evidence that the expected safety performance of the complex hydrides large scale storage including the regeneration section results higher than that of conventional cryogenic liquid storage including a liquefaction section. As shown in table 4.4.9 and in figure 4.4.11-(c), both potential and inherent hazard indexes, PI and HI, evaluated for the cryogenic storage result about two orders of magnitude higher than in the alternative technology. Similar results were obtained for the escalation hazard, as shown in figure 4.4.13. The PD index evaluated for the cryogenic alternative is strongly influenced by the bulk storage unit while the HD index, that takes into account the credit factors, is penalized also in this case by the hydrogen compression unit. Similarly, the escalation hazard KPIs evaluated for the complex hydrides technology result



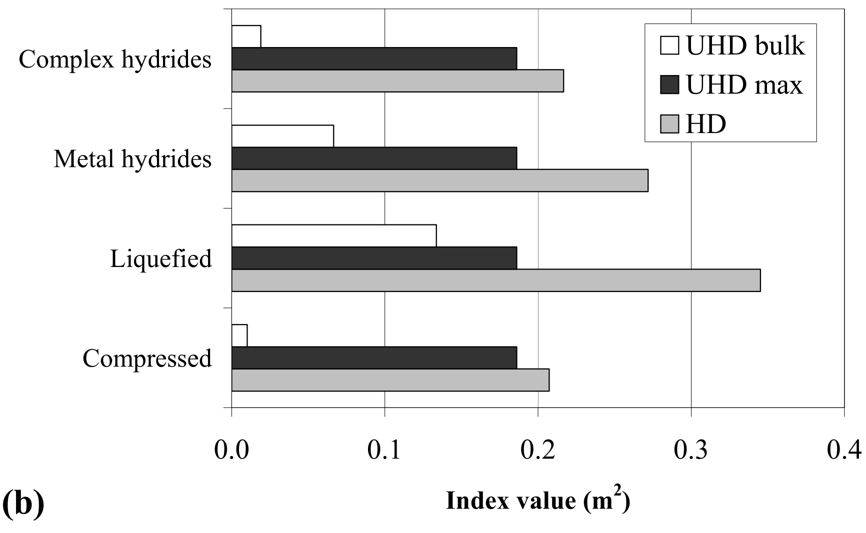
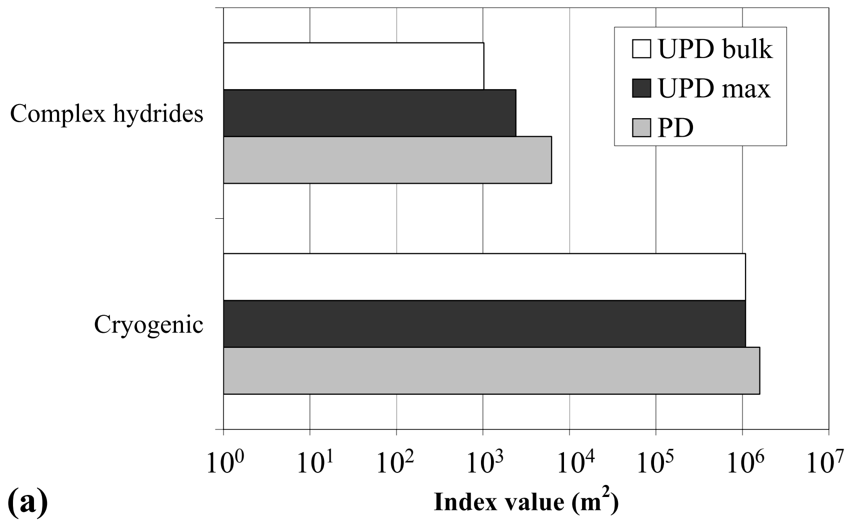


Figure 4.4.12: Medium scale hydrogen storage processes: overall, bulk storage and maximum unit values of domino potential (a) and inherent hazard (b) indexes.



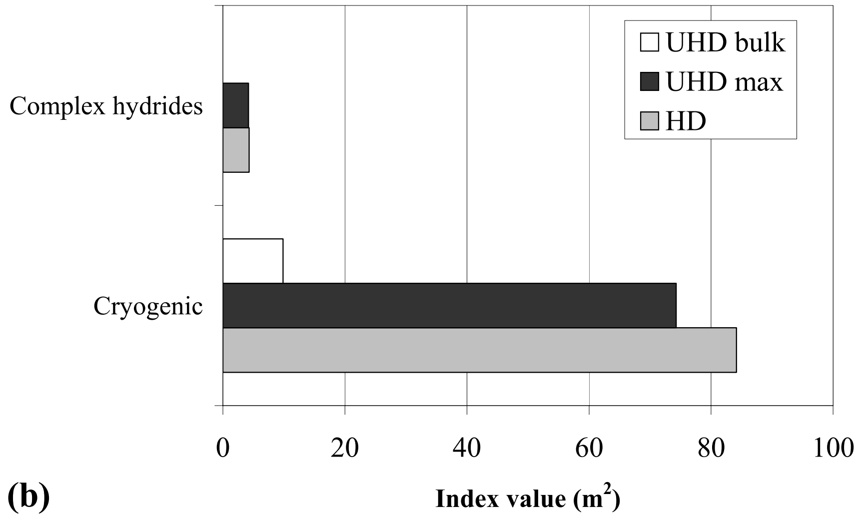


Figure 4.4.13: Large scale hydrogen storage processes: overall, bulk storage and maximum unit values of domino potential (a) and inherent hazard (b) indexes.

about two order of magnitude lower than those of the liquefied storage process. Is it worth to notice that in the case of escalation hazards, the contribution of the membrane separation unit (labelled as S1 in figure 4.4.9-(b)) to the overall index is much lower than in the case of hazards to humans, since the toxic dispersion of carbon monoxide is not taken into consideration as in the case of potential and inherent hazard indexes.

4.4.6 – Conclusions

In this chapter, the methods developed and presented in §1.2 and §2.3 were demonstrated by the application to case studies concerning industrial production and storage hydrogen. Several process options were compared, proving the applicability of the proposed methods in the various situations. The methodologies succeeded in evidencing the critical issues and the expected sustainability impact and inherent safety profile of alternative processes. Moreover it was possible to provide suggestions for improvement in the discussion of results. For inherent safety assessment comparison with literature methods was performed, evidencing that the proposed methodology, not only matches the expected results, but overrides several problems present in conventional approaches. All these elements prove the value of the developed methods.

In the analysis of the specific case studies, some key conclusions can be drawn:

- In the analysis of innovative technologies for hydrogen storage, evidenced as the potential hazard is always lower for the innovative technologies proposed (metal and chemical hydrides). This is mainly a consequence of the application of principles underlying the inherent safety “substitution” guideword, since in these alternative technologies hydrogen is stored as a less hazardous hydride. Moreover, metal hydrides and complex hydrides storage systems present less severe operative conditions than those of conventional technologies (inherent safety guideword “moderation”). Nevertheless, if the credit factors of LOC events are considered, based on standard equipment reliability data, the innovative technologies, and in particular metal hydrides storage, show lower safety performances than conventional storage processes. This is due to the more complex storage process (opposed to the guideword “simplification”), requiring a higher number of auxiliary units, and to the credit of LOC events in standard units as compressors or shell&tube heat exchangers. Thus, the results obtained evidence that in the perspective of an industrial implementation of these technologies, the reliability of the auxiliary equipment will be an important issue to be addressed.

- The comparative analysis of reference schemes for hydrogen production by steam reforming of natural gas evidenced that the *integrated reactor process (#5)* is expected to have the lowest impact on sustainability. The results were confirmed also for moderate variations of the reference parameters used in the analysis, as shown by a Monte Carlo approach. The *autothermal process (#2)* resulted the second best alternative with respect to sustainability, showing impacts slightly lower than the *traditional PSA (#1)* process. However it must be considered that the indexes calculated for both the *auto-thermal process (#2)* and the *integrated reactor process (#5)* receive a positive contribution from the allocation of part of the impacts to a co-product stream. Thus, the valorization of this by-product stream is an essential requirement to reduce the impact on sustainability of these processes. Among the other reference schemes, the *internal membrane separation (#3)* and the *external membrane separation processes (#4)* evidenced the lowest expected performances, due to the need to overcome limits in membrane separation efficiency. As expected, the consumption of raw materials, and in particular of natural gas, impacting on economic and environmental aspects, was identified as the most critical element influencing the sustainability performance of the different processes. Thus, the focus in proposing and developing innovative processes for hydrogen production from natural gas should be not only on the improvement of the reaction section, but also on the optimization of the overall separation efficiency and energy consumption.

4.5 - Inherent Safety of Materials

In the present chapter a few examples of application of the method described in §2.2 for inherent safety of materials are provided. The examples consist in typical results of comparison of hazard profiles of primary and secondary substances for thermally instable materials.

4.5.1 – Case study on Nitrobenzaldehyde

The present case study analyses some of the outcomes of the experimental survey on the isomers of nitrobenzaldehyde described in Section 3.
In the following the substances identified for 3-nitrobenzalheyde by Adiabatic Calorimetry tests are analysed. In particular the identification was possible for tests performed with different quantities of sample: tests where the final temperature reached 300°C (referred as “mild conditions” in the following) and tests where the final temperature reached 400°C and a large increase in pressure was detected (referred to as “severe conditions” in the following) (see §3.5.2). Tables from 3.5.8 to 3.5.10 list the compounds of interest.

Data on the proprieties of the identified substances were collected from available databases (see §2.2 for a list); in a few cases estimation was needed, resorting to structure-propriety relationships *[EPA, WPd]*. The application of the scoring procedure on this data resulted in the hazard matrix reported in Table 4.5.1 for “mild conditions”.

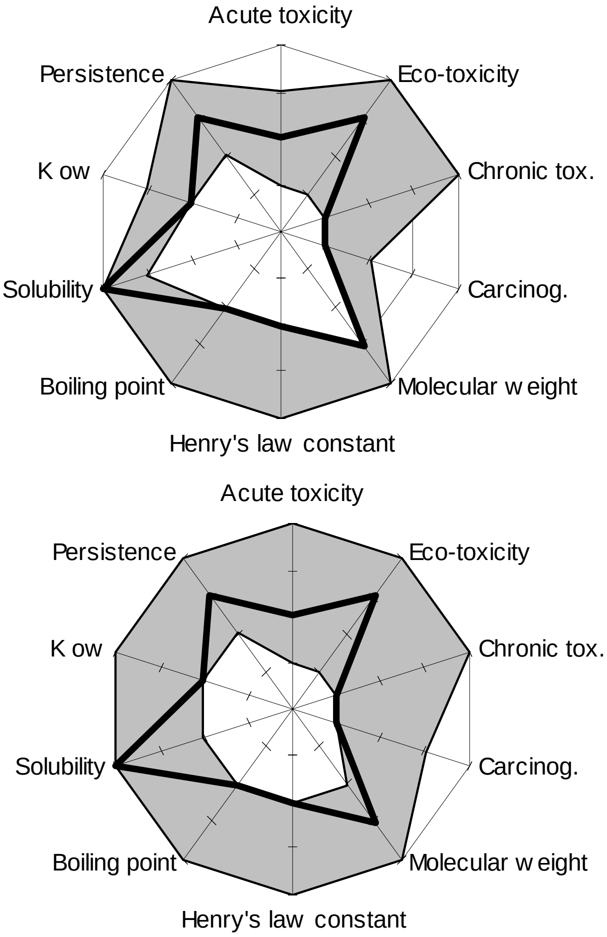


Figure 4.5.1: Hazard profile of 3-nitrobenzalehyde (black) compared to that of its decomposition products (grey) as obtained by tests in mild (top) and severe (down) conditions.

Compound name	P_{AT}	P_{ET}	P_{ChT}	P_C	P_{MW}	P_H	P_{Bp}	P_S	P_{Kow}	P_{to}	I_{AT}	I_{ET}	I_{ChT}	I_C	I_O
3-Nitrobenzaldeide	1	2	0	0	2	1	1	3	1	2	0	12	0	0	12
Benzaldehyde	1	2	1	1	2	2	1	3	1	1	0	6	1	1	8
Nitrobenzene	2	1	3	1	2	2	1	3	1	3	6	9	9	3	27
Benzoic acid	1	0	1	0	2	1	1	3	1	2	0	0	2	0	2
Biphenyl	0	3	2	1	2	2	1	2	2	1	0	6	4	2	12
Acenaphtene	0	3	2	1	2	2	1	2	2	1	0	6	4	2	12
1-Ethenyl Naphthalene	0	3	0	0	2	2	1	2	2	1	0	6	0	0	6
2-Hydroxybenzaldehyde	1	2	0	0	2	2	1	3	1	1	0	6	0	0	6
3-Hydroxybenzaldehyde	0	1	0	0	2	1	1	3	1	2	0	6	0	0	6
4-Hydroxybenzaldehyde	0	1	0	0	2	1	1	3	1	2	0	6	0	0	6
Phthalimide	0	0	0	0	2	1	1	2	1	2	0	0	0	0	0
3-Nitrophenol	1	3	0	0	2	1	1	3	1	2	2	12	0	0	14
Azobenzene	1	3	0	1	2	2	1	2	2	2	3	12	0	4	19
3-Nitrobenzoic acid	1	0	1	0	2	1	1	3	1	2	0	0	2	0	2
2-nitro biphenyl	1	2	0	1	2	2	1	2	2	2	0	8	0	4	12
3-Nitro biphenyl	0	2	0	1	2	2	1	2	2	2	0	8	0	4	12
4-Nitro biphenyl	0	2	1	1	2	2	1	2	2	2	0	8	4	4	16
5-Nitro acenaphthene	0	2	1	1	2	1	1	2	2	2	0	8	4	4	16
3-Nitrobenzamide	1	0	1	0	2	1	1	3	1	2	0	0	2	0	2
3-Nitrobenzophenone	0	2	0	0	2	1	1	2	1	2	0	8	0	0	8
2-Nitro-9-fluorenone	0	2	0	0	2	1	1	2	1	2	0	8	0	0	8
3-Nitro-9-fluorenone	0	2	0	0	2	1	1	2	1	2	0	8	0	0	8
N-(4-Nitrophenyl) methylenebenzamine	0	3	0	0	2	1	1	2	1	2	0	12	0	0	12
2,4'-Dinitrobiphenyl	0	2	0	1	2	1	1	2	1	2	0	8	0	2	10
2,2'-Dinitrobiphenyl	0	2	0	0	2	1	1	2	1	2	0	8	0	0	8
4,4'-Dinitrobiphenyl	0	2	0	1	2	1	1	2	1	2	0	8	0	2	10
3,4'-Dinitrobiphenyl	0	2	0	0	2	1	1	2	1	2	0	8	0	0	8
CO_2	0	0	0	0	3	3	3	3	1	3	0	0	0	0	0
Carbon monoxide	2	0	1	0	3	2	3	2	1	1	15	0	1	0	16

Table 4.5.1: Hazard matrix and hazard indices for 3-nitrobenzaldehyde, “mild condition” test.

The scores can be reported on a radar graph. A band or envelope of the different substances can be drawn on the graph, featuring the extremes of the hazard profile of the decomposition mixture. The envelope of the scores for the different proprieties of the substances formed is presented in the radial graph of Figure 4.5.1. As it is clear from the graph, substances characterized by different impact vectors compared to the original one are formed: in particular more dangerous substances are formed as, for instance, several nitro substituted aromatics and polycyclic aromatics as well as dangerous gases like nitrogen oxides and hydrogen cyanide.

This is more evident when comparing specific impact indexes (Figure 4.5.2). Substances characterized by a high toxicity, both for humans and ecosystem, and carcinogens are formed in detectable quantities in the degradation. It can be generally observed that as the more severe condition are reached (higher reaction temperatures and pressures) cyclization reactions are promoted, yielding to the formation of polycyclic compounds that frequently are carcinogen compounds. In these severe conditions, higher quantities of hazardous compounds, as nitrogen oxides and hydrogen cyanide, can be identified in the gas phase.

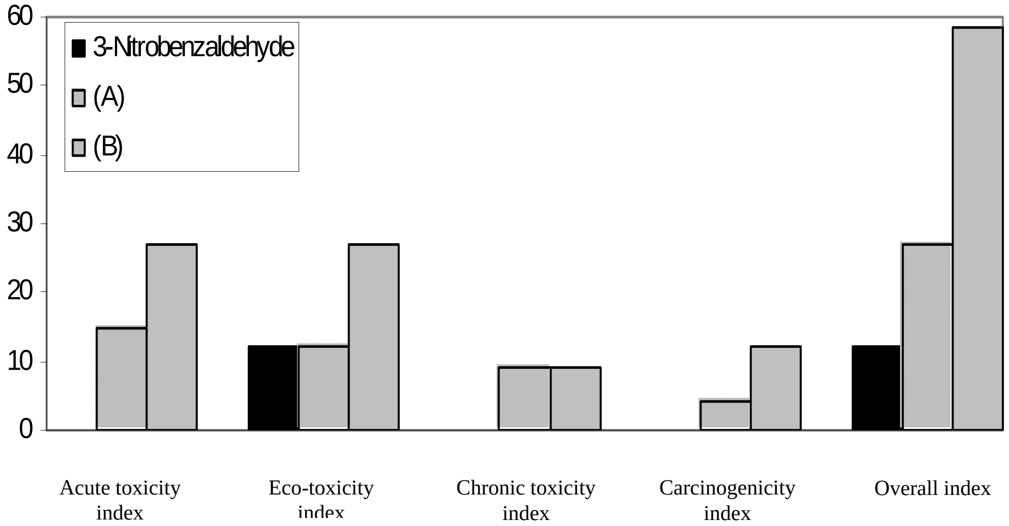


Figure 4.5.2: Hazard profile of 3-nitrobenzalehyde compared to that of its decomposition products as obtained by tests in mild (A) and severe (B) conditions. Some hazard indexes for 3-nitrbenzaldeyde are not visible in the histogram since their values are practically zero.

4.5.2 – Other cases-studies

The same procedure was applied to other cases studies, where it was possible to obtain from the literature data on qualitative and quantitative analysis of the product formed in accidental conditions. A few are reported in the following for sake of demonstration of typical results and conclusions.

4.5.2.1 – Tetrabromobisphenol A

Tetrabromobisphenol A (TBBA) is a material mainly used as flame retardant in the production of plastics. Quantitative and qualitative data for the thermal decomposition of tetrabromobisphenol A are reported by *Barontini et al., [2004a, 2004b]*.
Table 4.5.2 reports the hazard vector for the primary material, TBBA.

For each of the products identified, the hazard matrix and the hazard profile were calculated. Figure 4.5.3 and Table 4.5.3 reports the results obtained. As shown in the figure, the hazard profile of TBBA is that of an ecotoxic substance. The high molecular weight limit the acute toxicity hazard, while no evidence of chronic toxicity or carcinogenicity is reported. On the other hand, the identified decomposition products show more hazardous impact profiles: a first category of products, the brominated phenols, are again characterized by an ecotoxicity impact, although the lower molecular weight is responsible of the higher hazard scores detected. On the other hand, lower molecular weight products showing a high acute toxicity hazard are also formed, as hydrogen bromide and carbon monoxide. Thus, the impact profile of the decomposition products suggests that two different accidental scenarios should be assessed in the safety analysis of runaway or fire scenarios involving TBBA or materials containing TBBA as a flame retardant: the formation of a toxic cloud containing acutely toxic compounds, and the dispersion of an aerosol of ecotoxic decomposition products.

4.5.2.2 – Tert-butylperoxybenzoate

Data on the decomposition of tert-butylperoxybenzoate (TBPB) are reported in *CCPS, [1995]*. These data can be elaborated by the proposed methodology (§2.2), yielding the impact profile represented in Figure 4.5.4. In this case, the primary material show prevalent hazard for environment and, in minor terms, for chronic and carcinogen effects on humans. The mixture of decomposition products (grey band in the graphs) shows that more volatile products characterized by acute and chronic toxicity can be released. Since quantitative information are available on the composition of the mixture of secondary product *[CCPS,*

Score	P_{AT}	P_{ET}	P_{ChT}	P_{C}	P_{MW}	P_{H}	P_{Bp}	P_{S}	P_{Kow}	P_{to}
3		**X**							**X**	**X**
2										
1			**X**		**X**	**X**	**X**	**X**		
0	**X**			**X**						
	0	**3**	**1**	**0**	**1**	**1**	**1**	**1**	**3**	**3**

Table 4.5.2: Example of hazard vector evaluated for tetrabromobisphenol A (TBBA) .

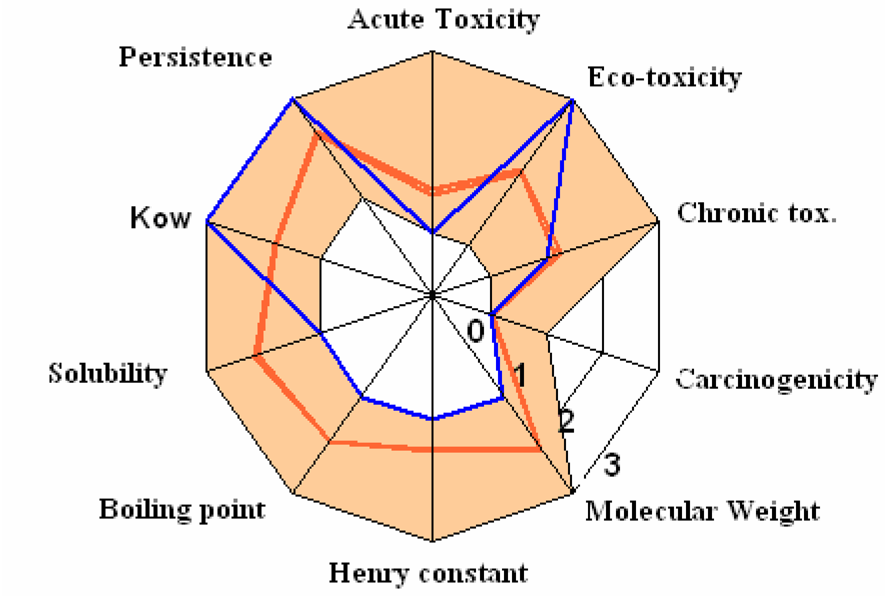


Figure 4.5.3: Hazard profile of TBBA compared to that of its decomposition products

1995], this profile can be reported on the graph (dark grey line). Thought the presence of a modest acute hazards are confirmed, the comparison with the primary material shows a reduction of eco-toxicity and a stable level of chronic and carcinogen hazards. This example clearly shows the importance of having quantitative information on the possible mixtures formed in decomposition.

	I_{acute}	I_{env}	$I_{chronic}$	I_{canc}
TBBA	**0**	**9**	**0**	**0**
2,4,6-tribromophenol	**0**	**12**	**0**	**0**
2,4-dibromophenol	**0**	**12**	**0**	**0**
2,6-dibromo-4-methylphenol	**0**	**12**	**0**	**0**
2,6-dibromophenol	**0**	**12**	**0**	**0**
2-bromophenol	**0**	**6**	**0**	**0**
4-bromophenol	**0**	**12**	**0**	**0**
bisphenol A	**0**	**12**	**6**	**0**
dibenzifuran	**0**	**8**	**0**	**0**
phenol	**6**	**12**	**2**	**0**
biphenyl	**0**	**8**	**0**	**0**
CO	**15**	**0**	**0**	**0**
HBr	**6**	**0**	**0**	**0**

Table 4.5.3: Decomposition products and hazard indices for tetrabromobisphenol A (TBBA) .

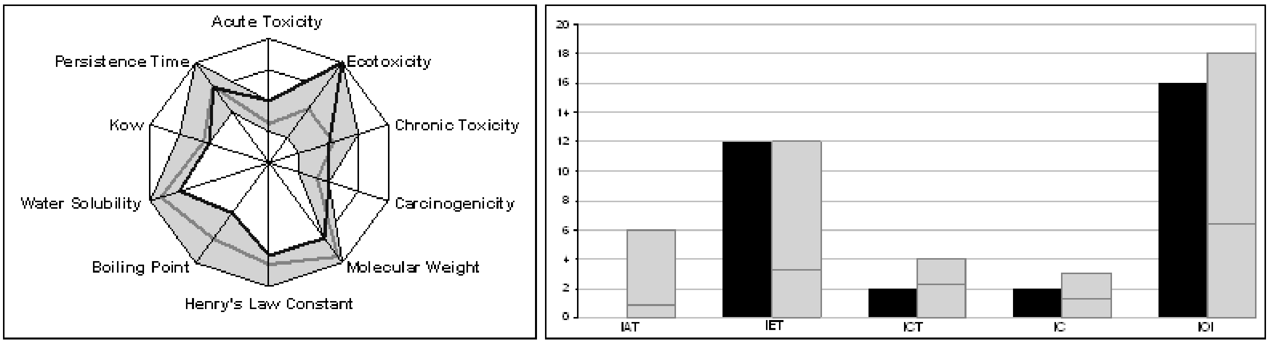


Figure 4.5.4: Hazard profile representation referred to the TBPB decomposition: black refers to TBPB and grey to its decomposition products. The grey line in the radial graph is the average hazard profile of the secondary products.

4.5.3 – Conclusions

The procedure developed to define the hazard profile of decomposition products (§2.2) was applied to some case studies. The input data for the selected set of hazard parameters were easily obtained from the available databases, allowing the application in all the cases studied. When necessary, predictive estimations were effective in the integration of scant data. The changes in the hazard profile of a chemical system due to the undesired decomposition of a substance were identified. The results proved that the developed method may be applied as a rapid and effective screening tool to represent the inherent hazard related to a substance present in a chemical system due to the possible decomposition products that may be formed. This allows a complete identification of the accidental scenarios that should be assessed following the emission in the environment of decomposition products formed in the loss of control of a chemical process.

4.6 – Upgrade of process sections in fine chemistry plant

In this section a couple of case studies about the implementation of alternative process and plant options in sections of an existing plant are discussed. The cases studies, featuring real industrial cases, were developed in collaboration with Ciba Speciality Chemicals. Some information, like the name of the substances involved, are not fully reported in the following for reasons of data confidentiality.

The case studies demonstrate the application of the sustainability and inherent safety assessment methods in the analysis of a section of a plant. Two problems are analysed: the storage and mixing of an hazardous reactant (§4.6.1) and the finishing of an oligomer (§4.6.5).

4.6.1 – Case study #1: Storage and mixing of an hazardous reactant: case study description

This case study deals with a specific section of a plant producing fine chemicals. The section prepares a reactant (B) used in the synthesis of the final product, by mixing it with a solvent (A). Two alternative options were identified for this plant section (the first one was in place at the moment of the analysis). The options differ in the physical state of the feedstock B:

- Option 1: the raw-material B is in solid state, as a powder at room temperature.
- Option 2: the raw-material B is in liquid state, since it is kept at temperature higher than its melting point.

The boundaries of the analysis include the preparation and mixing section of the plant as well as the storage of the material, since it changes according to the state of the material B. On the other hand, the production and transport of the different forms of B are beyond the goals of current analysis, since it is oriented to the assessment of the facility in the site.

4.6.1.1 - Option 1: raw-material B in solid state (powder)

In this option the raw-material B is a powder. The boundaries of option include the storage of the raw material in a dedicated warehouse, the transport of the material from the warehouse to the mixer and the mixing section of the plant (Figure 4.6.1).

The powder of B is supplied and stored in closed hoppers (GFK). The storage facility is a "open" warehouse in the raw-material storage section of the plant, that provides protection from rainfall, allowing natural ventilation. The GFKs can be of 3 different weights (600, 700 and 800 kg). The GFKs can be stacked and usually are stored in piles of two. The GFKs are handled both for truck unloading and for feed to the production by forklift truck.

In the mixing procedure, solvent A is fed to a mixing tank (R420-R1) from the storage tank (excluded from the boundaries of the analysis, since it is equal for both the options) and cooled to 10°C by chilled water in the mixer tank jacket. The desired quantity of solvent A is transferred from R420R1 to R445, in order to yield a solution of the required concentration. The content of tank R445 is kept to 10°C by chilled water in the jacket. The GFKs containing material B are lifted by a semi-automatic facility and connected to the feeding nozzle of the mixing tank (R445). The mixing tank (R445) is maintained to pressure lower than atmospheric, in order to prevent any release of powder when it is discharged. The discharge is by gravity and is promoted by the vibrating devices on the GFK. The disconnection of the empty GFK follow the inverse procedure than the feeding. Each time, the charging nozzle is washed by solvent A, in order to remove traces of B adhering the walls. Usually two GFKs are fed to the mixer in each batch. The discharged quantity is checked by a tank weight.

The mixing is done in R445 by an agitator. The mixture is then sent to the reactors (out of system boundaries) in the desired quantities. Tank R445 is then washed by the solvent A (the washing mixture is used in the reactor section as well) and flushed by nitrogen.

4.6.1.2 - Option 2: raw-material B in liquid state (melted)

In this option material B is stored and fed to the mixing as a liquid. Since the melting point of B is above room temperature (around 145°C), specific plant design is aimed to prevent the solidification of the material. The boundaries of option, similarly to the previous case, include the storage of the raw material, the transfer of the liquid to the mixer and the mixing section of the plant where the desired solution of A and B is obtained (Figure 4.6.2).

In this option the raw-material B is supplied to the plant in horizontal cylindrical tanks (isotanks) of the volume of 14.5 m^3 and equipped with steam coils. The isotanks are connected to the plant by flanged hoses. The hoses, as well as the piping carrying material B have steam heating system, in order to prevent the solidification of the substance.

When in use, the isotank is connected to the steam lines (1.2 MPa) in order to maintain the set point temperature (160°C). The hose of the isotank is connected to a closed loop transfer line, in order to keep the material moving. An injector feeds and meters the raw-material B from the transfer loop to the mixer (R2000).

The loading and storage facility allows 4 isotanks in place at a time. It is located in the plant storage area and is protected by a metallic roof. The isotanks are supplied to the plant with blind flanges on the connection nozzles (transfer line of the material and nitrogen line for

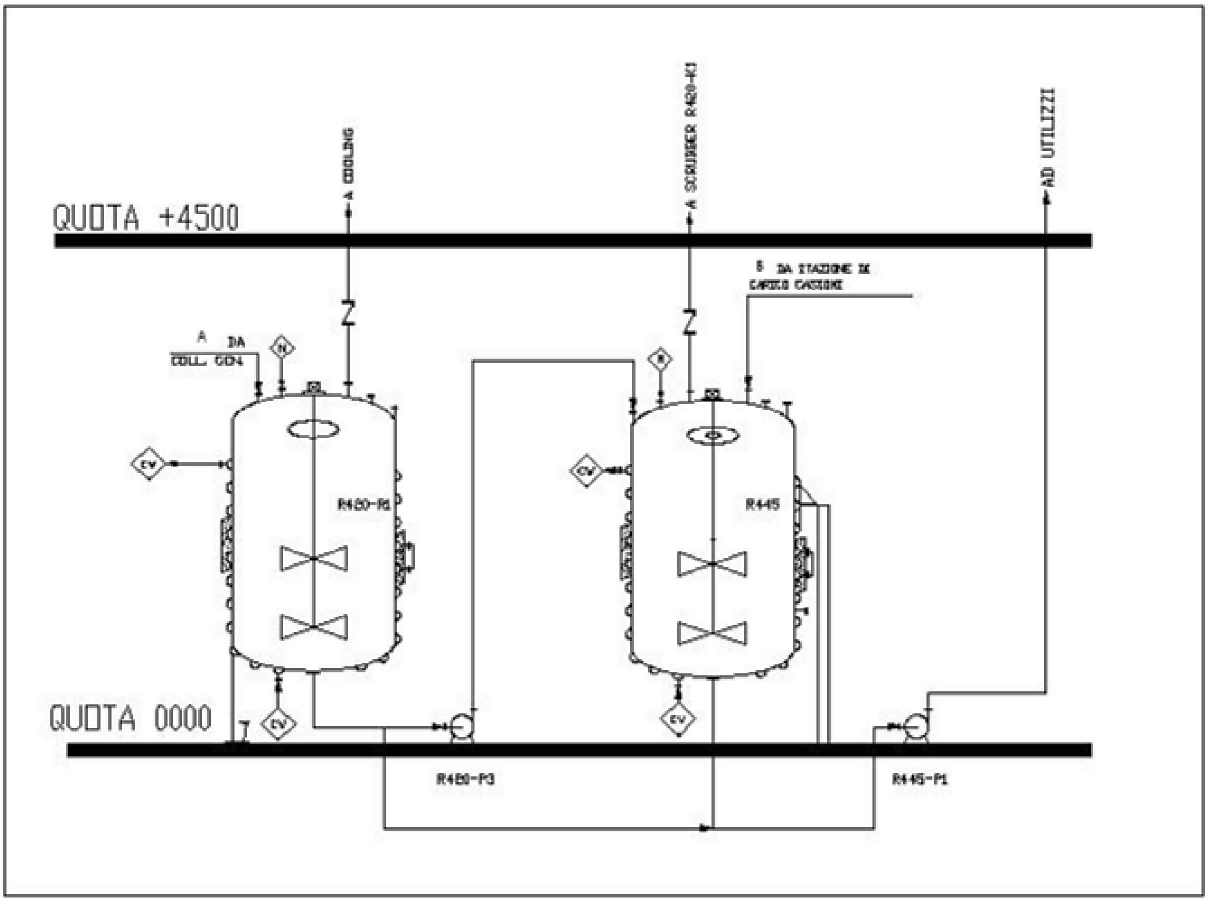


Figure 4.6.1: Diagram of the reactant preparation section for option 1 (material B in powder). The powder storage is not represented in this diagram.

pressurization). When the tanks are connected, the absence of leaks is tested by compressed nitrogen. Before disconnection, the transfer line is drained.

Solvent A is fed to a mixing tank (R2000) from the storage (excluded from the boundaries of the analysis, since it is equal for both options) by dedicated lines that do not enter the isotank storage facility, that is thus an area with no fire hazard (B is not flammable).
The circulation of B in the loop transfer line is provided by a canned pump. The piping of the line is installed with proper slopes, so it can be easily drained: if a shut down occurs, the line inventory flows back to the isotank. The piping is traced.
The mixer (R2000) is located in a building close to the storage of B. The solvent A is feed to the tank and cooled down by chilled water in an external shell-and-tube heat exchanger. The temperature around 10°C is required for process and safety (low partial pressure) issues. The weight of mixer (R2000) is a measured variable. The reagent B is metered (controlled flow and temperature) and injected by a nozzle that disperse it in fine droplets. Different compositions of mixture are produced.

4.6.2 – Case study #1: Collection of input data

The initial step of the analysis is the collection of the necessary data to define the options. Several data were collected from the design sheets of the options, but the need for estimated data was not completely eliminated (e.g. fugitive emissions).
The analysed process is a batch process. Four different composition of the final product (the mixture of A and B) are of interest in the production. Table 4.6.1 reports the summary of the production in a reference year, assumed for the calculation of the average annual production

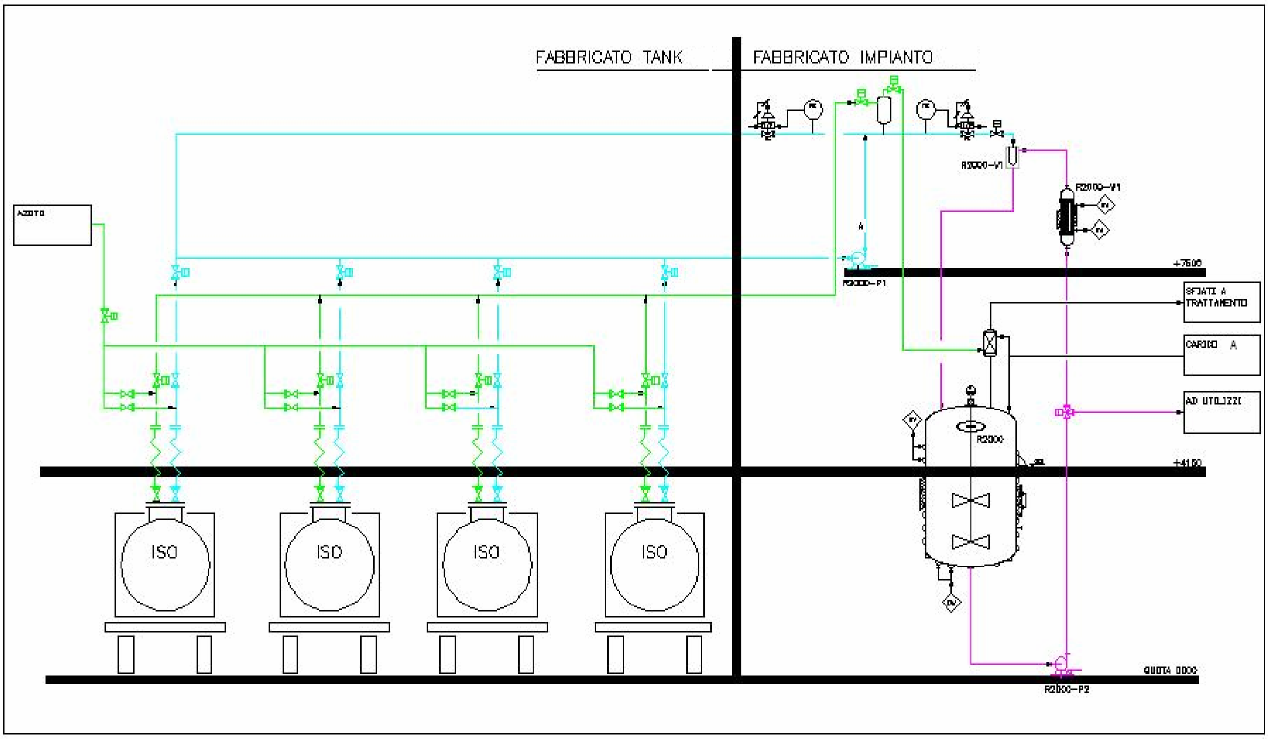


Figure 4.6.2: Diagram of the reactant preparation section with material B in liquid state (melted), option 2.

	B (t/y)	A (t/y)	Batch (y^{-1})	GFK (y^{-1})	Isotank (y^{-1})
Mixture 1	1575,00	3270,75	1050	2100	83
Mixture 2	201,60	657,72	168	336	11
Mixture 3	453,00	1527,18	566	566	24
Mixture 4	100,55	459,36	168	168	5
	2330,15	**5915,00**	**1952**	**3170**	**123**

Table 4.6.1: Number of batches and raw-material consumption in the production reference year.

	Steam Use (kg_{steam}/y)	Consumption CH_4 (Nm^3_{CH4}/y)[a]	Cost (€/y)[b]
1. Isotank warming up	161’900	12’900	3’730
2. Isotank maintaining	64’500	5’140	1’490
3. Loop line maintaining	373’500	29’800	8’600
	599’900	*47’800*	*13’800*

Table 4.6.2: Consumption of steam an natural gas for option 2. a) boiler efficiency 93%; b) natural gas cost 0.2885 €/Nm^3.

Unit	Power (kW)	Use (h/y)	Consumption (kWh/y)	Cost (€/y)[b]
R420-P3	3,00	488	1’463	143
R445-P1	7,50	976	7’319	717
Y2049-P3	2,00	8000	16’000	1’568
Y2049-P6	8,70	8000	69’333	6’795
Stirrer R420-R1	4,00	8000	32’000	3’136
Stirrer R445	4,00	8000	32’000	3’136
Refrig. Cycle (Y2049)[a]	27,88	8000	223’000	21’900
Total Option 1	-	-	*381’200*	*37’400*
R2000-P1	4,5	8000	36’000	3’528
R2000-P2	12,0	3253	39’036	3’826
R2000-P3	0,5	8000	4’000	392
Y2049-P3	3,0	8000	24’000	2’352
Y2049-P6	13,0	8000	104’000	10’192
Stirrer R2000	7,5	3253	24’400	2’391
Refrig. Cycle (Y2049)[a]	72,50	8000	580’000	56’840
Total Option 2	-	-	*811’400*	*79’500*

Figure 4.6.3: Electrical power consumption and related costs. a) refrigeration cycle has COP of 2.08; b) electrical energy cost assumed 0.098 €/kWh

potential used in the analysis. The consumption of solvent A is independent of the technological option adopted for the production. Table 4.6.1 reports the number of GFKs and of Isotanks needed to match that production.

Medium pressure steam is used in option 2. In particular steam is used for: i) warming up of the isotank once docked in the storage facility (in order reach the use conditions); ii) maintaining the docked isotanks at the desired standby condition; iii) maintaining the circulation loop at the desired condition. The thermal dispersions and, consequently, the steam consumption were evaluated. The consumption of natural gas and the costs for steam production were calculated from the characteristics of the existent boiler house. The results obtained are summarized in Table 4.6.2.

The principal users of electrical power, in both the options, are the refrigeration cycles, pumps and stirring drivers. The collected data are reported in Table 4.6.3.

Nitrogen is used for inerting of the vessels in the plant. The batch operation results in a cyclic variation of the level in the vessels, that expels nitrogen and, consequently, requires nitrogen make-up. The results of the estimation of nitrogen consumption are reported in Table 4.6.4.

	N_2 (kmol/y)	**A (kmol/y)**	**A (kg/y)**	**B (kmol/y)**	**B (kg/y)**
Option 1					
R445	376,7	0,964	102,3	2,43E-03	0,447
R420-R1	203,2	0,725	77,0	0	0
Total	579,9	1,689	179,3	2,43E-03	0,447
Option 2					
R2000	376,7	0,964	102,3	2,43E-03	0,447

Figure 4.6.4: Estimation of the emissions of A and B to air from inerting cycles.

(€/y)	**Option 1**	**Option 2**
Material B	3’791’000	3’346’000
Material A	4’732’000	4’732’000
Electrical Power	37’400	79’500
Steam	-	13’800
Maintenance	20’000	69’500
Labour	215’000	86’000
Total operative costs	8’795’400	8’326’800
Total savings	9’375’500	9’375’500
Initial capital investment	1’000’000	1’600’000
NPV	1’413’800	2’645’500

Table 4.6.5: Annual operative costs, initial capital investment and net present value of the two considered options

The compounds A and B are released in the same operations. The releases are calculated considering equilibrium of the liquid phase with the vapour phase released in cyclic variations, as suggested by *[Allen & Shonnard, 2002]*. This hypothesis is extremely conservative, since a demister and an alkaline scrubber are present on the venting line. The estimation of fugitive emissions from leaks (valves, flanges, pumps) are also estimated as proposed by *Allen & Shonnard, [2002]*.

The calculation of the Net present Value of each option required collection of data on costs and discount rates. Table 4.6.5 summarizes the operative and capital costs considered. The reference year is 2005. In the calculation of the savings a value added of 10% is considered for the product mixture compared to the prices of single components.

4.6.3 – Case study #1: Inherent safety assessment

The inherent safety assessment of the options is performed by the procedure described in §2.3. The accidental scenarios considered in the assessment are:

- DP1) toxic dispersion, deriving from release of B and accidental stoichiometric reaction with water (HCl is released from the reaction).
- DP2) pool fire of the flammable compound A

Tables 4.6.6 and 4.6.7 report a summary of the damage distances identified for the critical units considered in the assessment. Consequences were modelled by commercial software models. The release modes considered are:

- R1) continues release from a 10mm equivalent hole
- R2) continuous release of the hold-up in 10 minutes
- R3) instantaneous catastrophic rupture.

In the case of B in powder the release of HCl is supposed the result of reaction with water of superficial layer (thickness 10 cm) of a pile of released powder.

Figure 4.6.6 and 4.6.7 report also the credit factors considered in the analysis, derived from the literature on credibility of equipment release *[Uijt de Haag & Ale, 1999]*. In the case of the toxic cloud dispersion (DP2) the credit factors (theoretically depending only on the equipment) are multiplied by 0.192, representing the credit (probability) of rainfall in the specific site. In fact the accidental presence of water is required to derive from this condition.

It can be observed that pool fire scenarios usually result in modest damage distances, compared to toxic dispersions deriving from reaction of B with rainfall water.

Table 4.6.8 reports the hazard index calculated for the considered units. It can be observed that, even if maximum damage distances (and thus UPI, not reported in the table) are similar for different units, the credit factor influence the value of UHI. For instance, in option 2, R2000 and R2000-W1 have the same damage distance, but the release from a catastrophic failure of the condenser (R2000-W1) is much more credible.

The HI of option 1 is dominated by the UHI of the toxic dispersion following the rupture of a GFK. This is a combination of a large expected damage distance and a high credit factor, due to the high number of handling operations.

Unit	Top event	Credit factor	Release	Damage distance (m)
R420-R1	DP2	1 E-05	R1	43
		5 E-07	R2	45
		5 E-07	R3	42
R445	DP1	1 E-05	R1	183
		5 E-07	R2	2318
		5 E-07	R3	3680
	DP2	1 E-05	R1	39
		5 E-07	R2	40
		5 E-07	R3	37
GFK	DP1	1 E-05 x # of handlings	R3	1937

Table 4.6.6: Damage distances and credit factors for Option 1.

Unit	Top event	Credit factor	Release	Damage distance (m)
R2000	DP1	1 E-05	R1	183
		5 E-07	R2	2319
		5 E-07	R3	3680
	DP2	1 E-05	R1	19
		5 E-07	R2	19
		5 E-07	R3	16
R2000-W1	DP1	1 E-03	R1	183
		5 E-05	R3	3680
	DP2	1 E-03	R1	19
		5 E-05	R3	16

Table 4.6.7: Damage distances and credit factors for Option 2.

	UHI	HI
Option 1		
R420-R1	9,81E-03	2,27E+04
R445	1,87E+00	
GFK	2,27E+04	
Option 2		
R2000	1,87E+00	1,37E+02
R2000-W1	1,36E+02	

Table 4.6.8: Unit and overall hazard index for the two options considered.

4.6.4 – Case study #1: Sustainability assessment

Table 4.6.9 reports the normalized environmental indicators calculated for the 2 options. The material use (raw materials processed and natural gas) results the higher impact present. This is expected, since the process is basically a material treatment. The higher request of energy by option 2 pays significant effects on the environmental impact profile. In fact, the impacts linked to the emissions of exhaust gases negatively affect the categories of global warming, acidification, smog formation, toxicity and carcinogenicity. On the other side, the contribution of fugitive emissions on the value of the environmental indicators was identified as negligible.

Electrical power is another impact that shows a relatively high normalized indicator. As concerns this impact, the worse performance of Option 2 is linked to the higher requirement for chilled water.

Table 4.6.10 reports the calculated values of the level 2 and level 3 indices. The environmental index penalizes option 2, mainly due to the emissions from energy production. On the other side, the economic index is favourable for option 2, since annual operative costs are lower, mainly due to the minor labour costs and the different unitary cost of the two commercial forms of B. However, societal impacts, due in particular to inherent safety, are the dominant indices (see §4.6.3).

Impact category	Option 1	Option 2	Normalization factor	Weight factor
Global warming	5,16E-04	8,12E-02	1,16E+06 kg/(y·km^2)	0.051
Acidification	1,42E-04	6,99E-03	4,83E+03 kg/(y·km^2)	0.066
Smog formation	2,00E-01	1,15E-01	5,63E+03 kg/(y·km^2)	0.049
Air toxicity	1,33E-03	3,61E-02	3,77E+05 kg/(y·km^2)	0.095
Carcinogenicity	0,00E+00	5,68E+00	9,91E-01 kg/(y·km^2)	0.168
Materials	6,00E+01	5,70E+01	4,80E+05 kg/(y·km^2)	0.044
Electrical power	7,94E-01	1,69E+00	3,51E+05 kWh/(y·km^2)	0.064

Table 4.6.9: Normalized environmental indicators, normalization factors and weight factors used in the assessment.

	Option 1	Option 2	Weight factor
Level 2			
Environmental index	2,70	3,59	0,300
Economic index	-1,15	-2,11	0,300
Societal index	1,02E+04	6,17E+01	0,400
Level 3			
Overall index	4,07E+03	2,51E+01	

Table 4.6.10: aggregated indices for the two compared options.

The overall index follows the profile of the societal (inherent safety) aspect. The inherent safety index is recognized as important in the last aggregation step because of both: i) the significance compared to the background (i.e. normalization factor) and ii) the larger weight attributed to this impact aspect (i.e. the weight factor). Thus, in this case-study, the inherently safer option is also the more sustainable.

4.6.5 – Case study #2: Finishing of an oligomer

This case study deals with the final section of a specialty chemistry plant, where a product (named N), initially mixed with a solvent T, is treated in order to yield the commercial form. The pure oligomer N is a solid at room conditions.
Two plant options were proposed for the upgrade of the finishing section of an existing production plant, from 400 t/year to 600 t/y. The upgrade is required as a consequence of increased production from upgrades and de-bottlenecking in the production section. The aim of the present analysis is to compare and find out the critical issues of the two plant options.

- **Option1 (LIST)**: Use of a new technology for product finishing, called LIST (twin shaft extruder – solvent devolatilization). This option will produce a the oligomer in chips, one of the possible commercial form. The process is operated in continuous.
- **Option 2 (Traditional)**: This is the traditional batch process, adopted in the original section of the plant. The option consists in an upgrade of the present production potentiality with the realization of a new production line parallel to the original one in order to match the desired production potential. It produces a dry product in powder, that needs to be compacted to reach an acceptable commercial form. The compacting is realized in a facility out of the production plant boundaries.

4.6.5.1 - Option 1: LIST

In this process N is directly separated from the organic solvent (T). The principal piece of equipment, called LIST, requires auxiliary units to operate in steady state and to obtain the desired form of product: a buffer for storage of the mixture to be processed (which is produced by a batch process), two buffers for the storage of the solvent T, a vacuum pump, a pre-concentration, a laminator/cooler of the extruded oligomer, a “breaker” of the flakes resulting from the extruded product, a vibro-screen to split the coarse product from fines and the devices filling the Bulk Bags.

The mixture to be processed (about 35% of N) is stored in the buffer B640 (see figure 4.6.3). The solution is transferred to R641, where a continuous pre-concentration takes places (temperature 95°C, pressure 15 kPa). Pump G642 maintains the desired pressure in the system. The condenser R641-W1, operated with chilled water, allows to recover the solvent T. The solvent is stored in R641-B1, available for recycle back to production.
The solution leaving R641 contains around 80% of N. The LIST, G642, processes the mixture at 140°C and 2 kPa. A concentration of T lower than 0.5% is expected in the exiting stream of N.

The solvent T evaporated is condensed (G642-W1) and collected in R642-B1. The fused N leaves the extruder and it is cooled and laminated in G642-H1. The 2 mm thick layer produced in this operation is broken by G642-Z1, that produces the final chips. These are separated from fines by screening (G642-H2) and stored in bulk bags.

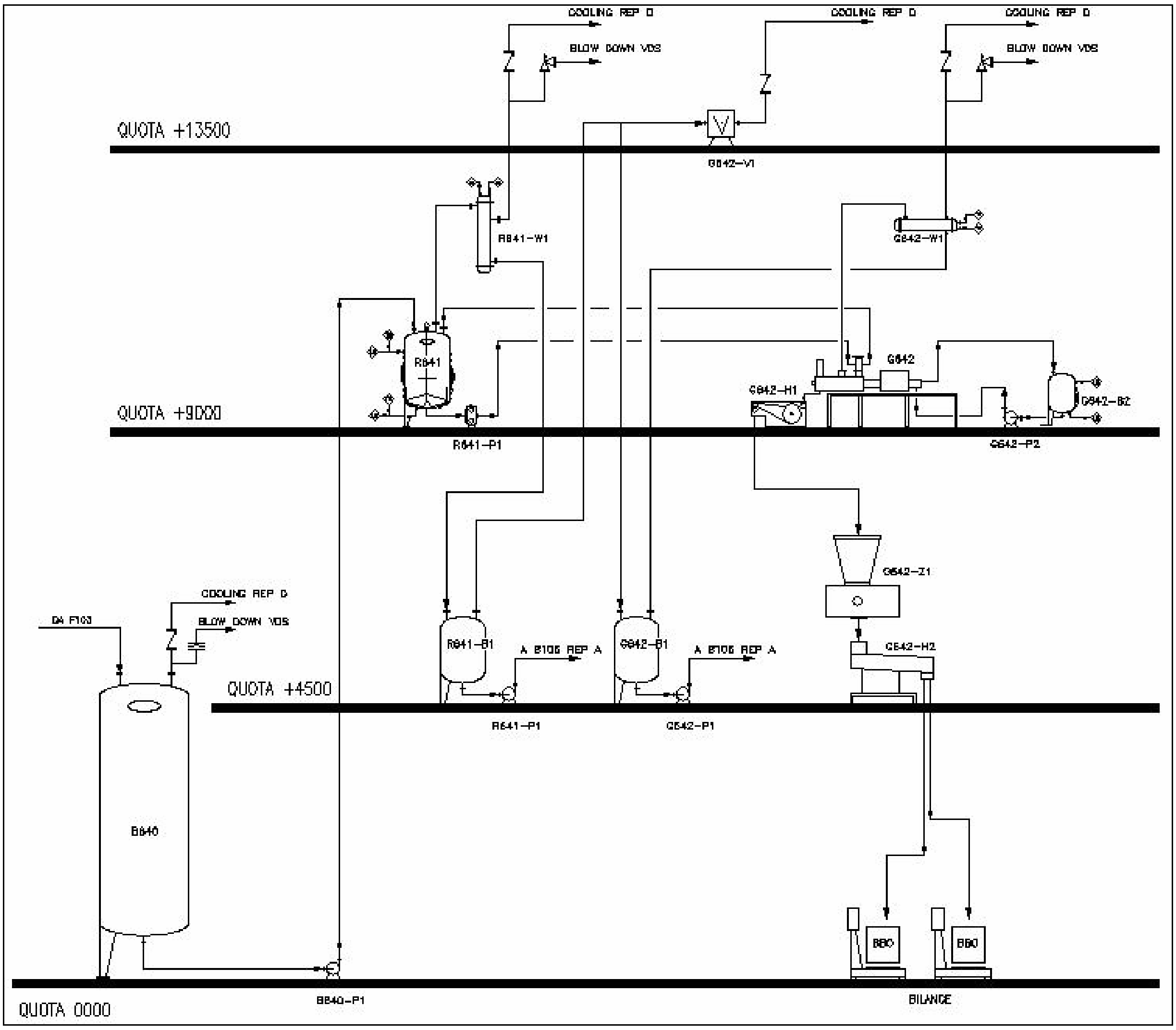


Figure 4.6.3: Plant scheme for option 1.

4.6.5.2 - Option 2: traditional plant

This option is the one currently in place in the plant. The upgrade can be realized building a similar production line. In the traditional process a the solvent T of the initial mixture is displaced by water and the drying step is realized on the water mixture.

The mixture to be processed (about 35% of N) is stored in L2023. A batch of 3150 kg of solution is transferred in R123 by the pump L2023-P1. The vessel R123 is stirred and heathen up to 70°C by 0.2 MPa steam. Pressure is lowered to 14 kPa by vacuum pump V130. The evaporated solvent T is condensed (R123-W1, by cooling water, and R123-W2, by chilled water) and sent to B106, where it is stored. The product of concentration contains more than 80% of oligomer N.
The product is transferred by P123-P1 to the vessel F123-E1, partially filled by demineralised water at 100°C. The oligomer is dispersed in the water. Vapours of T and water are condensed in F124-W1 and the two phases separated in a decanter. The solvent T is sent to the storage buffer (F124-B2). The next phase of the process cools down the vessel F123-E1 and sends the

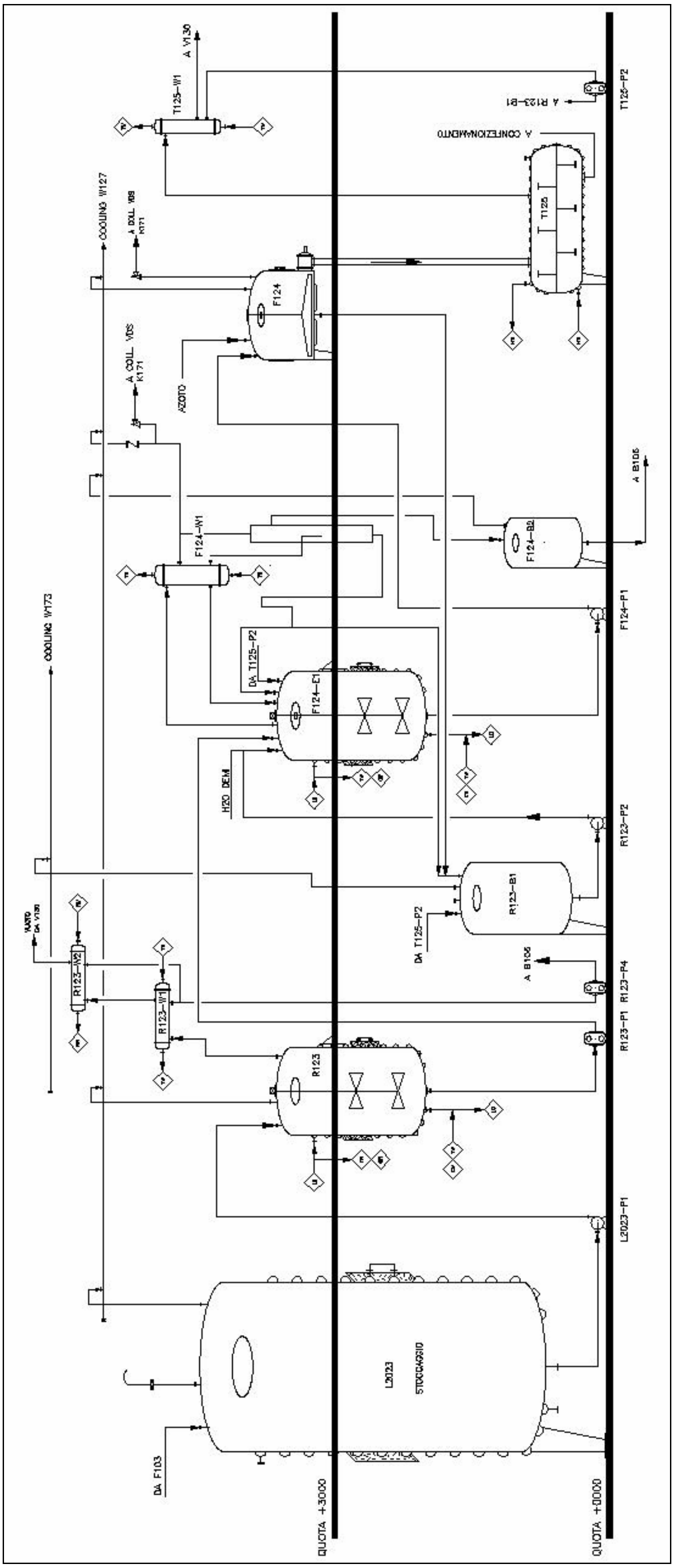


Figure 4.6.4: Plant scheme for option 2.

mixture (N and water) to a filter (F124). The mother liquor is stored in F123-B1 and recycled for the next batch.

The cake from the filter is transferred to a drying vessel (T125). This works at 7.5 kPa pressure and 65°C. The vacuum pump V130 removes the released vapours that are condensed (T125-W1) and sent to R123-B1. The drying ends when water content is lower than 0.5%.

The product is packed in bulk bags for transfer to the external compaction treatment.

4.6.6 – Case study #2: Collection of input data

The data on the plant were collected on-site and from the analysis of the design documentation, similarly to §4.6.2. Also in this case some additional estimations were necessary to complete the required data.

The production potential is the same 600 t/y of N in dry form. The finishing operations are realized in option 1 by a single treatment line and in option 2 by two equal parallel lines (in the following the combined effect of both is reported). The plant of option 1 is a continuous plant, and 8000 h/y of operation are considered. The plan of option 2 is batch and the design is such that vessels are slightly oversized; thus the number of batches required for the potentiality can be reached in 6000 h/y of operation on both the production lines.

Table 4.6.11 summarizes the principal material flow entering and leaving the two options.

The consumption of nitrogen for the cyclic operations in the batch vessels was evaluated similarly to previous case study (§4.6.2). This allows the evaluation of the quantity of T leaving the vessels. A large part of this T (about 95%) is recovered in the guard condensers on the vent lines. The condensed T is fed at the furnace for steam generation, while the gaseous stream is sent to incineration. Thus, no emission of T is expected from the inerting system. On the other hand, fugitive emissions may occur from leaks in flanges, valves and other equipment. These were evaluated by conventional emission factors *[Allen & Shonnard, 2002]*. These result around 1.3 and 1.4 kg/y of T emitted for option 1 and 2 respectively.

(t/y)	**Option 1**	**Option 2**
Input		
Feed mixture	1714	1714
Water	-	818
NaOH	-	136
Output		
Recovered T	1113	1112
Waste	1	957

Figure 4.6.11: Process input and output in the considered options.

	Option 1	**Option 2**
Steam use (kg/y)	402’100	1’148’800
Natural gas (Nm^3/y)	30’490	87’710
Cost (€/y)	9’147	26’310
Electric power use (kWh/y)	415’500	343’700
Cost (€/y)	44’000	36’400

Figure 4.6.12: Process energy consumptions and related costs in the considered options.

The heat balances allowed to estimate the amount of steam required for heating. As a consequence the use of natural gas (energy from solvent recovered in guard condensers as co-fuel was discounted) and the costs were accounted. The specifics on the use time and power consumption of the electrical motors allowed evaluation of the electrical power consumption. These data are reported in table 4.6.12.
The principal economic parameters used for the calculation of the net present value are summarized in table 4.6.13.

(€/y)	Option 1	Option 2
Materials (€/y)	18’000’000	18’000’000
Recovered T (€/y)	-777’200	-776’400
Electrical power (€/y)	44’000	36’400
Steam (€/y)	9’100	26’300
Nitrogen (€/y)	200	1’900
Cooling water (€/y)	200	2’200
Maintenance (€/y)	20’000	23’000
Labour (€/y)	215’000	344’000
Waste disposal (€/y)	-	49’000
Product compacting (€/y)	-	282’000
Total costs (€/y)	17’511’400	17’988’600
Total savings (€/y)	21’000’000	21’000’000
Initial invested capital (€)	18’00’000	600’000
Net Present Value (€)	11’187.406	10'386’594

Table 4.6.13: Annual costs, capital investments and net present value (NPV) for the two considered options.

4.6.7 – Case study #2: Inherent safety assessment

The procedure described in §2.3 is applied also in this case. The solvent T is a flammable liquid with moderate acute toxicity. The oligomer N can undergo dust explosion if a powder cloud is dispersed in air. The possible loss of containment were arranged in 5 release modes:

- R1: continuous release from a 10mm equivalent hole
- R2: continuous release of the hold-up in 10 minutes
- R3: catastrophic rupture
- R4: leak from pipe (10% of the nominal diameter)
- R5: full bore rupture

Table 4.6.14 and 4.6.15 report the damage distances ad the credit factors for the single units. The accidental scenarios considered are:

- DP1: toxic dispersion
- DP2: pool fire
- DP3: vapour cloud explosion

- DP4: flash fire
- DP5: internal explosion in vacuum equipment
- DP6: dust explosion

The critical unit for option 1 is the storage buffer B640, where the mixture of N and T to be processed is stored (Table 4.6.16). The other units have UHI at least one order of magnitude lower. The method identify an expected result: a continuous units have small inventories and are expected to result in smaller damage distances. This is an immediate consequence of the inherent safety principle of “minimization”. The sole UHI for B640 contributes to HI for about a half.

In the batch plant the most critical unit is pump L2023-P1, used for displacing the mixture from the storage buffer (L2023) to the concentrator (R123). The higher damage distanced are actually expected from the buffer. However the rupture of the pump and the release of the material from the buffer is considered more credible than the collapse of the vessel. This unit alone is practically responsible of the value of HI for the plant. Other hazardous units are the pieces of equipment handling large quantities of solvent (L2023 and R123) and the drying vessel (T125). It is worth noticing that any of these units alone has an UHI similar to the most critical unit of option 1 and, thus, half of the HI for option 1.

Unit	Scenario	Release	Credit factor (y^{-1})	Damage distance (m)
B640	DP1	R1	1 E-05	86
		R2	5 E-07	529
		R3	5 E-07	87
	DP2	R1	1 E-05	34
		R2	5 E-07	47
		R3	5 E-07	43
	DP3	R1	1 E-05	36
		R2	5 E-07	253
		R3	5 E-07	33
	DP4	R2	5 E-07	179
B640-P1	DP2	R5	5 E-04	7
R641	DP2	R3	1 E-05	25
	DP5		1 E-04	10
R641-B1	DP1	R3	1 E-05	20
	DP2	R3	1 E-05	14
	DP3	R3	1 E-05	19
	DP5		1 E-04	15
R641-P1	-	-	-	-
R641-P2	DP2	R5	5 E-04	11
R641-W1	DP2	R3	1 E-04	12
G642	DP2	R3	1 E-05	8
G642-B1	DP1	R3	1 E-05	20
	DP2	R3	1 E-05	14
	DP3	R3	1 E-05	19
	DP5		1 E-04	15
G642-W1	DP1	R3	1 E-04	7
	DP2	R3	1 E-04	12
G642-P1	DP2	R5	5 E-04	11
G642-H2	DP6		1 E-03	1

Table 4.6.14: Damage distances and credit factors for Option 1.

Unit	Scenario	Release	Credit factor (y^{-1})	Damage distance (m)
L2023	DP1	R1	1 E-05	81
		R2	5 E-07	509
		R3	5 E-07	71
	DP2	R1	1 E-05	35
		R2	5 E-07	34
		R3	5 E-07	41
	DP3	R1	1 E-05	35
		R2	5 E-07	230
		R3	5 E-07	29
	DP4	R2	5 E-07	157
L2023-P1	DP1	R5	5 E-04	136
	DP2	R4	1 E-04	14
		R5	5 E-04	19
	DP3	R5	5 E-04	48
R123	DP1	R3	1 E-04	136
	DP2	R3	1 E-04	30
	DP3	R3	1 E-04	48
	DP5		1 E-03	16
R123-P1	DP2	R4	1 E-04	14
R123-P4	DP2	R4	1 E-04	14
		R5	5 E-04	8
R123-W1	DP1	R3	1 E-04	10
	DP2	R3	1 E-03	14
F124-B2	DP1	R1	1 E-05	56
		R2	5 E-07	96
	DP2	R1	1 E-05	24
		R2	5 E-07	24
		R3	5 E-07	22
	DP3	R1	1 E-05	26
		R2	5 E-07	44
		R3	5 E-07	5
T125	DP6		1 E-03	14

Table 4.6.15: Damage distances and credit factors for Option 2.

4.6.8 – Case study #2: Sustainability assessment

The data collected in §4.6.6 are the input for the impact indices in sustainability assessment (§1.2).
Table 4.6.17 reports the normalized environmental indicators. Also in this case materials are identified as the most significant environmental category: this is a consequence of the process being the finishing of a final product, that has already caused impacts in the production stage. However the material index is practically identical among the alternatives. Similarly to case study #1, the impacts related to emissions from heat production (global warming, acidification, smog formation, air toxicity, carcinogenicity) are about one order of magnitude higher for option 2, which requires more steam in the operation (in particular in the drying section). Waste disposal is appreciable only for option 2, that produces a liquid waste form process water purge. Electrical power consumption is slightly higher for Option 1, because of the continuous operation of the vacuum pump and the refrigeration cycle.

Option 1			Option 2		
Unit	UHI	HI	Unit	UHI	HI
B640	2,19E-01	4,24E-01	L2023	1,97E-01	1,06E+01
B640-P1	2,44E-02		L2023-P1	9,29E+00	
R641	1,72E-02		R123	2,12E-01	
R641-B1	2,71E-03		R123-P1	1,91E-02	
R641-P1	-		R123-P4	4,98E-02	
R641-P2	6,40E-02		R123-W1	1,98E-02	
R641-W1	1,48E-02		F124-B2	3,57E-02	
G642	5,79E-04		T125	1,96E-01	
G642-B1	2,71E-03				
G642-W1	1,39E-02				
G642-P1	6,45E-02				
G642-H2	-				

Table 4.6.16: Unit and overall hazard indices for case study 2.

Impact category	**Option 1**	**Option 2**	**Normalization factor**	**Weight factor**
Global warming	5,45E-02	1,55E-01	1,16E+06 kg/(y·km^2)	0.051
Acidification	5,20E-03	1,43E-02	4,83E+03 kg/(y·km^2)	0.066
Smog formation	1,46E-03	2,86E-03	5,63E+03 kg/(y·km^2)	0.049
Air toxicity	2,62E-02	7,27E-02	3,77E+05 kg/(y·km^2)	0.095
Carcinogenicity	3,63E+00	1,04E+01	9,91E-01 kg/(y·km^2)	0.168
Materials	1,169E+02	1,17E+02	4,80E+05 kg/(y·km^2)	0.044
Electrical power	8,66E-01	7,16E-01	3,51E+05 kWh/(y·km^2)	0.064
Waste disposal	-	3,65E+00	2,32E+05 kg/(y·km^2)	0.030

Table 4.6.17: Normalized environmental indicators, normalization and weight factors for the assessment of case study #2.

The capital investment cost of option 1 is higher than option 2, due to the special and patented equipment required. However operative costs are lower for option 1, since a the requirement for utilities (steam, cooling, nitrogen, waste disposal, etc.) is lower (Table 4.6.13). This second effect prevail in the calculation of NPV, under the hypothesis assumed for the discount and tax rates.

The societal index is a combination of inherent safety and occupational impacts (Table 4.6.18). Inherent safety was discussed above (§4.6.7) and identifies the continuous option 1 to be largely preferable. The employees required (occupational index) for option 2 is larger, as it can be observed also in the analysis of operative costs. In this option also the allocation of part of the workers of the compacting plant is accounted. However, when the societal index is calculated inherent safety is prevalent, as expected from an highly automatic plant handling moderately hazardous materials.

The level 2 indices reported in table 4.6.19 evidence that, in this case, the impacts on the 3 spheres o sustainability are of the same order of magnitude. All the indices are favourable to option 1: environmental and economic indices reflect the lower consumption of utilities of this option and societal index reflects the applicability of the inherent safety guideword *minimization*.
The result of the aggregation to an overall index is, obviously, a clear preference of option 1. The index is negative since the more influent parameter for the calculation, the economic index, is negative.

Impact category	**Option 1**	**Option 2**	**Normalization factor**	**Weight factor**
Non normalized				
Occupational index	5 people	10.2 people	7,92E+01 peop./km^2	
Inherent safety index	1,33 m^2/y	33,3 m^2/y	7,00E+00 m^2/y km^2	
Normalized				
Occupational index	6,30E-02	1,29E-01		0,20
Inherent safety index	1,90E-01	4,75E+00		0,80
Societal index	1,39E-01	3,78E+00		

Table 4.6.18: Societal indices, normalization and weight factors for case study #2.

	Option 1	**Option 2**	**Weight factor**
Level 2			
Environmental index	5,81	7,07	0,30
Economic index	-9,09	-8,43	0,30
Societal index	0,14	3,78	0,40
Level 3			
Overall index	-0,926	1,103	

Table 4.6.19: Aggregated indices and weight factors for case study #2.

4.6.7 – Conclusions

In the case studies described above the methods developed for sustainability and inherent safety assessment are applied to alternative options for treatment of materials in speciality chemistry plants. This represent a rather particular kind of analysis, conceptually different than the process selection discussed in other cases studies. Nevertheless the methods were applicable and yielded valuable results. The results matched with the results expected from experience, thus, validating the proposed approach.

In particular the developed methods identified the following specific conclusions on the assessed options:

- The analysed processes are treatment of materials and mixtures, no reactions occur: thus differences in the impacts among the alternatives are mainly related to the hazard, costs and energy requirements of the handling operations.
- The use of highly hazardous materials, as material B in case study #1, makes inherent safety a dominant aspect for this kind of processes. This hazard is enhanced when manual operations (e.g. forklift truck handling) are performed, since this increases the credibility of release.
- Processes operating in continuous result inherently safer, since the material inventories are lower (minimization).
- The use of energy and utilities is the main element defining the marginal environmental performance in these kind of operations, since the prevalent impacts on many categories derives from the emission for the use of these utilities. The absolute value of the environmental index is, instead, dominated by the usage of materials processed, since impacts are accounted for their production in former lifecycle stages.
- Economic indices are influenced by the annual operative costs; turnover periods for the capital investments are usually very short for these applications.

4.7 – Layout definition

This chapter reports some case studiers demonstrating the analysis of layout plans as described in §2.4. The cases encompass different typologies of plant and different section of the facility (e.g. process and storage sections). This allows to test the applicability of the different methods to the various situations.
Further case studies with application of the KPIs for domino hazard assessment (§2.4.2.2) are described in §4.4.4 for hydrogen storage.

4.7.1 – Case study A: preliminary plant layout for production of acrylic acid

This case study depicts an application of the developed I2SI for layout assessment (§2.4.3.2). It concerns the definition of the preferable layout plan for an acrylic acid production plant. The analysis will compare three different options for the overall plan, aiming to select the better layout by an inherently safe approach.

The process for acrylic acid production was already studied in the literature on inherent safety *[Khan & Amyotte, 2005; Palaniappan et al., 2002b]*. However these analysis limited to chemical route and process selection, not assessing layout issues, since no suitable tools were available for the analysis (§2.4.1). The analysis in the literature lead to identify the one-step catalytic oxidation of propylene in the vapor phase as the inherently safer process for acrylic acid production. Further process details on this process are described by *Palaniappan et al., [2002b]*. Result in good agreement with the ones from Palaniappan and co-workers were obtained by the application of the I2SI from literature *[Khan & Amyotte, 2005]*. In the following the developed I2SI for layout assessment (§2.4.2) is applied to three possible layout options for a plant based on the one-step catalytic oxidation of propylene.

The set of units considered in the analysis includes the process units, the units of the storage section for feedstock materials and products (propylene, acrylic acid, acetic acid, solvent for make-up), the tank-truck loading facility and the principal plant utilities (a detailed list can be found in Table 4.7.1).
Figures 4.7.1 and 4.7.2 provide details of the general plot layout and the process area layout, respectively, of the three possible layout options are that have been proposed for comparison compared.
Each option thus presents a different solution for the design of both the overall plot plan and the process area configuration:

- Option 1 (base option) was designed in accordance with typical safety rules used in industrial practice for separation distances (*[Mecklenburgh, 1985; Lees, 1996]* and references cited therein). Because this option is taken as the base case, no passive protection devices were considered. The units of the process area are arranged in a single block, in two parallel rows following the process flow order. The storage area can be sub-divided into two main blocks – the pressurized storage of liquefied propylene (comprised of several horizontal vessels) and the atmospheric tank farm for storage of the liquids (acrylic acid, acetic acids and solvent).

- Option 2 presents an improved layout in the process area. The units are segregated in two blocks (reaction and product recovery block, and separation block). A wall, acting as both a fire resistant wall and a blast wall, is erected at the edge of the first block. All units have fire insulation in place. The layout of the loading and storage area has the same plot plan as option 1; however, passive protection measures (bunds and fire insulation) are considered in this case.

- Option 3 incorporates segregation of units, a modified spatial arrangement and passive protection devices, all aimed at enhancing layout safety. The units in the process area are arranged in two segregated blocks on a single row. The control room and laboratory are placed at a conveniently safe distance. Fire insulation is in place on all units. In addition, two firewalls to protect the quencher, and a bund to contain possible spills from the splitter, are in place. The layout of the tank farm is improved to limit escalation consequences. The distance of the loading facility from the propylene storage area is also increased.

4.7.2 – Results from layout safety assessment of case study A

For ease of discussion, the case study A is now analyzed before limiting the perspective to the process area layout and then expanding it to the overall plot plan.

4.7.2.1 – Process area layout of case study A

The results of the analysis of the three layout options are presented in Tables 7.4.1 through 7.4.8. The process area is discussed first because it consists of closely linked processing units and displays several hazardous features that can trigger escalation events. The process area units considered for all options are listed in Table 7.4.1. Data on the relative distances of the units were organized for each layout in the form of a distance matrix; an example for option 3 is given in Table 4.7.1.

Relevant primary events were identified and the DHI was calculated. An example of the domino hazard scoring is reported in Table 4.7.2 for option 3. As explained in §2.4.2, the assessment of the DHI is required for evaluation of the Inherent Safety Index, or ISI. This further requires consideration of the extent of applicability of the inherent safety guidewords *attenuation* and *limitation of effects*; thus DHI must be calculated twice for each option (i.e. both with and without passive protection measures). Assessment of the damage distances for each option (again, a requirement for ISI computation) was accomplished in the present case study by means of the SWeHI methodology *[Khan et al., 2001]*. Values of the principal indices for the case study analysis are reported in Tables from 4.7.3 to 4.7.5.

#	Unit	*01*	*02*	*03*	*04*	*05*	*06*	*07*	*08*	*09*	*10*	*11*
01	Compressor	-	10.2	12.6	20.3	26.7	25.0	31.0	26.0	26.2	21.8	23.0
02	Feed mixer	10.2	-	6.8	17.0	24.1	24.9	38.8	35.7	33.7	33.0	33.7
03	Reactor	12.6	6.8	-	10.2	17.3	18.4	35.7	33.7	30.5	33.6	33.0
04	Quencher	20.3	17.0	10.2	-	7.1	9.5	33.2	33.2	27.0	37.0	34.5
05	Absorber	26.7	24.1	17.3	7.1	-	6.3	33.2	34.6	27.1	40.7	37.2
06	Splitter	25.0	24.9	18.4	9.5	6.3	-	27.0	28.7	20.8	35.8	31.8
07	Acid extractor	31.0	38.8	35.7	33.2	33.2	27.0	-	6.8	6.2	20.1	13.5
08	Distillation I	26.0	35.7	33.7	33.2	34.6	28.7	6.8	-	9.2	13.3	6.7
09	Solvent mixer	26.2	33.7	30.5	27.0	27.1	20.8	6.2	9.2	-	21.0	14.9
10	Distillation II	21.8	33.0	33.6	37.0	40.7	35.8	20.1	13.3	21.0	-	6.6
11	Distillation III	23.0	33.7	33.0	34.5	37.2	31.8	13.5	6.7	14.9	6.6	-

Table 4.7.1: Example of distances among unit geometric centres in process area of option 3.

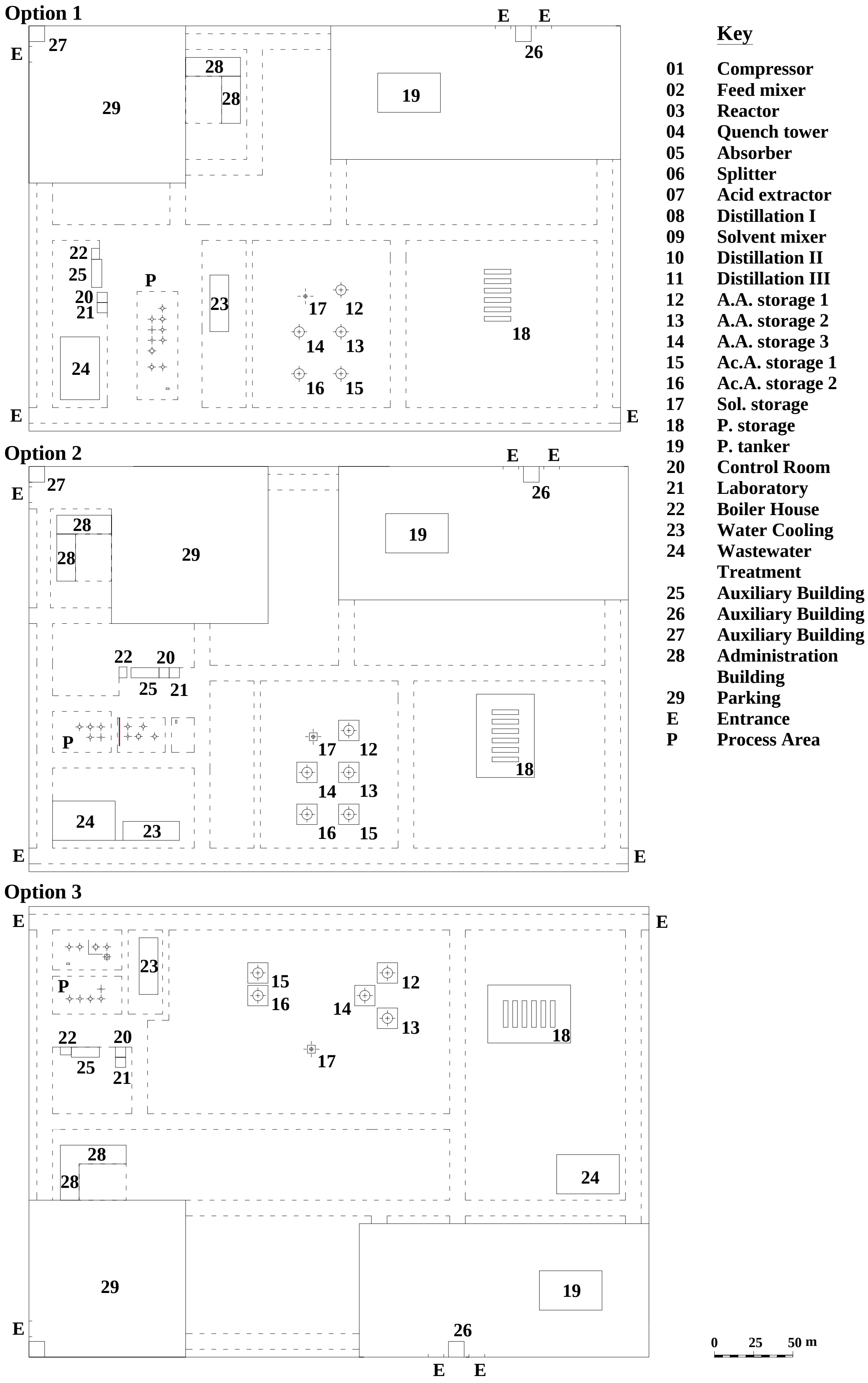


Figure 4.7.1 Layout plan of the three options in the case study.

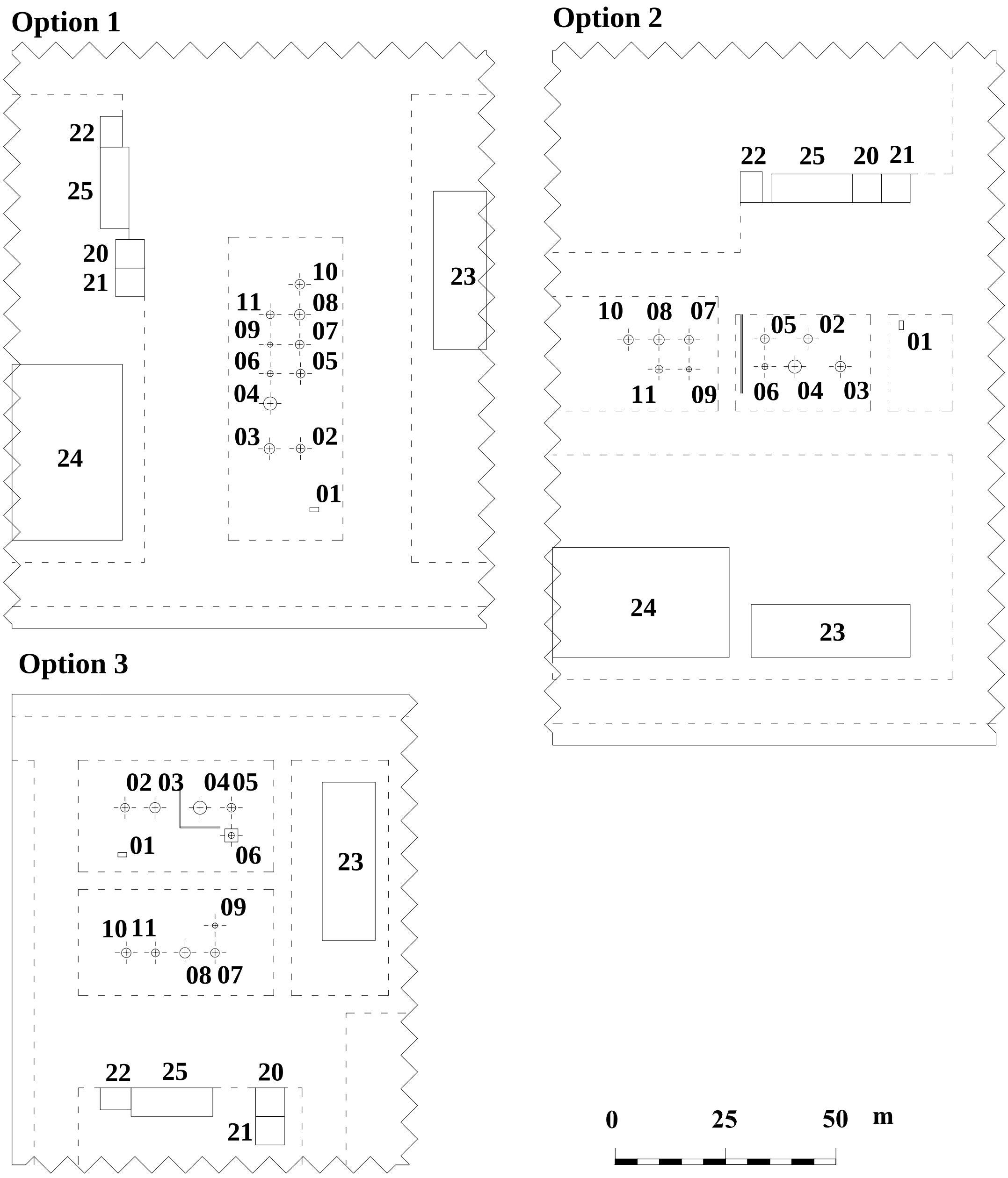


Figure 4.7.2: Layout of the process area of the three options in the case study.

Some general observations can be made concerning the DHS data such as those reported in Table 4.7.2. Units located in the same block are placed at close relative distances and domino effects within the block are extremely likely. However, some units have the potential to trigger escalation events at longer distances than others. When this distance is higher than (or at least comparable to) the block characteristic dimensions, placing these units in the same layout block implicitly means accepting a heightened escalation possibility. On the other hand, for units that trigger escalation only at short distances, the location within the block largely determines the possibility of initiating an escalation chain. In block layout design, therefore, the location of these latter units is of strategic importance in limiting the magnitude of accident consequences.

		Primary Unit										
	#	*01*	*02*	*03*	*04*	*05*	*06*	*07*	*08*	*09*	*10*	*11*
#	*Secondary Unit*											
01	Compressor	-										
02	Feed mixer	1	-	10	10	1	1	1	1.1	1	1.4	1.6
03	Reactor	1	10	-	10	1	1	1	1.3	1	1.3	1.7
04	Quencher	1	10	10	-	10	2	1	1	1	0.8	1
05	Absorber	1	10	10	10	-	5	1	1.2	1	1	1.5
06	Splitter	1					-			1.4	1.1	
07	Acid extractor	1	1.3	1.6	1	0.3	1	-	10	7	10	10
08	Distillation I	1					1		-	2.1	10	
09	Solvent mixer	1								-		
10	Distillation II	1								1.4	-	
11	Distillation III	1	1.6	1.7	1	1	1	2.5	10	1.8	10	-
	DHI	10	33	33	32	13	12	7	25	18	36	16

Table 4.7.2: Example of $DHS_{i,k}$ matrix for process area. Data refer to option 3, considering the effect of passive protection devices. Shaded areas correspond to negligible escalation effects (negative escalation test). Dashed lines group together units belonging to the same block.

4.7.2.1.1 – Option 1 (base case)

Table 4.7.3 depicts the I2SI values for option 1. Since this is the base case, these overall index values are mainly influenced by the HI values. Most of the units in the process area yield results for I2SI that are significantly less than unity. On the other hand, the (air) compressor displays relatively safer performance. This is a consequence of the low damage potential (low DI and hence, low HI) and the modest requirement for hazard control devices in the layout definition (low HCI, yielding an ISPI above the average value). Concerning the other units, distillation II is identified as being somewhat safer than the average – again, because of a lower HI, but this time due to extensive application of control devices (this is the product refining column and monitoring is critical for quality control purposes). As expected, the reactor, because it requires a high level of safety devices, has the poorest inherent safety performance (lowest I2SI).

The results of the cost indexing for option 1 are reported in Table 4.7.6. Again, no inherent safety measures are considered to be applied because this is the base case. Hence, the conventional and inherent safety cost indices are identical. It can be observed, however, that the cost indices for all units are below unity, meaning that the cost of safety devices is lower than the expected losses. That is mainly due to the possibility of domino effects which significantly increases the loss parameter values.

4.7.2.1.2 - Option 2

Focusing on option 2 (Table 4.7.4), the segregation of the two unit blocks in the process area is effective in reducing the escalation hazard of the units located close to the gap between the blocks. This leads to reduced values of DHI and increased values of ISI for the *attenuation* guideword as compared to the base case (option 1). Safety is further enhanced when passive

#	Unit	ISI_a	ISI_s	ISI_l	ISI	PHCI	ISPI	DI	HCI	HI	I2SI
01	Compressor	1.0	1.0	1.4	5.0	11	0.45	7	43	0.17	2.71
02	Feed mixer	1.0	1.0	1.4	5.0	31	0.16	29	56	0.53	0.31
03	Reactor	1.0	1.0	1.4	5.0	42	0.12	47	92	0.52	0.23
04	Quencher	1.0	1.0	1.4	5.0	26	0.19	25	51	0.48	0.40
05	Absorber	1.0	1.0	1.4	5.0	31	0.16	30	57	0.53	0.30
06	Splitter	1.0	1.0	1.4	5.0	21	0.24	21	51	0.41	0.58
07	Acid extractor	1.0	1.0	1.4	5.0	21	0.24	30	47	0.65	0.37
08	Distillation I	1.0	1.0	1.4	5.0	21	0.24	22	45	0.49	0.48
09	Solvent mixer	1.0	1.0	1.4	5.0	21	0.24	20	42	0.47	0.51
10	Distillation II	1.0	1.0	1.4	5.0	21	0.24	21	58	0.36	0.67
11	Distillation III	1.0	1.0	1.4	5.0	21	0.24	27	45	0.59	0.40
12	AA storage 1	1.0	1.0	1.4	5.0	24	0.21	36	56	0.64	0.32
13	AA storage 2	1.0	1.0	1.4	5.0	24	0.21	36	56	0.64	0.32
14	AA storage 3	1.0	1.0	1.4	5.0	24	0.21	36	56	0.64	0.32
15	AcA storage 1	1.0	1.0	1.4	5.0	24	0.21	38	56	0.68	0.31
16	AcA storage 2	1.0	1.0	1.4	5.0	24	0.21	38	56	0.68	0.31
17	Sol storage	1.0	1.0	1.4	5.0	24	0.21	14	55	0.25	0.82
18	P storage	1.0	1.0	1.4	5.0	36	0.14	40	73	0.55	0.25
19	P tanker	1.0	1.0	1.4	5.0	36	0.14	27	73	0.37	0.38

Table 4.7.3: Summary of all indices evaluated in the assessment for option 1 (case base). AA: acrylic acid, AcA: acetic acid, Sol: solvent, P: propylene.

#	Unit	ISI_a	ISI_s	ISI_l	ISI	PHCI	ISPI	DI	HCI	HI	I2SI
01	Compressor	1.0	1	1.4	5.0	11	0.45	7	43	0.17	2.71
02	Feed mixer	1.0	-10	5.7	5.0	25	0.20	29	56	0.53	0.38
03	Reactor	1.9	1	6.2	6.5	36	0.18	47	92	0.52	0.35
04	Quencher	1.1	1	6.7	6.8	22	0.31	25	51	0.48	0.65
05	Absorber	1.5	-10	7.1	5.0	23	0.22	30	57	0.53	0.41
06	Splitter	3.0	-10	21.5	19.3	17	1.13	21	51	0.41	2.74
07	Acid extractor	5.3	-10	32.6	31.5	17	1.85	30	47	0.65	2.86
08	Distillation I	2.4	1	15.0	15.2	17	0.89	22	45	0.49	1.82
09	Solvent mixer	2.2	1	28.9	29.0	17	1.71	20	42	0.47	3.64
10	Distillation II	3.7	1	9.3	10.0	17	0.59	21	58	0.36	1.66
11	Distillation III	2.0	1	32.3	32.3	17	1.90	27	45	0.59	3.23
12	AA storage 1	1.0	-10	45.1	44.0	24	1.83	36	56	0.64	2.85
13	AA storage 2	1.0	-10	34.1	32.6	24	1.36	36	56	0.64	2.11
14	AA storage 3	1.0	-10	34.5	33.0	24	1.38	36	56	0.64	2.14
15	AcA storage 1	1.0	-10	36.8	35.4	24	1.47	38	56	0.68	2.17
16	AcA storage 2	1.0	-10	41.8	40.6	24	1.69	38	56	0.68	2.49
17	Sol storage	1.0	-10	69.4	68.7	24	2.86	14	55	0.25	11.3
18	P storage	1.0	1	1.4	5.0	36	0.14	40	73	0.55	0.25
19	P tanker	1.0	1	1.4	5.0	36	0.14	27	73	0.37	0.38

Table 4.7.4: Summary of all indices evaluated in the assessment for option 2. AA: acrylic acid, AcA: acetic acid, Sol: solvent, P: propylene.

devices are considered, because the separation wall poses a physical barrier to escalation from one block to the other. The new position of the manned buildings (control room and laboratory) is verified as safer because these buildings are now located further from the units of the product separation block. As a consequence, the value of ISI for the *limitation of effects* guideword is significantly increased. On the other hand, ISI for the *simplification* guideword yields a negative contribution to all the units close to the wall, since the wall represents an obstacle. However, the absolute value of this contribution is judged to be quite small, because in the base option the same units were similarly obstructed by the absence of the gap between the blocks. The final result for I2SI is an increase above unity for all units belonging to the product separation block. This reflects the limited possibility of escalation from hazardous units (such as the reactor) in the other block.

From a cost perspective (Table 4.7.6), segregation of the process layout into two blocks and the presence of passive measures reduce the requirement for further safety measures – thus lowering overall safety costs. The costs of applied devices and of additional land (i.e. increased space requirements) were considered in the evaluation of the inherent safety cost. The overall effect is one of reducing the unit ISCI value from the base case (option 1). This decrease in ISCI is limited to a maximum factor of about 1.4 (reference unit 05, the absorber, in Table 4.7.6), meaning that the safety savings are usually an order of magnitude lower than the total costs. The units exhibiting better performance in this regard are those near the block spacing gap and thus protected by the wall – for example, the aforementioned absorber as well as the solvent mixer (unit 09 in Table 4.7.6).

4.7.2.1.3 - Option 3

In the process area of option 3, the unit arrangement increases segregation, effectively reducing the DHI values as compared to the base case. This yields high values of ISI for the *attenuation* guideword (Table 4.7.5). However, it also creates limitations on applicability of the *simplification* guideword, since the piping network for connection of the various units is made longer. The increased unit segregation makes the passive devices more effective, since the escalation vectors to be countered are mitigated by distance. This results in high values of ISI for the *limitation of effects* guideword. Some contribution to this index is also provided by the better building location (ISI_{lb}) and the fire resistant wall that limits the possible affected areas (ISI_{la}). Focusing on I2SI, values above unity are obtained for most of the units. In particular, the highest values are obtained for the splitter and acid extractor because the arrangement and the passive protection measures serve to limit escalation possibilities as compared to the base case (option 1). On the other hand, the units with the poorest performance are the reactor and the quencher. This is due to the domino effect from explosions which is not countered by the fire resistant wall.

In option 3 the values of ISCI for all units in the process area are lower than the corresponding CSCI values (Table 4.7.6). These cost reductions are limited in extent for the same reasons discussed for option 2. In particular, safety costs are significantly decreased for the reactor (due to unit segregation and the firewall), solvent mixer (due to location), absorber (due to location), and splitter (due to location and bund). It can be observed that the ISCI values are comparable to the results for option 2; thus both options can be considered to be at the same approximate level of cost effectiveness. It should be remembered, however, that option 3 generally displays better performance from an inherent safety perspective.

#		ISI_a	ISI_s	ISI_l	ISI	PHCI	ISPI	DI	HCI	HI	I2SI
01	Compressor	1.0	1	1.4	5.0	11	0.45	7	43	0.17	2.71
02	Feed mixer	1.7	1	12.0	12.1	21	0.58	29	56	0.53	1.10
03	Reactor	1.7	-10	12.0	6.9	38	0.18	47	92	0.52	0.35
04	Quencher	1.6	-30	12.8	5.0	22	0.23	25	51	0.48	0.47
05	Absorber	8.3	-30	38.3	25.1	27	0.93	30	57	0.53	1.75
06	Splitter	12.2	-30	55.5	48.2	17	2.84	21	51	0.41	6.86
07	Acid extractor	36.4	-30	75.2	78.0	17	4.59	30	47	0.65	7.10
08	Distillation I	3.1	1	16.4	16.7	17	0.98	22	45	0.49	1.99
09	Solvent mixer	5.8	-30	37.8	23.7	17	1.39	20	42	0.47	2.97
10	Distillation II	2.8	-10	13.1	8.9	17	0.53	21	58	0.36	1.48
11	Distillation III	2.7	1	27.0	27.1	17	1.59	27	45	0.59	2.71
12	AA storage 1	1.0	-20	54.6	50.8	24	2.12	36	56	0.64	3.29
13	AA storage 2	1.0	-20	54.6	50.8	24	2.12	36	56	0.64	3.29
14	AA storage 3	1.0	-20	54.6	50.8	24	2.12	36	56	0.64	3.29
15	AcA storage 1	1.0	-20	71.3	68.5	24	2.85	38	56	0.68	4.20
16	AcA storage 2	1.0	-20	71.3	68.5	24	2.85	38	56	0.68	4.20
17	Sol storage	1.9	-30	99.5	94.9	24	3.96	14	55	0.25	15.5
18	P storage	1.1	1	1.5	5.0	36	0.14	40	73	0.55	0.25
19	P tanker	42.9	1	42.7	60.5	36	1.68	27	73	0.37	4.54

Table 4.7.5: Summary of all indices evaluated in the assessment for option 3. AA: acrylic acid, AcA: acetic acid, Sol: solvent, P: propylene.

	Common to All Options (Base Case)			*Option 1*		*Option 2*		*Option 3*	
#	C_{Loss} ($)	$C_{ConvSafety}$ ($)	CSCI	$C_{InhSafety}$ ($)	ISCI	$C_{InhSafety}$ ($)	ISCI	$C_{InhSafety}$ ($)	ISCI
01	32680	23500	0.72	23500	0.72	20500	0.63	20500	0.63
02	127868	44500	0.35	44500	0.35	44423	0.35	37434	0.29
03	138266	63000	0.46	63000	0.46	54313	0.39	46120	0.33
04	126140	25500	0.20	25500	0.20	24333	0.19	23985	0.19
05	47699	32500	0.68	32500	0.68	22588	0.47	25851	0.54
06	101186	21000	0.21	21000	0.21	17324	0.17	16706	0.17
07	69381	21500	0.31	21500	0.31	18234	0.26	19738	0.28
08	105368	20000	0.19	20000	0.19	17652	0.17	17743	0.17
09	113504	24000	0.21	24000	0.21	17134	0.15	16695	0.15
10	114921	22000	0.19	22000	0.19	19751	0.17	20259	0.18
11	57392	18000	0.31	18000	0.31	15554	0.27	15698	0.27
12	118432	33500	0.28	33500	0.28	30135	0.25	30135	0.25
13	118432	33500	0.28	33500	0.28	30178	0.25	30135	0.25
14	118432	33500	0.28	33500	0.28	30176	0.25	30135	0.25
15	118432	33500	0.28	33500	0.28	30165	0.25	30028	0.25
16	118432	33500	0.28	33500	0.28	30146	0.25	30028	0.25
17	218434	33500	0.15	33500	0.15	30081	0.14	32354	0.15
18	437977	287500	0.66	287500	0.66	275500	0.63	309028	0.71
19	389648	69500	0.18	69500	0.18	69500	0.18	59664	0.15

Table 4.7.6: Summary of cost indices evaluated in the assessment for the three options. For item number, refer to Table 4.7.3. C_{Loss}, $C_{ConvSafety}$ and CSCI are the same for all options (being based on the values of the base case).

The analysis of the Loss Saving Index (Table 4.7.7) reveals that options 2 and 3 are by far more cost effective in limiting the expected loss from accidental events. This is once again due to the integrated effect of passive and inherent measures. The presence of several negative values means that the cost of these measures is fully compensated for by the expected decrease in loss in the event of an accident. Analyzing the details for each unit generally results in the same outcomes already discussed for the I2SI results. This is due to the predominant effect of the values of DHI on both indices (LSI and I2SI).

#	Unit	Option 1	Option 2	Option 3
01	Compressor	0.72	0.36	0.33
02	Feed mixer	0.35	0.42	0.49
03	Reactor	0.46	-0.19	-0.27
04	Quench tower	0.20	-0.03	-0.07
05	Absorber	0.68	0.16	-0.06
06	Splitter	0.21	-0.32	-0.65
07	Acid extractor	0.31	-0.24	-0.37
08	Distillation I	0.19	-0.36	-0.41
09	Solvent mixer	0.21	-0.60	-0.65
10	Distillation II	0.19	-0.32	-0.30
11	Distillation III	0.31	-0.30	-0.27
12	AA storage 1	0.28	-0.46	-0.47
13	AA storage 2	0.28	-0.44	-0.47
14	AA storage 3	0.28	-0.44	-0.47
15	AcA storage 1	0.28	-0.45	-0.50
16	AcA storage 2	0.28	-0.46	-0.50
17	Sol storage	0.15	-0.81	-0.82
18	P storage	0.66	0.57	0.52
19	P tanker	0.18	0.18	-0.47

Table 4.7.7: Loss saving indices of the case study. AA: acrylic acid, AcA: acetic acid, Sol: solvent, P: propylene.

4.7.2.2 – Overall plot plan of case study A

Application of the proposed index methodology to the plot plan of the base case (option 1) reveals that the safety distances from the literature are effective in preventing escalation from storage to process area and vice-versa. This is also due to the choice, derived by safety experience and common to all proposed layouts, of locating the propylene storage at the furthest feasible distance from the process area. This enhances the evaluation of the whole layout, since no significant interactions are then possible between the process and storage areas (except fragment or missile projection – which, as previously discussed, is difficult to limit in practice). Another observation concerning the propylene storage is that this area has the same tank layout in all options and therefore does not require assessment of safety improvement possibilities. (This again highlights the fact that indices such as I2SI are intended to be used in a relative, not absolute, manner to effect risk reduction.) Thus, in the following discussion, only the effect on the other storage units from a single propylene vessel is considered.

As shown in Table 4.7.3, the I2SI values for the storage and loading area in option 1 are below unity. The Inherent Safety Index (ISI) has low values, as expected for the base case. The values of Damage Index (DI) illustrate that all units have significant damage distances and hence significant potential to trigger escalation. As expected, propylene storage appears as a critical safety issue. The storage of solvent, however, is a relatively low hazard unit with respect to escalation.

In option 2 (Table 4.7.4), the spatial disposition of the units is the same as in option 1. Thus, the I2SI values principally reflect the effect of passive measures in escalation limitation. The combined protection of bunding and fire insulation increases the index values of the atmospheric storage units for flammable liquids well above unity.

In option 3 (Table 4.7.5), the improved unit spatial disposition has no effect in preventing escalation among unprotected atmospheric storage units (low values of ISI_a); however, if combined with passive protection, enhanced safety performance is obtained (high values of ISI_l, mainly due to *limitation of the effects of domino escalation*). On the other hand, the increased segregation does prevent, from an inherent safety perspective, escalation triggered by the propylene tank trucks at the loading station. The I2SI values are well above unity for all units, with good performance of the solvent storage unit made possible by adopting both inherent and passive measures.

Table 4.7.6 and 4.7.7 show the results of cost indexing for the storage and loading area. From Table 4.7.6, it can be observed that storage units usually have large costs of losses, mainly due to the large extent of damage propagation by domino effect. For storage, ISCI values are therefore lower than unity, suggesting that further protective measures should be applied. Option 2 shows only a minor decrease in ISCI values compared to those for CSCI for the storage area. This is a direct consequence of the similar values of costs for conventional safety and inherent safety. The same conclusions generally hold for option 3. Here, though, the inherent safety cost for propylene storage is higher than the conventional safety cost because of the high land cost for unit separation.

Analysis of the Loss Saving Index results in Table 4.7.7 leads to the same conclusions as those drawn for the process area. The loading facility offers a clear example of the previously discussed effect of DHI performance on both LSI and I2SI.

Table 4.7.8 reports the system I2SI for each of the three options. The better performance of the whole plant clearly belongs to option 3 due to the positive contribution of every unit. The contribution to the system index of the two identified plant areas (process area and storage area) is equally balanced in options 1 and 2, while a difference of one order of magnitude is shown by option 3. This is mainly due to the good performance achieved by coupling segregation and passive protection in facility layout.

	Process Units	Storage and Loading Units	Whole Plant
Option 1 (Base Case)	$1.8 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$	$2.9 \cdot 10^{-4}$
Option 2	$5.2 \cdot 10^{0}$	$8.6 \cdot 10^{0}$	$4.5 \cdot 10^{1}$
Option 3	$3.2 \cdot 10^{1}$	$1.1 \cdot 10^{2}$	$3.4 \cdot 10^{3}$

Table 4.7.8: System I2SI values for process area, storage area and the whole plant.

4.7.3 – Case study B: preliminary layout of an oil separation section

Case Study B shows an application of the KPIs for domino hazard assessment proposed in §2.4.2.2. The lay-out analyzed in this Case Study is a section of an off-shore separation train for oil extraction (Figure 4.7.3). Four main pieces of equipment were considered, as shown in Table 4.7.9. The Table also reports design details of the equipment and the primary scenarios considered in the analysis.

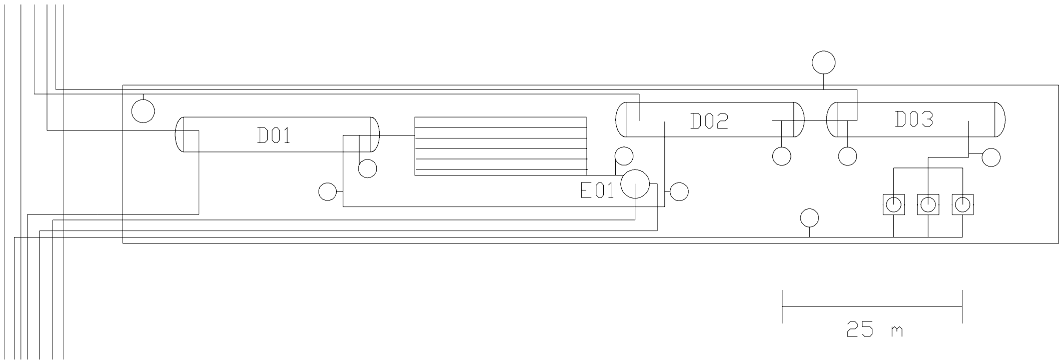


Figure 4.7.3: Layout analyzed in Case Study B.

The safety distances required for the analysis were calculated for the release scenarios using the swift approaches described in Appendix 2.2. This allowed the definition of the domino chain potential indices for the units (Table 4.7.10). The UPD values rank the units for the potential of triggering domino effects, no matter the actual position in the layout. The index may be used for a preliminary screening aimed to support an inherently safer design of the process, preliminary to layout definition. In this case study, three units have an equivalent UPD, since the considered accidental scenarios are the same. Unit E01 was identified as the potentially more critical unit since the VCE scenario may result in huge damage distances.

On the basis of the lay-out shown in Figure 4.7.3, the values of DCA, UDI and TDI were also calculated. The results are reported in Table 4.7.10. The domino chain actual hazard index, DCA, allows identifying the more hazardous domino escalation scenarios that may take place between each couple of units. As shown in Table 4.7.10, the DCA is never lower than 1.

Id.	Type	Substance	Inventory (t)	Release Type	LOC	Primary scenario
D01	Pressurized Vessel	Propane	300	continuous	Vessel Leak	Jet Fire
				continuous	PSV Opening	Jet Fire
E01	Pressurized Vessel	Propane	60	continuous	Vessel Leak	Jet Fire
				continuous	Vessel Leak	VCE
				continuous	PSV Opening	Jet Fire
D02	Pressurized Vessel	Propane	250	continuous	Vessel Leak	Jet Fire
				continuous	PSV Opening	Jet Fire
D03	Pressurized Vessel	Propane	250	continuous	Vessel Leak	Jet Fire
				continuous	PSV Opening	Jet Fire

Table 4.7.9: List of equipment units and accidental scenarios considered in Case Study B.

	D01	*E01*		*D02*	*D03*
UPD	$2.83\cdot10^{4}$	$2.06\cdot10^{6}$		$2.83\cdot10^{4}$	$2.83\cdot10^{4}$
	DCA				
	Primary unit scenario				
Target unit	*Jet fire*	*VCE*	*Jet fire*	*Jet fire*	*Jet fire*
D01	-	$2.03\cdot10^{1}$	1.75	2.00	1.08
E01	1.75	-	-	$1.40\cdot10^{1}$	2.50
D02	2.00	$1.62\cdot10^{2}$	$1.40\cdot10^{1}$	-	$1.40\cdot10^{1}$
D03	1.08	$2.89\cdot10^{1}$	2.50	$1.40\cdot10^{1}$	-
DCF	$8.6\cdot10^{1}$	$1.7\cdot10^{1}$		$7.1\cdot10^{1}$	$7.1\cdot10^{1}$
UDI	$4.83\cdot10^{1}$	$2.11\cdot10^{2}$		$3.00\cdot10^{2}$	$1.76\cdot10^{2}$
TDI	$5.10\cdot10^{1}$	$1.83\cdot10^{2}$		$3.22\cdot10^{2}$	$1.79\cdot10^{2}$

Table 7.4.10: Values of the Hazard Indices (UPD, DCA, DCF, UDI, TDI) for the equipment units considered in Case Study B.

Thus, as expected, none of the units in the lay-out is inherently safe with respect to escalation triggered by other units. This result should have been expected, since the layout is rather congested and inherent safety is considered in the approach (thus, the effect of passive and active protections is not considered).

The unit domino actual hazard index, UDI, identifies the more critical sources of domino effects, both for the capacity to damage target units and for the number of targets that may be damaged. Unit D02 appears to be particularly critical from this point of view, since the unit is very close to E01 and D03 and it has an inventory well above the critical one. On the other hand, unit D01, although having the same domino potential hazard, DPC, of D02, has a UDI value lower of about an order of magnitude due to the higher segregation.
The limited separation distances in the lay-out and the severity of the jet fire scenarios, common to all the units, are responsible as well of the high values of TDI for all the units, with the exception of D01 due to the higher separation distances present for this unit.

4.7.4 – Case study C: preliminary layout of a fuel storage section

Also Case Study C demonstrates the application of the KPIs for domino hazard assessment proposed in §2.4.2.2. This Case Study concerns the layout of a fuel storage area (Figure 4.7.4). This comprises an atmospheric tank farm for the storage of flammable liquids and several pressurized liquefied gas storage units. Table 4.7.11 summarizes the main features of the units of concern and of the primary scenarios considered.

Similarly to Case Study B, inherent safety distances were evaluated for each scenario by the swift approach described in Appendix 2.2. Quantification of inherent safety distances allowed the assessment of the hazard indices. Figure 4.7.5 summarizes the final results obtained for the UPD, the UDI and the TDI indices of the units. The figure shows that the UPD of the pressurized vessels for liquefied gas storage (D1-6) may result in scenarios (i.e. VCE) characterized by inherent safety distances well above those typical of the fire scenarios of atmospheric tanks T1-6. However, if the actual layout is considered the situation may change, since the location of the target units becomes important. The escalation is possible among the atmospheric tanks, even if the more segregated (T1 and T3 with respect to T5 and T6) are inherently safe from direct mutual domino effect. This is shown by the lower values of the UDI for these units (T1, T3, T5, T6) compared to the central ones (T2, T4). However UDI values for atmospheric tanks are lower than those for pressurized storages, since the escalation from the former to the latter is not considered credible for the fire scenarios defined in Table 4.7.11.

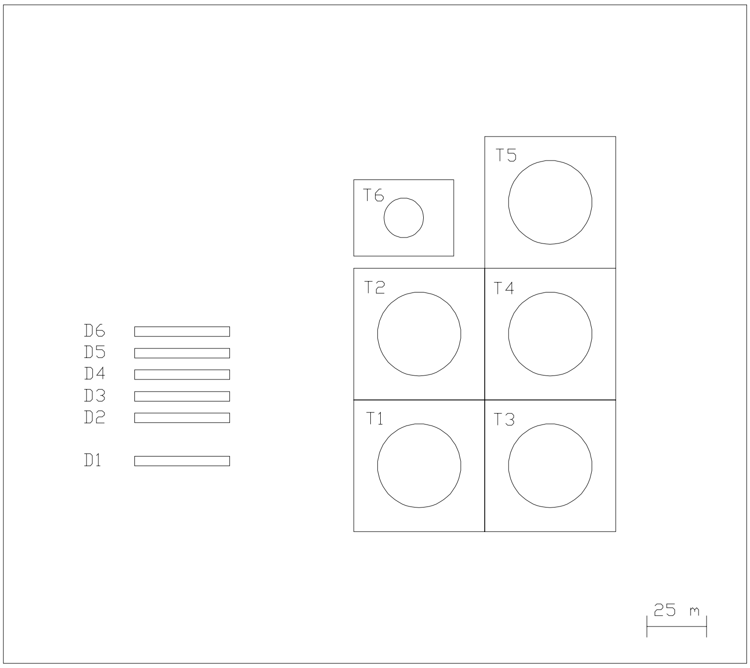


Figure 4.7.4: Layout analyzed in Case Study C.

Id.	Type	Diameter (m)	Height/ length (m)	Substance	Release Type	Primary scenario
T1-5	Atmospheric	35	10	gasoline	Continuous (50mm RD)	Pool fire (PD 15m)
					Instantaneous	Pool fire (PD 60m)
T6	Atmospheric	16.5	16.5	gasoline	Continuous (50mm RD)	Pool fire (PD 12m)
					Instantaneous	Pool fire (PD 40m)
D1-6	Pressurized	4	40	LPG	Continuous (10 min. release)	Jet Fire
					Continuous (10 min. release)	VCE
					Instantaneous	Fireball
					Instantaneous	VCE

Table 7.4.11: List of equipment units and accidental scenarios considered in case study 2. RD: release diameter; PD: pool diameter.

On the other hand any of the horizontal pressurized storage vessels may trigger escalation scenarios affecting the atmospheric storage tanks. The scoring of this effect is regulated by the relative distances of primary units and targets. As expected, units surrounded by a larger number of possible targets (e.g. D3-5) result in higher values of the indices. The TDI follow the same patterns of UDI, but the values are not, of course, identical since for a selected couple of units the mutual escalation vectors may be very different. The analysis of these results may provide useful information on the definition of add-on measures, e.g. in order to limit the possibility of escalation from pressurized to atmospheric storages or to install passive protections on the pressurized cylinders.

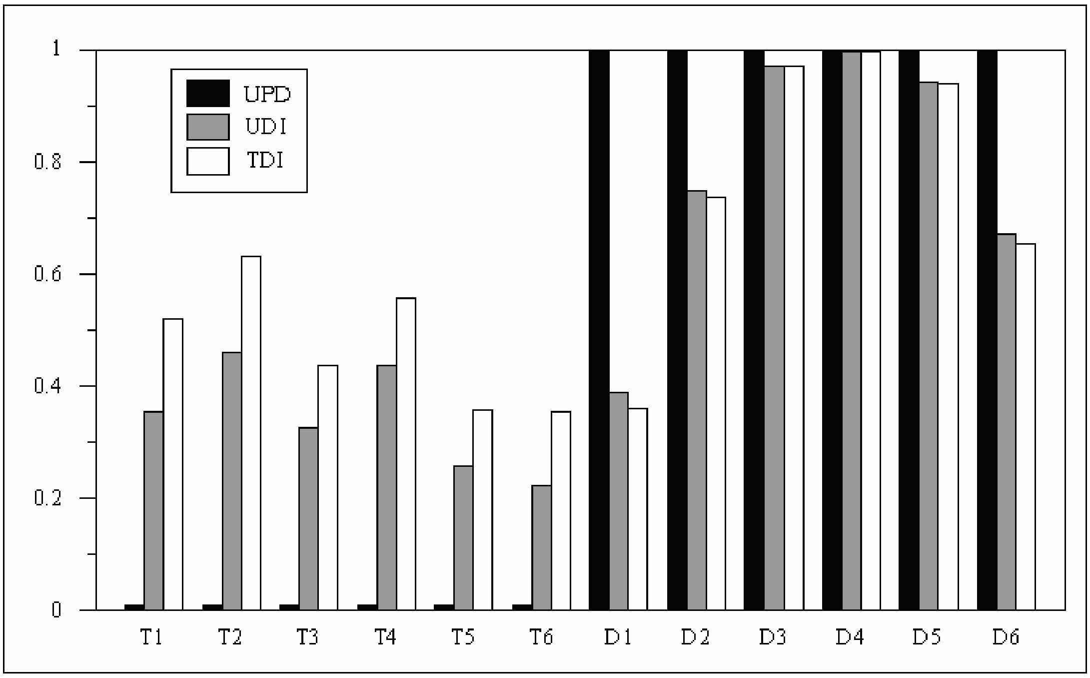


Figure 4.7.5: Hazard Indices (UPD, UDI, TDI) for the equipment units considered in Case Study C. The reported values were normalized by the highest value of each index among the units.

4.7.5 – Conclusions

In this chapter, the methods developed and presented in §2.4 were demonstrated by the application to case studies of different nature, both for plant section (layout of the process section of a plant, layout of storage area, overall layout) and plant type (chemical industry, oil-upstream and fuel storage). The case studies proved the applicability of the proposed methods in the various situations.

Moreover the methods permitted the identification of the critical units within a given layout and the assessment of the inherent safety performance of alternative options. Since in several cases the outcomes of the methods matched the results expected from the experience, this constitutes a validation of the applied methods.

From the analysis of the specific case studies, some general conclusions can be drawn about the implementation of inherent safety in layout design:

- The strategy of unit segregation is, as expected, effective in preventing domino chains, thus improving the inherent safety of the layout. Considering the whole plant, however, an integrated application of inherent and passive measures appears as the desirable way to achieve the best layout safety performance. Furthermore, the identification by the inherent safety approach of the hazards in the system cast the basis for the design of more effective the add-on measures.

- Grouping the units in blocks generally implies accepting the domino effects within a given block. This is a condition frequent in process area. The position of minor units should be carefully designed to limit initiation possibilities for chain effects.
- The economic consequences of loss for domino effects are typically significant. Therefore, limiting domino possibility by improved layout design yields important savings in terms of the avoided costs of accidents.

4.8 – Conclusions

In the current section the assessment methods presented in sections 1 and 2 were applied to several cases studies. The application successfully met both the goals initially proposed (§4.0): the demonstration of the applicability of the procedure and the validation of the methods.

The case studies concern a large variety of design problems. They differ both in the type of design activity to be analysed (choice of materials, design of the process, of the plant, of the layout) and in the function of process/plant analyzed (chemical process, storage, waste disposal). For each case study a detailed demonstration of the application and of the interpretation of the results was provided.
The application of the pertinent method was possible for each case with an amount of information comparable to that available in early design phases. This proves the applicability and the flexibility of proposed methods as a comprehensive portfolio of design support tools.
The sensitivity analysis confirmed the ability of the method to yield unambiguous results, even if the values used in the analysis were affected by a modest degree of uncertainty in the weight factor used.

With respect to the validation of the method, all the cases studies were successful in identifying the critical aspects expected from process experience or from engineering judgement. It is worth noticing that the developed methods are able to match the variety of cases expected from specific process experiences. Moreover the methods yield a quantitative picture of the impact profile, more easily interpretable than the qualitative outcomes from experience or arbitrary indices of other methods proposed in the literature.
The comparison of the results with those obtained from other literature methods evidences the better performance of the developed approach. In particular in the case studies on inherent safety assessment of alternative processes, it was possible to show that the built-in and subjective assumptions embedded in literature methods negatively affected the ability to perform the analysis. Moreover, some aspect of the safety performance, as the hazard coming from minor and auxiliary units quite prone to loss of containment (e.g. pump, compressors, heat exchangers, etc.), are frequently overlooked by conventional inherent safety approaches. These units were accounted by the methodologies developed in the present study.

In conclusion, the portfolio of developed methods is suitable to evidence the critical issues and the expected sustainability and inherent safety profile of alternative design options. It can be effectively used to support decision making and design improvement, also in the early stages of design activities. It overrides several problems and gaps present in conventional approaches for this kind of application.

Section 5

5.1 – Conclusions

In the present study, quantitative assessment tools to support the implementation of sustainability and inherent safety in process and plant design activities were developed. These approaches are suitable for the analysis of the early phases of conceptual and basic design, when the project is still open to changes (due to the large number of degrees of freedom), that may as well encompass strategies to improve sustainability and inherent safety. The development of such tools gives a substantial contribution to fill the present gap in the availability of sound supports for safety and sustainability implementation in early design. The portfolio of the developed tools is devoted to encompass different phases of the design activities, all through the lifecycle of a project.
The principal outcomes of the study are listed in the following:

- **Definition of design support tools for the analysis of the sustainability profile of process options.** The methodology consists in the assessment of a comprehensive system of key performance indicators aimed at mapping the performance of a process scheme. The indicators are combined in aggregated indices to yield a sharp representation of the sustainability issues and of the critical elements of the analysed process. The proposed procedure results in a simple and flexible tool, which allows a straightforward application to practical situations. In particular, the definition of the methodology required the development of:
  - A system of representative leading key performance indicators (KPIs) which are able to capture the impacts on sustainability of industrial process schemes. The integrated system contains technological and economic KPIs as well as KPIs for inherent safety and environmental performance aspects. The indicators were either selected from widely accepted literature approaches, if suitable, or were developed within the present study. The KPIs are based on impact models (also complex), but are easy and swift in the practical application. Their full evaluation is possible also starting from the limited data available during early process design.
  - Rules for the normalization and aggregation of the KPIs. Innovative reference criteria were developed to compare and aggregate the impact indicators on the basis of the actual site-specific impact burden and the sustainability policy. On the one hand this links the assessment of the process to the general sustainability management of the site and, on the other hand, it allows a straightforward comparison and aggregation of aspects belonging to economic, societal and environmental spheres.

- **Definition of design support tools for the analysis of the inherent safety performance of process options.** The methodology follows an innovative approach in the analysis of inherent safety, based on both the calculation of the expected consequences of potential accidents and on the evaluation of the hazard of the substances and related to equipment. The calculation of the consequences takes advantage of the progress in the availability of user-friendly commercial software that significantly reduced the time requirements for consequence analysis. In the framework of a comparative assessment of the inherent safety of process options, the methodology overrides several problems present in the previous methods proposed for quantitative inherent safety assessment. Introducing a direct relation among hazard factors and consequence analysis of potential scenarios, the proposed methodology avoids the use of arbitrary indexes and of subjective elements. The final result is expected to be a more realistic and sound representation of the inherent safety performance. The method is extremely flexible, allowing the assessment of the pertinent scenarios for each unit (e.g. FMEA can be used for non-standard units) and the application of the more appropriate model for the analysis of specific consequences in the scenario. Thus, built-in assumptions and generalizations typical of other tools are avoided, yielding a more specific assessment of the expected accident severity. The methodology produces quantitative KPIs that are suitable for both the stand-alone analysis of inherent safety performance and the integration of inherent safety as a key element in the sustainability (societal sphere) of a process scheme. With respect to the latter option, the method is fully compatible with the developed sustainability assessment tool.

- **Definition of design support tools for the analysis of the inherent safety performance in layout definition.** The specific features in the application of inherent safety principles in layout design were explored and defined. As a matter of fact, very limited efforts were devoted in the literature to this kind of application and no assessment tools were present. A consequence-based approach, built on the framework of the process assessment tool previously defined, was developed for the identification and ranking of the expected hazards related to escalation chains. In fact, the hazard of a domino effect was identified as a core feature in the inherent safety profile of layout. A set of KPIs was defined within the tool for the analysis and representation of unit specific parameters useful as a reference in layout design. In a second step, an integrated safety screening method was developed, which considers not only the domino hazard, but also the compliance to inherent safety principles, the residue requirement for risk control measures, and the safety economics. The proposed tool is based on the framework of an integrated method for process analysis described in the current literature, in order to produce a common approach for both process and layout assessment. However the application within the constraints and specific characteristics of layout design required a systematic update of the indexing system.

- **Definition of a screening procedure for the identification of hazardous scenarios related to the formations of undesired substances in chemical systems undergoing anomalous or “out of control” conditions.** This procedure provides key information on the inherent safety of materials that is required for the application of further steps of inherent safety analysis of processes and plants. The procedure consists of two parts: the application of an array of experimental protocols for the assessment of the behaviour of the material in anomalous conditions and a hazard interpretation phase that analyses the experimental results defining the hazard profile of the material. The former part is based on the combination of calorimetric an analytic techniques that allow for the controlled reproduction of standardized accidental conditions on a safe laboratory scale. The latter part consists of a systematic procedure both for the collection of the hazard data of concern and for the representation and interpretation of the hazard profile. The hazard analysis is based on the physio-chemical and toxicological proprieties of the substances identified in the experimental survey. The results are presented through index scoring approaches developed “ad-hoc”. The current work produced a demonstration and testing of this procedure, by the development of an experimental activity aimed at the analysis of the thermal stability of chlorinated and non-chlorinated isomers of nitrobenzaldehyde.

- **Validation and demonstration of the developed methods by the application to cases studies.** The proof of the effectiveness and value of the methods was obtained by the application to a large number of case studies concerning different kinds of design activities (choice of materials, design of the process, of the plant, of the layout) and different types of processes/plants (chemical industry, storage facilities, waste disposal). For all cases the methods were able to match the results expected “a priori” by the specific experience that was possible to collect about the single cases. This constitutes a validation, since the assessment procedure is able to identify critical elements that otherwise required specific knowledge to be addressed. When applicable methods exist in the literature (e.g. inherent safety of processes), the comparison of the results for the cases studies showed positive matches with the outcomes of the proposed methods. Furthermore, it clearly demonstrated all the limits and deficiencies of the former, that were overcame by the new approach. In the cases studies, the application of the pertinent method was possible for each system analysed, requiring an input of information comparable to the early phases of design. This proves the applicability and the flexibility of the proposed tools. The sensitivity analysis confirmed the ability of the method to yield meaningful results even in the presence of limited degrees of uncertainty affecting input data and weight factors.

5.1 – List of publications

a. *Fully referenced publications*

a.1. Cozzani V., Tugnoli A., Salzano E.
Prevention of domino effect: From active and passive strategies to inherently safer design.
Journal of Hazardous Materials, v. 139, n. 2, (2007), 209-219.

a.2. Tugnoli A., Cozzani V., Landucci G.
A Consequence Based Approach to the Quantitative Assessment of Inherent Safety
AIChE Journal, vol. 53, no. 12, (2007), 3171-3182

a.3. Cordella M., Tugnoli A., Spadoni G., Santarelli F., Zangrando T.
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International Journal of Life Cycle Assessment, 13 (2), (2008), 133-139.

a.4. Tugnoli A., Khan F., Amyotte P., Cozzani V.
Safety Assessment in Plant Layout Design using Indexing Approach: Implementing Inherent Safety Perspective; Part 1 – Guideword applicability and method description
Journal of Hazardous Materials, in press.

a.5. Tugnoli A., Khan F., Amyotte P., Cozzani V.
Safety Assessment in Plant Layout Design using Indexing Approach: Implementing Inherent Safety Perspective; Part 2 – Domino Hazard Index and Case Study
Journal of Hazardous Materials, in press.

a.6. Landucci G., Tugnoli A., Cozzani V.
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Journal of Hazardous Materials, in press.

b. Conferences

b.1. Tugnoli A., Cozzani V., Santarelli F., Salzano E., Trifirò F.
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b.2. Tugnoli A., Cozzani V., Santarelli F.
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