



## Design of Sustainable Chemical Processes: Systematic Retrofit Analysis Generation and Evaluation of Alternatives

Carvalho, Ana Isabel Cerqueira de Sousa Gouveia; Matos, Henrique A.; Gani, Rafiqul

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**Universidade Técnica de Lisboa**  
**Instituto Superior Técnico**

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**DESIGN OF SUSTAINABLE CHEMICAL  
PROCESSES: SYSTEMATIC RETROFIT ANALYSIS  
GENERATION AND EVALUATION OF  
ALTERNATIVES**

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Ana Isabel Cerqueira de Sousa Gouveia Carvalho  
(Licenciada)

Dissertação para a obtenção do Grau de Doutor em Engenharia Química

**Orientador:** Doutor Henrique Aníbal Santos Matos

**Co-Orientador:** Doutor Rafiqul Gani

**Júri**

**Presidente:** Presidente do Conselho Científico do IST

**Vogais:** Doutor Rafiqul Gani

Doutora Maria de Ascensão Carvalho Fernandes de Miranda Reis

Doutor Paulo Jorge Sintra Almeida Partidário

Doutor Henrique Aníbal Santos de Matos

Doutora Maria Cristina de Carvalho Silva Fernandes

Doutora Maria Joana Castelo Branco de Assis Teixeira Neiva Correia

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# Abstract

This thesis presents a new generic and systematic methodology to design new sustainable alternatives for any chemical process. The methodology uses a set of indicators to identify the critical points in the process. The indicators with the highest potential for improvements are identified and then selected to generate the new design alternatives. The new design alternatives are evaluated through the use of performance criteria parameters (sustainability metrics and safety indices). A software, called *SustainPro*, has been developed and performs the whole methodology.

Nowadays the concerns about the future of humanity are growing due to an increase of environmental problems, the depleting of natural resources as well as the social effects generated because of industrial activity. Consequently, one issue that has gained importance is Sustainability. It is possible to define sustainability as a development strategy that meets the needs of the present without compromising the ability of future generations to meet their own needs. One way to apply this strategy to industry is to retrofit the processes by generating new process/ operation alternatives. These alternatives will integrate the economic, the environmental and the social aspects into industry production. All the previous factors have motivated the development of this methodology and the respective software. With this work, it is now possible to analyse and consequently generate new sustainable alternatives in any chemical process operating in batch and continuous mode that improve the aforementioned concerns. The software allowed a more precise and faster analysis that can be reproduced by any person at any time. The methodology and the software were highlighted through the use of case studies using processes operating in continuous and batch mode. Some of those the data was collected from real plant.

**Keywords:** Process design/retrofit, Sustainability, Indicators, Safety, Software, Continuous and Batch Processes



# Resumo

Nesta tese é apresentada uma nova metodologia, genérica e sistemática, que visa a obtenção de alternativas processuais sustentáveis em processos químicos. A metodologia utiliza um conjunto de indicadores que identificam os pontos críticos do processo. Os indicadores que apresentam maior potencial para serem melhorados são identificados e seleccionados para criar a nova alternativa. As novas alternativas são avaliadas através do uso de métricas de sustentabilidade e de índices de segurança. Um software, *SustainPro*, foi desenvolvido para facilitar a aplicação da metodologia.

Existe, hoje em dia, uma crescente preocupação com o futuro da humanidade, devido aos problemas ambientais, ao esgotamento de recursos naturais e ao impacto social que advêm da actividade industrial. Assim sendo o termo Sustentabilidade tem ganho importância. Sustentabilidade, pode ser definida como estratégia de melhoramento que satisfaça as necessidades actuais sem comprometer as necessidades futuras. Uma das formas de aplicar esta estratégia na indústria é criar novas alternativas processuais sustentáveis, ou seja alternativas para uma produção industrial que tenha em consideração factores económicos, sociais e ambientais. Os factores apresentados serviram então, de motivação para o desenvolvimento desta metodologia e do respectivo software. Com este trabalho, é agora possível, analisar e consequentemente sugerir novas alternativas processuais mais sustentáveis em qualquer processo químico (contínuo ou batch). O software permitiu uma análise mais precisa, rápida e reproductível.

A metodologia e o software foram aplicados a diferentes casos estudo que englobam processos operando em contínuo e em batch. Os dados de alguns dos casos estudo foram obtidos de indústrias em funcionamento.

**Keywords:** Design de processos, Sustentabilidade, Indicadores, Segurança, Software, Processos em contínuo e em batch



# Preface

This thesis is submitted as partial fulfillment of the requirements for the Ph.D. degree at Instituto Superior Técnico and at The Technical University of Denmark. The work has been carried out at Center of Chemical Processes (CPQ) at Department of Chemical and Biochemical Engineering, in Lisbon and at the Computer Aided Process-Product Engineering Center (CAPEC) at Institut for Kemiteknik (Department of Chemical and Biochemical Engineering), in Lygby, from January 2006 to August 2009 under the main supervision of Prof. Henrique Matos from Portugal and Prof. Rafiqul Gani from Denmark.

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# 1. Introduction

Increased industrial activities combined with new economic, environmental and societal constraint means that energy consumption, raw materials depletion and environmental impact are also receiving increased attention by the modern society. Due to these factors, new as well as old industries need to achieve balance between the negative impacts from their activity and the positive benefits (due to the products they provide) to the society. Consequently, concerns about the sustainability of the modern society are growing everyday and demands for improving the industrial plant operations and designs are also increasing. The use of green chemicals and process operability at sustainable conditions are two factors, among many others, that should be taken into account in the retrofitting of the already existing processes. In order to address these issues, it is useful to develop systematic methods and tools, which enable the generation of more sustainable alternatives for process design and to improve the ability to adapt to the future needs.

In the past decades, different methodologies have been proposed in order to determine the retrofit potential of a chemical process, operating in continuous mode, with respect to improvement of the cost-efficiency. Some methodologies were introduced using heuristic rules for the generation of new design alternatives (Rapoport *et al.*, 1994). Other methodologies based on mathematical concepts and optimization methods, such as mixed integer nonlinear programming (MINLP) have also been proposed (Ciric and Floudas, 1989 and Jackson and Grossmann, 2002). Another approach for the analysis of continuous processes is based on the resynthesis of the entire process by

incorporating operating units with enhanced performance (Liu *et al.*, 2006). Recently, an indicator-based methodology was proposed (Uerdigen *et al.*, 2003 and Uerdigen *et al.*, 2005) in order to identify and screen processes operating in the continuous mode. The indicators determine the critical points in the process and based on their values new (feasible) design alternatives are generated. These feasible alternatives are compared in terms of economic aspects that help to select the best alternatives. Jensen *et al.*, 2003 extended the first part of this methodology where the previously defined indicators were retained but the choice of the best alternative was obtained using new parameters related to economic, safety and environmental factors. The sustainability metrics defined by Azapagic *et al.*, 2002, the safety indices developed by Heikkilä, 1999 and the waste reduction, algorithm, WAR, proposed by Cabezas and Young, 1999 were incorporated in the new version as measures of process performance.

For processes operating in batch, some methodologies for process retrofitting have also been proposed during the past decades. Much work has been done in developing optimization models for scheduling of batch operations (Chakraborty and Linninger, 2002 and Montagna, 2003). In a review paper, Póvoa (2007) covered various approaches for design of batch plants and on retrofit design problems. However, all these approaches only take into account retrofitting analysis regarding the scheduling of batch operations and they do not consider the further improvements that can be achieved in terms of sustainable design.

In addition, methodologies taking into account environmental aspects have been developed ( Zhao-Ling and Xi-Gang, 2000 and Lee and Malone, 2000). Recently, due to concerns about of the time consumed and the complexity of the problems considered in previous analyses, systematic methodologies to generate new design alternatives have been proposed (Halim and Srinivasan, 2006 and Halim and Srinivasan, 2008). A different approach where indicators, heuristics, and process model are combined to provide decision support in retrofitting of chemical batch processes has also been proposed (Simon *et al.*, 2008).

The retrofit methods of chemical processes presented before are an analysis that may potentially involve a very large search space and therefore, generation and evaluation of many alternatives. Therefore, this analysis can be very complex and time consuming. These earlier methodologies while very useful are not generic and therefore need additional effort on their implementation and application. Consequently, and using the advances in computer science and computational algorithms for process analysis, makes it advantageous and helpful to employ computer-aided modeling systems and tools for integrated process retrofitting analysis. These computational tools make the retrofitting process become easier and allow at the same time a more accurate and systematic process analysis. Developments of a number of software with varying lists of implemented methods and tools for retrofit analysis have been reported. These software tools can be divided into two groups. The first group is those that evaluate process performance in terms of sustainability, life cycle assessment and environmental impact (GaBi Software, 2009, SimaPro -Product Ecology Consultants – PRé, 2009, Bare et al., 2003 and Curzons *et al.*, 2007). The second group are those that determine new design alternatives in order to reduce the environmental impact (AquoMin - Relvas *et al.*, 2008, ENVOPEXpert - Halim and Srinivasan, 2002 and DESASS - Ferrer *et al.*, 2008)

The motivation for this work is to improve and extend the already established methodology, which was able to identify critical points to certain processes operating in continuous mode. The new analysis should be done taking into account the urgency of results that means that the results should be available in a short time. Consequently, the objective of this thesis is to present a new generic and systematic methodology, to generate new sustainable design alternatives for a given process, which might operate in batch or in continuous mode. The other main objective is to create a software that applies the previous methodology allowing a systematic, generic and fast analysis of the problem. The methodology (Carvalho *et al.*, 2008 and Carvalho *et al.*, 2009<sup>1</sup>) is divided into six main steps: (1) the data from simulation results or real plant data needs to be collected; (2) a flowsheet decomposition is performed in order to “break-down”



the process in paths; (3) a set of mass and energy indicators is calculated to each path, in order to give information about the localization of the process bottlenecks; (4) through a sensitivity based analysis the target indicators for improvements are identified; (5) a sensitivity analysis is then performed to the target indicators in order to determine the target variables for improving the process; (6) a set of synthesis methods are used to generate new sustainable process alternatives. These alternatives are then evaluated through the performance criteria parameters (Sustainability Metrics and Safety Indices). A new software called *SustainPro*, which allows the analysis and the generation of process alternatives that are more sustainable has been developed. The software performs all the steps of the methodology automatically, giving the user the opportunity to decide, whenever that can happen.

The software has been integrated with other tools, such as ENVOPEExpert (Halim and Srinivasan, 2002), in order to combine the strength points of the two methodologies/software and create a tool for the analysis of a given process in terms of sustainability, Carvalho *et al.*, 2009<sup>2</sup>.

This PhD-thesis is organized in seven chapters including this chapter (Introduction). Chapter 2 gives an overview of the theoretical background related to the proposed methodology. This includes an overview of retrofit approaches, a summary of synthesis methods that can be used to generate new design alternatives, an introduction to the performance criteria parameters which includes the sustainability analysis and process safety study and finally an overview about the computational tools available in the market for retrofit analysis and sustainability evaluation. The next chapter (Chapter 3) presents the description of the proposed methodology. This chapter is divided into two parts: one presenting the methodology for continuous processes and the other presenting the extended methodology to batch processes. This chapter provides the full picture of the developed methodology for designing new sustainable alternatives for continuous and batch processes and therefore a comparison between the two approaches is also presented. In the end of each section, a case study is presented to illustrate the sustainable design methodology for continuous and batch process

respectively (MTBE production- continuous process and Laundry case study- batch process). In Chapter 4, the *SustainPro* software is presented. Issues such as software architecture, supporting tools, the development of a knowledge base and the main features of the software are presented in this chapter. In the end of the chapter, a simple case study is presented to illustrate the application of the software (Acetone-Chloroform Case Study). The developed methodology and the corresponding software have been applied in several case studies, which are presented in Chapter 5. This chapter is divided into two sub-sections, in the first sub-section, the processes operating in a continuous mode are presented while in the second sub-section the batch processes are presented. These case studies highlight application of the developed methodology to different types of design/retrofit problems faced by the chemical and biochemical industries. In the continuous processes sub-section, VCM production, Ammonia production, Biodiesel production and Copper extraction were presented as case studies. For batch processes, the retrofit analysis has been performed for Insulin Production and  $\beta$ -Gal Production. Chapter 6 presents the integration of the software *SustainPro* with ENVOPExpert. The proposed joint framework is described and the ammonia process and the acetone production have been used as case studies to highlight the applicability of this framework. Finally, Chapter 7 presents conclusions and directions for future work.

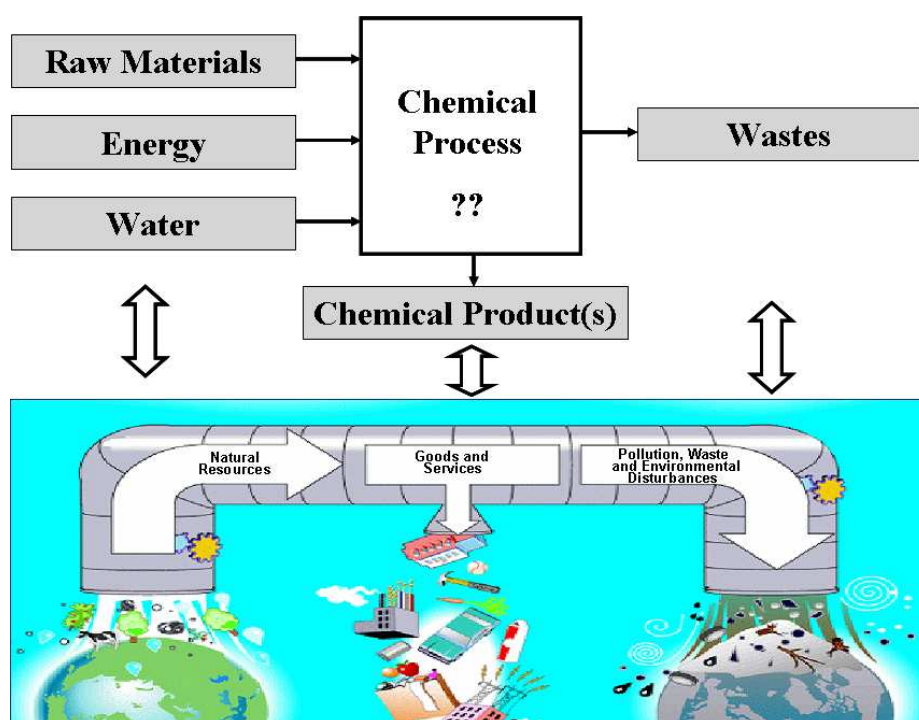


## 2. Theoretical background

### 2.1 Introduction

The industrial chemical processes transform a set of raw materials into useful product(s). Usually the chemical processes use energy and water, to physically or chemically, promote the transformation of the raw materials. These chemical processes help to meet the world's most of the fundamental needs in terms of food, shelter and health, as well as products that are vital to such advanced technologies as computing, telecommunications and biotechnology.

These industries face major challenges to meet the needs of the present without compromising the needs of the future generations in the face of increasing industrial competitiveness. This translates into the need to make processes much more energy efficient, safer and more flexible, and to reduce emissions to meet the competitive challenges within a global economy, or in other words the need of more sustainable processes. The simplified flowsheet of a chemical process showing its impact in the surrounding is represented in Figure 2.1.



**Figure 2.1:** Simplified representation of chemical processes impact

Figure 2.1 shows that a chemical process uses the natural resources in the form of raw materials, water and energy as input. The chemical processes transform the input into goods and services, however this transformation leads to the production of large amounts of wastes, which increase the pollution and make environmental disturbances. These problems create concerns in the modern society, which lead to important questions:

- 1) How should we reduce the impact of chemical processes?
- 2) How should we improve an existing process (that is, generate sustainable retrofit alternatives) without too much effort?
- 3) How can we identify the process bottlenecks?
- 4) Which are the process bottlenecks that significantly improve the process performances?
- 5) What should be done in order to make the processes more sustainable?
- 6) How can we generate design alternatives to achieve the desired targets (means sustainable process)?

Some work has been done to solve the above questions. Many different approaches have been developed and used to address them. A review of the previous work in the different related areas of this thesis is presented in this chapter.

## 2.2 Processes Analysis

### 2.2.1 Processes Retrofitting

The study of process retrofit methods has always been important and has recently become a major issue.

Retrofit has been defined by Guinand (2001) as:

*“Process retrofitting is the redesign of an operating chemical process to find new configuration and operating parameters that will adapt the plant to changing conditions to maintain its optimal performance.”*

From an engineering point of view, retrofitting shares common characteristics with the two extreme problems in process engineering: the optimization of chemical plants and the design of new plants. From this point of view, retrofitting is an optimization of real plant that includes not only operating variables but also structural characteristics related to the process topology. It is also similar to the design of new plants since it includes both a systematic procedure to develop process alternatives and a procedure to select the optimal configuration.

The main objectives of process retrofits are to identify the bottlenecks in the process, recognize the bottlenecks that when removed will lead to improvements and suggest new design alternatives that match the identified bottlenecks. Typically, these objectives are related to increasing the capacity, efficiently handle the raw materials, utilizing new process technologies to improve the energy-use efficiency, reducing the environmental impact, increasing the safety of the process and/or reducing the operating costs.

Rong *et al.*, 2000 identified six types of bottlenecks that are primarily found in the industry:

- Bottleneck of Scale

These problems are related to the operation conditions used for a given size of the equipments. Sometimes these conditions are not optimized and they lead to wastes of energy, inefficient operations and additional operational costs. Typically the bottlenecks of this section are related to the diameter of the columns, area of heat exchangers, stirring velocity, retention time of reactors, equipment operating temperature and pressure, etc.

- Bottleneck of Energy Consumption

Here the problems are related to the demands of utilities used for cooling and heating the equipments (unit operation). The utilities used in each unit operation might not be the adequate ones and sometimes generation of utilities may be necessary but is not available in the process. Also, sometimes the energy integration among the heat exchanger networks is not taken into account which leads to wastes of energy and consequently to inefficient energy processes.

- Bottleneck of Raw Material Consumption

These problems appear due to the inefficient reaction and/or separation operations, which causes excessive consumptions of raw materials.

- Bottleneck of Environmental Impact

These bottlenecks are also related to inefficient reaction and/or separation processes. If the reactions and the recovery of the compounds are not done in an efficient way, wastes will be produced and consequently the pollution caused by the process will increase.



- Bottleneck of Safety

The properties of the compounds involved in the process might present a big risk in the safety of the process. Some hazardous compounds (for example, solvents) might be substituted by harmless compounds increasing the safety of the process. The process operational conditions and the respective layout may not be optimized, which therefore compromises the safety of the process.

- Bottleneck of Feedstocks

These problems might appear due to market conditions that could change during the plant lifetime.

To identify the above bottlenecks, different methods may be used.

- **Experience-based Approach**

The experienced engineers might indicate the unit that is the source of the bottleneck. However, this analysis always needs to be checked with theoretical analysis to prove the veracity of the suggested bottleneck. This method can be useful as a starting point for further and deeper analysis.

- **Experimental Tests of Specified Equipment**

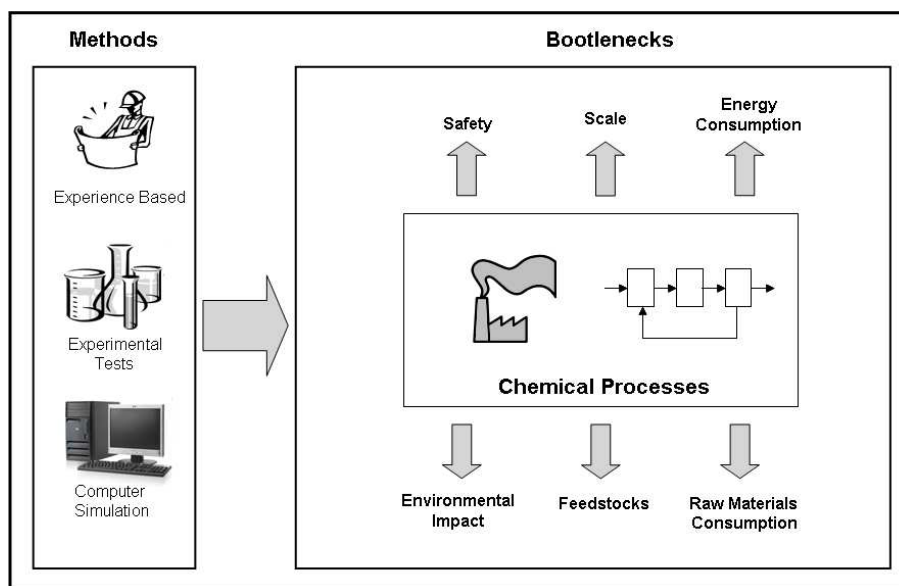
Experiments can be done in the equipments in order to study the influence of specific conditions in the desired output. This method is commonly used in identifying the bottleneck of scale, especially in reactors and separation units.

- **Computer Simulation**

Simulation of the process is a good method to identify the process bottlenecks and thereby locate the problems in these unit operations. Another way of retrofitting is the use of computer based methodologies that allow the identification of the bottlenecks and help in the solution of the problem.

These methods can be used together in order to combine their strengths.

Figure 2.2 summarizes the different types of methods, which may be used to identify the bottlenecks in a chemical process.



**Figure 2.2:** Retrofitting methods and bottlenecks in a chemical process

In this thesis, we have focused our efforts in developing a computer aided methodology for retrofit analysis. Consequently, only point three (Computer Simulation) will be taken into account and a review on methodologies using computational tools will be presented.

The current available methodologies can be divided into three main categories: Heuristic Methods, Optimization Formulations and Hybrid and Novel Methodologies.

### 2.2.1.1 Heuristic Methods

Pahl *et al.*, 1996, describe a heuristic as the structure, which includes explicit knowledge (i.e. knowledge that can be explained) as well as implicit knowledge. The authors state that this is necessary in order to organize the sequence of thinking operations, including modifying operations (searching and finding) and testing operations (checking and assessing).

Rapoport *et al.*, 1994 presented a retrofit design algorithm, which uses a process synthesis approach with heuristic rules based on engineering experience, detailed process calculations and detailed economical evaluations leading to an optimal design.

Smith, 1995 presented a set of heuristics to use in the design/retrofit of distillation columns. New approaches have been developed in order to improve and extend the applicability of the heuristic methods. Schembecker and Simmrock, 1997, presented a method involving heuristics, for systems containing azeotropic mixtures with close boiling point, which are going to be separated in distillation columns.

These earlier approaches were focused in the economical process point of view. Further work has been done in order to extend the heuristics to pollution prevention concerns. Based on the studies by Pennington, 1997 related to chemical engineering principles for continuous processes in the context of pollution prevention two methods based on heuristics were proposed for retrofit/design of chemical processes (Pennington, 1997 and Butner, 1999). These heuristics were the guidelines for strategies in pollution prevention.

Recently, new sets of heuristics have been added to take into account different process operation modes, such as semi-continuous processes (Adams and Seider, 2009). New approaches to evaluate workflow in process designs have also been developed based on heuristics (Vanderfeesten *et al.*, 2008).

The heuristic methods have some limitations, for example:

- The heuristics can be general. Its use follows a hierarchical procedure to identify process opportunities that can be considered similar to using guidelines or brainstorming techniques, although more structured. This means that sometimes a more in-depth analysis might be done by using detailed design procedures.
- The heuristics are fallible. The heuristic models are based on the analysis of a certain set of simplified rules and assumptions, trying to avoid the complexity associated with the real detailed models. Therefore, they are good approaches to be used as a support in order to make quick estimates and preliminary process designs.
- The heuristics might not lead to the optimal solution. This means that these methods have to compromise on the precision of the solution in terms of its optimality and settle for a near-optimal solution.
- These methodologies cannot find the exact place for the bottleneck in the process. They give a guideline and a range of options to justify a given event. This might lead to some confusion and extra effort to discover the most critical point in the process.

### *2.2.1.2 Optimization Formulations*

For process retrofit by optimization, superstructures may be used. Here, one determines the changes in costs resulting from modifications in process needed for retrofit design. The superstructure represents all possible design alternatives within the specified flowsheet. These types of problems lead to mixed-integer linear programming (MILP)

and mixed-integer nonlinear programming (MINLP) problems, which require efficient numerical solvers and a good knowledge of the mathematical programming techniques. Methods for redesigning systematically an existent process flowsheet to increase its flexibility were developed and used for process retrofit analysis (Pistikopoulos and Grossmann, 1988 and Pistikopoulos and Grossmann, 1989). To define a superstructure, which describes fully the process and the possibilities for retrofit is not easy. Due to this fact, other methodologies have been developed to focus on specific parts of the process or in specific areas of the flowsheet for improvements. Methodologies taking into account reduction of energy consumption or heat exchanger networks were developed and presented as retrofit methods. Gundersen and Grossmann, 1990, presented a heuristic approach for improving current automatic heat exchanger network. They took into account the various sets of matches that all achieve the minimum or the specified number of units was rated according to their potential for being able to transfer heat vertically between the composite curves, and thus giving the minimum total area in the corresponding network.

Kovac and Glavic, 1995, developed a combined approach that includes two methods (two steps), the thermodynamic step and the algorithm step. In the first step, the unpromising structures are eliminated and the new promising structures are added based on the Extended Grand Composite Curve. In the second step, the obtained superstructure is optimized using Mixed-Integer Non Linear Programming.

Bjork and Nordman, 2005, developed an extended model for design of large-scale retrofit heat exchanger network problems and a rigorous optimization framework based on both a genetic algorithm and a deterministic MINLP-approach.

Finally, Ponce-Ortega *et al.*, 2008, showed a new formulation for the retrofit of heat exchanger networks considering process modifications. The method accounts for the interactions between the process conditions and the heat integration options to provide an optimal structure for a redesigned heat exchanger network.

Some work has also been done in retrofitting networks consisting of several interconnected processes (Jackson and Grossmann, 2002).

The optimization methods present some disadvantages, such as:

- These types of methods involve heavy mathematical programming, which require experts to develop and solve them.
- The optimal solution can only be guaranteed with respect to the alternatives that have been considered in the superstructure a priori. For complex problems, it is difficult to involve all possible alternatives in the mathematical model. Therefore, the retrofit analysis automatically excludes some alternatives that might be promising with respect to achieving a good improvement.
- These methods are usually only valid for the type of process they were developed for. Usually, it is difficult to extend the models in order to make them generic enough to be applicable to any chemical process.
- The optimization methods may require huge computational efforts and consequently it may take a long time to obtain results.

### *2.2.1.3 Hybrid and Novel Methodologies*

Hybrid methodologies combine approaches creating tools that are more powerful. Fischer *et al.*, 1987 presented a systematic procedure for developing and screening process retrofit opportunities. The procedure considers modifications on the structure of the flowsheet as well as the equipment sizes for a fixed flowsheet. The sequence of the methodology is based on heuristics. In one of the steps, a simple optimization problem is used to find optimum design with respect to minimum operating costs. Dantus and High, 1996 presented a methodology that consists of identifying waste minimization options through a sensitivity analysis and flowsheet configurations through a hierarchical procedure. The alternatives identified together with the heat-exchanger

network were used to construct a superstructure that was formulated as an MINLP problem. This approach uses the heuristics as a first step and then solves an optimization problem to determine the optimal alternatives.

Halim and Srinivasan, 2002 developed a systematic methodology to guide users wishing to achieve waste minimization. The methodology determines the origins of waste in any process and through a set of rules based on process insights suggests new possible actions to reduce the identified wastes.

Linnhoff and Flower, 1978, first introduced the pinch analysis, which is a thermodynamically orientated method for the synthesis of heat exchanger networks. This method points out feasible solutions, which preferably exhibit maximum energy recovery and it has been applied to a wide range of chemical processes.

Some novel approaches have also been developed. These methodologies follow a completely different way of thinking about process retrofitting and lead to interesting results. Liu and Fan, 2006 introduced a novel holistic approach for process retrofitting. The proposed approach resynthesizes the entire process. It can take into account all possible outcomes, including the inevitable restructuring of the flowsheet's network structure. El-Halwagi, 1998 proposed a framework for integrating environmental issues with other process objectives such as profitability, yield, enhancement, debottlenecking and energy reduction. The methodology involves process integration, offering a framework for fundamental understanding of the global insights of the process, methodically determining its attainable performance targets and systematically making decisions leading to the realization of these targets.

Uerdingen *et al.*, 2002 presented a new approach for process retrofitting. This approach does not use heuristics and does not use the common optimization problems. This approach was the bases for this PhD thesis.

### *New Retrofit Design Methodology*

Uerdingen *et al.*, 2003 presented a new systematic methodology for screening retrofit options to improve the economics of a continuous chemical process. The methodology was organized in three main steps: 1) Base case analysis, where the process was decomposed in path-flows 2) Generation of retrofit options, where a set of mass and energy indicators were used to the path flow assessment and 3) Rough economic evaluation using the economic indicators. This author further introduced a step 4 and 5 (Uerdingen *et al.*, 2005). In step 4 a process optimization with regard to retrofit options that do not require investments are studied. In step 5 a feasibility study as well as the economic profitability of the retrofit options that require investment is done. Jensen *et al.*, 2003, added to this methodology an evaluation of the alternatives using sustainability metrics and safety indices.

In this PhD thesis, the flow-path definitions and the mass and energy indicators (Uerdingen *et al.*, 2003), were used in the proposed methodology. For a better understanding, these concepts will be presented during the methodologies description. This methodology also incorporates the sustainability metrics and the safety indices added by Jensen *et al.*, 2003. The limitations presented by the previous approaches were used as the motivation of this PhD work and they are presented in more detail in the motivation section (3.1.1 Motivation).



### 2.2.2 Process Synthesis

After locating the bottlenecks in the process, suggestions for improvements in the critical areas are needed. For that, synthesis methods should be used to generate new design alternatives.

The process synthesis and design is described by Hostrup (2002) as:

*“Given the feed and product specifications in the process, determine a flowsheet including the required tasks, appropriate equipments and solvents needed”*

Processes are synthesized by using heuristics, thermodynamic, algorithm methods or combined approaches. D’Anterrosches, 2005<sup>1</sup> divided the synthesis methods into three main classes: 1) methods dealing with heuristics based, 2) methods that employ mathematical and optimization techniques and 3) hybrid methods combining two previous approaches into one method.

#### *2.2.2.1 Heuristic Methods*

The heuristic methods are based on a set of rules, which were defined based on the experience and available knowledge. This means that these are empirical methods.

Douglas, 1985, showed early in the eighties, that the heuristic methods could be very useful for a rapid identification of the process options and a good help in terms of process synthesis design. The hierarchical decomposition technique proposed by Douglas, 1985, where heuristic rules are applied at different design levels to generate the flowsheet alternatives divides the synthesis problem into five hierarchal decision levels:

- 1) Batch versus continuous.
- 2) Input–output structure of the flowsheet.
- 3) Recycle structure and reactor considerations.
- 4) Separation system synthesis.
- 5) Heat exchange network.

A sequence of rules is given to solve the above problems. Those rules were defined based in previous experiences and they represent the knowledge acquired by men experience.

Even nowadays, studies are being done using heuristic rules for process synthesis. Martin, *et al.*, (2006) presented a methodological procedure based on the intelligent and practical application of heuristic rules developed by experience. This holistic methodology decomposes the original problem in four simpler problems, caller phase: reaction, localization, separation and integration; the result of each exercise could modify the former exercises and forward exercises, providing a holistic character to the methodology.

### *2.2.2.2 Optimization based methods*

The mathematical models developed to describe the process synthesis, take into account the investment costs, the operational costs different alternatives for improvements, etc. Based in an objective function, a solution will be presented, suggesting the optimal configuration for the proposed problem.

Lin and Miller, (2004) presented a meta-heuristic optimization algorithm, Tabu Search (TS), for solving stochastic optimization problems for process synthesis. Angira and Babu, (2006), developed a novel modified differential evolution algorithm, for solving process synthesis and design problems. They compare the performance of modified differential evolution with the Genetic Algorithm, Evolution Strategy, and MINLP-Simplex Simulated Annealing (M-SIMPASA). Raeesi *et. al.*, (2008), presented a

mathematical formulation of a superstructure model and proposed an ant colony algorithm for solving the nonlinear combinatorial problem. Li et al, (2009), presented an environmentally conscious integrated methodology for design and optimization of chemical process especially for separation process. The methodology incorporates environmental factors into the chemical process synthesis at the initial design stage.

### *2.2.2.3 Hybrid methods*

Hybrid methodologies combine approaches creating tools that are more powerful for process synthesis.

- Method based on thermodynamic insights

Jakslund (1996) developed a methodology, which employs reliable property information for process separation synthesis. The methodology relies on the knowledge (thermodynamic insight) of the properties of the mixture to be separated and the relation between properties and the theories of separation.

Jakslund's methodology is divided into multiple steps that are grouped into two levels, where level 1 employs pure compound properties for separation technique identification and level 2 employs pure compound and mixture properties for separation task selection, separation technique validation and process design. The main steps of each level are briefly described below.

#### **Level 1 (6 steps):**

- 1) Mixture analysis (generates information on type of mixture, phase identity at the specified condition, presence of azeotropes, presence of mutual solubilities, etc.);
- 2) Computation of a binary ratio matrix (represents the property differences between all binary pairs of compounds in terms of property ratios);

- 3) Separation process identification (determines the feasible separation techniques for each binary pair of compounds taking into account the binary ratio matrix and a matrix of allowable values for the property values);
- 4) Screening of alternatives (reduces the number of feasible alternatives to at least one per binary pair);
- 5) Initial estimates of split factors (determines estimates for split factors so that mass balance calculations can be made);
- 6) Choice of the first separation task (determines the binary pair, which splits the multicomponent mixture into two).

### **Level 2 (6 steps):**

- 1) Identification of separation task alternatives: pure compound properties and mixture properties are considered to simultaneously order and select the separation tasks and separation techniques;
- 2) Selection of mass separation agent (MSA): select compounds or mixtures for MSA (when required);
- 3) Selection of external agents (when required);
- 4) Estimates of operating conditions: conditions that allow the required separation are estimated;
- 5) Screening of alternatives: further screening of separation techniques per separation task;
- 6) Selection and sequencing of separation tasks: generation of a flowsheet with alternatives for each separation task and determination of conditions of operation.

After applying both levels of the methodology, a physically feasible alternative is generated. This approach is very useful for generating new design alternatives for a given process.

- The reverse approach for synthesis and design of chemical processes

This method presents a reverse approach to formulation and solution of problems related to synthesis/design of chemical product-processes. The basis for this method is the computer aided molecular design (CAMD) idea. CAMD approach uses a group contribution approach for molecular property prediction where the building blocks are molecular groups. In this case, D'Anterrosches and Gani, 2005 presented a new approach called computer aided flowsheet design (CAFD), which follows the same idea of CAMD but in this case for flowsheet synthesis. CAFD is a combination of two reverse problems; the first problem involves the synthesis of process flowsheet alternatives similar to a reverse target property estimation approach: defining property targets for the structure, alternatives matching the targets are generated. In the second part, the reverse simulation approach is applied to get from the process-groups in the structure the minimum set of design parameters to fully describe the flowsheet, in the same way as a process stream is fully described knowing pressure, temperature and compound molar flowrates.

CAFD consists of eight main steps:

- Definition of the process synthesis problem. User defined available materials and desired products.
- Analysis of the process synthesis problem. Using physical insights and knowledge based methods a set of feasible process operations are defined.
- Selection of the process groups matching with synthesis problem. The process groups are matched between appropriate process tasks selected in the analysis and the mixture involved in the problem.
- Synthesis and test of the flowsheet structure alternatives. Based on the developed connectivity rules, the process groups are combined into the flowsheet alternatives.

- Ranking of the generated alternatives and selection of the most promising alternatives. Based on flowsheet property model, the performance of the alternatives are predicted and compared.
- Design of the selected flowsheet structure alternatives. It is achieved by applying a reverse simulation approach to determine the design parameters of the unit operations from specifications inherited from underlining process groups.
- Post analysis of the designed alternatives. Issues related to heat integration and environmental impacts are considered.
- The final flowsheet is verified through rigorous simulation and/or plant data.

With the CAFD framework it is possible to generate the process alternatives for given problem specification. Given a desired output with the respective input for a given unit, the reverse approach method should be applied in order to obtain the operational conditions that fulfill the specified requirements. D'Anterrosches, 2005 states that this method is applicable to a large range of problems (e.g. includes various process operations like distillation column, solvent based separation, fixed conversion reactor and many more), and does not need to employ rigorous models at each decision step (rigorous models are used in the final step).

- Computer aided molecular design

The goal of a computer aided molecular design (CAMD) techniques is to identify compounds capable of performing a specific task or series of tasks. This is achieved by generating compounds matching a set of specifications with respect to compound type, physical and chemical properties. Harper and Gani, 2000 presented a methodology for finding compounds suitable for a particular purpose. This method is especially useful in this work when new solvents need to be identified. The method will give as an output the suitable candidates for a specified separation process. The approach presents three-steps, which address the need for problem formulation, problem solution and solution analysis.

### 1) *Pre-design step*

The methodology starts with the definition of the overall goal for the design process. The overall goal for the design process is the definition of the overall function the compounds should fulfill along with specifications of additional requirements. Based on the overall goal the formulation in terms of design constraints is achieved using a knowledge base where the properties of interest are identified on the basis of the operational involved.

### 2) *CAMD design step*

The employed CAMD solution method is a hybrid of generate and test type where all feasible molecules are generated from a set of building blocks and subsequently tested against the design specifications. A multi-level approach of Harper et al., 1999 is employed to generate only the most promising candidates. In this approach, a set of groups is used to assemble the compound structures. This can either be done by using a simple approach (generation of a vector of groups describing one or more compounds) or more rigorously by connecting the fragments to form molecular structures.

### 3) *Post-design step*

Here the answers from the CAMD design step are analyzed and verified with respect to properties and behavior that could not be part of the design considerations. The results need to be analyzed and verified because a number of factors cannot be assessed using the prediction techniques employed in the CAMD design step. The post-design analysis includes structural searches of suppliers' databases in order to determine if the identified candidates are commercially available at a financially viable price. Database searches are also valuable sources of experimental and environmental data used to verify the results of predictions and to obtain environmental information impossible to predict but important when choosing the final candidates.

## 2.3 Measures of process performance

When different design alternatives are presented to a given process it is necessary to evaluate the new alternatives when compared with the base case. The interaction of the process with its surroundings it is a very important factor to decide whether the new alternative is better than the base case or not. This interaction can be evaluated using the sustainability metrics. The safety of the process is also another issue that should be taken into account when a new alternative is designed. Therefore, a set of safety indices is used to evaluate the process performance. A review about these two issues is given in the following paragraphs.

### 2.3.1 Sustainability

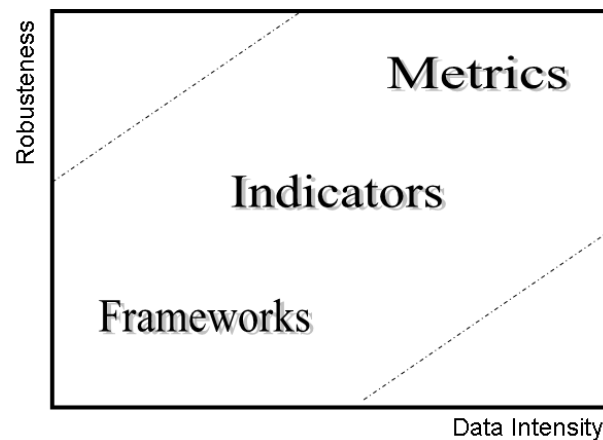
The concept of Sustainability first emerged in 1970, but it has only become an important issue in the modern society with the Brundtland Report, (1987), in which sustainable development is defined as:

*“Sustainable development is a development that meets the needs of the present without compromising the ability of future generations to meet their own needs”.*

It is a very useful definition. However, it implies an objective interpretation and it is a bit hard to operationalize. In the recent years, many companies have adopted the concept of sustainable development. For these companies it was necessary to understand how to implement it and how to measure sustainability.

Different approaches have been developed to measure sustainability. These approaches can be divided into three main areas: Frameworks, indicators and metrics (see Figure 2.3)





**Figure 2.3:** Sustainability Technologies (Adapted from Butner, (2007))

Figure 2.3, shows the relation between the robustness of the technologies for sustainability measurement and the data intensity used to calculate the respective methodologies. The frameworks are the more generic methodologies, requiring less data to use them. This makes these methods more generic and not so accurate to a specific problem. The indicators are the intermediate methodology in terms of robustness and data intensity. The metrics are in the top, being the more specific methods and consequently the most robust and the ones requiring high data intensity. A review about the available methodologies is presented in the following sections.

#### *2.3.1.1 Framework*

A framework for sustainable development is a generic framework used to understand and plan progress towards a sustainable society using back casting from sustainability principles to prioritize strategic actions. The objective of these frameworks is to obtain a global path towards sustainable development. The frameworks are developed based on international standards, representing common visions of sustainability targets. Generally, they make use of indicators, which are relevant to the majority of countries. Usually these approaches are developed by organizations, which have access to a wider range of meetings and exchange more ideas.

Brundtland Report: In late 1983 Brundtland, the former Prime Minister of Norway, was asked by the Secretary-General of the United Nations to establish and chair the World Commission on Environment and Development, a special, independent commission convened to formulate "a global agenda for change". The Brundtland Report issued a multitude of recommendations to help attain sustainable development and to address the problems posed by a global economy that is intertwined with the environment. The report recommends ways to deal with the debt crisis in developing nations, and insists on linking poverty and environmental deterioration.

The Natural Step: is an international not-for-profit organization founded in Sweden in 1989 by Swedish scientist Karl-Henrik Robèrt (<http://www.naturalstep.org/>) The Natural Step has pioneered a "Backcasting from Principles" approach to effectively move society towards sustainability. They present a 5-level framework: (1) *System Level* – identification of the scope of the system in study; (2) *Success Level* – That means “sustainability” (sustainability means that nature is not subject to systematic increases in concentrations of substances from the Earth’s crust, concentrations of substances produced by society, degradation by physical means and people are not subject to conditions that systematically undermine their capacity to meet their needs.); (3) *Strategic Level* – some strategic guidelines for organizations to follow in implementing the framework and taking actions towards sustainability are given; (4) *Action Level* – concrete actions that are taken on the path to sustainability are represented here; (5) *Tools Level* - tools that help organizations managing their path towards sustainability are the last step. This method has being effective as much for the power of its narrative as its ability to be acted upon.

These two frameworks are examples of the work that has taken place in the past decades. However, the work in this area is continuously growing. Some examples are Agenda 21, which is a plan of action (Rio Declaration on Environment and Development, and the Statement of principles for the Sustainable Management of

Forests) to be taken globally, nationally and locally by organizations of the United Nations System, Governments, and Major Groups in every area in which human impacts on the environment (<http://www.un.org/esa/dsd/agenda21/>). Some companies are also creating their frameworks, in order to improve their activity towards sustainability (International Federation of Accountants - <http://web.ifac.org/sustainability-framework/overview> and Regional Sustainable Development Forum, (2007)).

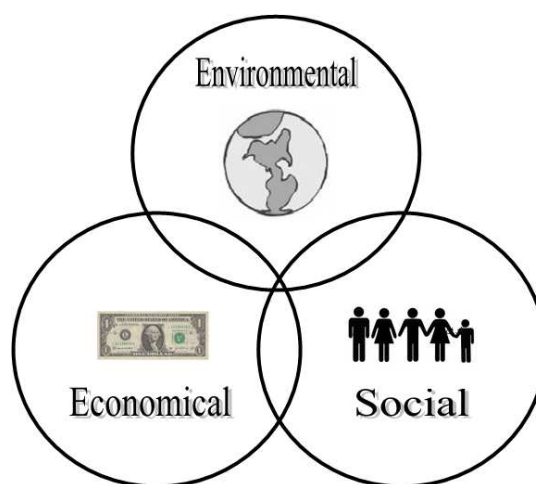
### *2.3.1.2 Indicators*

An indicator is a tool for simplifying, quantifying and communicating information. (Jo and Langenhove, 2006). These tools are more specific and usually they are related to a given area that can be a continent, country, city, etc. The indicators analysis, require extra data for their calculations. They are very often, based on regulatory measures, and imposed for example by laws. Since the indicators are usually applied locally, it was created at the International Sustainability Indicators Network's Web site (<http://www.sustainabilityindicators.org/>), which presents information regarding sustainability indicators at the community level. Work has also been done in order to give directives on how to build sustainability indicators. Valentin et. al., 2000 proposed a model on how local sustainability indicators can be developed and how they can help to reduce the complexity of sustainability and to concretize a program for the Local Agenda 21. Hueting and Reijnders, 2004, gave a list of proposals for the proper way to construct sustainability indicators. Tanzil and Beloff, 2006, wrote an overview about sustainability indicators and metrics. They highlight the work that has been done in the companies regarding the creation of indicators and metrics for sustainability.

All these studies pointed out the importance of the triple bottom line concept, where environmental, social and economical issues should be taken into account. The term 'triple bottom line', is often attributed to John Elkington, a co-founder and chair of Sustainability, a sustainable business consultancy, in 1994 (Elkington, 2004)

The triple bottom line, abbreviated as "TBL" or "3BL", and also known as "people, planet, profit" is any analysis that takes into account a spectrum of values and criteria

for measuring organizational (and societal) success: economic, ecological and social (see Figure 2.4). The triple bottom line succinctly describes the main objective of sustainability. The social concerns (“People”) take into consideration issues such as salaries, safe environment work, tolerable working hours, etc. Environmentally (“Planet”) the companies should make an effort to have a chemical production with a low ecological footprint, which carefully manages the energy consumption, the non-renewable consumption and which reduces the manufacturing waste disposing it in a safe and legal manner. Finally, economical concerns are taken into account in this analysis (“Profit”). The economic value created by the organization after deducting the cost of all inputs is the major concern.



**Figure 2.4:** Triple Bottom Line

### *2.3.1.3 Metrics*

In order to characterize various aspects of a complex phenomenon, cumulative indices or a collection of indicators are turned into a metric. Usefulness of a metric depends on the number of indicators: too few may not provide an adequate description of a phenomenon, too many would make the cost of completing the metric prohibitively high. Because a metric is defined based on indicators, this means that the required data

to calculate them is higher than to calculate the indicators and consequently its robustness is also higher.

Schwarz *et al.*, 2002, define the criteria for useful Sustainability metrics. The metrics should fulfil the following criteria:

- Simple to use: They should not require large amount of time and manpower to calculate them
- Useful as a management tool: They should help in the decision-make regarding to business
- Understandable: The metrics should be understandable from a variety of audiences, from people in operations to finance to strategic planning
- Reproducible: The results must be consistent, allowing the comparison among them
- Cost-effective: The cost related to data collection should be effective
- Robust and non-perverse: The metrics should indicate progress towards sustainability when improvement has in fact been made
- Stackable along the supply chain: They should be usable beyond the particular fence line for which the calculation was performed
- Protective: The metrics should be protective of proprietary information to prevent the back-calculation of confidential information

One of the roles of the metrics is to guide future process and product development. In this way the companies are “forced” to create their own metrics to generate their external reports, to mark their market position and for their product and/or technology development. For instance, GlaxoSmithKline developed a set of metrics to guide the development of new routes to complex organic molecules, while adhering to principles of green chemistry (Constable *et al.*, 2009). Another effort in developing sustainability metrics was undertaken by the Center for Waste Reduction Technologies (CWRT). They developed a set of metrics that examined the production-normalized intensity of manufacturing. This involves material intensity, energy intensity, water consumption, toxics dispersion and green house gases (Beloff, *et.al.*, 2001). BRIDGES to

Sustainability (Tanzil, *et.al.*, 2003) further extended these metrics. The developed metrics follow the simple rule that the lower is the metric the lower is the impact.

Recent progress has also been made by Britain's Institution of Chemical Engineers (IChemE), with the sustainability metrics expanded to include subsets of economic and societal indicators (Azapagic *et al.*, 2002). Detail information is given about these metrics once they are the ones applied in the present methodology.

### *IChemE Metrics:*

These metrics were built upon the “triple bottom line” framework, so they comprise environmental, economic and social indicators. These metrics are intended to be applied at operating units or process basis. IChemE is an important institution, which gives credibility to the developed metrics. Also looking at the metrics, they respect the criteria described before for a good metric. Due to these reasons, this set of metrics has been selected as performance criteria, to evaluate/ compare the new design alternatives with the base case.

The metrics related to each area of the triple bottom line are shortly described in the following points:

#### ➤ *Environmental indicators*

These metrics should give a balanced view of the environmental impact of inputs – resource usage, and outputs – emissions, effluents, waste and product and services produced.

##### ▪ *Energy*

To calculate the energy metrics it is necessary to collect some process data. The parameters that must be obtained are described in Table 2.1.

**Table 2.1:** Data required for energy metrics calculation

	Energy Value	Conversion Factor	Primary Energy Value	Quantity Used/y	Usage Rate GJ/y
Electricity	kJ		kJ		
Fuel Oil	kJ/kg	1	kJ/kg		
Gas	kJ/kg	1	kJ/kg		
Coal	kJ/kg	1	kJ/kg		
Steam	kJ/kg		kJ/kg		
Other (specify)	kJ/kg		kJ/kg		
<b>Total</b>					

In order to calculate the Primary Energy Value, the Energy Value must be multiplied by the Conversion Factor. This factor corrects the efficiency of the generation and supply of the secondary energy source, in order to yield comparable figures for the primary energy usage rate. The conversion factors are available from the energy suppliers and vary from provider to provider. The energy metrics are calculated using the parameters presented in the tables above and the expressions, which describe them, are:

<b>Total Net Primary Energy Usage Rate = Imports – Exports</b>	_____ GJ/y
<b>Percentage Total Net Primary Sourced from Renewals</b>	_____ %
<b>Total Net Primary Energy Usage Rate per kg Product</b>	_____ kJ/kg
<b>Total Net Primary Energy Usage per Unit Value Added</b>	_____ kJ/\$

These metrics are very useful on the evaluation of new alternatives, because they capture process improvements, such as enhanced heat recovery, better heat integration or higher production capacity. The metrics also reflect improved efficiencies of power and steam generation through technologies such as cogeneration.

- *Material (excluding fuel and water)*

The material metrics are the following one:

<b>Total raw materials used per kg product</b>	_____ kg/kg
<b>Total raw materials used per unit value added</b>	_____ kg/\$
<b>Fraction of raw materials recycled within company</b>	_____ kg/kg
<b>Fraction of raw materials recycled from consumers</b>	_____ kg/kg
<b>Hazardous raw material per kg product</b>	_____ kg/kg

The material metrics indicate the consumption of raw materials in the process, and, consequently, they can be useful to determine the impact on the resources. These metrics are also useful in the definition of good alternatives that might improve the recycle of raw materials and, therefore, reduce the consumption of the raw materials.

- *Water*

Based on the following equation, Net water consumed = Total used – recycled t/y, the water metrics can be obtained.

<b>Net water consumed per unit mass of product</b>	_____ kg/kg
<b>Net water consumed per unit value added</b>	_____ kg/\$

The water metrics are related to the information about the process water and the cooling water, therefore these metrics will be useful in order to identify good alternatives related to the decrease of the utilities and to the decreasing of fresh water in the process.

- *Land*

In the set of environmental metrics, the land must be taken into account. These metrics determine the area of land occupied and affected by the process.



## 2. Theoretical background

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<b>Total land occupied + affected for value added</b>	_____ m <sup>2</sup> /\$/y)
<b>Rate of land restoration</b>	_____ (m <sup>2</sup> /y)/ m <sup>2</sup>

- *Emissions, effluents and waste*

The metrics involved in this section take into consideration the atmospheric, aquatic and land impact that comes out from the emissions, effluents and wastes.

The metrics, which define the process impact in the environment, are the following.

<b>Atmospheric acidification burden per value added</b>	_____ te/\$
<b>Global warming burden per value added</b>	_____ te/\$
<b>Human Health burden per value added</b>	_____ te/\$
<b>Ozone depletion burden per value added</b>	_____ te/\$
<b>Photochemical ozone burden per value added</b>	_____ te/\$
<b>Aquatic acidification per value added</b>	_____ te/\$
<b>Aquatic oxygen demand per value added</b>	_____ te/\$
<b>Ecotoxicity to aquatic life per value added</b>	_____ te/\$
<b>Eutrophication per value added</b>	_____ te/\$
<b>Hazardous solid waste per value added</b>	_____ te/\$
<b>Non-hazardous solid waste per value added</b>	_____ te/\$

These metrics allow identifying alternatives that decrease emissions, effluents and wastes. They also identify alternatives that substitute compounds less toxics and consequently less hazardous for the environment.

➤ *Economic indicators*

A key element of sustainability is the success of the industry in creating wealth. The economic indicators go somewhat further than conventional financial reporting in

describing the creation of wealth or value, and in reporting its distribution and reinvestment for future growth. Some of the economic metrics are the following:

<b>Value Added*</b>	_____	\$/y
<b>Value Added per unit value of sales</b>	_____	\$\$
<b>Profit**</b>	_____	\$/y

\* *Value Added* = Revenues – Raw Materials Costs

\*\* *Profit* = Revenues – Variable Costs

The rest of the metrics take into account employee's information, such as the qualification degree, investment in education, number of jobs, etc. These metrics required very detailed data about the company's situation, limiting the calculations from outside the company.

➤ *Social indicators*

Indicators of social performance reflect the company's attitude towards the treatment of its own employees, suppliers, contractors and customers, and also its impact on society at large. These metrics give information about the employment situation (example of metrics: benefits as percentage of payroll expenses, employee turnover, promotion rate, etc), health and safety at work (example of metrics: lost time accident frequency, expenditure on illness and accident prevention, etc) and the opinion of the stakeholders, which includes customers, residents and other community groups, about the production (example of metrics: number of stakeholders meetings, number of complaints, number of legal action, etc).

These metrics are very helpful to evaluate the sustainability of the processes, however they require some data that might not be easy to find. Due to that reason, the metrics described in the emissions, effluents and wastes section were replaced by the use of the Waste Reduction Algorithm (WAR) presented by Cabezas et al (1999). The availability of large database of compounds and their environmental related properties make the

WAR algorithm an easier tool to evaluate the environmental impact. The WAR algorithm is available as a tool in ICAS (Integrated Computer Aided system - Gani *et al.*, 1997). The input data for the tool is the entire data about all inlets and the outlets streams, such as the flowrates, compositions and operational conditions. As an output the WAR algorithm parameters are given.

### *WAR – Algorithm*

Cabezas et al, 1999 firstly introduced The Waste Reduction Algorithm (WAR), then Young and Cabezas, 1999, further extended the algorithm including the specific indices to measure the environmental impact.

The WAR algorithm is based on a potential environmental impact (PEI) balance for chemical processes. The PEI is a relative measure of the potential for a chemical to have an adverse affect on human health and the environment (aquatic ecotoxicology, global warming, etc). The result of the PEI balance is an impact index, which provides a quantitative measure of the impact of the waste generated in the process. This value indicates the unrealized effect or impact that the emission of mass and energy would have on the environment on average.

The WAR algorithm includes eight categories as environmental impact factors:

- HTPI (Human Toxicity Potential by Ingestion)
- HTPD (Human Toxicity Potential by Exposure both Dermal and Inhalation)
- TTP (Terrestrial Toxicity Potential)
- ATP (Aquatic Toxicity Potential)
- GWP (Global Warming Potential)
- ODP (Ozone Depletion Potential)
- PCOP (Photochemical Oxidation Potential)
- AP\* (Acidification Potential)

All these parameters are combined using weights for each environmental factor to achieve the PEI value.

Lower values of PEI show less environmental impact, so to achieve a more sustainable process this value should be as lower as possible.

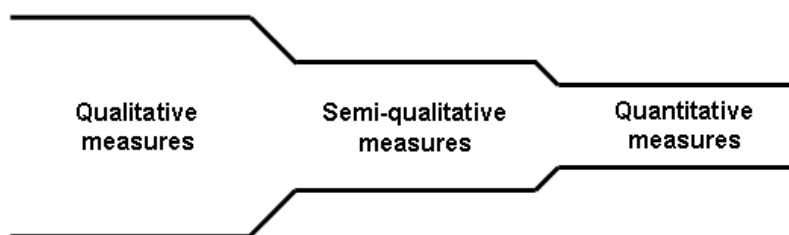
### 2.3.2 Process Safety

It is required that the safety of a process plant fulfils a certain required level, due to general legal requirements, the company image, as well as economic reasons, since an unsafe plant cannot be profitable on account of losses of production and capital. Therefore, safety should influence design decisions from the first moment of the design project.

The safety evaluation is a very difficult point, and it is usually done by safety analysis methods. Safety analysis is a systematic examination of the structure and functions of the process system aimed at identifying potential accident contributors, evaluating the risk presented by them and finding risk-reducing measures.

The safety criteria needs to be considered in different ways depending on the presented problem.

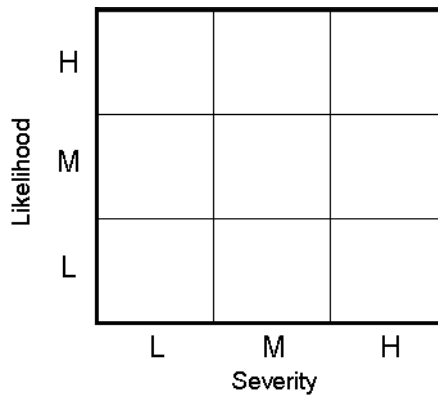
The safety methods can range from purely qualitative to fully quantitative, accompanied by uncertainty analysis (Ian and Raman, 2005). These methods can be divided into three main groups: Qualitative methods, Semi-quantitative methods and Quantitative methods (see Figure 2.5)



**Figure 2.5:** Spectrum of the safety measurements (Adapted from Ian and Raman, 2005)

2.3.2.1 *Qualitative methods*

Qualitative analysis can be applied early in the safety management process to sort those events or incidents that need further detailed consideration. These are simple methods to apply. In adopting a two-dimensional view of safety that considers impact and likelihood as two principal factors, we can develop simple tools to first rate the impacts or severity as well as the likelihood for identified event or incident in the system. The simple qualitative analysis is the safety matrix represented in Figure 2.6.



**Figure 2.6:** Safety Matrix (Ian and Raman, 2005)

In Figure 2.6 the two factors of severity and likelihood have three classes designated as low (L), medium (M) and high (H). The different types of risks should be placed in the appropriate square taking into account its levels of severity and likelihood.

It is also common in this type of analysis to present safety graphs.

This type of analysis allows to rank the risks and consequently to prioritize efforts to be done. This analysis is useful as an initial analysis, however is too broad to a deep safety analysis.

### 2.3.2.2 *Semi-quantitative methods*

These methods come in different forms. The use of indices is one of the methods extensively used for safety analysis. Dow's fire and explosion index or F&EI (AICHE, 1994) allow to estimate of both consequence and likelihood factors in a process unit. This allows a relative ranking of safety within a process.

Heikkilä, 1999, developed the Inherent safety index ( $I_{TI}$ ). The index is subdivided in sub-indices. These sub-indices can be divided into two groups, one group, which takes into account the chemical inherent safety, and the other group that is dependent on the process inherent safety.

Khan, and Amyotte, 2004, presented a conceptual framework of an integrated inherent safety index (I2SI). This index considers the life cycle of the process with economic evaluation and hazards potential identification for each option. The I2SI is composed of sub indices, which account for hazard potential, inherent safety potential, and add-on control requirements.

Another approach was the iSafe Index (Palaniappan *et al.*, 2004). This index identifies the hazards that are associated with the reactions and the chemicals involved in the process route and ranks the available process routes for the product chosen in the product specification stage. Information used for analysis are reaction conditions, materials involved, heat of reaction, catalysts, phase of reaction, unit process involved, and process yield.

These methods are very useful to the safety calculations because they do not require extensive data for the calculations and they already cover important aspects of the process safety.

### 2.3.2.3 Quantitative methods

Qualitative methods are normally undertaken when acceptance or tolerability criteria are available for comparison or acceptance purposes. This method usually involves the description of the problems using mathematical models. Despite of making a very deep analysis about process safety, the qualitative methods require a lot of data and heavy computational effort. In addition, these methods are not so generic, because the models are mainly developed for a given type of process.

In this thesis the inherent safety index Heikkilä, (1999) has been selected as a method for evaluate the safety of the process. A qualitative method would not be sufficiently accurate for evaluating the safety of the process and a quantitative method requires a lot of information, it is too detailed and consequently it might not be sufficiently generic to any process. Therefore a semi-qualitative method should be selected. The inherent safety index, takes into consideration important chemical and process factors that cover the main issues related to the process safety. It is also easy to calculate and analyse.

#### *Inherent safety index ( $I_{TI}$ )*

The safety index can be divided into two groups of sub-indices, one group, which takes into account the chemical inherent safety, and the other group that is dependent on the process inherent safety (See Table 2.2)

**Table 2.2:** Inherent safety sub indices

Total inherent safety index ( $I_{TI}$ )			
Chemical inherent safety index, $I_{CI}$	Score	Process inherent safety index, $I_{PI}$	Score
<u>Subindices for reactions hazards</u>		<u>Subindices for process conditions</u>	
Heat of the main reaction, $I_{RM}$	0-4	Inventory, $I_I$	0-5
Heat of the side reactions, $I_{RS}$	0-4	Process temperature, $I_T$	0-4
Chemical Interaction, $I_{INT}$	0-4	Process pressure, $I_P$	0-4
<u>Subindices for hazardous substances</u>		<u>Subindices for process system</u>	
Flammability, $I_{FL}$	0-4	Equipment, $I_{EQ}$	
Explosiveness, $I_{EX}$	0-4	ISBL	0-4
Toxicity, $I_{TOX}$	0-6	OSBL	0-3
Corrosivity, $I_{COR}$	0-2	Process structure, $I_{ST}$	0-5
Maximum score $I_{CI}$	28	Maximum score $I_{PI}$	25
<b>Maximum <math>I_{TI}</math> Value</b>		<b>53</b>	



➤ *Sub-indices of Chemical Inherent Safety Index*

In this subsection, there are indexes related to reaction hazards, which are the first three indexes; and the others are related to hazardous substances.

▪ *Reaction Heat Subindex for the Main Reaction ( $I_{RM}$ )*

The heat of the reaction is very important in the process safety, because reactions in which large quantities of heat or gas are released are potentially hazardous, particularly during fast decomposition or complete oxidations.

From the safety point of view it is important to know, how exothermic the reaction is. The classification for this index based in the heat of the reaction is described in Table 2.3.

**Table 2.3:** Determination of Reaction Heat Sub-indices  $I_{RM}$  and  $I_{RS}$

Heat of reaction/total reaction mass	Score
Thermally neutral $\leq 200$ J/g	0
Mildly exothermic $< 600$ J/g	1
Moderately exothermic $< 1200$ J/g	2
Strongly exothermic $< 3000$ J/g	3
Extremely exothermic $\geq 3000$ J/g	4

If there are several main reactions, for instance a series reaction, the score of  $I_{RM}$  is determined on the basis of the total reaction. If there are several reactors in the process under consideration, the score is determined on the reactor with the greatest heat release.

- *Reaction Heat Subindex for the Side Reaction ( $I_{RY}$ )*

This subindex is determined as the same way as the last one. Therefore, the same classification described in Table 2.3 is applied.

- *Chemical Interaction Subindex ( $I_{INT}$ )*

Chemical interaction considers the unwanted reactions of process substances with materials in the plant area. These reactions are not expected to take place in the reactor and therefore they are not discussed in the side reaction subindex. The worst interaction that appears between the substances present in the plant area is used in the calculations for the Chemical Inherent Safety Index.

The following table shows the different scores in relation to the different conditions.

**Table 2.4:** Determination of Chemical Interaction Sub-index  $I_{INT}$ .

Chemical interaction	Score
Heat formation	1-3
Fire	4
Formation of harmless, non-flammable gas	1
Formation of toxic gas	2-3
Formation of flammable gas	2-3
Explosion	4
Rapid polymerization	2-3
Soluble toxic chemicals	1

- *Flammability Subindex ( $I_{FL}$ )*

This subindex describes the flammability of the liquid in the case of a leakage. Flammability of liquids is measured by their flash points and boiling points. The classification used to determine the subindex is the following:

**Table 2.5:** Determination of Flammability Subindex  $I_{FL}$ .

Flammability	Score
Non-flammable	0
Combustible (flash point $>55^{\circ}\text{C}$ )	1
Flammable (flash point $\leq 55^{\circ}\text{C}$ )	2
Easily flammable (flash point $\leq 21^{\circ}\text{C}$ )	3
Very flammable (flash point $\leq 0^{\circ}\text{C}$ & boiling point $\leq 35^{\circ}\text{C}$ )	4

- *Explosiveness Subindex ( $I_{EX}$ )*

The explosiveness is considered through a chemical property which is not directly the same as the process explosion hazard, but can be a fire estimate.

The subindex of explosiveness describes the tendency of gas to form an explosive mixture with air. It can be calculated by the difference between the upper and the lower explosion limits (LEL and UEL) of the substances. With this value and using the ranges presented in the next table it is possible to determine the subindex.

**Table 2.6:** Determination of Explosiveness Subindex  $I_{EX}$ .

Explosiveness (UEL-LEL) vol %	Score
Non explosive	0
0-20	1
20-45	2
45-70	3
70-100	4

- *Toxic Exposure Sub-index ( $I_{TOX}$ )*

Health hazardous caused by chemicals are represented by the Toxic Exposure Subindex. The toxic exposure is based on the Threshold Limit Value (TLV) because TLV data is readily available for most substances in the process industry. TLV values

express the harmful exposure limits of substances in the threshold time of 8 hours. The scores related to the values of TLV are in Table 2.7.

**Table 2.7:** Determination of the Toxic Exposure Sub-index  $I_{TOX}$ .

Toxic limit (ppm)	Score
TLV >10000	0
TLV ≤10000	1
TLV ≤1000	2
TLV ≤100	3
TLV ≤10	4
TLV ≤1	5
TLV ≤0.1	6

▪ *Corrosiveness Subindex ( $I_{COR}$ )*

Corrosion is usually measured as corrosion rates mm/a. The material is selected so that the corrosion allowance is not exceeded during the life time of the equipment. However, the corrosion rates are not always known during the predesign, therefore, in order to determine the corrosive conditions of the process the material used in the process must be examined. The best material often indicates conditions that are more corrosive; consequently, a classification based on the type of construction material can be justified (see Table 2.8).

**Table 2.8:** Determination of Corrosiveness Sub-index  $I_{COR}$ .

Construction material required	Score
Carbon steel	0
Stainless steel	1
Better material needed	2

➤ *Sub-indices of Process Inherent Safety Index*

In this section, the indices are all related to the equipment and to the operational conditions.

▪ *Inventory Subindex ( $I_I$ )*

An exact calculation of inventory is difficult to make in the conceptual design phase, since the size of the equipment is not usually known. The total inventory is the sum of inventories of all process vessels. The indexes related to the inventory are the following:

**Table 2.9:** Determination of Inventory Subindex  $I_I$

ISBL	Score
0-1 t	0
1-10 t	1
10-50 t	2
50-200 t	3
200-500 t	4
500-1000 t	5

▪ *Process Temperature Subindex ( $I_T$ )*

Temperature is an indicator of heat energy in the system. The hazard increases in higher temperatures because the energy contents itself and because the strength of materials result in high or very low temperatures. The different temperatures match different scores and the temperature ranges were chosen based on the danger to humans, as well as of material strength as a function of temperature.

**Table 2.10:** Determination of Temperature Subindex  $I_T$ .

Process Temperature	Score
<0 °C	1
0-70 °C	0
70-150 °C	1
150-300 °C	2
300-600 °C	3
> 600 °C	4

When there are many temperature levels in the process area under study, the highest temperature is chosen to obtain the sub-index value.

- *Process Pressure Subindex ( $I_P$ )*

Pressure is an indicator that affects the leak rates in the case of loss of containment. Higher pressures also present stricter requirements to the strength of vessels. Leak in vacuum equipment may cause inlet of air and consequent explosion.

In the Inherent Safety Index ( $I_{TI}$ ) the process pressure is determined on the basis of the maximum pressure in the process area under normal operation. The pressure limits are described in the table below:

**Table 2.11:** Determination of Pressure Subindex  $I_P$ .

Process Pressure	Score
0.5-5 bar	0
0-0.5 or 5-25 bar	1
25-50 bar	2
50-200 bar	3
200-1000 bar	4

▪ *Equipment Safety Subindex ( $I_{EQ}$ )*

Equipment safety tries to measure the possibility of a piece of equipment being unsafe. Here, the equipment includes all major pieces of equipment such as pumps and vessels and others, but not pipes, valves or instruments. For the Equipment Safety Subindex the process plant area is divided into two different areas, which have different properties. The onsite area is the area where the raw materials are converted into products. This is referred to as the Inside Battery Limits Area (ISBL). A large number of equipment concentrated in a small area characterizes this area. The rest of the plant is referred to as the Offsite Battery Limits Area (OSBL). The OSBL is characterized by large inventories of fluids, which are often flammable and/or toxic.

▪ *ISBL*

The plant layout is a crucial factor in the safety of a process plant due to the segregation of different risks, the containment of accidents and the limitation of exposure. These are often called the minimum clearances between equipment.

In order to measure the safety of a process in relation to the equipment, the scores will be given by the existing equipment in the process. Using the description of the equipment it will be easy to know whether a process is more or less safe due to the defined distances between them.

In short, the process items have been arranged into five groups as shown in the table below.

**Table 2.12:** The scores of Equipment Safety Subindex  $I_{EQ}$  for ISBL.

Equipment items	Score
Equipment handling non-flammable, non-toxic materials	0
Heat exchangers, pumps, towers, drums	1
Air coolers, reactors, high hazard pumps	2
Compressors, high hazard reactors	3
Furnaces, fired heaters	4

- *OSBL*

For the offsite equipment the scores 0-3 have been used instead of 0-4 for ISBL equipment, since the offsite represents only one third of all losses and are therefore not as essential as ISBL. Also much of the risks of OSBL are due to large inventories of flammable or toxic chemicals, which are discussed in the inventory, flammability and toxicity indices, and not in the equipment safety index. Furthermore, the equipment of the same size is probably safer in OSBL than in ISBL on account of a larger spacing in the layout.

**Table 2.13:** The scores of Equipment Safety Subindex  $I_{EQ}$  for OSBL.

Equipment items	Score
Equipment handling non-flammable, non-toxic materials	0
Atmospheric storage tanks, pumps	1
Cooling towers, compressors, blowdown systems, pressurised or refrigerated storage tanks	2
Flares, boilers, furnaces	3

- *Safe Process Structure Subindex ( $I_{ST}$ )*

The Process Structure Subindex approaches the process from the systems engineering point of view. Therefore, it is much more difficult to estimate. In fact, there is no explicit way of estimating the safety of the process structure but one has to rely on experience-based data, which are documented as standards, design recommendations and accident reports.

Process structures are divided into six groups of scores from 0 to 5 according to the knowledge of their safety behaviour in operation.



**Table 2.14:** Values of the Safe Process Structure Sub-index  $I_{ST}$ .

Safety level of process structure	Score
Recommended (safety standard)	0
Sound engineering practice	1
No data or neutral	2
Probably unsafe	3
Minor accidents	4
Major accidents	5

The final score of the sub-index is chosen based on the worst case.

With all the indexes, described before, it is possible to determine the Total Inherent Safety Index ( $I_{TI}$ ). This index is the sum of Chemical Inherent Safety Index ( $I_{CI}$ ) and the Process Inherent Safety Index ( $I_{PI}$ ). They are calculated for each process alternative separately and the results are compared with each other. The equations which describe them are the following ones:

$$I_{TI} = I_{CI} + I_{PI} \quad \text{Eq (2.1)}$$

$$I_{CI} = I_{RM,max} + I_{RS,max} + I_{INT,max} + (I_{FL} + I_{EX} + I_{TOX})_{max} + I_{COR,max} \quad \text{Eq (2.2)}$$

$$I_{PI} = I_I + I_{T,max} + I_{P,max} + I_{EQ,max} + I_{ST,max} \quad \text{Eq (2.3)}$$

## 2.4 Computational Tools

A number of software with varying lists of implemented methods and tools and different architectures are being developed as a result of the advances in computer science and computational algorithms. Tools for process retrofit analysis have also been reported. Nowadays with increased interest on sustainability issues, many software have been developed to help with the sustainability measurements. The available software tools can be divided into two groups: those that evaluate process performance in terms of sustainability, life cycle assessment and environmental impact; and those that determine new design alternatives in order to reduce the environmental impact.

### 2.4.1 Performance Tools - Software

In this group of software different approaches to measure sustainability are considered. Some of the tools perform life cycle assessment, some calculate and employ sustainability metrics for process evaluation and some use specific parameters to measure sustainability.

- Software BRIDGESworks Metrics (Tanzil and Beloff, 2006) is a metrics management software tool that identifies key sustainability indicators and offers a variety of metrics for measuring sustainability performance. It incorporates a base set of metrics and their heuristics for calculation and a data base for use in identification of pollutant effects.
- U.S. EPA (Bare et al., 2003) has developed TRACI, the Tool for the Reduction and Assessment of Chemical and other environmental Impacts. This tool was developed to assist in impact assessment for Sustainability Metrics, Life Cycle Assessment, Industrial Ecology, Process Design, and Pollution Prevention.

- Curzons et al., (2007) developed a tool for Life Cycle Assessment called, FLASCTM (Fast Life cycle Assessment of Synthetic Chemistry). This tool was developed from a detailed assessment of the cradle-to-gate life cycle environmental impacts associated with the manufacture of materials used in a typical pharmaceutical process.
- GaBi (GaBi Software, (2009)): a software, which includes tools and databases for product and process sustainability analysis. This software includes tools for Life Cycle Assessment (LCA), Carbon Footprint calculation and Greenhouse analysis.
- SimaPro (Product Ecology Consultants – PRé, (2009)) is another software, performing LCA. This software uses Eco-Indicator 99 in order to determine the parameters need for LCA.

These tools although very useful, present some limitations. They measure sustainability parameters that can be used to compare the performance of different processes or different design alternatives, however they do not suggest alternatives to solve the identified problems.

### 2.4.2 Process retrofit - Software

Many approaches for retrofit design have been presented covering different issues such as, waste water reduction, energy reduction, environmental impact reduction etc.

- ENVOPExpert, Halim and Srinivasan, (2002), which is an expert system that given the information concerning the process in the form of a flowsheet, process chemistry, and material information, can automatically detect the waste compounds in the process, diagnose the sources of their origin, and suggest intelligent design alternatives (heuristic) to eliminate or minimize them.
- AquoMin, Relvas et al., (2008), which is a software tool dealing with water and wastewater minimization. This software was developed to study the problem of wastewater minimization in a set of mass-exchange operations and the subsequent distributed effluent system.
- DESASS, Ferrer et al., (2008), has been developed to design, simulate and optimize wastewater treatment plants. The software allows the simulation of the most important physical, chemical and biological processes.

Now, there are several software available with varying degrees of implemented methods and tools. However, these software do not include options for retrofit analysis as well as process evaluation. In addition, the principal emphasis of these software has been on process improvement through waste and energy reduction. These facts highlight the need for some other tools that involve options for time retrofit analysis and evaluation of the generated alternatives. It also points out the need of more generic software that take into consideration energy and water reduction, but also economic, other environmental and safety issues.



## 3. Methodology for Sustainable Process Design

### 3.1 Introduction

In this section, the motivation for this thesis (section 3.1.1) is discussed and the problem formulation is presented (section 3.1.2). Then the methodology for Sustainable Process Design is described in detail for continuous and batch processes (sections 3.2 and 3.4 respectively). After the description of the methodology, a case study is presented in detail in order to illustrate the application of the methodology (section 3.3 for continuous processes and section 3.5 for batch processes). Finally, the main conclusions are presented (section 3.6).

#### 3.1.1 Motivation

As stated before the motivation for this PhD work is to present a new systematic and generic methodology to study any chemical process, based in some concepts already presented by Uerdingen, 2002 (paths definition and mass and energy indicators). These concepts presented some limitations, which were used as motivation of this work. In addition, to present a methodology able to deal with any kind of process some other considerations have to be taken into consideration.

- The closed-path concept defined by Uerdingen *et al.*, 2002 was not able to deal with nested loops. How can these flowsheets be analyzed?

- Uerdingen *et al.*, 2002 determined the mass and energy indicators, but it did not select the most critical ones. How can the indicators be selected? Which indicators should be considered to a better improvement?
- Design alternatives must be proposed after identifying bottlenecks in the process. How can we generate new design alternatives to match the target indicators?
- Only flowsheets with small number of compounds (10), streams and units (25) could be analyzed. What should be done in order to extend the application of the method to any chemical process? Should the computer aided techniques be considered?
- Only processes operating in continuous mode are considered in the previous methodology. What should be done to study batch and semi-continuous processes? How can the batch operations be taken into account?
- The previous concepts have only been applied to data from simulations results. Is it possible to apply the methodology to real plant data? Which are going to be the main problems?
- The methodology did not include the possibility of combining strengths with some other methodologies. Is it possible to combine the extended methodology with other approaches?

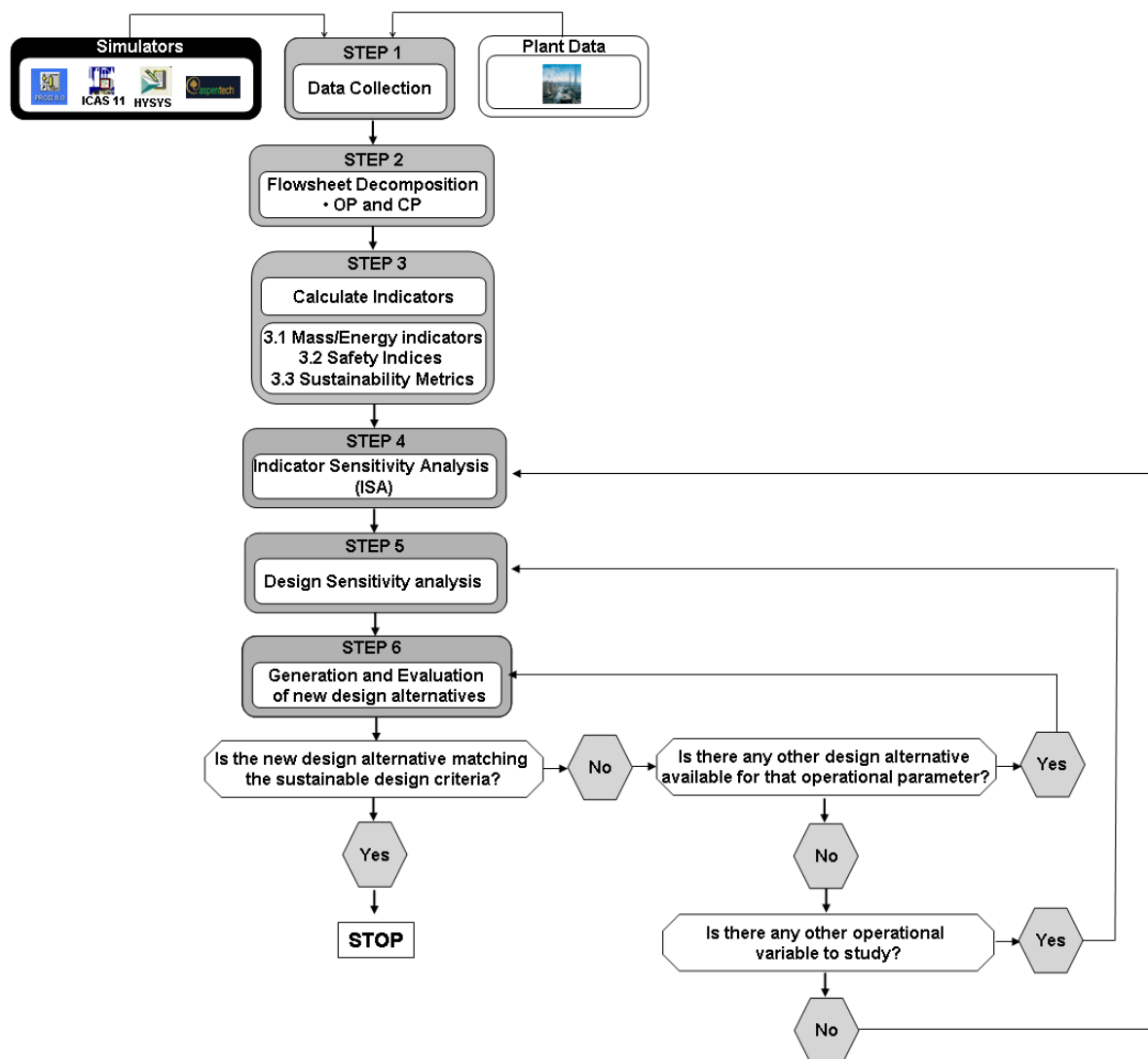
#### 3.1.2 Problem formulation

From all the questions raised in the previous subsection (3.1.1), the focus of this work is on the development of an extended methodology, which will be able to analyze any chemical process. The methodology will guide the user through a step by step procedure for a sustainable design, which includes analysis of the retrofit problem, generation of new design alternatives and evaluation of new design alternatives. The methodology should deal with any type of process operating in continuous, batch and semi-batch mode. A software that follows the methodology should be developed in order to make the methodology systematic and applicable to complex flowsheets. The software and consequently the methodology should be applied to case studies in order to illustrate their applicability. The integration of the software with other tools should also be tested and verified.



### 3.2 Methodology for continuous processes

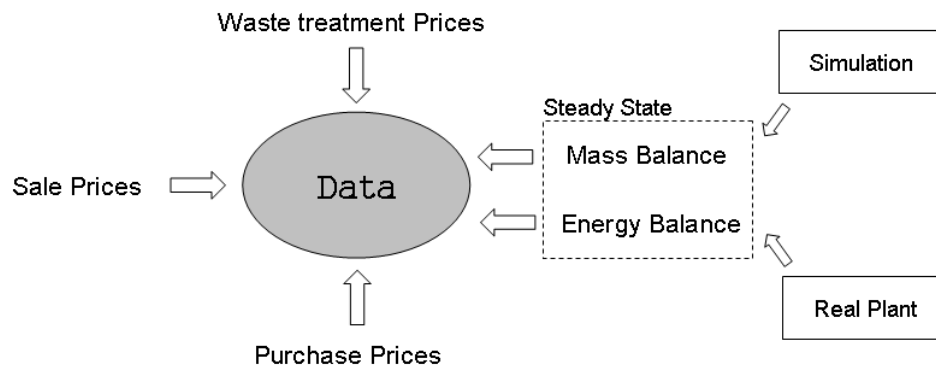
The main objective of this methodology is to screen, analyse and then identify new sustainable design alternatives (Carvalho *et al.*, 2008). The work flow of the methodology can be seen in Figure 3.1.



**Figure 3.1:** Flowdiagram of the sustainable process design methodology for processes operating in continuous mode

### 3.2.1 Step 1- Data Collection

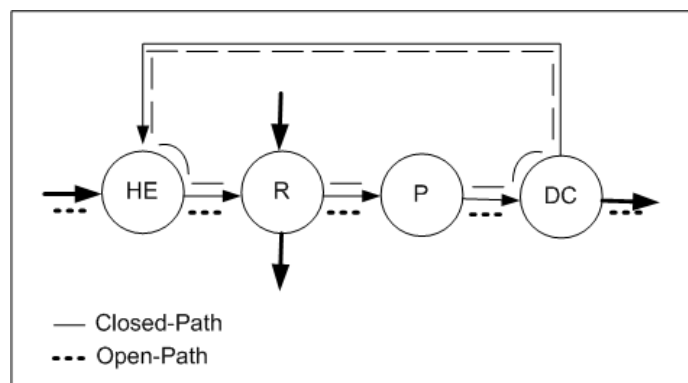
The objective of this step is to collect the mass and energy data corresponding to the steady state operation of the process under investigation. This data can be provided as steady state simulation results (for example, from commercial simulators such as *PRO/II*, *Aspen*, *HYSYS*, or *ICAS* simulator (Gani et al. 1997)) or operational data collected from the plant. Therefore, the methodology can be applied to any chemical process, for which steady state operational data is available. All the prices involved in the process need also to be specified in this step. The purchase prices of each compound, the sale prices as well as the waste treatment prices are included in the methodology input. Figure 3.2, presents a summary of the necessary data for the methodology application.



**Figure 3.2:** Input data for the Sustainable Process design methodology

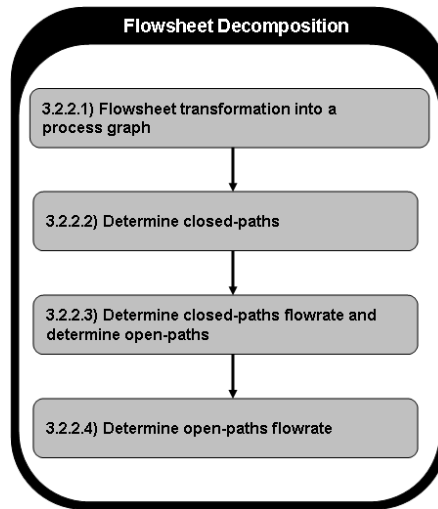
### 3.2.2 Step 2- Flowsheet Decomposition

The objective of this step is to identify all the mass and energy flow-paths in the process by decomposing the process into open- and closed- paths for each compound. The closed-paths (CP) are the process recycles with respect to each compound in the process. In other words, they are the flow-paths, which start and end in the same unit of the process. An open-path (OP) consists of an entrance and an exit of a specific compound in the process. The entrance of the compound in the system can be due to its entrance through a feed stream or by its production in a reactor unit. The exit of the respective compound can be due to a “demand” (exit) stream or by its reaction in a reactor unit (Uerdingen *et al.*, 2003). See Figure 3.3 to a better understanding of the concepts.



**Figure 3.3:** Illustration of closed- and open-paths

Figure 3.4 highlights the main steps of the flowsheet decomposition algorithm (Carvalho *et al.*, 2008).



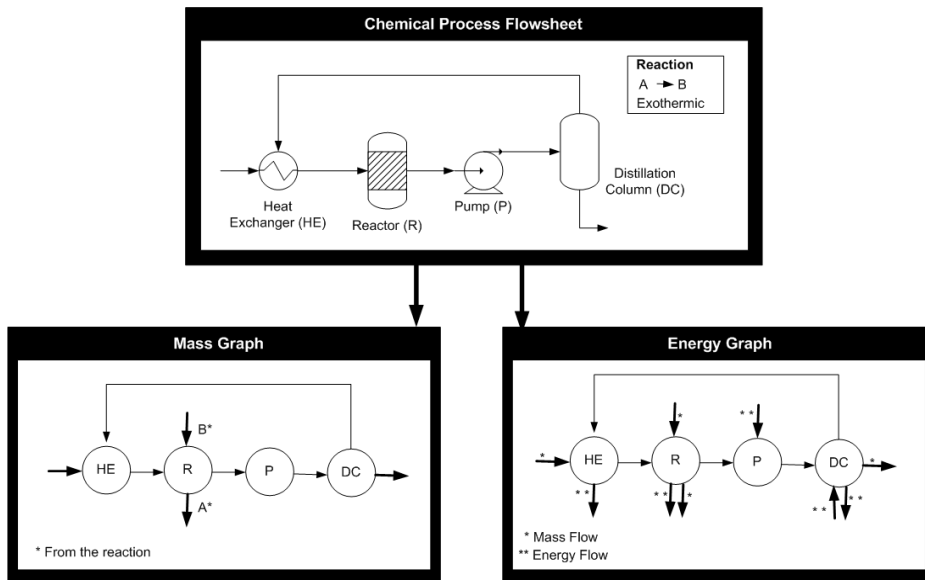
**Figure 3.4:** Main steps for the flowsheet decomposition algorithm (Step 2)

#### *3.2.2.1) Flowsheet transformation into a process graph*

The flowsheet decomposition is based on the graph theory applied to process design analysis, described by Mah, 1983. The units of the flowsheet are called vertices ( $v$ ). These vertices are connected through intermediate streams, called edges ( $f$ ). Bold arrows pointing the vertices are referred to supply flows ( $s$ ) and the bold arrows leaving the vertices are the demand flows ( $d$ ). When reactions occur in a process, reactants disappear from the process and products are generated. These flows cannot be visualized in a flowsheet representation however in graph representation those flows are represented and they can be visualized. In this way the graph representation helps the visualization of the processing tasks in general.

Mass and energy graphs are different. Energy is not limited to follow the mass paths, it can be split into flow heat and transferred heat with the surroundings (for example heat transfers to the utilities). Example 3.1 illustrates the application of the graph theory for mass and energy graphs representing a simple flowsheet.

**Example 3.1**



**Figure 3.5:** Transformation of a process flowsheet into a process graph (Example 3.1)

*Mass Graph*

In Figure 3.5, in the mass graph two bold arrows are represented in the reactor, one entering and the other one leaving the reactor. The arrow entering the reactor represents compound B produced in the reaction. A is disappearing from the process, since it is being consumed in the reaction. This fact is then represented in the mass graph by a bold arrow leaving the reactor.

*Energy Graphs*

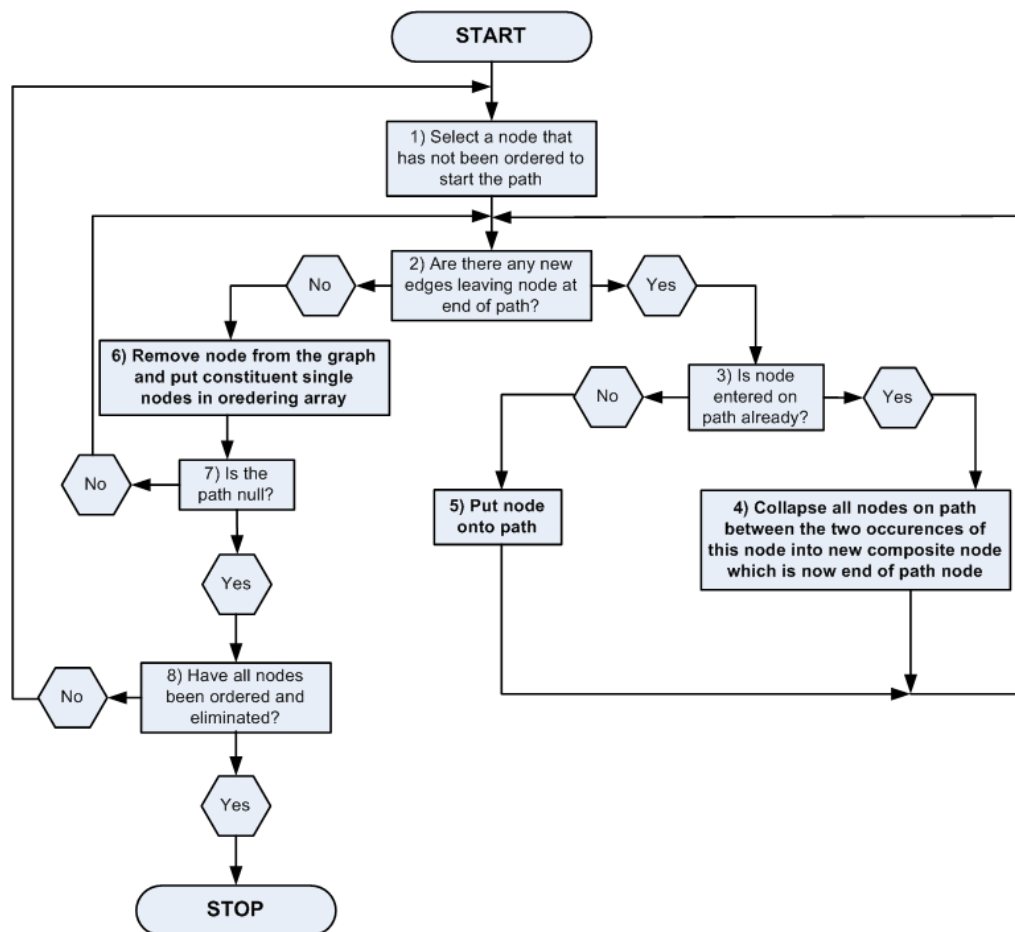
Extra bold arrows are represented in the energy graph. All the streams carrying mass into the process will consequently carry an inherent enthalpy associate to them. Therefore, they are also represented in the energy graph. The remaining bold arrows are related to energy exchanged with utilities. For example in the heat exchanger, when the mixture is cooled, energy is being released from the process and consequently it is represented with a bold arrow leaving the unit. Electricity is being supplied to the pump, which is therefore represented by a bold arrow entering the pump. In a distillation column there is energy entering in the reboiler and energy leaving in the condenser, this explains the two arrows represented in that unit.

With the graph representation it is possible to trace all mass and energy fluxes, making this analysis a simpler and more efficient process.

#### *3.2.2.2) Determine Closed-paths*

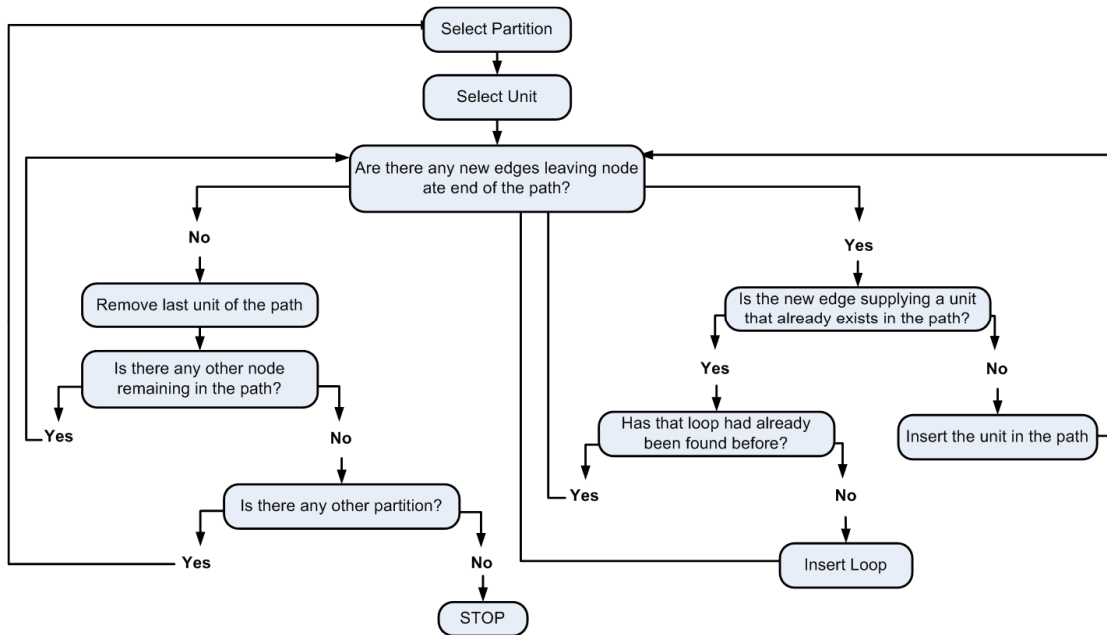
##### *Mass Closed-Paths*

Before identifying the closed-paths within the flowsheet, it is necessary to decompose the flowsheet into different partitions. A partition is a strongly connected and a strong compound subgraph (Duff and Reid, 1978). In other words, a partition is a subgraph (subset of nodes and all edges that are pairs of nodes belonging to this subset), where there is a path from any of its nodes to any other node in that subgraph and the subgraph cannot be enlarged to another strongly connected subgraph by adding extra nodes and associated edges. Clearly, each node can belong to only one partition (which may consist of a single node). The Sargent and Westerberg algorithm (Sargent and Westerberg, 1964), which determines the different partitions in a process has been implemented here (see Figure 3.6).



**Figure 3.6:** Flowchart of Sargent and Westerberg's algorithm adapted from Duff and Reid, (1978)

After identify all the partitions, it is possible to determine the closed-paths within each partition. Biegler *et al.*, 1997, presented an algorithm to determine closed-loops. This algorithm has been adapted, and has been used in this methodology (See Figure 3.7)



**Figure 3.7:** Flowchart of for loops determination based on Biegler *et al.*, 1997 theory

Following these two algorithms, all possible closed-paths are identified in a systematic way.

#### *Energy Closed-paths:*

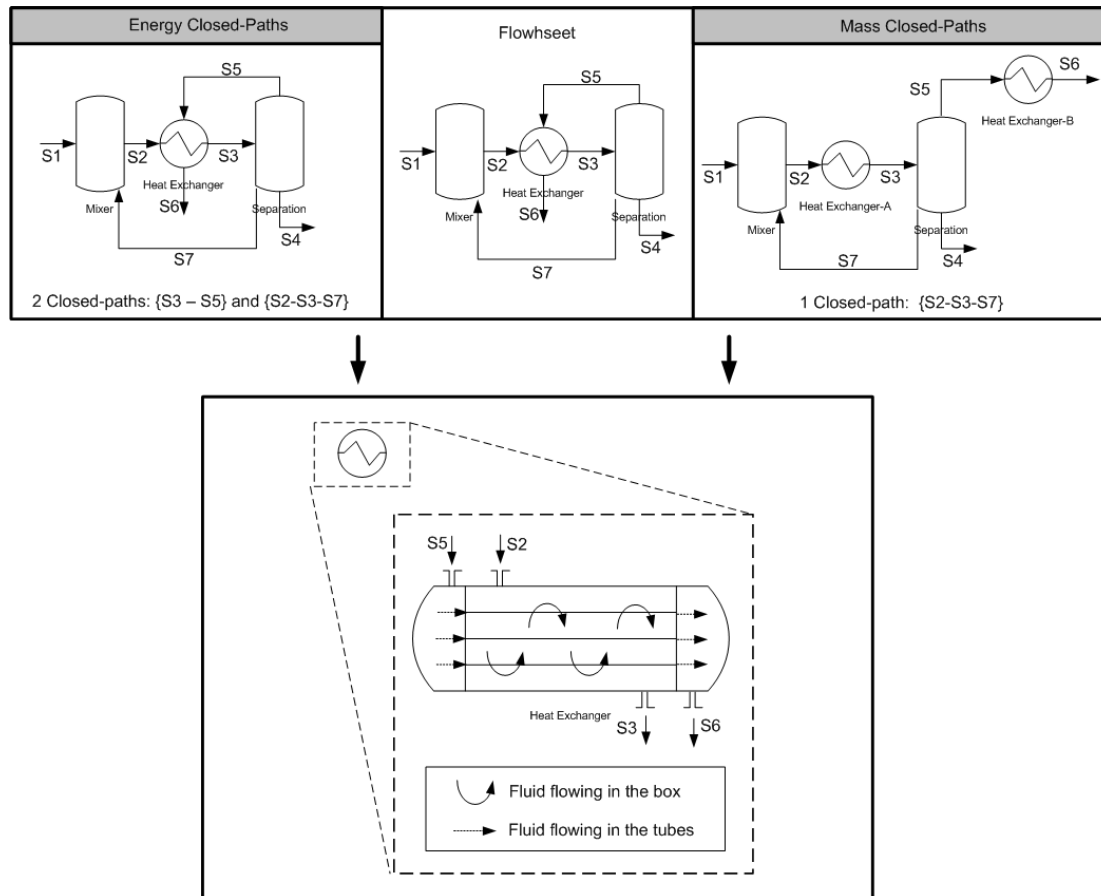
The flowsheet decomposition, into energy closed-paths, is identically performed as for the mass flowsheet decomposition, however there are some differences. The flowsheet decomposition into different partitions is performed as presented in mass section, through the application of Sargent and Westerberg algorithm. Then the algorithm described by Biegler *et al.*, 1997 is also applied to determine the energy closed-paths. The main difference between the mass and the energy flowsheet decomposition is that the energy closed-paths are not related to a given compound. Instead, they are related to streams. It is also important to mention that some of the energy closed-paths are not defined in the mass flowsheet decomposition. This happens due to the heat integration that might occur in a given flowsheet. When heat integration appears in a flowsheet, an



energy loop is presented because there are energy exchanges within that equipment. However, these closed-paths are not listed in the mass closed-paths, because the mass of different streams pass through the same unit but in separate parts of the equipment without mass interaction.

Example 3.2 illustrates, the closed-paths determination in a simple flowsheet, which includes heat integration.

**Example 3.2**



**Figure 3.8:** Example of flowsheet decomposition into closed-paths with heat integration (Example 3.2)

*Mass Graph:* One closed-path has been found in terms of mass. The heat exchanger with heat integration is represented by two separate heat exchangers in the mass graph, because there is no mass interaction.

*Energy Graph:* Two closed-paths were found in terms of energy, which means an extra path when compared to the mass graph.

In the bottom part of Figure 3.8, it is represented the fluid circulation across a heat exchanger. The two fluids do not mix up, since one fluid is running in the box and the other in the tubes, which means that these unit can be represented by two independent equipments (no mass closed-path, because no mass interaction). However, the two fluids are constantly exchanging energy through the walls of the tubes, which means energy interaction between the two fluids and consequently on single unit in the graph representation (extra energy closed-path).

#### *3.2.2.3) Determine closed-paths flowrate and determine open-paths*

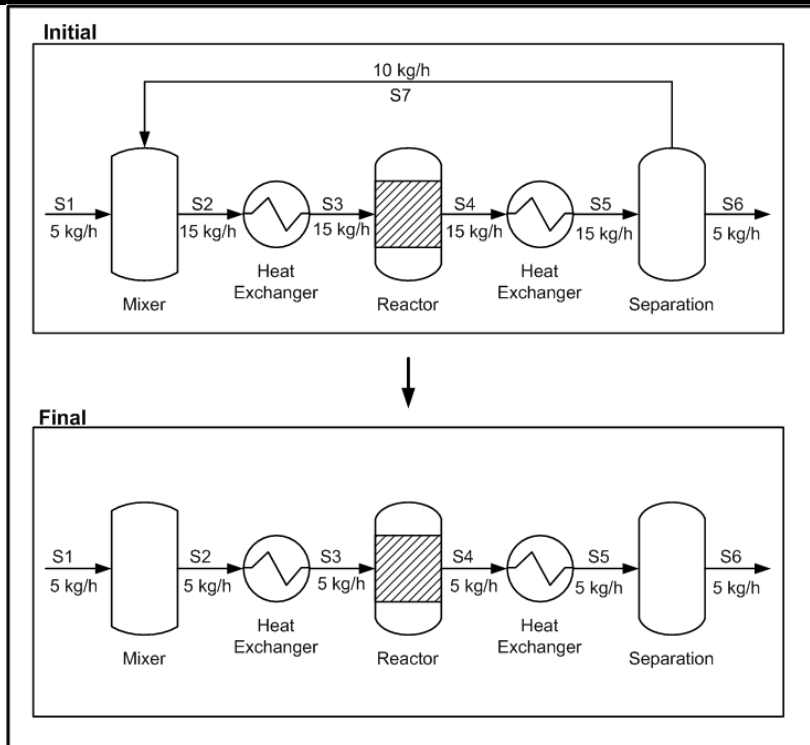
The closed-paths flowrates represent the mass and energy accumulation/recirculation in the process. The closed-paths flowrates need to be identified before the identification of the open-paths and their associated flowrates. This is because the mass accumulated in the loops needs to be subtracted from the corresponding open-path streams. This allows defining a new graph presenting only the amounts related to the entrance and the exit of a given compound.

#### *Mass closed-paths flowrate and open-paths*

The determination of the flowrate for the closed-path was firstly presented in Uerdingen *et. al* (2002). This author developed an optimization problem to calculate the mass flow of a compound in each closed-path. After that, Andersen and Engen (2002) further developed this work and determined an easier way to calculate the flowrate for the closed-path achieving the same results. These authors determine the minimum flow of each compound in the closed-path. This value is referred to be the mass base level and consequently the closed-path flowrate.

The starting point of this thesis was based on the approach developed by Andersen and Engen (2002). A simple example (Example 3.3) is given in order to illustrate the closed-path flowrate determination defined by Andersen and Engen (2002).

**Example 3.3**



**Figure 3.9:** Example for closed-path flowrate calculations for independent loops (Adapted from Andersen and Engen (2002)) -Example 3.3

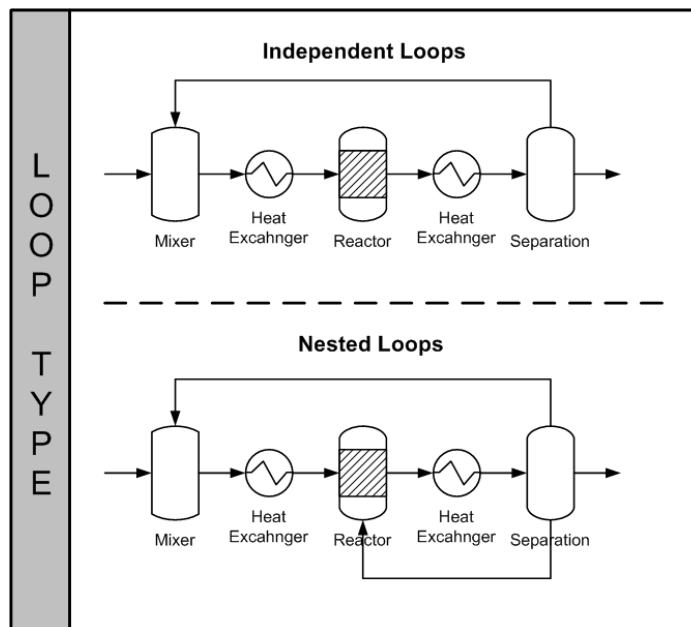
Figure 3.9 shows a simple process with a recycle. The values of the flowrates refer to a single compound. It is assumed that the compound is an inert and enters the process together with a reactant. The closed-path includes the following streams {S2, S3, S4, S5, S7}. The stream with the lowest flowrate within the streams of the closed-path is identified. In this case stream S7 presents the lowest flowrate (10 kg/h) and consequently flowrate of S7 is the closed-path flowrate. This closed-path flowrate can now be subtracted from the original process graph shown in Figure 3.9 (top). The new updated process graph without the recycles is shown in Figure 3.9 (bottom). For this process, removal of the single recycle leaves only one open-path. This is the open-path supplied from the inlet, S1, and leaving in the demand stream, S6.

Example 3.3 illustrates the basic steps to subtract the closed-paths from the original flowsheet, leaving only the open-paths in the flowsheet. The approach presented in the previous example is appropriated to simple flowsheets where only independent loops are present. However, when nested loops appear, the previous methodology fails. In some flowsheets, when applied that approach, negative mass closed-path flowrates appear as a result. In this way it was necessary to develop a new flowsheet decomposition technique to enlarge the application of this methodology to any chemical process.

In the new flowsheet decomposition technique, it has been considered two different types of loops:

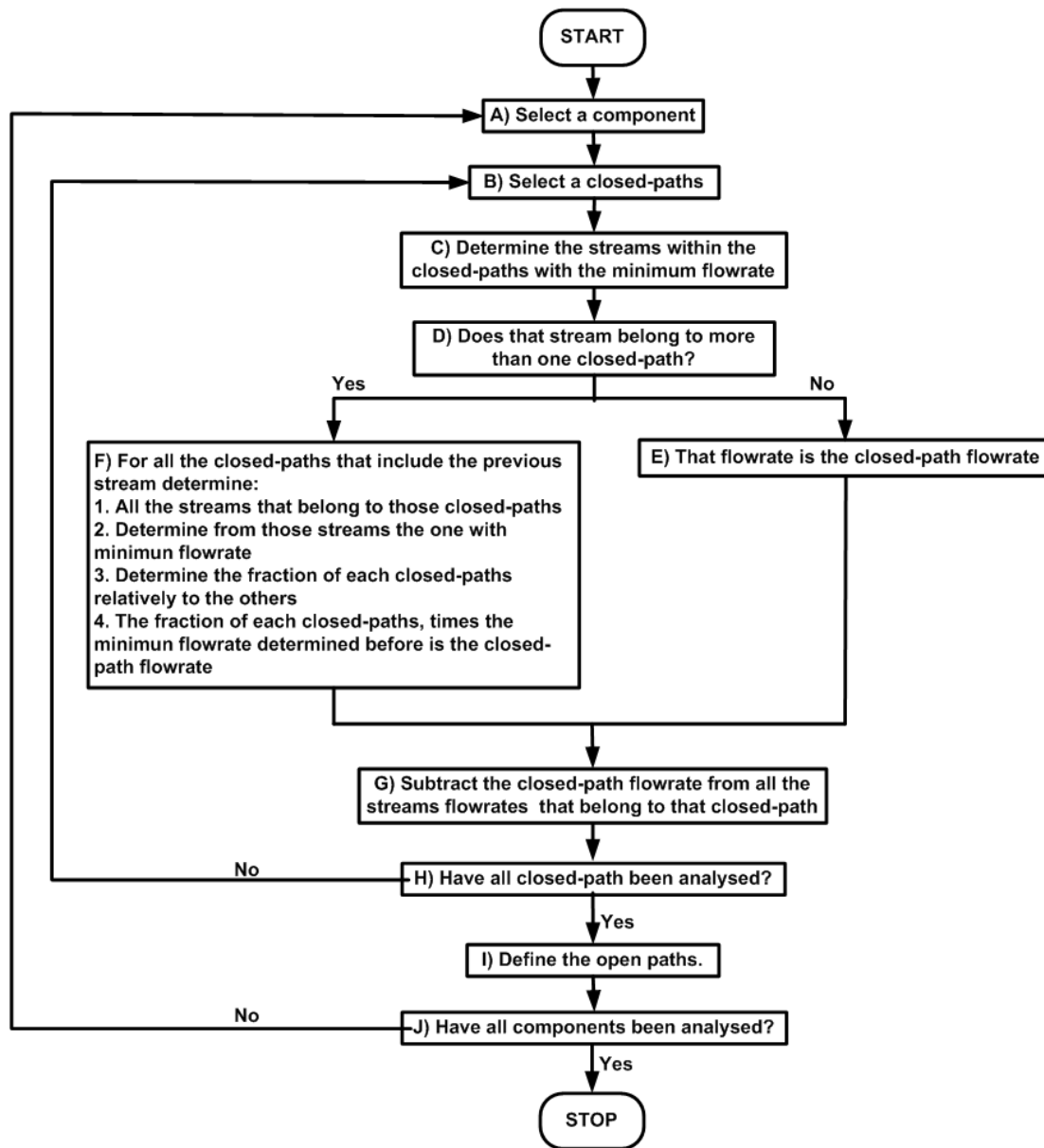
- Flowsheets with independent loops
- Flowsheet with nested loops

The different types of loops are illustrated in Figure 3.10.



**Figure 3.10:** Different types of loops that can appear in a process flowsheet

Nested loops are the loops with streams in common. A new algorithm, which determines the loop type and the respective procedure for calculating the closed-path flowrates, has been developed. The algorithm implemented to determine the closed-paths flowrates is highlighted in Figure 3.11 (Carvalho *et al.*, 2008).



**Figure 3.11:** Schematic diagram of the algorithm for step 3.2.2.3 of the flowsheet decomposition

- **Step A:** The first step of the new algorithm is to select the compound to analyze. This step needs to be repeated for all compounds whose accumulation is different in each closed-path.
- **Step B:** Here a closed-path should be selected. All the closed-path should be analyzed for each compound.
- **Step C:** The stream, within the selected closed-path, which corresponds to the minimum compound flowrate, needs to be located. This value represents the amount of material, which is being recycled.
- **Step D:** Here it should be analyzed if the selected stream is belonging only to the closed-path in study or to more closed-paths. Depending on the result obtained by the previous analysis the way of calculating the closed-path flowrate will vary.
- **Step E:** If this stream only belongs to an independent loop, it is clear that this is the accumulated amount of the compound in that closed-path and consequently this value is the compound flowrate in the closed-path in study.
- **Step F:** If the minimum compound flowrate appears in a stream that is common to more than one nested loop (Stream called  $S_{NL}$ ), then it is necessary to find a way to quantify the percentage of the compound flowrate that belongs to each closed-path.
  - F-1:** Here all the closed-paths that belong to the stream  $S_{NL}$  (found in Step C) need to be determined. For those closed-paths, some procedures should be executed (described in the following steps).
  - F-2:** For each closed-path determined in Step F-1 it is necessary to find the streams, which belong to them.
  - F-3:** From the streams determined in Step F-2, the one presenting the lowest flowrate should be determined. This stream will be called  $S_E$ . This procedure

will be done for all the closed-paths passing in  $S_{NL}$ , so there will be a  $S_E$  stream for each closed-path determined in Step F-1.

**F-4:** Here the fraction of each closed-path, determined in Step F-1, relatively to the remaining closed-paths passing through  $S_{NL}$ , is calculated using Eq (3.1).

$$fr_{cp}^{(c)} = \frac{m_{cp,S_E}^{(c)}}{\sum_{cp=0}^{NL} m_{cp,S_E}^{(c)}} \quad \text{Eq (3.1)}$$

Where  $fr_{cp}^{(c)}$  is the fraction of the closed-path  $cp$  in the total of the flowrates of the streams,  $S_E$ , for compound  $c$ .  $m_{cp,S_E}^{(c)}$  represents the minimum flowrate of compound  $c$  in the close-path  $cp$  within the streams that belong to that closed-path ( $S_E$ ) and  $NL$  is the number of closed-path which belong to the stream  $S_{NL}$ .

With this fraction, it is possible to break the nested loops, determining the mass in  $S_{NL}$  stream that corresponds to each closed-path. Without this approach, negative flowrates might appear when the accumulated mass would be discounted from the streams remaining to the open-paths.

The flowrate for each closed-path passing in stream  $S_{NL}$  should be determined by the multiplication of the flowrate of stream  $S_{NL}$  times the fraction of each closed-path (Eq 3.1). The expression used to calculate the flowrate is the following one.

$$m_{cp}^{(c)} = m_{s_{NL}}^{(c),cp} \times fr_{cp}^{(c)} \quad \text{Eq (3.2)}$$

Where  $m_{cp}^{(c)}$  is the flowrate for compound  $c$  in the closed-path,  $cp$ , which pass through  $S_{NL}$ .  $m_{s_{NL}}^{(c),cp}$  is the flowrate of stream  $S_{NL}$  and  $fr_{cp}^{(c)}$  is the fraction of the closed-path  $cp$  in the total of the flowrates of the streams (see Eq (3.1)).

- **Step G:** Once the flowrate of the closed-path in study is already known (Step E or Step F-4) the accumulation in that closed-path is also known. Consequently, the stream determined in Step C should be removed from the flowsheet in order to allow the determination of the open-paths. The closed-path flowrate should be subtracted from all the streams belonging to the closed-path, in order to leave only the flow that is entering and leaving the process and not the accumulated value.
- **Step H:** In this step, it is checked if all the closed-paths have been analyzed. If not, Step B and the follows need to be executed again.
- **Step I:** Here the entire open-paths related to that compound are going to be determined. Uerdingen et al., 2003, firstly described the algorithm for open-path decomposition as a step by step routine. In this work, the algorithm is presented as a work-flow diagram, which allows an easier application of the algorithm. The algorithm described in Figure 3.12 can be easily computed and programmed

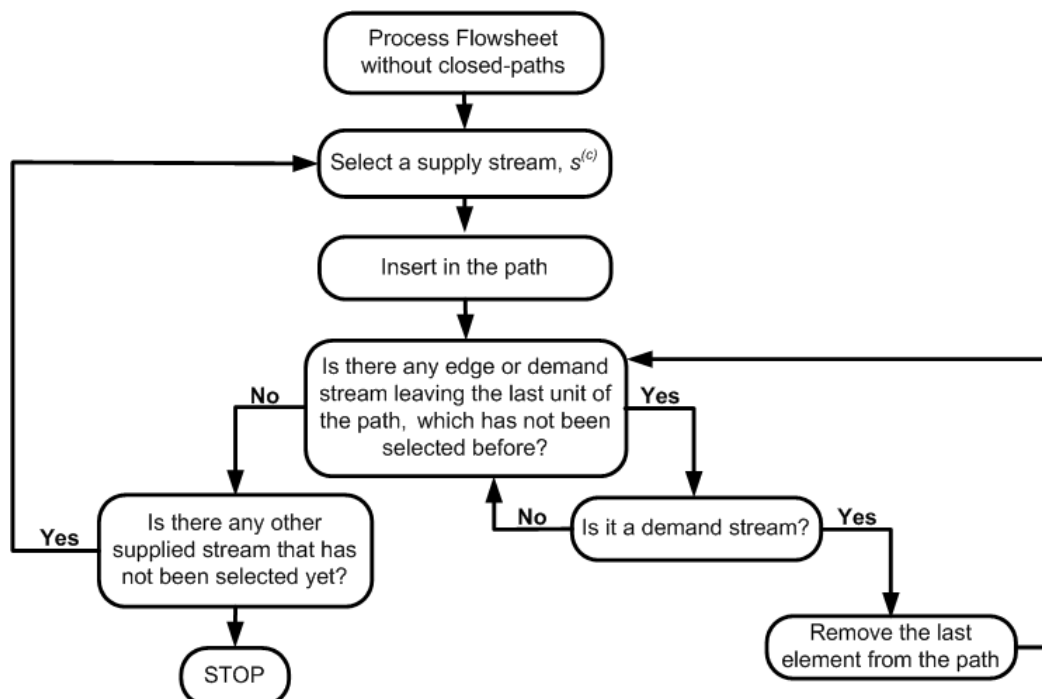


Figure 3.12: Flowdiagram with the algorithm for open-path decomposition



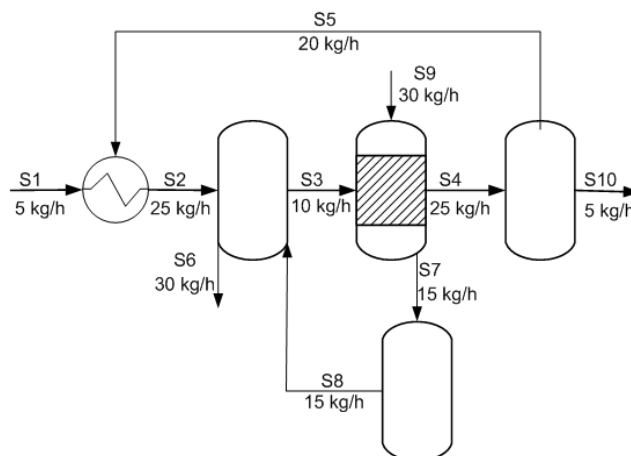
- **Step J:** Here it is verified if all the compounds have been analyzed. If not, Step A and the follows need to be executed again.

#### *Energy closed-paths flowrate and open-paths*

For the energy closed-paths flowrate and for the open-paths determination the procedure is exactly the same as the one described for the mass flowsheet decomposition (see Figure 3.11). The only difference appears when energy is exchanged with utilities. In that case, those streams are represented in the process graph as supply and demand streams (see section 3.2.2.1-Flowsheet transformation into a process graph). This means that some open-paths obtained in the energy flowsheet decomposition do not appear in the mass flowsheet decomposition. The energy open-paths are determined to each stream and not to a particular compound.

Example 3.3 has already presented the flowsheet decomposition in flowsheets without nested loops. Since one of the developments achieved in this thesis is to deal with nested loops Example 3.4 is given to illustrate the flowsheet decomposition in a simple flowsheet presenting nested loops.

#### ***Example 3.4***



**Figure 3.13:** Process flowsheet with nested loops (Example 3.4)

In this flowsheet, flowrate of stream 3 ( $f_3$ ) is the minimum flowrate for closed-paths CP1: [S3-S7-S8] and CP2: [S2-S3-S4-S5]. Since  $m_3$  flowrate represents both closed-paths, the total amount of  $m_3$  cannot be subtracted from both closed-paths, because stream 3 is a  $S_{NL}$  stream. The flowrate for each closed-path needs to be determined, but this is only possible if the fraction of each closed-path in that stream is known.

For this example the necessary data are the following:

- Stream belonging to more than one nested loop: ( $S_{NL}$ ): Stream 3
- Streams belonging to each cycle, ( $S_E$ ): **CP1:** (7, 8); **CP2:** (2, 4, 5)
- Stream with the minimum flowrate,  $m_{cp,S_E}^{(c)}$ , in the domain of  $S_E$  streams: **CP1:**  $S_7$  and  $S_8$ , **CP2:**  $S_5$

With the above data and applying Eq (3.1) it is possible to calculate the fraction of each closed-path.

$$fr_{C1}^{(A)} = \frac{m_{C1,S7}^{(A)}}{\sum_{cp=0}^2 m_{cpj,si}^{(A)}} = \frac{15}{20+15} = 0.43$$

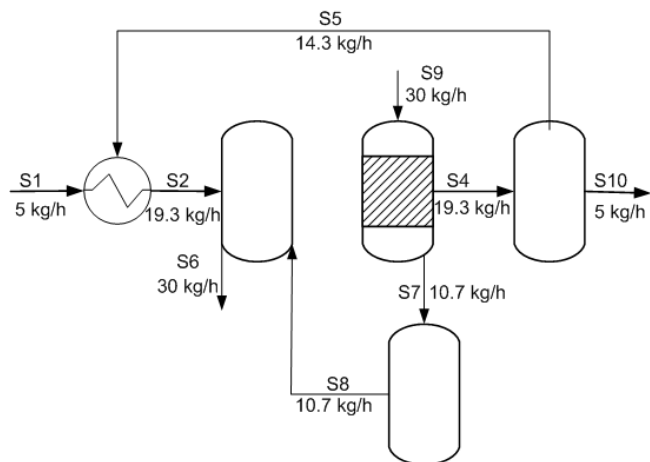
$$fr_{C2}^{(A)} = \frac{m_{C2,S5}^{(A)}}{\sum_{cp=0}^2 m_{cpj,si}^{(A)}} = \frac{20}{20+15} = 0.57$$

With the fractions of each closed-path known, the closed-path flowrates can now be calculated through Eq (3.2).

$$m_{C1}^{(A)} = m_{S3}^{(A),C1} \times fr_{C1}^{(A)} = 10 \times 0.43 = 4.3$$

$$m_{C2}^{(A)} = m_{S3}^{(A),C2} \times fr_{C2}^{(A)} = 10 \times 0.57 = 5.7$$

The closed-path flowrates of C1 and C2 will be subtracted to the flowrates of compound A in streams [S7-S8] and [S2-S4-S5] respectively to each closed-path. Removing stream 3, both closed-paths become open (see Figure 3.14).



**Figure 3.14: Process flowsheet with the opened nested loops (Example 3.4)**

The open-paths determined following the algorithm presented in Figure 3.12 are:

- {S1-S2-S6}
- {S9-S4-S5-S2-S6}
- {S9-S4-S10}
- {S9-S7-S8-S6}

#### 3.2.2.4) Determine Open-path flowrate

The open-paths flowrates are calculated using the rules presented in Uerdigen *et al.*, (2003), who recommends the calculation of the open-path flowrate as the multiplication of the flowrate for the feed stream by the distribution factors across the path.

The distribution factors must always be calculated when a unit has more than one supply or exit stream. This factor gives the mass fraction of the leaving stream related to the exit streams.

The general equation to calculate the distribution factor for stream  $S_t$  is given by the following equation.

$$w_c^s = \frac{m_{St}^{(c)}}{\sum_{es} m_{St,e}^{(c)}} \quad \text{Eq (3.3)}$$

Where  $w$  is the distribution factor, for stream  $St$  and compound  $c$ ,  $m$  is the flowrate,  $es$  is the exit stream (when multiple exits) or the entering stream (when multiple entries) and  $Es$  is the total number of exit stream or the entering streams respectively.

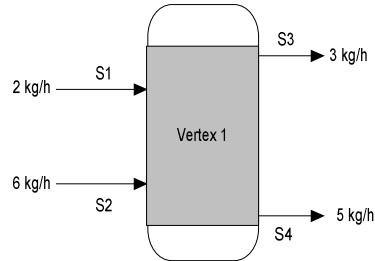
Determining all the distribution factors for the entire set of unit it is possible to determine all open-paths flowrates for all compounds. The general equation to calculate the respective flowrates is given by the multiplication of the original supply by the entire distribution factors encountered in the path.

$$m_{op}^{(c)} = m_{Su} \prod_u^U w_{s,u}^{(c)} \quad \text{Eq (3.4)}$$

Where  $m$  is the flowrate of compound  $c$  in open-path  $op$ ,  $Su$  is the supply stream,  $w$  is the distribution factor,  $u$  is the unit,  $U$  is the total number of units in that open-path.

Example 3.5 illustrates open-paths flowrate calculations.

**Example 3.5**



**Figure 3.15:** Units with multiple supplies and exits (Andersen and Engen, 2002)- Example 3.5

This example shows a unit with two inlet and two outlet streams. For this example four open-paths were found: {S1,S3}; {S1,S4}; {S2,S3}; {S2,S4}.

The distribution factor represents the fraction of mass that leave the unit in S3 or S4 by the total mass supplied to that unit (Mass of S1 plus mass of S2). The distribution factors are the following:

$$w_c^4 = \frac{m_4^{(c)}}{m_4^{(c)} + m_3^{(c)}} = \frac{5}{8}; w_c^3 = \frac{m_3^{(c)}}{m_4^{(c)} + m_3^{(c)}} = \frac{3}{8}$$

With this fraction it is possible to determine the open-path flowrate for {S1,S3}, {S1,S4}, {S2,S3} and {S2,S4}.

$$m_{op}^{S1-S3} = m_c^1 \cdot w_c^3 = 2 \times \frac{3}{8} = 0.75 \text{ kg / h}$$

$$m_{op}^{S1-S4} = m_c^1 \cdot w_c^4 = 2 \times \frac{5}{8} = 1.25 \text{ kg / h}$$

$$m_{op}^{S2-S3} = m_c^2 \cdot w_c^3 = 6 \times \frac{3}{8} = 2.25 \text{ kg / h}$$

$$m_{op}^{S2-S4} = m_c^2 \cdot w_c^4 = 6 \times \frac{5}{8} = 3.75 \text{ kg / h}$$

*Energy open-path flowrate*

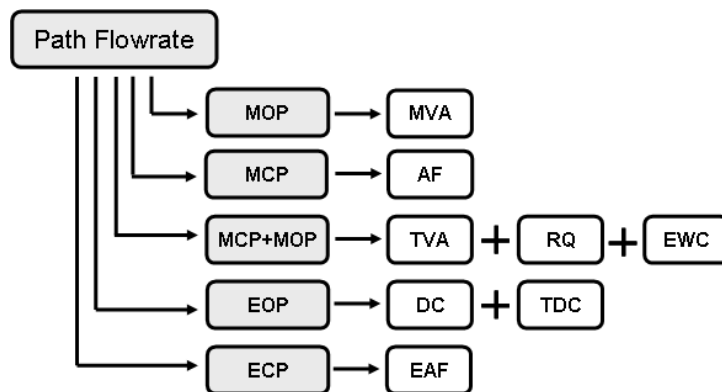
The procedure for the energy open-paths flowrate calculation is the same as the one presented for the mass case.

### 3.2.3 Step 3- Indicators/ Sustainability Metrics/Safety Indices calculation

In this step the mass / energy indicators, the safety index and the sustainability metrics are calculated.

#### 3.2.3.1) Calculate mass and energy indicators

There are five mass indicators and three energy indicators, Uerdigen et al., (2003). A brief description about these indicators is going to be given in the following paragraphs. Figure 3.16 shows an overview of the indicators application.



**Figure 3.16:** Indicators for continuous processes- Overview

MOP- Mass Open-Path; MCP- Mass Closed-Path; EOP- Energy Open-Path; ECP- Energy Closed-Path; MVA-Material Value Added; AF-Accumulation Factor; TVA Total Value Added; RQ-Reaction Quality; EWC-Energy and Waste Cost; DC- Demand Cost; TDC-Total Demand Cost; EAF: Energy Accumulation Factor

#### *Material Value Added (MVA)*

This indicator gives the value added between the entrance and the exit of a given compound. In other words, this means the value generated between the start and the end point of the path. Consequently, this mass indicator is only applied to mass open-

paths (MOP). To calculate this indicator it is necessary to know the purchase price or the costs related to the production of a given compound as well as its sale price.

For the open-paths with compounds, which are not, involved in reactions the following equation is to be used for the indicator calculation:

$$MVA_{op}^{(c)} = m_{op}^{(c)} (PP_{op}^c - PR_{op}^c) \quad \text{Eq (3.5)}$$

Where  $m_{op}^{(c)}$  is the flowrate of the compound  $c$  in open-path  $op$ ,  $PP_{op}^c$  and  $PR_{op}^c$  represent the sale price and the purchase price, respectively.

When the open-path is related to a compound produced in the system the production price needs to be estimated from the raw material price. The equation to calculate the indicator is the following.

$$MVA_{op}^{(c)} = m_{op}^{(c)} \left( PP_{op}^{(c)} - CA_{op}^{(c)} \left( \sum_{rm=1}^{RM} \frac{v_{op}^{(rm)} MW^{(rm)}}{v_{op}^{(c)} MW^{(c)}} PR_{op}^{(rm)} \right) \right) \quad \text{Eq (3.6)}$$

Where  $rm$  is the raw material index and  $RM$  is the total number of raw materials involved in the overall reaction equation,  $MW^{(rm)}$  are the molecular weights of raw materials, the  $v^{(rm)}$  are the stoichiometric coefficients from the reaction equation, the purchase price  $PR^{(rm)}$  of raw materials,  $CA$  is the cost allocation factor. The allocation factor can be calculated using the following expression, if and only if one of the products generated in the overall reaction equation represents a value outside the process boundaries (means that is going to be sold).

$$CA_{op}^{(c)} = \frac{PP_{op}^{(c)}}{\sum_{pd=1}^{PD} PP^{(pd)}} \quad \text{Eq (3.7)}$$

Where  $pd$  denotes a product and  $PD$  is the total number of products in the overall reaction equation.

Otherwise the allocation factor has to be determined using,

$$CA_{op}^{(c)} = \frac{MW_{op}^{(c)}}{\sum_{pd=1}^{PD} MW_{op}^{(pd)}} \quad \text{Eq (3.8)}$$

Negative values of this indicator show that the compound has lost its value in this open-path and consequently point to potential for improvements. The indicator value is given in terms of monetary units per year.

#### *Energy Waste Cost (EWC)*

This indicator is applied to both open- and closed-paths. It takes into account the energy costs, EWC. The value of EWC represents the maximum theoretical amount of energy that can be saved in each path within the process. The expression to calculate this indicator is the following one:

$$EWC_k^{(c)} = \sum_{u=1}^U PE_u Q_u \frac{m_k^{(c)} A_{u,k}^{(c)}(T, p)}{\sum_{uk=1}^{UK} m_{uk} A_{u,uk}(T, p)} \quad \text{Eq (3.9)}$$

Where  $k$  is the open- or the closed-path depending to the type of path that the indicator is being applied,  $u$  is the unit index and  $uk$  is the index of all compound path flows in  $u$ .  $U$  represents the total number of units in the path and  $UK$  the total number of compound path flows in a sub-operation.  $PE_u$  represents the specific price of the utility needed in sub-operation  $u$  and  $Q_u$  is the energy consumption in the same sub-operation.  $A$  is an allocation factor calculated at the average temperature  $T$  and pressure  $p$  and it is normally a physical property which depends of the unit operation.



As a rule of thumb the properties used for each unit operations as allocation factor  $A$  are:

- Heat capacity,  $C_p$ : Heat exchangers (non-evaporators)
- Heat of vaporization,  $\Delta H_{vap}$ : Heat exchangers (evaporative and condensing units)
- Density,  $\rho$ : Compressors and pumps

High values of this indicator show high consumption of energy and consequently these paths should be considered in order to reduce the indicator value. This can be done in two ways, reducing the path flowrate or changing the conditions in order to decrease the duties. The EWC value is given in terms of monetary units per year.

#### *Reaction Quality (RQ)*

This indicator measures the influence of a given path with respected to process productivity. This indicator is applied to both closed- and open-paths. Positive values of RQ show a benefit of this path with respect to process productivity, while, negative values show a decrease in the process productivity. The path where negative values appear is therefore a good target for improvement.

The value of RQ is obtained by the following expression:

$$RQ_k^{(c)} = \frac{\sum_{r=1}^R \sum_{rk=1}^{RK} \xi_{r,rk,k} E_{r,rk,k}^{(c)}}{\sum_{fp=1}^{FP} MM^{(fp)}} \quad \text{Eq (3.10)}$$

Where  $\xi_{r,rk,k}$  is the extent (in kmol/h) of reaction  $rk$ ,  $MM^{(fp)}$  is the molar flowrate of the final product  $fp$  leaving the process boundaries,  $FP$  represents the total number of desired products in the process,  $r$  is the index of the reactive unit operations,  $R$  is the total number of reactive unit operations in the path  $k$ ,  $rk$  is the index of the reactions and  $RK$  is the total number of reactions in the unit operation affected by the path  $k$ .

The parameter  $E_{Hr,rk,k}^{(c)}$  is dependent on the effect of a given compound in the reactions involved in the path flow. The value can be determined using the following rule of thumb:

$$E_{Hr,rk,k}^{(c)} = \begin{cases} +1, & \text{If component } c \text{ in } k \text{ path affects reaction } rk \text{ such that the} \\ & \text{total productivity of the desired product } n^{(fp)} \text{ is favored} \\ 0, & \text{If component } c \text{ in } k \text{ path has no effect on reaction } rk \text{ and} \\ & \text{total productivity of the desired product } n^{(fp)} \text{ is unchanged} \\ -1, & \text{If component } c \text{ in } k \text{ path affects reaction } rk \text{ such that the} \\ & \text{total productivity of the desired product } n^{(fp)} \text{ is inhibited} \end{cases}$$

#### Accumulation Factor (AF)

This indicator determines the accumulative behavior of the compounds in the closed-paths. This corresponds to the amount that is recycled relative to the input to the process and not the inventory. High values of this indicator show high potentials for improvements.

The expression representing this indicator is described by:

$$AF = \frac{m_{cp}^{(c)}}{\sum_{iv=1}^{Iv} \left( \sum_{k=1}^{EN} f_{iv,k}^{(c)} + \sum_{op=1}^{OP} d_{iv,op}^{(c)} \right)} \quad \text{Eq (3.11)}$$

Where  $m_{cp}^{(c)}$  is the flowrate of compound  $c$  in the closed-path,  $cp$ ,  $f_{iv,k}^{(c)}$  and  $d_{iv,op}^{(c)}$  are the compound flows leaving the cycle flow and  $i$  is the index of vertices in the cycle from where the compound leaves,  $Iv$  is the total number of such vertices. EN is the total number of leaving streams from a closed-path excluding the demand streams.

*Total Value Added (TVA)*

This indicator describes the economic influence of a compound in a given path. TVA joins two of the previous indicators EWC and MVA and the following expression determines its value:

$$TVA = MVA - EWC \quad \text{Eq (3.12)}$$

Negative values of this indicator show high potential for improvements in terms of decrease in the variable costs. The values of this indicator should be analyzed carefully, due to the fact that MVA can have a high positive value and consequently hide the problems in EWC. Therefore, even if the TVA value does not present a very negative value, the values of EWC and MVA should be analyzed separately in order to confirm that they really do not show any problem.

*Energy accumulation factor (EAF)*

This indicator determines the accumulative behavior of energy in the closed-paths. Low values of this indicator highlight the potential for saving energy consumption in the system.

The EAF can be calculated by using the following expression:

$$EAF = \frac{ebl_{ec}}{\sum_{iv=1}^{Iv} \left( \sum_{k=1}^{EN} f_{iv,k} + \sum_{op=1}^{OP} d_{iv,op} \right)} \quad \text{Eq (3.13)}$$

Where  $Iv$  is the total number of the vertices encountered in the energy closed-path flow, and  $i$  is the index of these.  $ec$  is the index of the cycle energy path flows.  $ebl$  is the energy base level, i.e the amount of energy recycled in the particular recycling.

*Demand Cost (DC) and Total demand cost (TDC)*

This indicator is applied only to open-paths and traces the energy flows across the process. For each demand stream in the process the sum of all DC, which pass through it, are calculated. DC can be calculated using the following equation:

$$DC_{su,d} = Pr D_{su} \cdot EOP_{su,d} \quad \text{Eq (3.14)}$$

Where  $PrD$  is the utility/stream cost, in units of price/energy and EOP is the flowrate of the energy open-path. The total cost for all the paths is expressed by:

$$TDC_d = \sum_{su=1}^{SS} DC_{su,d} \quad \text{Eq (3.15)}$$

Where  $SS$  is the total number of supplies that energy contributes are significant to the demand,  $d$ .

High values of this indicator identify the demands that consume the largest values of energy, so these are the process parts, which are more adapted to heat integration.

*3.2.3.2) Calculate Safety Indices*

The safety of the process is another important parameter that should be taken into account. In this thesis the inherently safety index, developed by Heikkilä, (1999), has been implemented. In order to achieve the inherently safety index the value for some sub-indices need to be calculated. These sub-indices are divided into two groups, one group, which takes into account the chemical inherent safety, and the other group that is dependent on the process inherent safety. Heikkilä, (1999) defined a scale of scores for each sub-index. These scales are based on the values of some safety parameters, such as the explosiveness, the toxicity, the pressure of the process and so on. The sum of all the sub-indices scores is the Inherent Safety Index value; this parameter has the maximum

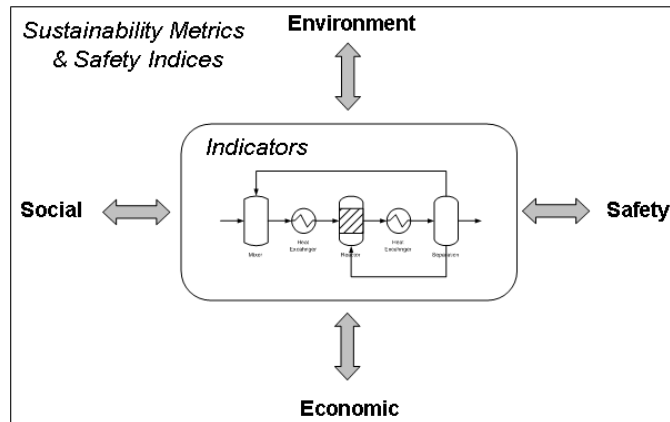
value of 53 (see section 2.3.2). Note that the higher is the Inherent Safety Index value the more unsafely is the process, so the aim in all the design alternatives is to try to reduce its value as much as possible. In Table 2.2 section 2.3.2, the entire sets of sub-indices, as well as the respective scales, are specified.

#### *3.2.3.3) Calculate Sustainability Metrics*

In this methodology the sustainability metrics defined by the Institution of Chemical Engineers by Azapagic *et al.*, (2002) have been used (see section 2.3.1). The author has defined 49 metrics divided into three main areas: environmental, social and economical.

For the environmental impact related metrics, instead of using the definition of Azapagic *et al.*; the definition proposed by Cabezas *et al.*, (1999) have been used (see section 2.3.1).

Summarizing, the mass and energy indicators are applied to the entire set of mass and energy open- and closed-paths. With their values the critical points of the process as well as the areas that should be improved in the process are determined. The sustainability metrics and the safety index are calculated using the steady state data for the global process and they are used to measure the impact of the process in its surroundings. They evaluate the interaction of the process with the exterior in terms of environment, social, economical and safety aspects. They will be used as performance criteria in the evaluation of the new suggested design alternatives. Figure 3.17 summarize the process connection with the indicators, the sustainability metrics and the safety indices.

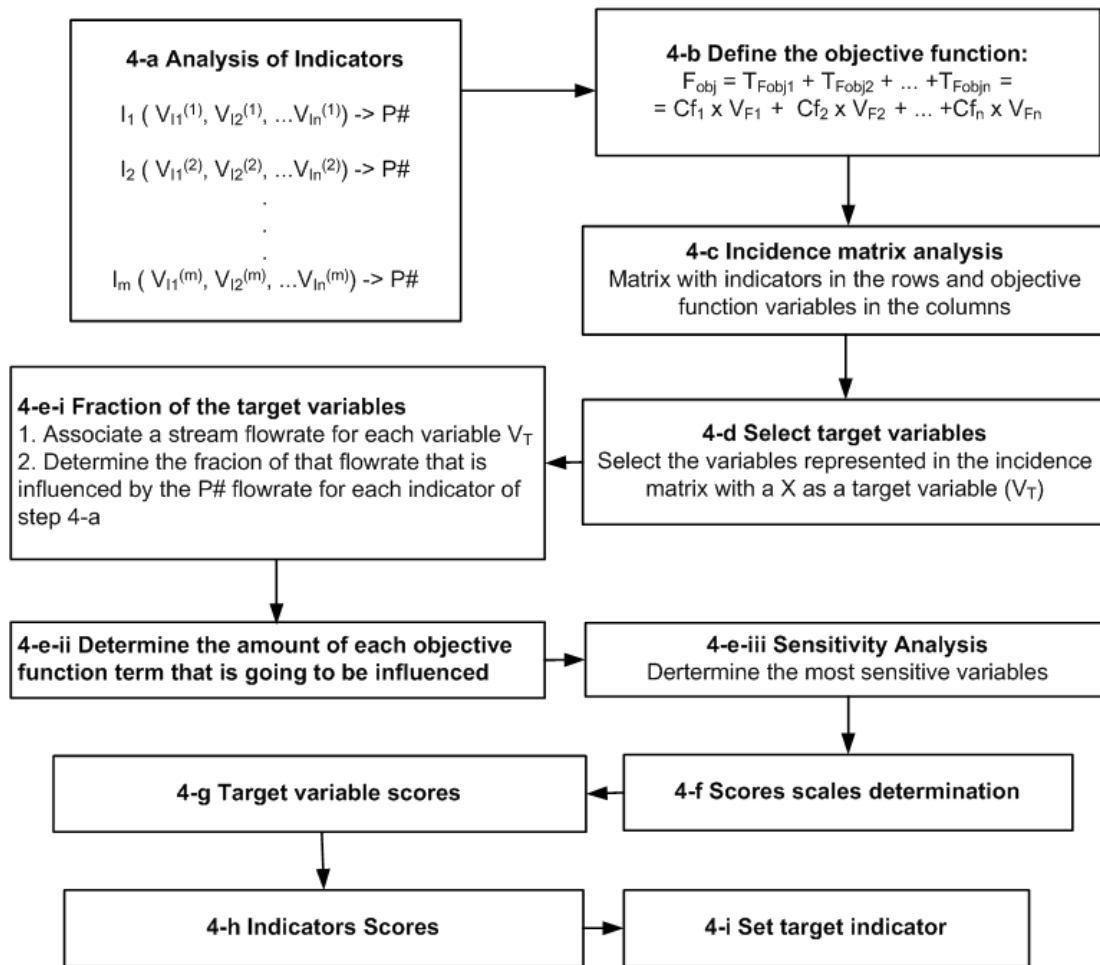


**Figure 3.17:** Schematic representation of sustainability metrics, safety indices and indicators application

### 3.2.4 Step 4- Indicator Sensitivity Analysis (ISA Algorithm)

An algorithm to identify the design targets and to determine their desired “target” values has been developed for this step (Carvalho et al., 2008).

With this algorithm it is possible to identify the indicators that have the potential to make significant improvements in the process. These indicators are then designated as targets (design) for generation of new process alternatives. Since the variables which define the indicators are the same that define the process alternatives, it is also possible to simultaneously determine (without additional simulation or optimisation) how much of the targeted process improvements can be actually achieved. The main steps of ISA algorithm are described in the diagram present in Figure 3.18.



**Figure 3.18:** Main steps for the ISA algorithm

In Figure 3.18 I is the indicator,  $V_I$  are the variables influencing the indicators, P# is the path,  $F_{obj}$  is the objective function,  $T_{Fobj}$  are the terms of the objective function, Cf are the coefficients of the objective function and  $V_F$  are the variables influencing the objective function.

4-a) Analysis of Indicators

The objective here is to identify and select the indicators that show the highest potential for improving the process. That is, locate the critical points in the process flowsheet with respect to potential design-operational deficiencies. This determination is done comparing the indicators values and selecting the ones presenting the highest potential

for improvements. For a better understanding on how to compare the indicators values, Table 3.1 summarizes the meaning of each indicator and which one should be selected when compared to the others.

**Table 3.1:** Summary of the interpretation of the mass and energy indicators

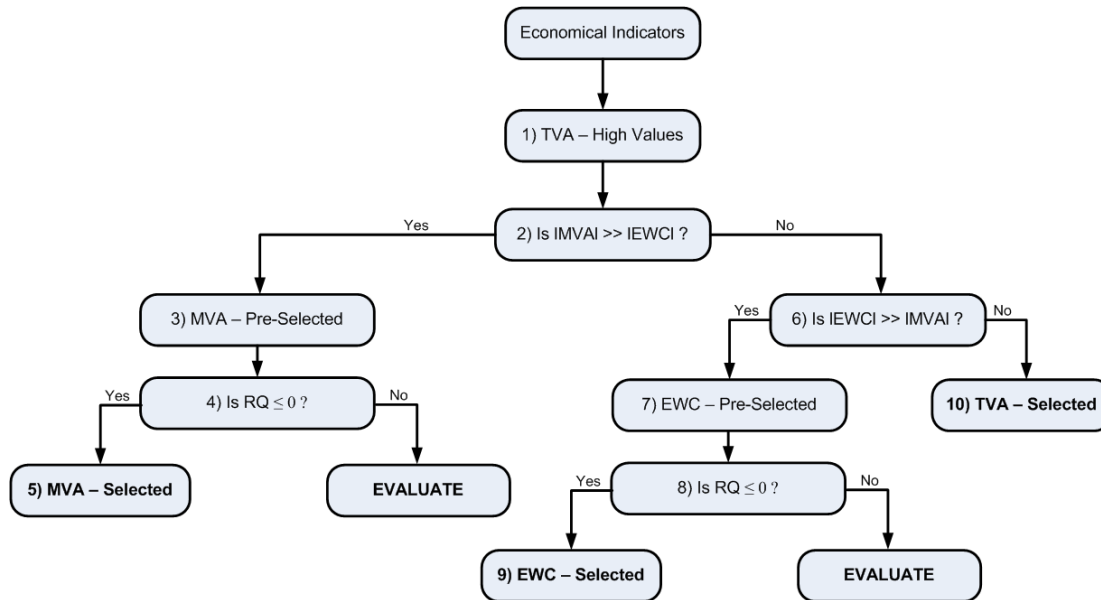
Indicator	Meaning	Negative Value	High Positive Value	Low Positive Value
MVA	Material Value Added	High Potential Improvement	-	-
EWC	Energy consumption	-	High Potential Improvement	-
TVA	Total Value Added	High Potential Improvement	-	-
RQ	Productivity Impact	High Potential Improvement	-	-
AF	Accumulation	-	High Potential Improvement	-
EAF	Accumulation	-		High Potential Improvement
DC	Energy Cost	-	High Potential Improvement	-
TDC	Energy Cost	-	High Potential Improvement	-

From Table 3.1 it can be seen the indicators that should be selected within a given category of indicators. It can be seen that the indicators presenting the most negative values of MVA, TVA and RQ, should be selected. However for EWC, AF, DC and TDC the indicators presenting the highest positive values are the ones that should be selected. For EAF the lowest positive values are the ones showing high potential for improvements. In this way it possible to order the indicators taking into account their values and consequently the top indicators are the ones that should be selected. To compare indicators from different categories the algorithm presented in Figure 3.19 and Figure 3.20 should be followed respectively to mass open-path, mass closed-path. The energy paths should be analysed separately and consequently their analysis is explained after the ISA algorithm description.



*Select indicators related to mass open-path*

In Figure 3.19 it is represented a flowdiagram describing the guidelines for the selection of the indicators among the mass open-paths indicators.



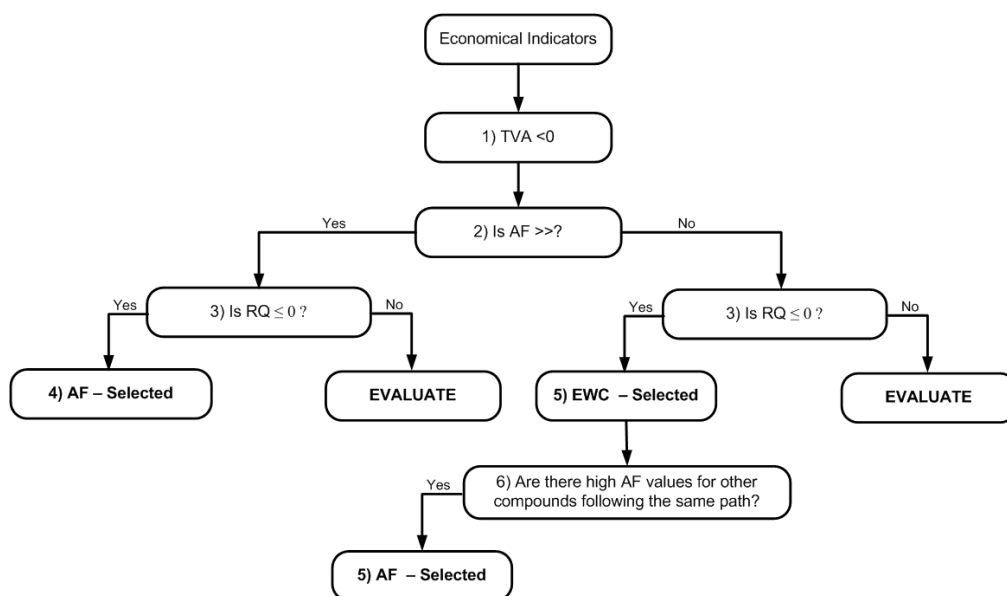
**Figure 3.19:** Flowdiagram representing the selection of the indicators for the mass open-paths

- 1) TVA gives the economical influence in a given path and consequently this should be the first indicator to be analysed. The indicators presenting the highest negative values are the ones that are losing more value across the path and therefore they present higher potential for improvements. These indicators should be selected firstly.
- 2) After selecting TVA indicators it is necessary to verify if the responsible for the very negative value of TVA is MVA or EWC or even both (see Eq (3.12)).
- 3) If the TVA negative value is due to very negative MVA and EWC presents an insignificant value, then MVA for that path should be pre-selected.
- 4) Here RQ should be analysed in order to verify if the path is favourable for the final production or not. If RQ is negative step 5, Figure 3.19, should be done, otherwise it needs to be evaluated if it is a good decision to improve that path or not.
- 5) MVA for that path should be selected.
- 6) If the TVA negative value is due to very high EWC and the MVA does not present high potential for improvements.

- 7) EWC indicator for that path should be pre-selected instead of selecting TVA.
- 8) Here RQ should be analysed in order to verify if the path is favourable for the final production or not. If RQ is negative step 9, Figure 3.19, should be done, otherwise it needs to be evaluated if it is a good decision to improve that path or not.
- 9) EWC for that path should be selected.
- 10) If both indicators contribute almost equally to the negative value of TVA, then either it can be selected EWC and MVA for that path or only TVA indicator can be selected for that path.
- 11) Check if there are MVA or EWC in the top indicators (highest potential for improvements), that have not been selected yet. This must be verified due to the stated reasons presented in TVA indicator (see section 3.2.3.1).

*Select indicators related to mass closed-path*

In Figure 3.20 it is represented a flowdiagram describing the guidelines for the selection of the indicators among the mass closed-paths indicators.



**Figure 3.20:** Flowdiagram representing the selection of the indicators for mass closed-paths

- 1) Again, the TVA indicators showing the highest values should be selected in first place. In this case a very negative value of TVA means a high positive value of EWC, because MVA is not applied to closed-paths.
- 2) After selecting TVA/EWC indicators it is necessary to verify if the compound related to those close-paths is highly accumulated in the system or not. To verify the accumulation of a compound in a closed-path, AF value should be analysed. If AF presents high positive values then the compound is accumulated in the process and needs to be reduced.
- 3) Here RQ should be analysed in order to verify if the path is favourable for the final production or not. If RQ is negative step 4 or 5 should be done, otherwise it needs to be evaluated the possibility of improving that path or not.
- 4) AF of that closed-path should be selected, because if this indicator is improved then EWC will be consequently improved.
- 5) If AF does not present a high value for that given path, then EWC is high due to other factors which are not the accumulation of that compound and consequently that indicator should be selected.
- 6) One factor that can affect the high EWC of the path can be the high accumulation of other compounds. If that happen, high AF values for other compounds are present and they need to be selected.

After selecting the indicators, those indicators are decomposed in their basic variables. As can be seen in Figure 3.18, the indicators are related to a given path, P#, and they are depending on variables,  $V_I$  (variables influencing indicators).

#### 4-b) Define the objective function

The goal here is to derive an expression, which defines the criteria for process (performance) improvement objective. This equation should be a function of process-manipulated variables and process operational parameters such as the cost of materials and utilities. The general expression for an objective function ( $F_{obj}$ ) is given by:

$$F_{obj} = Cf_1V_{F1} + Cf_2V_{F2} + \dots + Cf_nV_{Fn} \quad \text{Eq (3.16)}$$

Where,  $Cf$  are the coefficients, which multiply by the variables  $V_F$  (variables influencing  $F_{obj}$ ). Variables  $V_F$  are taken from the mass and the energy balance (flowrates or exchanged energies). Consequently it is possible to see that these variables are a function of some other variables ( $V_F = f(\text{operational variables})$ ). This means that despite of the linearity shown in Eq (3.16), the objective function is dependent on variables that were calculated through models that can be non-linear.

Eq (3.16) provides a flexible definition of  $F_{obj}$  for different processes. This function can be divided in terms,  $T_{Fobj}$ , and each term is determined by  $CfV_F$ .

For example, a process that produces large quantities of a desired product,  $F_{obj}$  could improve the profit margin while simultaneously improving waste reduction potential (and therefore, also the environmental impact) but keeping all other metrics and indices constants or within insignificant changes. In another case, such as a pharmaceutical product manufacturing, where the process operational cost may be less important than, for example, the reliability of the product quality, the environmental impact and the time needed for production.

#### 4-c Incidence matrix

This analysis identifies the variables  $V_F$  (determined in 4-b) that also influence the selected set of indicators (Step 4-a) through an incidence matrix, where each row represents an indicator (model) equation and each column represents the variables  $V_F$ . See Table 3.2 for a better understanding.

**Table 3.2:** Incidence matrix example (ISA algorithm-step 4)

	$V_{F1}$	$V_{F2}$	...	$V_{Fn}$
$I_1$	X		X	
$I_2$		X		
...				
$I_n$	X	X		X

#### 4-d Select target variables

From the analysis of the incidence matrix of step 4-c, identify the common set of variables that belong to the  $F_{obj}$  expression as well as the selected indicators. These variables will determine by how much the “targeted” value can be attained. The target variables,  $V_T$ , are all the variables that satisfy the following condition:  $V_I = V_F$ . Each space fulfilled with a X in Table 3.2 is a common variable and consequently a target variable. These variables are the ones that are going to be modified in order to improve the target indicators (that is, match the target values); consequently these are the variables that are going to influence our objective function.

#### 4-e Sensitivity Analysis of the target variables on the objective function

The objective in this step is to identify the variables that will effect the largest changes in the objective function for the smallest changes in its values. This is done by analysing the effect of each variable on the objective function and studying their sensitivity. Through this analysis, it is possible to identify the set of target variables that makes the largest impact on the objective function, and therefore, in the target indicator.

#### ***4-e-i) Fraction of the target variables***

The aim here is to see the influence of the target variable,  $V_T$ , on the  $F_{obj}$ . These  $V_T$  are not going to influence the variables  $V_F$  in their total amount, in this way it is necessary to define  $V_T$  as a function of P# for each indicator ( $V_T = f(P\#)$ ). This means that just the fraction of the total amount of the variable,  $V_T$ , which is related to the selected path, can be changed to improve  $F_{obj}$ . In order to see the fraction of each  $V_T$  that is going to be influenced by each path, a flowrate stream that represents that variable,  $V_T$ , is going to be determined. This means that, if  $V_T$  is already a flowrate, this flowrate will be the representative flowrate of that variable. However if for example the variable  $V_T$  is a heat duty exchange in a unit, the flowrate of the leaving stream is the representative flowrate for variable  $V_T$ . Once all the variables  $V_T$  have a flowrate associated to them,

it is possible to see which influence has the path, P#, in the variable  $V_T$ . The expression to determine that fraction is the following one:

$$x_{n,k} = \frac{m_k}{m_n} \quad \text{Eq (3.17)}$$

Where  $x_{n,k}$  is the fraction of the path ( $k$ ) flowrate by the flowrate associated to a target variable,  $V_T$ .  $m_k$  is the path flowrate and  $m_n$  is the total flowrate associated to the variable  $n$  which is being studied. When the variable in study is not a flowrate then  $m_k$  is assumed to be represented by the outlet flowrate of the unit. When the unit has more than one outlet stream it should be assumed the one where the path has been defined.

***4-e-ii) Determine the amount of each objective function term that is going to be influenced***

In this step, for each target variable,  $V_T$ , selected in step 4-d, the terms of the objective function,  $T_{Fobj}$ , that are related to  $V_T$  are determined. This means, if the study is being done in variable  $V_{T1}$  the correspondent profit term is given by  $T_{V_{T1}} = C f_{V_{T1}} V_{T1}$ . The values of the terms represent the total amount of  $F_{obj}$  that is influenced by a target variable; however here the objective is to determine which part of that term,  $T$ , is influenced by the paths P# (See step 4-a). To calculate the part of the term value that is influenced by a given variable in a given path, the objective function term,  $T_{Fobj}$ , should be multiplied by the fractions determined in 4-e-i.

$$T_{Fobj(n,k)} = x_{(k)} \times T_{Fobj(n)} \quad \text{Eq (3.18)}$$

Where  $T_{Fobj(n,k)}$  is the amount of the  $F_{obj}$  term that is influenced by a given path  $k$  and a given variable  $n$ ,  $x$  is the fraction determined by Eq(3.17) and  $T_{Fobj(n)}$  is the total amount of the  $F_{obj}$  term that is influenced by a given variable  $n$ .

Summing all the terms influenced by all the variables in the selected paths it is possible to achieve the total amount in the objective function that can be changed-improved. In order to make a comparison between the target variables and to see which of them have the relative higher effect in  $F_{obj}$  the fraction between the objective function terms, calculated using Eq(3.18), by the total amount in the objective function that can be changed, is determined using the following equation.

$$y_{(n,k)} = \frac{T_{Fobj(n,k)}}{\sum_k \sum_{va} T_{Fobj(va,k)}} \quad \text{Eq (3.19)}$$

Where  $T_{Fobj}$  is the profit term and  $y$  is the fraction of a given term in the sum of all the terms related to the selected variables.  $va$  is the variable in study and  $VA$  is the total number of variables selected in step 4-d.  $k$  is the path in study and  $K$  is the total number of paths selected in step 4-a.

With this fractions,  $y$ , it is possible to define which are the variables within a given path that can achieve a higher improvement in  $F_{obj}$ .

For each target variable  $V_T$  and each path  $P\#$  there will be a  $y_{(n,k)}$  (see Table 3.3)

**Table 3.3:**  $y_{(n,k)}$  for the target variables- example (ISA algorithm-step 4)

		$V_{F1}$	$V_{F2}$	...	$V_{Fn}$
$I_1$	$P\#$	$y_{(V_{F1},P\#)}$		$y_{(n,k)}$	
$I_2$	$P\#$		$y_{(V_{F2},P\#)}$		
....	...				
$I_n$	$P\#$	$y_{(V_{F1},P\#)}$	$y_{(V_{F2},P\#)}$		$y_{(V_{Fn},P\#)}$

**4-e-iii) Sensitivity Analysis**

This last sub-step is to identify the most sensitive variables by determining the coefficients,  $Cf$ , which are multiplied by the variables  $V_T$ , and then calculate their

percentage in the sum of all coefficients. These coefficients are collected from Eq (3.16),  $C_f$ . The equation used to determine the relative sensitivity between the  $C_f$  associated to each variable  $V_T$  is the following one:

$$z_n = \frac{C_{f(n)}}{\sum_{va=0}^{VA} C_{f(va)}} \quad \text{Eq (3.20)}$$

$z$  is the fraction of the coefficient  $C_f$  for the variable  $n$ , in the sum of all coefficients related to all the variables selected in step 4-d.

Through this analysis, it is possible to conclude which are the variables that with smaller modifications are going to achieve higher improvements in the objective function.

For each target variable there will be a  $z_n$ . Table 3.4 illustrates the representation of these values for the target variables.

**Table 3.4:**  $z_n$  for the target variables- example (ISA algorithm-step 4)

		$V_{F1}$	$V_{F2}$	...	$V_{Fm}$
$I_1$	P#	$z_{F1}$		$z_n$	
$I_2$	P#		$z_{F2}$		
....	...				
$I_n$	P#	$z_{F1}$	$z_{F2}$		$z_{Fm}$

4-f Define a score scale for steps 4-e-ii and 4-e-iii

This step is to establish limiting values for the selected variables, based on a relation between percentage changes in the variables against improvements achieved, on a scale of 0-5. This will allow the determination of two different scales for steps 4-e-ii and 4-e-iii respectively. The increment for the scale determination is calculated through:



$$In^{(T)} = \frac{Max y_{(n,k)} - Min y_{(n,k)}}{5} \quad \text{Eq (3.21)}$$

$$In^{(SA)} = \frac{Max z_n - Min z_n}{5} \quad \text{Eq (3.22)}$$

Where  $In$  is the increment used in the determination of the scores scale for the weight terms in the profit expression (T) or for the sensitivity of the variables (SA).  $Min y_{(n,k)}$  and  $Min z_n$  are the minimum value presented for the fractions  $y_{(n,k)}$  and  $z_n$  respectively.  $Max y_{(n,k)}$  and  $Max z_n$  are the maximum value presented for the fractions  $y_{(n,k)}$  and  $z_n$  respectively. Table 3.5 and Table 3.6 show how the scale is defined for both cases.

**Table 3.5:** Ranges and scores for the weight terms in the Fobj function (ISA algorithm-step 4)

Weight in the profit expression			
Weight Terms	Inferior limit	Superior limit	Scores
Extremely high	Min y + 4 In <sup>T</sup>	Max y	5
High	Min y + 3 In <sup>T</sup>	Min y + 4 In <sup>T</sup>	4
Normal	Min y + 2 In <sup>T</sup>	Min y + 3 In <sup>T</sup>	3
Low	Min y + In <sup>T</sup>	Min y + 2 In <sup>T</sup>	2
Extremely low	Min y	Min y + In <sup>T</sup>	1

**Table 3.6:** Ranges and scores for the target variable sensitivity (ISA algorithm-step 4)

Sensitivity			
Kind of sensitivity	Inferior limit	Superior limit	Scores
Extremely sensible	Min z + 4 In <sup>SA</sup>	Max z	5
Much sensible	Min z + 3 In <sup>SA</sup>	Min z + 4 In <sup>SA</sup>	4
Sensible	Min z + 2 In <sup>SA</sup>	Min z + 3 In <sup>SA</sup>	3
Small sensitivity	Min z + In <sup>SA</sup>	Min z + 2 In <sup>SA</sup>	2
Almost no sensible	Min z	Min z + In <sup>SA</sup>	1

4-g Transform the target variables in scores

Analyze the percentages defined in sub-steps 4-e-ii and 4-e-iii and transform them into scores through the scales set in step 4-f. Each value of  $y_{(n,k)}$  will be included in one of the ranges of the scales (Table 3.5), which corresponds to a score. Therefore each value  $y_{(n,k)}$  will be represented by a score. For  $z_n$  the same procedure is done using Table 3.6. Each score is related to a path, P# and a variable,  $V_T$ . Summing the scores obtained for the two parameters,  $y_{(n,k)}$  and  $z_n$  a table such as Table 3.7 will be achieved.

**Table 3.7:** Scores for the target variable (ISA algorithm-step 4)

		$V_{F1}$	$V_{F2}$	...	$V_{Fm}$
$I_1$	P#	Score		Score	
$I_2$	P#		Score		
...	...				
$I_n$	P#	Score	Score		Score

4-h Indicators scores

Determine the score for all indicators by the sum of the points given by the target variables, which influence them. The indicators scores are obtained summing the scores of their row (see Table 3.7);

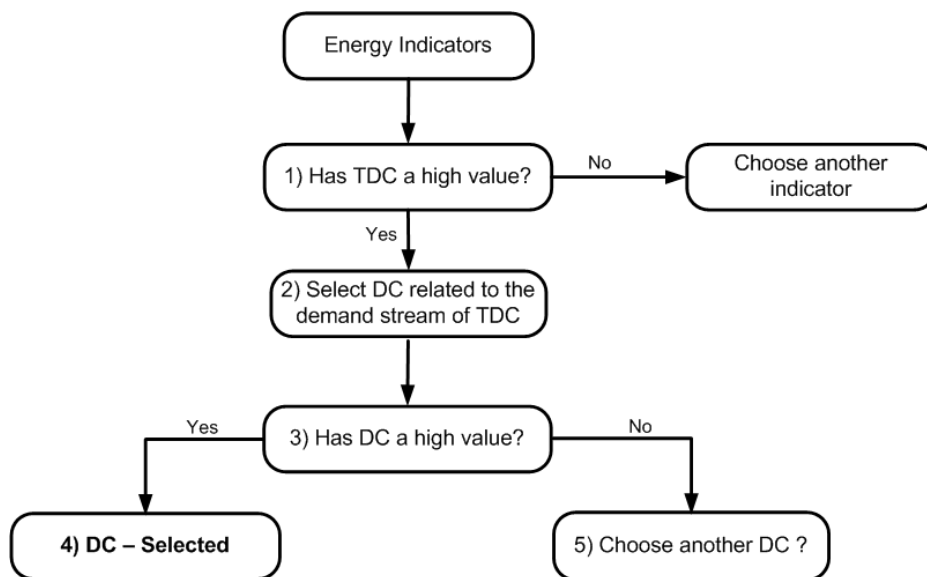
4-i Set the target indicator

Set the highest scored indicator as the first target for improvement.

*Energy Indicators Selection*

The energy indicators are used to complement the information achieved from the previous algorithm. These indicators are used to analyze the possibility of heat integration. They are used after the analysis of the mass indicators.

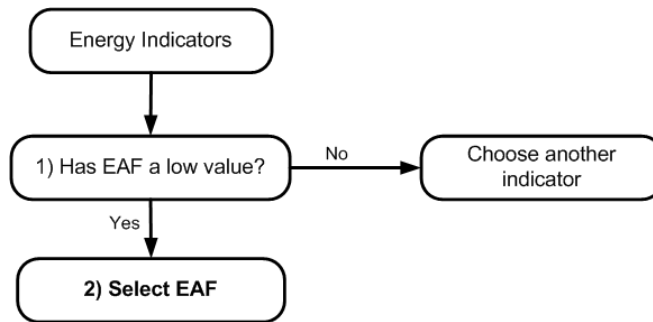
Some guidelines are given to select TDC and DC indicators (see Figure 3.21).



**Figure 3.21:** Flowdiagram representing the selection of the indicators for energy open-paths

- 1) The TDC indicators presenting high values show that a lot of energy is being released, and consequently that energy might be used in the process.
- 2) DC related to that demand stream should be analyzed.
- 3) When DC has a high values that indicator shows that there is a high potential for integration.
- 4) Select the indicator.
- 5) Analyze another DC related to the demand stream of TDC.

Some guidelines are given to select EAF indicators in Figure 3.22.



**Figure 3.22:** Flowdiagram representing the selection of the indicators for energy closed-paths

- 1) When EAF has a low value, it shows high potential for improvements using heat integration.
- 2) Select the indicator.

### 3.2.5 Step 5- Design Sensitivity analysis

With the target indicators and their variables identified in step 4 the next task is to determine the process-operational variables that cause the biggest changes in the target indicators for smallest changes in their values. This analysis is done by checking the influence of step increments, 5, 10 and 15%, in all the operational variables that influence the selected target indicator and the consequent effect in the target indicator (see Figure 3.23).

The value of the new operational variable is done using the following equation:

$$\Delta OPV = \frac{OPV_{final} - OPV_{initial}}{OPV_{initial}} \quad \text{Eq (3.23)}$$

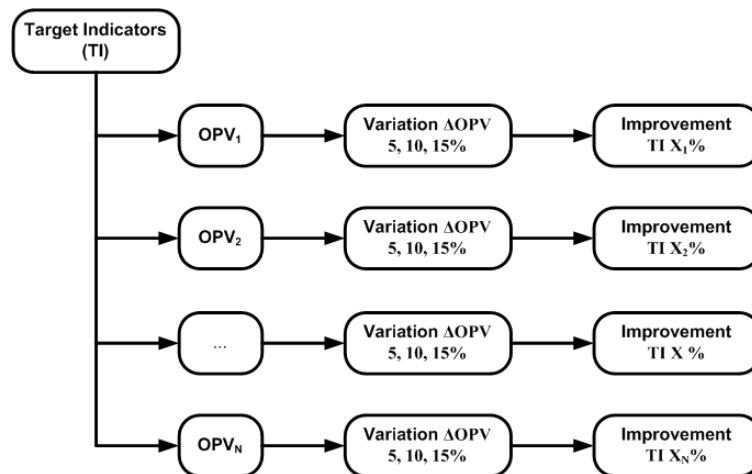
Where, OPV is the operational value.

After changing the variable the improvement in the target indicator is calculated through:

$$\text{Improvement} = \frac{TI_{final} - TI_{initial}}{TI_{initial}} \quad \text{Eq (3.24)}$$

Where, TI is the target indicator value.

Through this analysis, it is possible to determine the highest improvement in the indicator value. The results determine the operational variable which presents the highest improvement in the process and consequently the operational variable that must be improved to generate new design alternatives. From Figure 3.23 it is possible to see that for each target indicator (TI) there is a list of operational variables (OPV). Each OPV is locally analyzed changing their values, which allows the determination of an improvement in the target indicator. The highest improvement in the target indicator corresponds to the target operational variable.

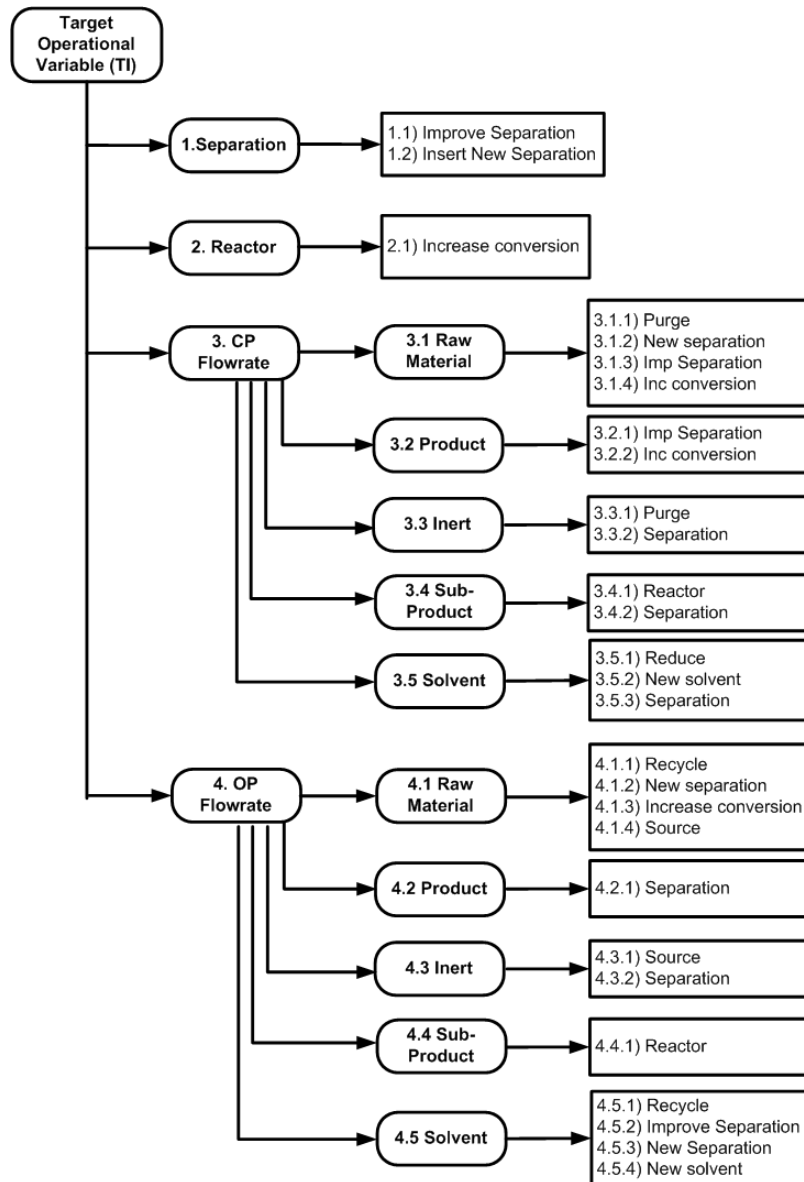


**Figure 3.23:** Sensitivity analysis to the operational variables- Summary

### 3.2.6 Step 6- Generation and evaluation of new design alternatives

#### *Generation of a new design alternative*

To generate the new sustainable design alternatives the diagram showed in Figure 3.24 is used.



**Figure 3.24:** Workflow for generation of sustainable alternatives (Step 6)

The target variable, selected in step 5 of the methodology, should be included in one of the four categories considered in the flowdiagram of Figure 3.24.

**Category 1:** Operational variables associated with a separation

**Category 2:** Operational variables associated with a reaction.

**Category 3:** Operational variables associated with flowrate reduction in a closed-path.

**Category 4:** Operational variables associated with flowrate reduction in an open-path.

Once the categories have been identified some suggestions are given to improve the process in that respective case. A synthesis algorithm is needed to generate the new sustainable alternative. For each category there is a suggested synthesis algorithm. The following synthesis algorithms are going to be used.

**Separation synthesis:** Apply algorithm of Jaksland et al., 1996

**Improvement in a separation unit:** Apply algorithm of D'Anterrosches and Gani, 2005

**Improvement in a reactive unit:** Apply algorithm of D'Anterrosches and Gani, 2005

**Selection of new solvents:** Apply algorithm of Harper and Gani, 2000

For a further clarification about these methods, section 2.2.2 should be consulted.

Table 3.8 summarizes the synthesis algorithms that can be applied to all the categories shown in the flowdiagram presented in Figure 3.24.

**Table 3.8:** Synthesis algorithm that should be applied to each category in the flowdiagram represented in Figure 3.24.

Methodology	Approach
D'Anterrosches (2005)	1.1; 2.1; 3.1.3; 3.1.4; 3.3.1; 3.4.1; 3.4.2; 3.5.3; 4.1.3; 4.2.1; 4.3.2; 4.4.1; 4.5.2
Jaksland (1996)	1.2; 3.1.2; 3.3.2; 3.4.2; 3.5.3; 4.1.2; 4.2.1; 4.3.2; 4.5.2
ICAS (ProCamd) Harper and Gani, 2000	3.5.2; 4.5.1

These methods give the directives to improve the process, such as new separation processes that should be used, the operational conditions required to achieve a specific output in a reaction/separation, the new solvents that must be used to perform a given separation, etc. The proposed new alternatives are simulated using the new flowsheet configuration or the new operational conditions.

#### *Evaluation of the new design alternative*

The final step of this methodology is to evaluate and compare the new alternatives that match the design targets in terms of their improvements with the performance criteria (sustainability metrics and safety indices). With the simulation results data, the performance criteria are calculated again and a comparison between the base case and the new alternatives is done taking into account the following criteria.

*“An alternative is considered more sustainable if and only if it improves the indicator targets without compromising the performance criteria in more than 1-2% comparing with their initial value”.*

If this criteria is not respected then a new design alternative suggested in step 6 needs to be checked (see Figure 3.1). When all the alternatives have been analyzed and none of them respect the design criteria, another operational variable should be selected followed by step 6 application. If any operational variable is still available for studying then a new target indicator should be selected and steps 5 and 6 must be performed again.

When the criteria is respected a new sustainable alternative is available and the methodology stops. If more than one alternative is proposed, the one with the better results will be the one selected.

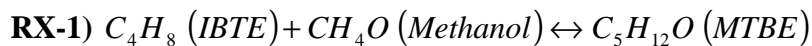


### 3.3 Illustration of the methodology for continuous processes – MTBE Case Study

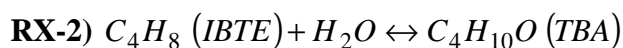
#### 3.3.1 Process description

Methyl ter-butyl ether (MTBE) is manufactured by catalytically reacting iso-butylene and methanol. This process involves 11 compounds, n-Butane (NC4), Isobutane (IC4), 1-Butene (1-butene), cis/trans 2-Butene (BTC2 and BTT2), tert-Butanol (TBA), Di-isobutylene (DIB), water plus isobutylene (IBTE), water and methanol (MEOH). The first 5 compounds are fed with isobutylene in the process. The tert-butanol and the Di-isobutylene are secondary products which are produced by the reaction of water with isobutylene and the dimerization of isobutylene, respectively. Water enters the system as the solvent used for the recovery of methanol.

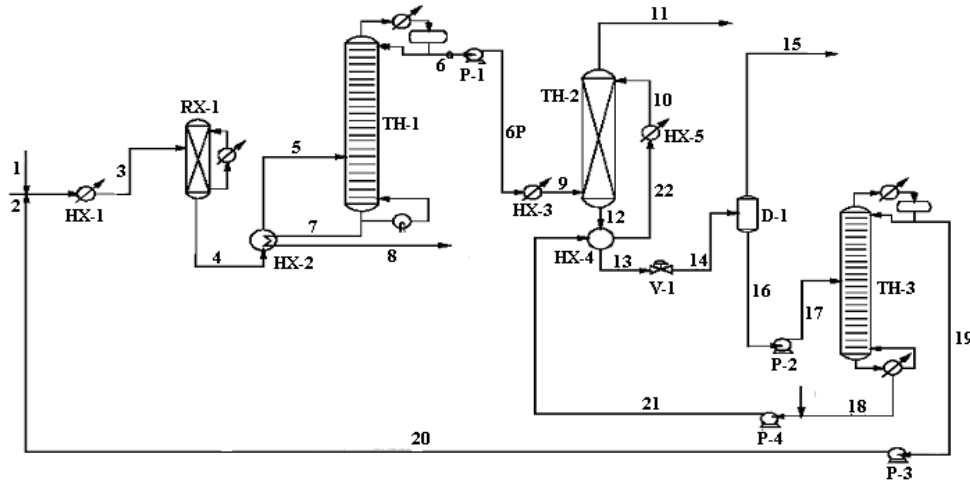
The process starts with the reaction of isobutylene and methanol in the reactor (RX-1), followed by reaction-separation in a reactive distillation column.



Nevertheless, in the reactor there is not only the main reaction because any water in the reactor feed is instantly converted to TBA. Another impurity, DIB, is formed by dimerization of isobutylene. While the formation of DIB and TBA should be minimized, their presence in small concentrations in the MTBE product is acceptable, since these byproducts also have very high octane numbers. The two side reactions are the following ones:



The next section in the process is the recovery of methanol with a wash column (TH-2). Water is used to extract the methanol from the other impurities (fed with isobutylene). The section of the process involves a distillation column (TH-3) to separate methanol and water for recycle. Figure 3.25 shows the flowsheet for MTBE production.



**Figure 3.25:** Process flowsheet for MTBE process

### 3.3.2 Methodology results

#### ***Step 1: Data Collection***

The required detailed process data for the MTBE plant is given as a sample PRO/II (version 8) files (PRO/II Casebook, (1992)). The steady state operational data were generated through PRO/II. The prices and costs were also collected. The required data to apply *SustainPro* to MTBE case study can be found in Appendix A1.

#### ***Step 2: Flowsheet decomposition***

##### ***Step 2.1) Flowsheet transformation into a process graph***

For the flowsheet decomposition the first step is to transform the flowsheet into a process graph. Based on the rules explained in section 3.2.2.1 the mass and energy graphs for MTBE process have been determined (see Figure 3.26 and Figure 3.27).



*Step 2.2) Determine closed-paths*

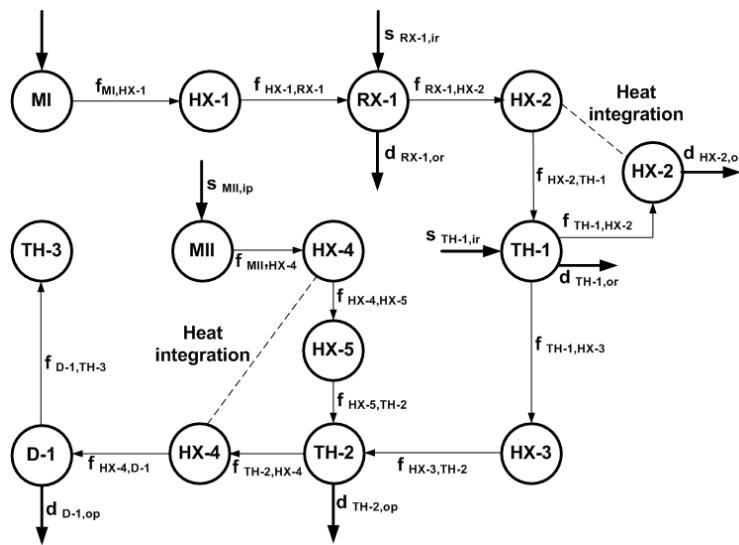
Applying the algorithms described in Figure 3.6 and Figure 3.7, 22 mass closed-paths have been determined for this case study (CP1-CP11 different compounds same streams {20-3-4-5-6-6P-9-12-13-14-16-17-19} and CP11-CP22 different compounds same streams {12-13-14-16-17-18-21-22-10}).

*Step 2.3) Determine closed-paths flowrates and determine open-paths*

Since this algorithm has been developed in this thesis a detailed analysis is presented.

The algorithm described in section 3.2.2.3, Figure 3.11, is followed step by step:

- A) *Select a compound*- For this case study, 11 compounds have been analysed;
- B) *Select a closed-path* – For each compound the respective closed-paths have been analysed, in this case 2 closed-paths for each compound ({20-3-4-5-6-6P-9-12-13-14-16-17-19} and {12-13-14-16-17-18-21-22-10});
- C) *Determine stream within the CP with minimum flowrate*- For all the compounds the streams with the minimum flowrate were stream 20 and stream 18 respectively for the first and the second closed-paths;
- D) *Does that stream belong to more than one CP?* No. Those streams are independent streams, they belong exclusively to the respective closed-paths.
- E) The flowrate of each compound in stream 20 and stream 18 are the flowrates of the closed-paths.
- F) It is not applied to this case study. It will be illustrated in section 5.2.1- VCM production case study.
- G) The compound flowrate of streams 20 and 18 were subtracted from the rest of the streams in the closed-path ({3-4-5-6-6P-9-12-13-14-16-17-19} and {12-13-14-16-17-21-22-10}). A new mass graph is obtained (see Figure 3.28). This graph allows the determination of open-paths.



**Figure 3.28:** Mass Graph for MTBE Production after removing the closed-paths

- H) This step was performed until all closed-paths have been studied.
- I) Following the algorithm described in Figure 3.12 the open-paths were identified. For this case study a total of 77 mass open-paths have been identified.
- J) This step was performed until all the compounds have been studied.

*Step 2.4) Determine open-paths flowrates*

Applying the rules described in section 3.2.2.4 the open-paths flowrate have been determined.

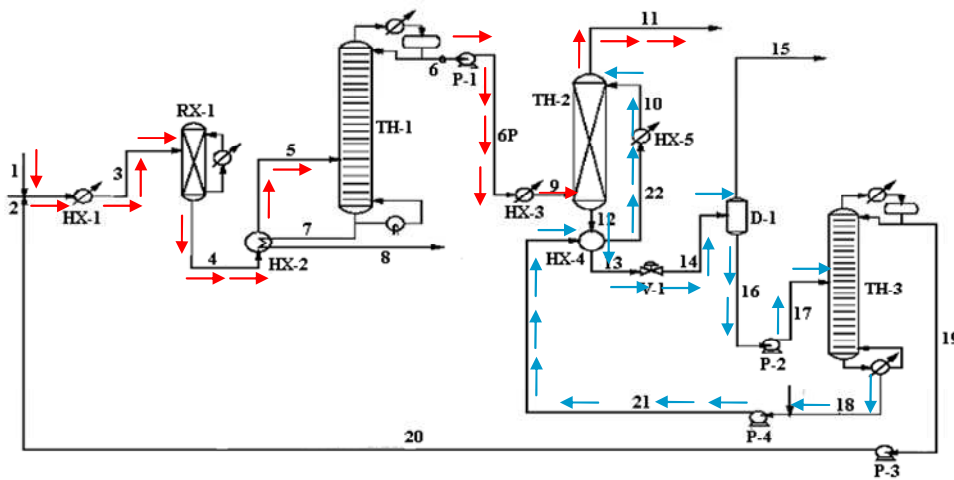
To determine the energy paths the same algorithms have been applied. For this case study 4 energy closed-paths ( $\{5-7\}$ ,  $\{12-22-10\}$ ,  $\{20-3-4-5-6-6P-9-12-13-14-16-17-19\}$  and  $\{12-13-14-16-17-18-21-22-10\}$ ) and 27 energy open-paths were identified.

All the paths are listed in Appendix A1. The most critical paths are listed in Table 3.9. The selection of these paths is going to be explained in step 4-a.

**Table 3.9:** Characterization of the most relevant paths for the MTBE process flowsheet

Path #	Compound	Streams within the path	Flow-rate (kg/h)
OP 1	n-butane	2 – 3 – 4 – 5 – 6 – 6P – 9 – 11	4446
OP 10	Isobutane	2 – 3 – 4 – 5 – 6 – 6P – 9 – 11	20256
OP 19	1 Butene	2 – 3 – 4 – 5 – 6 – 6P – 9 – 11	3338
OP 28	BTC2	2 – 3 – 4 – 5 – 6 – 6P – 9 – 11	1908
OP 37	BTT2	2 – 3 – 4 – 5 – 6 – 6P – 9 – 11	2861
CP21	H2O	12-13-14-16-17-18-21-22-10	6744

Figure 3.29 represents the open- and closed-paths listed in Table 3.9. The open-paths are represented in red colour and the closed-path is represented by the blue arrows.



**Figure 3.29:** Process flowsheet for MTBE process with the open- (red) and closed-paths (blue) presented in Table 3.9

**Step 3.1) Calculate mass and energy indicators**

Applying the equations for the mass and energy indicators presented in section 3.2.3.1 the full set of indicators has been determined for all open-and closed-paths.

Comparing the values obtained for all the indicators, the paths which present the most negative values of MVA, RQ and TVA and the highest values of AF and EWC were selected. Those indicators are the ones with highest potential for the improvements. The top 10 mass indicators for open-paths are listed in Table 3.10. The top 5 mass

indicators for closed-paths are listed in Table 3.11. The indicators listed in these tables are the ones presenting highest potential for improvements.

**Table 3.10:** Top 10 indicators for open-paths-MTBE Case Study

Path	MVA( $10^3$ \$/yr)	RQ	Path	EWC( $10^3$ \$/yr)	RQ	Path	TVA( $10^3$ \$/yr)	RQ
OP 10	-32084.8	0	OP 49	1588.5	-4157	OP 10	-32216.3	0
OP 1	-7042.9	0	OP 10	131.5	0	OP 1	-7074.3	0
OP 19	-5288.0	0	OP 54	92.3	0	OP 19	-5311.4	0
OP 37	-4532.6	0	OP 1	31.4	0	OP 37	-4553.9	0
OP 28	-3021.7	0	OP 19	23.4	0	OP 28	-3035.9	0
OP 42	-356.8	-63674	OP 37	21.3	0	OP 42	-357.7	-63674
OP 75	-111.1	0	OP 46	16.6	59272	OP 75	-113.8	0
OP 63	-29.7	0	OP 28	14.2	0	OP 63	-31.3	0
OP 58	-7.9	63552	OP 72	12.0	-42	OP 46	-16.6	59272
OP 11	-1.9	0	OP 60	12.0	59394	OP 72	-12.0	-42

**Table 3.11:** Top 5 mass indicators for closed-paths-MTBE Case Study

Path	EWC( $10^3$ \$/yr)	RQ	Path	AF	RQ
CP8	374.1	63552	CP21	626.5	0
CP21	313.3	0	CP8	0.015	63552
CP2	0.36	-63674	CP19	0.005	0
CP1	0.23	-63674	CP1	0	-63674
CP19	0.01	0	CP2	0	-63674

Table 3.12 and Table 3.13 summarize the energy indicators values.

**Table 3.12:** Energy indicators for closed-paths-MTBE Case Study

ECP	EAF
CP1	0.2264
CP2	0.1620
CP3	0.0001
CP4	0.5078

**Table 3.13:** Energy indicators for open-paths-MTBE Case Study

Supply	Demand	DC (\$/G.J)	TDC (\$/G.J)
H TH3	C TH3	34.56	45.6
E P4	C TH3	7.43	
H TH3	C TH3	3.58	
H HX1	C RX1	19.56	19.6
H HX1	C HX5	7.92	18.7
E P4	C HX5	7.27	
H TH3	C HX5	3.50	
E P1	11	5.41	9.1
H HX1	11	3.64	
H HX1	C TH1	4.26	4.3
E P1	C HX3	0.84	1.4

**Step 3.2: Calculate Safety Indices**

Using the available process data and the additional information provided by the material safety data sheets, MSDS, (<http://www.msds.com/>) it has been possible to calculate all the indices involved in the safety index determination. The scores were determined using the ranges available for each sub-index in Heikkilä, 1999 (see section 2.3.2). The scores for each index are listed in Table 3.14.

**Table 3.14:** Safety Indices – MTBE Production Case Study

<b>Total inherent safety index (<math>I_{TI}</math>)</b>			
<b><i>Chemical inherent safety index, <math>I_{CI}</math></i></b>	<b><i>Score</i></b>	<b><i>Process inherent safety index, <math>I_{PI}</math></i></b>	<b><i>Score</i></b>
<u>Subindices for reactions hazards</u>		<u>Subindices for process conditions</u>	
Heat of the main reaction, $I_{RM}$	1	Inventory, $I_I$	4
Heat of the side reactions, $I_{RS}$	0	Process temperature, $I_T$	1
Chemical Interaction, $I_{INT}$	4	Process pressure, $I_P$	1
<u>Subindices for hazardous substances</u>		<u>Subindices for process system</u>	
Flammability, $I_{FL}$	4	Equipment, $I_{EQ}$	
Explosiveness, $I_{EX}$	1	ISBL	2
Toxicity, $I_{TOX}$	6	OSBL	3
Corrosivity, $I_{COR}$	1	Process structure, $I_{ST}$	2
Maximum score $I_{CI}$	17	Maximum score $I_{PI}$	13
<b><math>I_{TI}</math></b>		<b>30</b>	



The Chemical inherent safety index value was 17 and the Process inherent safety index value was 13, finally the value of the total safety index has been found to be 30, which indicates that the process is on the safe side.

### ***Step 3.3: Calculate Sustainability Metrics***

The sustainability metrics were also calculated. In this work, only 23 sustainability metrics were determined, because it was assumed that the corresponding parameters would remain unchanged (for example, new investment, tax-benefits, etc.) and since data related to the social metrics was not available.

The calculated metrics are presented in the following table.

**Table 3.15:** Sustainability metrics for the different areas excluding the environmental metrics - MTBE Production Case Study

Area	Sustainability Metrics	Value
Energy	Total Net Primary Energy Usage Rate	$3.33 \times 10^5$ GJ/y
	Total Net Primary Sourced from Renewals	99.92 %
	Total Net Primary Energy Usage Rate per kg Product	1257 kJ/kg
	Total Net Primary Energy Usage per Unit Value Added	5.3 kJ/\$
Material	Total raw materials used per kg product	1.74 kg/kg
	Total raw materials used per unit value added	0.0073 kg/\$
	Fraction of raw materials recycled within company	0.0023 kg/kg
	Fraction of raw materials recycled from consumers	0 kg/kg
	Hazardous raw material per kg product	1.74 kg/kg
Water	Net water consumed per unit mass of product	22.87 kg/kg
	Net water consumed per unit value added	0.096 kg/\$
Economic	Value Added	$7.84 \times 10^6$ \$/y

The environmental metrics were calculated using ICAS. This software has a tool to calculate the WAR algorithm described by Cabezas (1999). In order to apply this

algorithm the specifications of the feed and the demand streams of the global process should be specified, so in this case study the data related to streams 1, 2, Make-up, 8, 11 and 15 were inserted in the program. The results obtained from ICAS are listed in Table 3.16.

**Table 3.16:** WAR algorithm results- MTBE Production Case Study

Stream No	Total PEI	HTPI	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
1	107962	17809.6	323	874,681	17809.6	0	0	72011.1	0
2	4.24x10 <sup>6</sup>	809068	223	109567	809068	0	0	2.52x10 <sup>6</sup>	0
Make-up	0	0	0	0	0	0	0	0	0
<i>Input sum</i>	<i>4.35 x10<sup>6</sup></i>	<i>826878</i>	<i>546,302</i>	<i>109576</i>	<i>826878</i>	<i>0</i>	<i>0</i>	<i>2.59x10<sup>6</sup></i>	<i>0</i>
8	388390	190315	4417.12	3315.1	190315	0	0	275,356	0
11	2.56x10 <sup>6</sup>	548884	223.04	105137	548884	0	0	1.36x10 <sup>6</sup>	0
15	696	149	0.009	341	149	0	0	363	0
<i>Output sum</i>	<i>2.95 x10<sup>6</sup></i>	<i>739214</i>	<i>4640.17</i>	<i>108455</i>	<i>739214</i>	<i>0</i>	<i>0</i>	<i>1.36x10<sup>6</sup></i>	<i>0</i>
<b>Impact generated</b>	<b>-1.40 x10<sup>6</sup></b>	<b>-87664.2</b>	<b>4093.87</b>	<b>-1120.24</b>	<b>-87664.2</b>	<b>0</b>	<b>0</b>	<b>-1.23x10<sup>6</sup></b>	<b>0</b>

The previous values are the environmental metrics.

#### ***Step 4: Indicator Sensitivity Analysis (ISA Algorithm)***

Following the steps described in Figure 3.18, ISA algorithm will be illustrated step by step for the target indicator determination among the open-paths indicators. The results for the closed-path will be given after the detailed explanation.

##### *Step 4-a:*

From Table 3.10 and Table 3.11 and following the algorithms described in Figure 3.19 and Figure 3.20 respectively to open- and closed-paths the indicators showing highest potential for improvements have been selected and they are listed in Table 3.9. From Table 3.10 OP1, OP10, OP19, OP28 and OP37 have been selected, since these indicators are in the top of the table, presenting very negative values of TVA when compared to the others. Following the algorithm of Figure 3.19, step 5 of the algorithm has been achieved and consequently MVA has been selected for all of them. Regarding the closed-paths, CP8 presented high values of EWC, however this path is related to the

raw material recycle (see appendix A1) and consequently the chances for improvements are very low (indicator is not selected as a potential target indicator). Following the algorithm described in Figure 3.20, step 4 of the algorithm has been achieved and consequently AF of CP21 has been selected as a potential target indicator. It can be noted that the most sensitive open-paths (traced in red in Figure 3.29) correspond to the mass of inert compounds present in the process, which enter the process as impurities of the reactant, isobutylene. As stated before these open-paths show a very negative value of MVA, indicating that the impurities lose their value through this path. The compounds are bought at a high price, but their value added is lost across the path. Closed-paths, CP21 (traced in blue in Figure 3.29) is related to water which is the solvent used to recover methanol (see appendix A1). In this closed-path, high values of AF and EWC can be observed. The high values of AF indicate the high accumulative behaviour of water in the recycle, and consequently, high energy consumption.

At this point, six paths are available as potential target indicators (OP1, OP10, OP19, OP28, OP37 and CP21).

*Step 4- b:*

To set target indicators, it is necessary to define the improvement objective in order to apply ISA algorithm. In this case study the main objective has been to increase the process profit without compromising the performance criteria (sustainability metrics and safety indices).

The profit expression selected for  $F_{obj}$  is the following:

$$\begin{aligned} \text{Profit} = & m_8 \cdot Pr_8 + m_{11} \cdot Pr_{11} - m_{15} \cdot Pr_{15} - m_1 \cdot Pr_1 - m_2 \cdot Pr_2 - m_{MKUP} \cdot Pr_{MKUP} \\ & - (Q_{RX1} + Q_{HX3} + Q_{HX5} + Q_{CondT3} + Q_{CondTH1}) \cdot Pr_{cooling} - (Q_{HX1} + Q_{RebTH1} + Q_{RebT3}) \cdot Pr_{steam} \\ & - (Q_{P1} + Q_{P2} + Q_{P3} + Q_{P4}) \cdot Pr_{electricity} \end{aligned}$$

Where  $m_c$  is the flowrate for compound  $c$ ,  $Pr_c$  is the price for compound  $c$ ,  $Q$  is the heat exchange in a given unit.

Step 4-c and Step 4-d:

The incidence matrix of target indicators expressions and their variables is given in Table 3.17. In Table 3.17,  $V_F$  variables appear in the columns of the table.

**Table 3.17:** Incidence matrix to solve the ISA algorithm- MTBE Production Case Study

Path	Indicator	Streams Flowrates			Heat exchanged in units													
		1	2	MKUP	P3	HX1	RX1	TH1	P1	HX3	HX5	P2	P4	Cond T3	Cond TH1	Reb T3	Reb TH1	
OP 10	MVA		X			X	X	X	X	X					X			
OP 1	MVA		X			X	X	X	X	X					X			
OP 19	MVA		X			X	X	X	X	X					X			
OP 37	MVA		X			X	X	X	X	X					X			
OP 28	MVA		X			X	X	X	X	X					X			

The selected variables ( $V_T$ ) are the ones where an X is presented. For this case study  $m_2$ ,  $Q_{HX1}$ ,  $Q_{RX1}$ ,  $Q_{TH1}$ ,  $Q_{P1}$ ,  $Q_{HX3}$  and  $Q_{CondTH1}$  are the  $V_T$  variables.

Step 4-e:

i) For the selected target variables,  $V_T$ , the values of the associated flowrates are listed in Table 3.18.

**Table 3.18:** Design variables flowrates- MTBE Production Case Study

Variable ( $V_T$ )	Stream of the associated flowrate	Flowrate (kg/h)
$m_2$	$m_2$	48548
$Q_{HX1}$	$m_3$	57576
$Q_{RX1}$	$m_4$	57576
$Q_{TH1}$	$m_6$	33071
$Q_{P1}$	$m_{6p}$	33071
$Q_{HX3}$	$m_9$	33071
$Q_{CondTH1}$	$m_6$	33071

Using the path flowrates (see Table 3.9) and the respective variables flowrates (see Table 3.18) the influence of the paths in the selected variables has been calculated.

The fraction of variable  $m_2$ , which is influenced by open-path 1, is given below as an example.

$$x_{m_2,OP1} = \frac{m_{OP1}}{m_{m_2}} = \frac{4446}{48548} = 0.091$$

The fractions of all the paths, which influence  $V_T$  variables, has been calculated for the entire set of variables determined in step 4-d. The fractions values,  $x_{n,k}$ , are listed in Table 3.19.

**Table 3.19:**  $x_{n,k}$  values - MTBE Production Case Study

Path	Indicator	Flowrate (kg/h)	$m_2$	$Q_{HX1}$	$Q_{RX1}$	$Q_{TH1}$	$Q_{P1}$	$Q_{HX3}$	$Q_{CondTH1}$
OP 1	MVA	4446	0.091	0.077	0.077	0.134	0.134	0.134	0.134
OP 10	MVA	20256	0.417	0.352	0.352	0.612	0.612	0.612	0.612
OP 19	MVA	3338	0.069	0.058	0.058	0.101	0.101	0.101	0.101
OP 28	MVA	1908	0.039	0.033	0.033	0.058	0.058	0.058	0.058
OP 37	MVA	2861	0.059	0.050	0.050	0.087	0.087	0.087	0.087

ii) Once all the fractions have been obtained, it is necessary to determine for each variable  $V_T$  (see Table 3.18) the profit terms that are influenced by each variable and sum all of them. Table 3.20 gives the amounts influenced by these variables.

**Table 3.20:** Profit terms for each  $V_T$  variable- MTBE Production Case Study

Variable	Variable Value	Price	Total amount in profit (\$/h)
$m_2$	48548 (kg/h)	0.353 (\$/kg)	17137
$Q_{HX1}$	5.0 (GJ/h)	8.75 (\$/GJ)	44
$Q_{RX1}$	11.6 (GJ/h)	0.96 (\$/GJ)	11
$Q_{TH1}$	0 (GJ/h)	0.96 (\$/GJ)	0
$Q_{P1}$	5.4 (kW)	0.05 (\$/kWh)	0.25
$Q_{HX3}$	0.5 (GJ/h)	0.96 (\$/GJ)	0.46
$Q_{CondTH1}$	23.7 (GJ/h)	0.96 (\$/GJ)	22.74

Using the values from Table 3.20, the maximum value by which the variables can be changed is determined. The involved calculations are highlighted for open-path 1 and variable  $m_2$ . Applying Eq(3.18), the influence of variable  $m_2$ , within open-path 1, in the profit term related to that variable is determined by the following expression.

$$T_{(m_2,OP1)} = x_{(OP1)} \times T_{(m_2)} = 0,091 \times 17137 = 1569 \text{ \$ / h}$$

Applying the same expression to all the variables and paths and summing all the  $PT$  values the maximum amount in the profit that can be changed by these target variables is determined. Then Eq(3.19) is applied to determine the fraction of each profit term by the maximum amount of profit that can be changed. In the case of the open-path 1 the fraction is calculated as shown below:

$$y_{(m_2,OP1)} = \frac{T_{(m_2,OP1)}}{\sum_k \sum_{va} T_{(v,k)}} = \frac{1569}{11636} = 0,13\%$$

Table 3.21 lists the  $y_{(n,k)}$  values.

**Table 3.21:**  $y_{(n,k)}$  values- MTBE Production Case Study

Path	Indicator	$m_2$	$Q_{HX1}$	$Q_{RX1}$	$Q_{TH1}$	$Q_{P1}$	$Q_{HX3}$	$Q_{CondTH1}$
OP 1	MVA	0.13	$2.93 \times 10^{-4}$	$7.42 \times 10^{-5}$	0	$2.92 \times 10^{-6}$	$5.37 \times 10^{-6}$	$2.63 \times 10^{-4}$
OP 10	MVA	0.61	0.001	$3.38 \times 10^{-4}$	0	$1.33 \times 10^{-5}$	$2.45 \times 10^{-5}$	$1.20 \times 10^{-3}$
OP 19	MVA	0.10	$2.20 \times 10^{-4}$	$5.57 \times 10^{-5}$	0	$2.19 \times 10^{-6}$	$4.03 \times 10^{-6}$	$1.97 \times 10^{-4}$
OP 28	MVA	0.06	$1.26 \times 10^{-4}$	$3.18 \times 10^{-5}$	0	$1.25 \times 10^{-6}$	$2.31 \times 10^{-6}$	$1.13 \times 10^{-4}$
OP 37	MVA	0.09	$1.89 \times 10^{-4}$	$4.78 \times 10^{-5}$	0	$1.88 \times 10^{-6}$	$3.46 \times 10^{-6}$	$1.69 \times 10^{-4}$

iii) The coefficients present in the profit expression that are multiplied by each target are listed in Table 3.22.

**Table 3.22:** Coefficients,  $C_f$ , to each variable  $V_T$ - MTBE Production Case Study

Variable	Coefficients ( $C_f$ )
$m_2$	0.353
$Q_{HX1}$	8.75
$Q_{RX1}$	0.96
$Q_{TH1}$	0
$Q_{P1}$	0.047
$Q_{HX3}$	0.96
$Q_{CondTH1}$	0.96
<b>Sum</b>	<b>12.03</b>

These coefficients correspond to the sum of the material or utilities prices, which influence each variable. The percentage of each coefficient in the total amount of the coefficients should be determined using Eq(3.20).

For open-path 1 and variable  $m_2$  the percentage of sensitivity coefficient is given by the following expression.

$$z_{m_2} = \frac{Cf_{(m_2)}}{\sum_{v=0}^7 Cf_{(v)}} = \frac{0.353}{12.03} = 0.029$$

Applying the same expression for all the paths and variables the fraction of the coefficients in the sum of all the coefficients,  $Z_n$ , are listed in Table 3.23.

**Table 3.23:**  $z_n$  values- MTBE Production Case Study

Path	Indicator	$m_2$	$Q_{HX1}$	$Q_{RX1}$	$Q_{TH1}$	$Q_{P1}$	$Q_{HX3}$	$Q_{CondTH1}$
OP 1	MVA	0.029	0.727	0.080	0	$3.91 \times 10^{-3}$	0.080	0.080
OP 10	MVA	0.029	0.727	0.080	0	$3.91 \times 10^{-3}$	0.080	0.080
OP 19	MVA	0.029	0.727	0.080	0	$3.91 \times 10^{-3}$	0.080	0.080
OP 28	MVA	0.029	0.727	0.080	0	$3.91 \times 10^{-3}$	0.080	0.080
OP 37	MVA	0.029	0.727	0.080	0	$3.91 \times 10^{-3}$	0.080	0.080

*Step 4-f:*

The increment to define the scales has been calculated through Eq(3.21) and Eq(3.22) ( $In^T = 0.12$  and  $In^{SA} = 0.15$ ). The scales for the profit terms fraction,  $y_{(n,k)}$  (see Table 3.21) and the fraction of the coefficients  $Z_n$  (see Table 3.23), are listed in Table 3.24 and Table 3.25 respectively.

**Table 3.24:** Ranges and scores to the Step 4-e-ii in ISA algorithm-MTBE case study.

Weight in the profit expression			
Weight	Inferior limit	Superior limit	Scores
Extremely high	0.49	0.61	5
High	0.37	0.49	4
Normal	0.25	0.37	3
Low	0.12	0.25	2
Extremely low	0	0.12	1

**Table 3.25:** Ranges and scores to the Step 4-e-III in ISA algorithm-MTBE case study

Sensitivity			
Type of sensitivity	Inferior limit	Superior limit	Scores
Extremely sensible	0.58	0.73	5
Much sensible	0.44	0.58	4
Sensible	0.29	0.44	3
Small sensitivity	0.15	0.29	2
Almost no sensible	0	0.15	1

*Step 4-g, Step 4-h and Step 4-i:*

In Step g the percentages presented in Table 3.21 and Table 3.23 are transformed into scores using the scales available in Table 3.24 and Table 3.25, respectively. The scores to each variable and the final scores to each indicator are listed in Table 3.26.

**Table 3.26:** Scores for the different open-paths-MTBE case study

Path	Indicator	m <sub>2</sub>	Q <sub>HX1</sub>	Q <sub>RX1</sub>	Q <sub>TH1</sub>	Q <sub>P1</sub>	Q <sub>HX3</sub>	Q <sub>CondTH1</sub>	Scores
OP 1	MVA	2+1	1+5	1+1	1+1	1+1	1+1	1+1	19
OP 10	MVA	5+1	1+5	1+1	1+1	1+1	1+1	1+1	22
OP 19	MVA	1+1	1+5	1+1	1+1	1+1	1+1	1+1	18
OP 28	MVA	1+1	1+5	1+1	1+1	1+1	1+1	1+1	18
OP 37	MVA	1+1	1+5	1+1	1+1	1+1	1+1	1+1	18

Following the same procedure the scores for closed-paths have also been determined. Table 3.27 lists the scores for closed-paths.

**Table 3.27:** Scores for the different closed-paths-MTBE case study

Path	Indicator	Scores
CP 21	AF	16



*Step 4-J:*

According to Table 3.26, the most sensitive indicators have been identified to be the MVA in open-path OP10 and AF for the closed-path CP21 (highest score).

**Step 5: Design Sensitive Analysis**

The rest of the methodology is illustrated taking into consideration the closed-path improvements, or in other words the AF reduction in CP21.

The operational variables that influence the value of AF in the closed-path CP 21 are the following:

- **Closed-paths flowrate:** CP 21 flowrate
- **Stream flowrates:** Flowrate of stream 15 and Flowrate of stream 19

Variations of 5, 10 and 15% on the reference (design) values for all the identified operational variables.

Table 3.28 lists the improvements in the target indicator obtained by the variations on the operational variables.

**Table 3.28:** Summary of the sensitivity analysis to measure the influence of operational variables in AF of closed-path CP21— MTBE case study

Variation (%)	Improvement in target indicator (%)		
	Flowrate CP21	Flowrate 15	Flowrate 19
5%	5.00%	0.09%	1.54%
10%	10.00%	0.19%	3.04%
15%	15.00%	0.28%	4.49%

Analyzing the results it is possible to conclude that the flowrate of closed-path 21 is the most sensitive variable for the target indicator and consequently the one that allows higher improvements.

**Step 6: Generation and evaluation of new design alternative**

Step 5 identified the operational variable to achieve an improvement in the target indicator as the reduction of the flowrate of a solvent (Water) in a closed-path (CP 21). From Figure 3.24 it can be noted that the improvement category for this variable is the category 3.5. To improve the variables of category 3.5 there are three alternatives available:

- Reduce the flowrate
- New Solvent
- Improve/ Insert a new separation process

- **Reduce the flowrate**

First an analysis to verify if it is possible to reduce the solvent flowrate without compromising the separation efficiency has to be tested. This would be the best alternative since it does not involve additional investment costs.

To verify the new design alternative, the process has been simulated, with 20% less of water in the washed system. This new alternative presents very interesting results. First with this reduction the efficiency of the wash column can be kept at 99.9% recovery of methanol and water.

The target indicators improved by 20%, respectively, for AF and EWC.

**Table 3.29:** Improvements in target indicators - MTBE production Case Study

Target Indicator	Initial	Final
AF –CP21	626	500
EWC – CP21	$3.13 \times 10^5$ \$/y	$2.50 \times 10^5$ \$/y

The process is now more sustainable as the energy metrics per kg of final product and per value added decreased by 3%, the water metrics per kg of final product and per

value added decreased by 4% and the material metrics per value added improved 0.2%. The profit improved by 1.7%, while all the other metrics and indices remained constant (see Table 3.30).

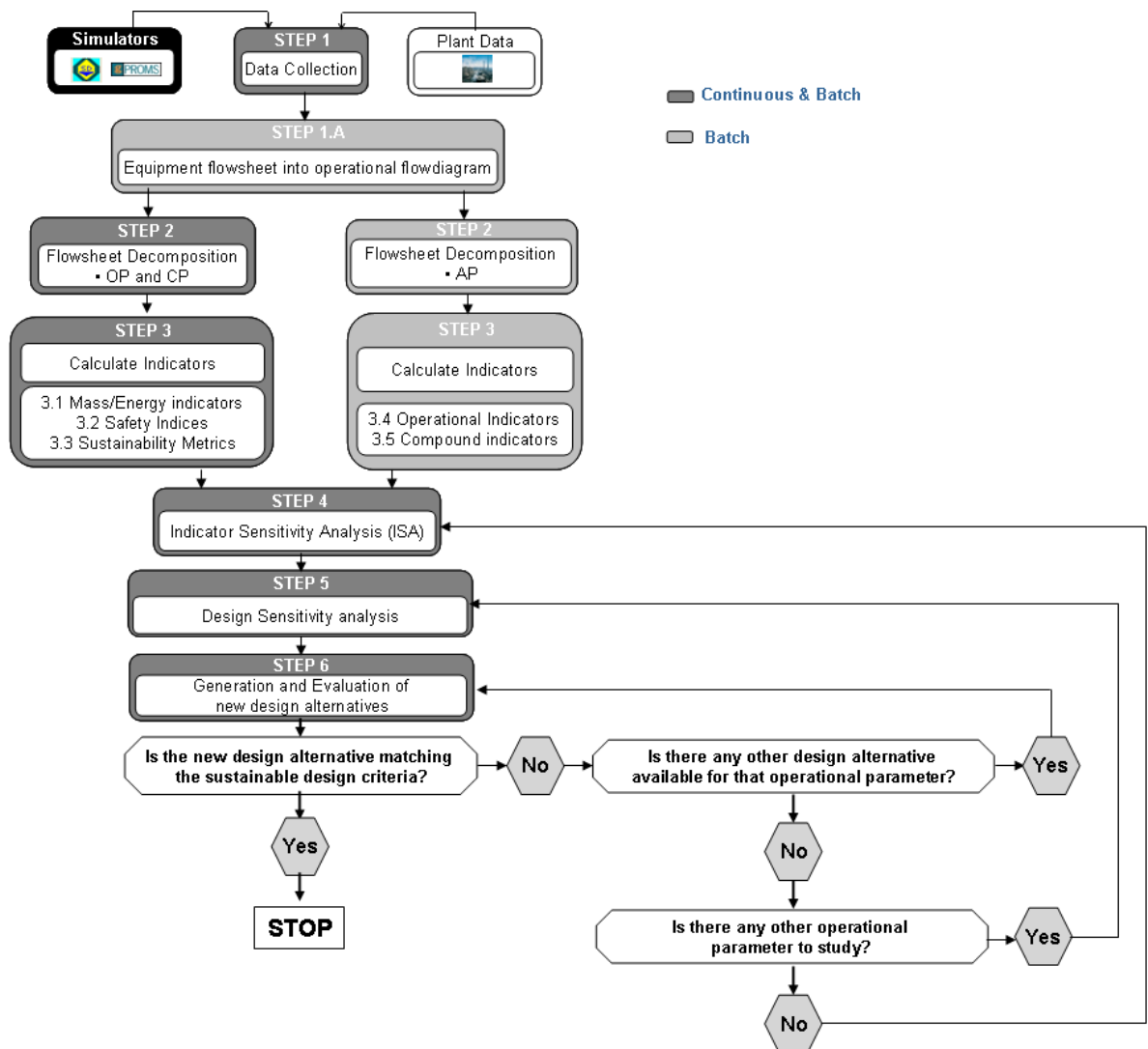
**Table 3.30:** Comparison of the performance criteria between the base case and the new sustainable design alternative - MTBE Production Case Study

Sustainability Metrics	Base Case	New Design	Improvement
Total Net Primary Energy Usage rate (GJ/y)	332623	322726	3.0%
% Total Net Primary Energy sourced from renewables	0.999	0.999	0.0%
Total Net Primary Energy Usage per kg product (kJ/kg)	1257	1220	3.0%
Total Net Primary Energy Usage per unit value added (kJ/\$)	5	5	3.1%
Total raw materials used per kg product (kg/kg)	2	2	0.0%
Total raw materials used per unit value added (kg/\$)	0.00733	0.00732	0.2%
Fraction of raw materials recycled within company	0.00234	0.00231	1.6%
Fraction of raw materials recycled from consumers	0	0	0.0%
Hazardous raw material per kg product (kg/kg)	2	2	0.0%
Net water consumed per unit mass of product (kg/kg)	23	22	3.8%
Net water consumed per unit value added (kg/\$)	0.0965	0.0927	4.0%
Safety index	30	30	0%
WAR	$-1.4 \times 10^6$	$-1.4 \times 10^6$	0%
Profit (\$/y)	$5.20 \times 10^6$	$5.29 \times 10^6$	1.7%

Since the validation has been done with the verification of the improvements in the targets as well as in the performance criteria, the established criterion has been satisfied and consequently this can be considered and more sustainable alternative (none of the performance parameters got worse than 1-2%).

### 3.4 Methodology for Batch processes

The methodology previously described for continuous processes has been further extended to batch processes (Carvalho *et al.*, 2009). With the extended methodology it is possible to analyze a wide range of processes that operate, in semi-continuous and/or in batch mode. The main steps of the extended methodology are described below. The workflow for the extended methodology is organized in terms of six steps with an extra sub-step, as shown in Figure 3.30.



**Figure 3.30:** Flowdiagram of the sustainable process design methodology for processes operating in batch mode

In Figure 3.30, the boxes in light grey represent the steps, which are exclusively performed in batch processes. The dark grey boxes are the steps applied for processes operating in continuous mode, in semi-continuous and/or in batch mode.

#### 3.4.1 Step 1- Data Collection

Process data needed to apply the methodology is collected. For continuous processes, steady state data related to the mass and the energy balance are needed, however, for batch operations the information required is not the same. For the batch case, data on the time of each operation, the equipment volume, the initial and the final mass for each compound in each operation, the mass entering and leaving each batch operation during the operation time and the energy used in each step are required. The purchase and sale prices for each chemical are also needed. All these data can be collected from the real plant and/or generated through model-based simulations.

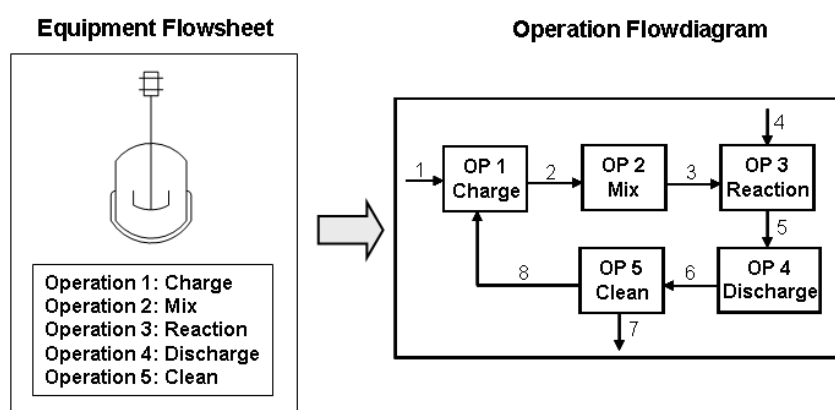
#### 3.4.2 Step 1A- Transform equipment flowsheet in an operational flowsheet

For continuous processes the flowsheet diagram is a sequence of different equipments, where in each equipment a specific operation takes place. When the process is operating in a batch mode the individual equipments may present a sequence of operations. In this methodology the batch process will be treated as a “continuous” process in terms of the material and energy (data) flow from operation to operation (Carvalho *et al.*, 2009). Thus, the equipment based-flowsheet is transformed to an operation based flowdiagram. To illustrate the new concept of flowdiagram a simple example is presented (see example 3.6).

**Example 3.6**

The equipment process presented in Figure 3.31 consists of five operations, as specified in the figure.

- Charge: One reactant and a solvent are charged
- Mix: Mixing the previous mixture
- Reaction: Reaction operation, where the second reactant is charged during the reaction time
- Discharge: Discharged of the reaction effluent
- Clean: Clean the equipment.



**Figure 3.31:** Example for the transformation of equipment flowsheet in an operational flowdiagram (Example 3.6)

Although the equipment flowsheet has only one unit (tank-reactor), a sequence of five operations is taking place in that unit. To transform the equipment flowsheet to an operation flowdiagram the operations are represented as “units”. In the first operation, the tank is charged (fed) with two compounds (Stream 1). Assuming that the time for operation 1 (charge) is  $t_1$ , the mass of stream 1 will be the sum of the mass flowrate entering from  $t = 0$  till  $t = t_1$ . Then, the second operation consists of mixing the charged compounds. Stream 2 represents the mass inside the tank at time  $t_1$ , which can be seen as the mass entering the second operation, at the initial time of operation 2,  $t_{i2} = t_1$ . Assuming that the time for operation 2 is  $t_2$  stream 3 will be the mass at time  $t = t_1 + t_2$ . Following this procedure, it is possible to determine the mass in the other streams of the process at other times of operation. After the remaining operations take place (reaction, discharge and clean) there may remain a small residue of compounds in the equipment, even after cleaning. Consequently, when the first operation starts again that residue will be still present inside the equipment. Therefore, it can be considered that there is a recycle of mass from the last batch operation to the first one.

Based on the previous example, three types of streams are considered. The masses for the respective streams are calculated in the following way.

- Streams entering/leaving the operation during the operation time (see streams 1 and 4 in Figure 3.31). The mass for these streams are calculated as:

$$M_{S,j}^{OF} = \int_{t=0}^{t=t_j} F_S dt \quad \text{Eq (3.25)}$$

- Streams at the end/beginning of an operation (see streams 2, 3, 5 and 7 in Figure 3.31). The mass for these streams are the mass at the final times of the previous adjacent operation.

$$M_{S,j}^{OF} = M_{j-1}^{t=t_{j-1}} \quad \text{Eq (3.26)}$$

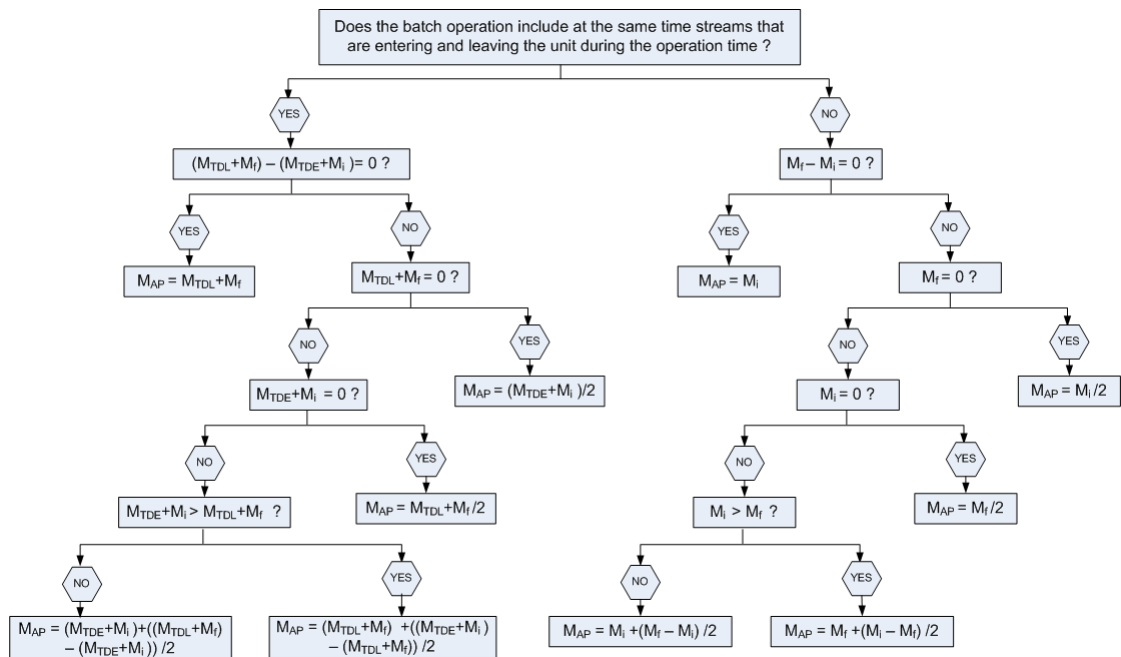
- Streams of residues in the equipment (see stream 8 in Figure 3.31). These streams are recycled from the last operation to the first in the new sequence of operations and their mass are calculated as follows.

$$M_{S,j}^{OF} = M_R^{t=t_j} \quad \text{Eq (3.27)}$$

In Eqs 3.25- 3.27,  $M_s$  is the mass of stream  $s$  which is entering/leaving an operation,  $M_j^t$  is the mass in the operation  $j$  at time  $t$ ,  $t$  is the time,  $t_j$  is the final time for operation  $j$ ,  $M_R$  is the residual mass and  $F_S$  is the flowrate of stream  $s$  in the operation flowdiagram.

## 3.4.3 Step 2- Flowsheet decomposition

The flowsheet decomposition consists of identification of all open- (OP) and closed-paths (CP) for each compound in the batch operation flowdiagram. For a batch process, it is possible to perform the identification of all the open- and closed-paths for each compound as in the continuous mode once the flowdiagram has been generated. However, for batch operation flowdiagram, a new path related to the accumulation of mass and energy is introduced. This new path is called accumulation-path (AP) and corresponds to the accumulation in a given operation (Carvalho *et al.*, 2009). This path represents an average of the mass for each compound during the operation time. The procedure for calculating the accumulated mass ( $M_{AP}$ ) is illustrated in Figure 3.32.



**Figure 3.32:** Flowdiagram of the algorithm to determination of the accumulated mass

In Figure 3.32,  $M_{AP}$  is the mass of the accumulation path,  $M_i$  is the initial mass of a given compound,  $M_f$  is the final mass of a given compound,  $M_{TDL}$  is the mass of a time dependent stream that leaves the process (this means streams leaving the operation



during the operation time) and  $M_{TDE}$  is the mass of a time dependent stream that enters the process (this means streams entering the operation during the operation time).

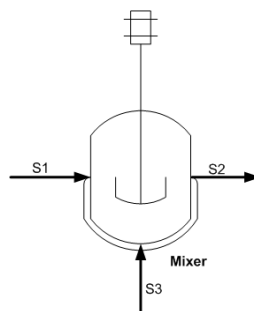
Once the accumulated mass has been determined, the corresponding AP flowrate is calculated through the use of Eq (3.28).

$$F_{AP} = \frac{M_{AP}}{t_j} \quad \text{Eq (3.28)}$$

In Eq (3.28)  $F_{AP}$  is the accumulation-path flowrate,  $M_{AP}$  is the mass of accumulation-path AP (see Figure 3.32) and  $t$  is the time spent in operation  $j$ .

**Example 3.7**

Consider the flowdiagram for a tank that is supposed to mix the compounds during 2 hours. S1 represents the initial mass ( $M_i = 50$  kg at  $t_i=0$ ). S2 represents the final mass that leaves the unit after the batch operation ( $M_f = 70$  kg at  $t_f=2h$ ). S3 is a stream that enters at a fixed flowrate during the operation time (time dependent stream  $M_{TDE} = \int_{t_i}^{t_f} F_{TDE} dt$ ).



**Figure 3.33:** Unit with a stream entering during the operation time (Example 3.7)

Using the algorithm described in Figure 3.32 the mass of the accumulation-path has been determined in the following way:

- 1) Does the batch operation include streams that are entering and leaving the operation during the operation time?

*The unit includes a stream entering during operation time (S3), however there is no stream leaving the unit during operation time. Right hand side of the algorithm is followed.*

2)  $M_f - M_i = 0?$

No ( $M_f - M_i = 70 - 50 = 20$ )

3)  $M_f = 0?$

No ( $M_f = 70$ )

4)  $M_i = 0?$

No ( $M_i = 50$ )

5)  $M_i > M_f?$

No ( $M_i = 50 < M_f = 70$ )

6) Determine the mass of the accumulation-path.

$$M_{AP} = M_i + \frac{(M_f - M_i)}{2} = 50 + \frac{70 - 50}{2} = 60\text{kg}$$

7) Using Eq (3.28) the flowrate of the accumulation-path is calculated

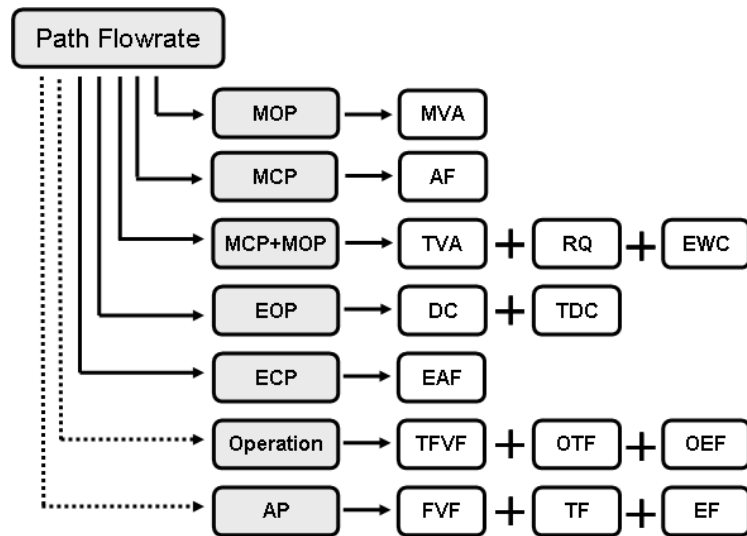
$$(A_{AP} = \frac{60}{2} = 30\text{kg/h})$$

### 3.4.4 Step 3- Indicators/ Sustainability Metrics/ Safety Indices Calculation

In this section, the indicators (open-paths, closed-paths, accumulation-paths (batch operation and batch compound- operation)) the sustainability metrics and the safety indices (see sections 2.3.1 and 2.3.2) are calculated, using the results from step 1-3. The indicators presented in section 3.2.3.1 are calculated for all open- and closed-paths. Through the values obtained for these indicators it is possible to identify the locations within the process (or operations) where the mass/energy “paths” face “barriers” with respect to costs, benefits, or accumulation. These critical points therefore indicate high potential for process (or operation) improvements.

In order to take into account characteristic problems related to batch operations, a new set of batch indicators have been developed, addressing issues such as the time, the volume occupancy and the energy used per operation (Carvalho *et al.*, 2009). Figure 3.34 gives an overview of the application of indicators for each type of path.

For the batch operation, two new indicators are proposed (see dashed lines Figure 3.34): *Operation Indicator* (compares the performance of the operation) and the *Compound Indicator* (indicates for each operation, the compound most likely to cause operational problems). These new indicators provide important information about the batch processes in terms of which operation of a process flowsheet has comparatively more potential for improvements than the others.



**Figure 3.34:** Indicators overview including batch indicators

MOP- Mass Open-Path; MCP- Mass Closed-Path; EOP- Energy Open-Path; ECP- Energy Closed-Path; MVA-Material Value Added; AF-Accumulation Factor; TVA Total Value Added; RQ-Reaction Quality; EWC-Energy and Waste Cost; DC- Demand Cost; TDC-Total Demand Cost; EAF: Energy Accumulation Factor; AP: Accumulation-path; TFVF: Total Free Volume Factor; OTF: Operation Time Factor; OEF: Operation Energy Factor; FVF: Free volume Factor; TF: Time Factor; EF: Energy Factor

### Operation Indicators

There are three Operation Indicators, the Total Free Volume Factor (TFVF), the Operation Time Factor (OTF) and the Operation Energy Factor (OEF). With these indicators it is possible to have an analysis of the performance of the batch operations in terms of volume, time and energy respectively.

#### ***Total Free Volume Factor (TFVF)***

This indicator gives the percentage of free volume compared to the total volume of the equipment.

$$TFVF_j = \frac{V_{eq}^j - \sum_c \frac{M_{AP,c}}{\rho_c}}{V_{eq}^j} \quad \text{Eq (3.29)}$$

In Eq (3.29),  $V_{eq}^j$  is the equipment volume in operation  $j$ ,  $\rho_c$  is the density of compound  $c$ ,  $C$  is the total number of compounds present in operation  $j$  and  $M_{AP}$  is the mass of accumulation-path  $AP$ .

*High values of this indicator indicate that the equipment volume is not filled to a high level and consequently points to a potential for improvements.* Knowing where the equipment is not being fully occupied, there is a good chance of changing the material disposition among the operations in order to improve the performance of the sequence of operations. The indicator value is given as a fraction.

***Operation Time Factor (OTF)***

This indicator points to the fraction of time that a given operation spends compared to the total time taken by the whole sequence of operations.

$$OTF_j = \frac{t_j}{\sum_j t_j} \quad \text{Eq (3.30)}$$

In Eq (3.30),  $t$  is the time spent in operation  $j$ .

*High values of this indicator show that a given operation is taking too much time and consequently this operation can be seen as the bottleneck in the operations flowdiagram.* This is also the limiting operation with respect to time. This indicator value is given as a fraction and it should be reduced in order to improve the process.

***Operation Energy Factor (OEF)***

This indicator gives the percentage of energy used in a given operation compared to the total amount of energy consumed.

$$OEF_j = \frac{E_j}{\sum_j E_j} \quad \text{Eq (3.31)}$$

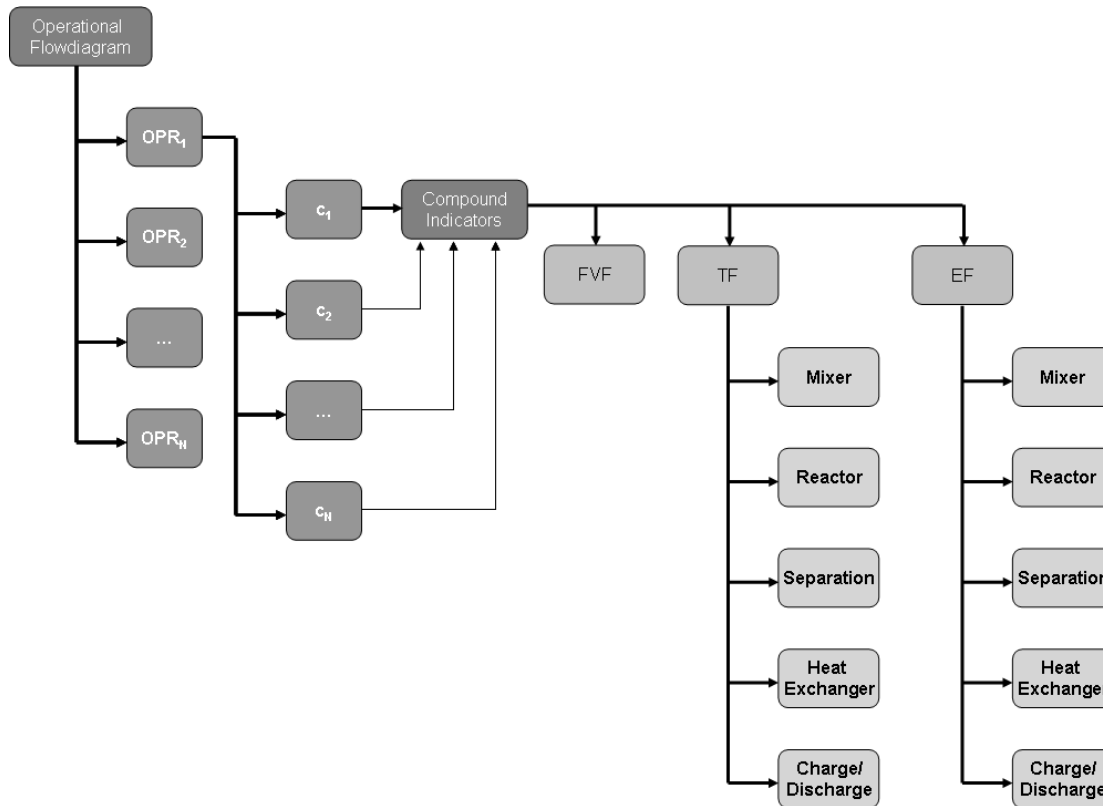
Where  $E_j$  is the energy consumed in operation  $j$ .

*High values of this indicator point to an operation consuming too much energy when compared to others.* This indicator also helps in identifying opportunities for heat integration and to trace the heat integration possibilities among different equipments/operations. This indicator should be reduced to improve the process and its value is given as a fraction.

**Compound Indicators**

A set of compound indicators, which allow the identification of the compound causing a bottleneck in a given operation, have been developed. There are three different compound indicators the Free Volume Factor (FVF), the Time Factor (TF) and the Energy Factor (EF). The TF and the EF are applied for each accumulation-path and their calculations are dependent on the type of operation, such as, mixing, reacting and separating operations.

Figure 3.35 summarizes the application of batch compound indicators.



**Figure 3.35:** Batch compound indicators - Summary

OPR- Operation; C- Compound; FVF: Free volume Factor; TF: Time Factor; EF: Energy Factor

As it can be seen from Figure 3.35, a operational flowdiagram includes a set of operations (OPR<sub>1</sub>, OPR<sub>2</sub>, ..., OPR<sub>n</sub>). For each operation the set of operational indicators is applied and the ones showing high potential for improvements are selected. The selected operations involve different compounds (c<sub>1</sub>, c<sub>2</sub>, ..., c<sub>n</sub>). The compound indicators (FVF, TF and EF) are applied to each compound in the respective operation. To identify the problems related to volume occupancy it is not necessary to take into consideration the type of operation. However, to identify bottlenecks in time and energy the type of operation has to be taken into consideration and consequently there is an indicator for each type of operation (see Figure 3.35).

***Free Volume Factor (FVF)***

This indicator gives the percentage of free volume compound to the total volume of the equipment, which is not occupied by the accumulation-path compound.

$$FVF_{j,c} = \frac{V_{eq} - \frac{M_{AP}^c}{\rho_c}}{V_{eq}} \quad \text{Eq (3.32)}$$

In Eq(3.32),  $V_{eq}$  is the equipment volume,  $j$  is the batch operation,  $M_{AP}^c$  is the mass of compound  $c$  with respect to the accumulation-path  $AP$  and  $\rho_c$  is the density of the compound  $c$ . *High values of this indicator indicate that the corresponding compound has a high contribution to the problem already identified by TFVF (equipment not filled in a high level) and consequently also point out to potential for improvements.* The indicator value is given as a fraction.

***Time Factor (TF)***

This indicator points out the compounds that are responsible for the time spent in a given operation. Tracing the compound, which is making the operation slow, it is possible to identify what can be done in order to improve the time for the corresponding operation. However, it is not possible to have only one indicator for all types of batch operation, since in each operation there are different properties/factors that could make the process slower. In the text below the compound indicators for each type of batch operation are explained.

- Mixer

When a mixing operation is taking place, the compound with the lower flowrate is the one that will define the time to achieve uniform mixing. The compounds with lower flowrates have more influence in the mixing operation time and consequently they are



the ones having the higher values for the TF indicator. The equation to calculate TF for mixing operations is the following.

$$TF_{j,c} = \frac{1}{\frac{F_{AP}^{(c)}}{\sum_{c=0}^C F_{AP}^c}} \times \frac{t_j}{\sum_{j=0}^J t_j} \quad \text{Eq (3.33)}$$

In Eq (3.33),  $F_{AP}^{(c)}$  is the flowrate of compound  $c$  for accumulation-path  $AP$ ,  $t_j$  is the time of operation  $j$ ,  $J$  is the total number of operations in the process and  $C$  is the total number of compounds involved in the mixing operation.

- Reactor

In a reactor operation, the influence of each compound in the operation time will be dependent on the compound type. Four categories of compounds are considered and for each category the indicator may have different values.

- *Desired Product*

The TF indicator for an accumulation-path corresponding to the desired product is not necessary because other compounds in the system affect its production time.

- *Inert/Solvent*

When the TF indicator is being calculated for an accumulation-path related to a solvent or an inert, TF is zero as these types of compounds do not affect the time of reaction, and consequently, their value is set to zero. When this compounds present an influence in the reaction rate they should be considered as raw materials.

- *Compound involved in the reaction*

Reactant: When the accumulation-path is representing a reactant, the indicator TF, should show if that reactant is a limiting reactant. Limiting reactants are those that determine the residence time, and consequently, the operation time. *In the TF*

expression, the accumulation-paths with limiting reactants present high values of  $TF$ , and consequently, they would need to be reduced.

**By-Product:** The by-products influence the reaction time when they are being produced from the same raw material as the desired product or when they are being produced directly from the desired product. This happens because they are consuming the raw materials from the desired product production which means a bigger residence time to achieve the same desired conversion. *If the  $TF$  value for the accumulation-paths of by-products has high values they will need to be reduced.*

Incorporating all the information from above a generic formula for  $TF$  calculation in reaction operations has been developed. This equation takes into account all the facts discussed before.

$$TF_{j,c} = y_1 \left( y_2 \left( \frac{k}{\frac{F_{AP}^{(c)}}{MW^{(c)}} \sum_{j=0}^J t_j} \times \frac{t_j}{\sum_{j=0}^J t_j} \right) + (1 - y_2) \times \underset{RM}{Max} \left( (1 - z_1) \frac{k}{\frac{F_{AP}^{(c)}}{MW^{(c)}} \sum_{j=0}^J t_j} \times \frac{t_j}{\sum_{j=0}^J t_j} \right) \right) \quad \text{Eq (3.34)}$$

In Eq(3.34),  $F_{AP}^{(c)}$  is the flowrate of accumulation-path  $AP$  for compound  $c$ ,  $t_j$  is the time of operation  $j$ ,  $J$  is the total number of operations in the process,  $MW^{(c)}$  is the molecular weight of compound  $c$ ,  $k$  is the reaction rate constant and  $\nu$  is the stoichiometric coefficient of compound  $c$ .  $y_1$  is the binary variable for the inert/solvent presence ( $y_1 = 0$  if a compound is a inert/solvent and  $y_1 = 1$  otherwise),  $y_2$  is the binary variable for the reactants/by-products presence ( $y_2 = 1$  if a compound is a reactant and  $y_2 = 0$  if a compound is a by-product).  $z_1$  is the fraction of raw materials mass that reacts to give our desired product.  $z_1$  is given by the following expression.

$$z_1 = \frac{MM_{DP}}{MM_{DP} + MM_{BP}} \quad \text{Eq (3.35)}$$

Where, MM is the molar flowrate of the desired product, *DP*, and the by-product *BP*. It is important to mention that when the reaction rate constant (*k*) is not known, it is set equal 1, in order to calculate TF indicator.

The term  $1-z_1$  (see Eq(3.34)) represents the measure of time that is spent in the production of the by-product. When  $z_1$  is close to 1, the TF for the by-product will be very similar to the TF of the reactant, which means that the reaction process is producing too much by-product (when compared to the desired product), and consequently, the by-product is responsible for the high TF value.

When TF is much bigger for a reactant, it indicates that this compound is the limiting reactant, causing in this way the increase in the reaction time. To improve the reaction operation focus needs to be made on this reactant to generate new sustainable design alternatives.

- Heat Exchanger

When a heat exchanger operation is taking place, the compound with the higher heat capacity is the one that will define the time for uniform heating. The equation to determine TF for heat exchanger operations is given by,

$$TF_{j,c} = \frac{F_{AP}^{(c)} \times Cp^{(c)}}{\sum_{c=0}^C F_{AP}^c \times Cp^{(c)}} \times \frac{t_j}{\sum_{j=0}^J t_j} \quad \text{Eq (3.36)}$$

In Eq(3.36),  $F_{AP}^{(c)}$  is the flowrate of compound *c* for accumulation-path *AP*,  $t_j$  is the time of operation *j*, *J* is the total number of operations in the process, *C* is the total number of compounds involved in the heat exchange operation and *Cp* is the heat capacity. The compound with the higher factor of  $F_{AP}^{(c)} \times Cp^{(c)}$  will have higher TF values as they are

the ones that will consume more energy and consequently will be responsible for a bigger time consumed.

- Separation

A separation process transforms a mixture of compounds into two or more distinct products in order to recover a specific compound. Specific properties of the separated compounds need to be different in order to perform the desired separation. These properties are called the inherent separation properties (ISP). *The time consumed in the separation process is high when the ISP values of the compounds being separated are similar.* In this way the compounds that have ISP values closer to the compound that should be recovered, are the ones that have more influence on the time spent in the separation operation.

Based on this definition, the TF for separation operations is derived as,

$$TF_{j,c} = \frac{F_{AP}^{(c)}}{|ISP^R - ISP^c|} \times \frac{t_j}{\sum_{j=0}^J t_j} \quad \text{Eq (3.37)}$$

In Eq(3.37),  $F_{AP}^{(c)}$  is the flowrate of accumulation-path  $AP$  for compound  $c$ ,  $t_j$  is the time of operation  $j$ ,  $J$  is the total number of operations in the process,  $ISP^R$  is the inherent separation property value for the recovery compound and  $ISP^C$  is the inherent separation property value for any compound  $c$ .

The ISP value to be used in Eq(3.37) to calculate TF can be taken from Jaksland *et al.* (1996) who classified separation techniques in terms of their corresponding separation related property (see appendix B).

- Charge / Discharge / Clean

For this set of operations, the operational times are not influenced by any of the compounds. Consequently, the compound indicators are not necessary for these operations and only operational indicators are calculated to them.

*Summarizing, for all types of operations, high values of TF show high potential for improvements and consequently they should be reduced. For all operations, the compound with the highest TF value is the one that most affect the high OTF values (see Eq( 3.30)).*

### **Energy Factor (EF)**

This indicator points out the compounds that are responsible for the energy consumed in a given batch operation. For EF calculations it is also not possible to use a generic indicator expression for all types of batch operations. Therefore, different indicator expressions have been developed for each type of operation, which are explained below.

- **Mixer**

For the mixing operation, the energy consumed is a consequence of the energy spent by the impeller. The energy spent in the mixing operation increases as the differences in densities and/or the viscosities of the compounds increase. The equation to determine EF for mixing operations is given by.

$$EF_{j,c} = \frac{F_{AP}^{(c)} \sum_h^H \Delta\rho_h + F_{AP}^{(c)} \mu^{(c)}}{\sum_n^N F_{AP}^n \sum_h^H \Delta\rho_h + \sum_n^N F_{AP}^n \mu^n} \times \frac{E_j}{\sum_{j=0}^J E_j} \quad \text{Eq (3.38)}$$

Where  $F_{AP}^{(c)}$  is the flowrate of accumulation-path AP for compound c,  $E_j$  is the energy of operation j, h is a pair of compounds, H is the total number of compound pairs, n is a compound and N is the total number of compounds,  $\mu$  is the viscosity and  $\Delta\rho_h^{(c,n)}$  is the difference between the density of compound c and n represented as the compounds pair h ( $\Delta\rho_h^{(c,n)} = |\rho^c - \rho^n|$ ). It is important to mention that when the density and/or

viscosity of the compounds are not available, then the corresponding term in Eq(3.38) is neglected, in order to calculate EF indicator.

*This indicator points to the compound with the higher flowrate and a bigger density/viscosity difference compared to the other compounds, and consequently, points to the compound indicating a higher potential for improvement.*

- Reactor

The energy spent in a reactor is directly proportional to the heat of the reaction. Therefore, determine the influence of the compounds, it is necessary to correlate the compounds with respect to the heat of the reaction.

- *Desired Product*

The EF indicator for an accumulation-path corresponding to the desired product is not needed since other compounds in the system affect its production.

- *Inert/Solvent*

The EF indicator for an accumulation-path related to a solvent or an inert compound, is given by:

$$FE_{Cp} = \frac{F_{AP}^{(c)} \times Cp^{(c)} \times (T_{Reac} - T_{Ent})}{M_{React} \Delta H_R + \sum_c^C F_{AP}^{(c)} \times Cp^{(c)} \times (T_{Reac} - T_{Ent})} \quad \text{Eq (3.39)}$$

In Eq(3.39),  $F_{AP}^{(c)}$  is the flowrate of accumulation-path AP for compound c, Cp is the heat capacity, C is the total number of compounds present in the reactional operation,  $T_{Reac}$  is the temperature of the reaction,  $T_{Ent}$  is the entry temperature,  $M_{React}$  is the mass that reacted,  $\Delta H_R$  is the heat of the reaction and  $FE_{Cp}$  is the fraction of energy that is spent to heat/cool compound c till  $T_{Reac}$ .  $FE_{Cp}$  points to

the fraction of energy that is spent to heat/cool the respective compound until the reaction temperature.

▪ *Compounds involved in the reaction*

For the compounds involved in the reaction, the energy consumption is due to two parameters: the heat of the reaction and the energy spent to heat/cool the respective compound to the reaction temperature. Consequently, a new term representing the fraction of energy consumed by a compound in the heat of reaction is added.

$$FE_{\Delta H_R} = \frac{F_{AP}^{(c)} \times \Delta H_R}{M_{React} \Delta H_R + \sum_c F_{AP}^{(c)} \times Cp^{(c)} \times (T_{Reac} - T_{Ent})} \quad \text{Eq (3.40)}$$

In Eq(3.40),  $F_{AP}^{(c)}$  is the flowrate of accumulation-path  $AP$  for compound  $c$ ,  $Cp$  is the heat capacity,  $C$  is the total number of compounds present in the reactional operation,  $T_{Reac}$  is the temperature of the reaction,  $T_{Ent}$  is the entry temperature,  $M_{React}$  is the mass that reacted,  $\Delta H_R$  is the heat of the reaction and  $FE_{\Delta H_R}$  is the fraction of energy that is spent from the heat of the reaction by compound  $c$ .

The heat of the reaction is given by the following equation.

$$\Delta H_R = \sum \Delta H_f^{Products} - \sum \Delta H_f^{Reactants} \quad \text{Eq (3.41)}$$

In Eq(3.41),  $\Delta H_R$  is the heat of the reaction and  $\Delta H_f$  is the formation heat.

Using Eq(3.43), the following observations can be made:

**Endothermic:** If  $\Delta H_R > 0$ , then  $\sum \Delta H_f^{Products} > \sum \Delta H_f^{Reactants}$ . Some energy should be added to the system. In this case the products with higher energy or the reactants

with the lower energy will be the ones with more effect in the energy exchanged and consequently in the EF indicator.

Exothermic: If  $\Delta H_R < 0$ , then  $\sum \Delta H_f^{Products} < \sum \Delta H_f^{Reactants}$ . Some energy should be released to the system. In this case the products with lower energy or the reactants with the higher energy will be the ones with more effect in the energy exchanged and consequently in the EF indicator.

The generic expression for the EF indicator Eq(3.42) becomes therefore,

$$EF_{j,c} = y_1 FE_{cp} \times \frac{E_j}{\sum_{j=0}^J E_j} + (1 - y_1) \left( FE_{cp} + FE_{\Delta H_R} (y_3 ((1 - y_2)g + y_2(1 - g)) + (1 - y_3)((1 - y_2)(1 - g) + y_2(g))) \right) \times \frac{E_j}{\sum_{j=0}^J E_j}$$

Eq (3.42)

In Eq(3.42),  $F_{AP}^{(c)}$  is the flowrate of accumulation-path AP for compound c,  $E_j$  is the energy of operation j,  $\Delta H_R$  is heat of the reaction,  $\Delta H_f$  is the heat of formation and g is given by:

$$g = \frac{\Delta H_f}{\sum_{c=0}^C \Delta H_f^{(c)}}$$

Eq (3.43)

In Eq(3.42) the binary variable  $y_1$  represents if a compound is a solvent/inert ( $y_1 = 1$  if a compound is a inert/solvent and  $y_1 = 0$  otherwise). The binary variable  $y_2$  represents if a compound in an accumulation-path is a reactant or a product ( $y_2 = 1$  if a compound is a reactant and  $y_2 = 0$  if a compound is a by-product). The binary variable,  $y_3$ , is used to



define if the reaction is exothermic or endothermic ( $y_3 = 0$  if the reaction is exothermic and  $y_3 = 1$  if the reaction is endothermic).

- Heater

When a heat exchanger operation is taking place, the compound with the higher heat capacity is the one that defines the energy consumption for a uniform heating. The equation to determine EF for heat exchanger operations is similar to the expression for the TF, considering that the time and the energy spent in a heat exchange operation are interrelated.

$$EF_{j,c} = \frac{F_{AP}^{(c)} \times Cp^{(c)}}{\sum_c F_{AP}^{(c)} \times Cp^{(c)}} \times \frac{E_j}{\sum_{j=0}^J E_j} \quad \text{Eq (3.44)}$$

In Eq(3.44),  $F_{AP}^{(c)}$  is the flowrate of accumulation-path  $AP$  for compound  $c$ ,  $E_j$  is the energy of operation  $j$ ,  $J$  is the total number of operations,  $C$  is the total number of compounds involved in the heat exchange operation and  $Cp$  is the heat capacity. The compound with the higher factor of  $F_{AP}^{(c)} \times Cp^{(c)}$  has higher EF provided they are the ones that consume the most energy.

- Separation

When a separation operation needs utilities, it indicates that some heat/energy needs to be exchanged, which consequently means that a property is related to the exchanged heat/energy. These properties can be called Inherent Energy Properties (IEP). The properties are dependent on the type of the separation technique used. When the separation involves phase change the property that must be used to calculate EF is the enthalpy variation during the phase change ( $\Delta H_{Vap}$ ,  $\Delta H_{Sub}$ , etc), Uerdingen *et al.* (2002). When there is no phase change, the procedure proposed by Jaksland *et al.* (1996) is adopted to determine the IEP values (see appendix B). An expression for EF indicator for separation operations is given by:

$$EF_{j,c} = \frac{F_{AP}^{(c)} \times IEP^c}{\sum_c F_{AP}^{(c)} \times IEP^c} \times \frac{E_j}{\sum_{j=0}^J E_j} \quad \text{Eq (3.45)}$$

In Eq(3.45),  $F_{AP}^{(c)}$  is the flowrate of accumulation-path  $AP$  for compound  $c$ ,  $E_j$  is the energy of operation  $j$ ,  $J$  is the total number of operations in the process,  $IEP^c$  is the inherent energy property value for the compound  $c$ .

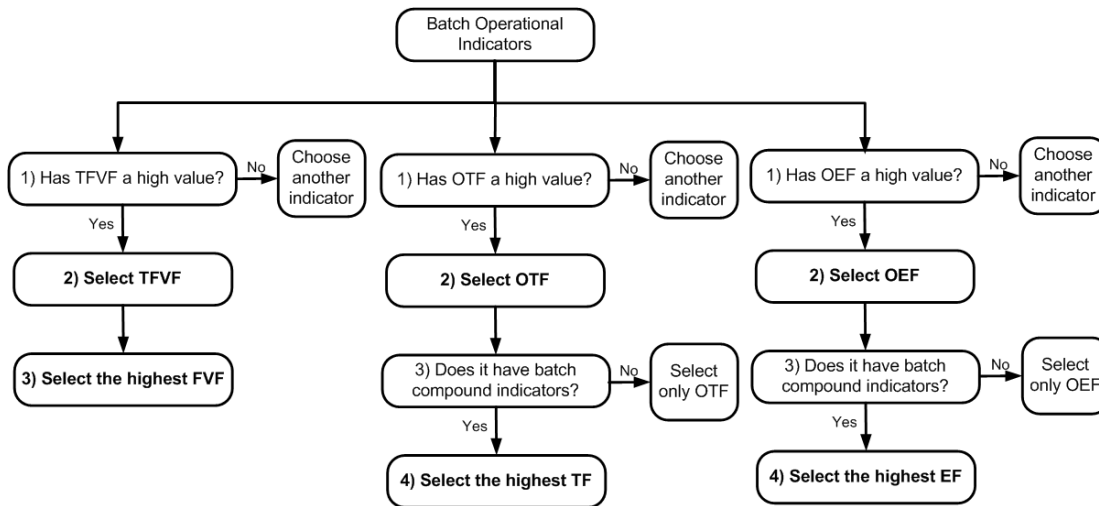
*Summarizing, in all operations, high values of EF show high potential for improvement, and consequently, they should be reduced. For all operations, the compound with the higher EF value is the one responsible for the high OEF values (see Eq(3.31))*

### ***Sustainability Metrics and Safety Indices***

The safety of the process is taken into account through the calculation of the inherently safety index, developed by Heikkilä, (1999). The sustainability of the process is determined by the use of the sustainability metrics defined by the Institution of Chemical Engineers by Azapagic *et al.*, (2002). For further details about the safety indices and the sustainability metrics see sections 3.2.3.2 and 3.2.3.3, which describe the application of these parameters in the methodology.

### 3.4.5 Step 4- Indicator Sensitivity Analysis (ISA algorithm)

In this step the target indicators are determined using the ISA algorithm (see section 3.2.4). To apply this algorithm the indicators having the highest potential for improvements are identified first. Then an objective function such as the gross-profit or the process total cost is specified. A sensitivity analysis is then performed to determine the indicators that allow the largest positive (for profit) or negative (for cost) change in the objective function. The most sensitive indicators are selected as targets for improvements (see section 3.2.4). The batch indicators are used to complement the information given by the principal indicators. The analysis of the batch indicators is done in a similar way as the energy indicators (see section 3.2.4 energy indicators). Guidelines are given to select the batch indicators presenting high potential for improvements (see Figure 3.36)



**Figure 3.36:** Flowdiagram with the guidelines for the selection of batch indicators

### 3.4.6 Step 5- Design Sensitivity Analysis

A sensitivity analysis with respect to the operational (parameters) variables, which influence the target indicators, is performed. The analysis identifies the operational variables that need to be changed to improve the process in the desired direction (See Section 3.2.5).

### 3.4.7 Step 6- Generation and Evaluation of new design alternatives

Using the information related to the indicators applied for open- and closed paths, synthesis algorithms are applied to generate new design alternatives (see section 3.2.6). For batch processes a flowdiagram is presented with suggestion to improve the batch indicators (see Figure 3.37).

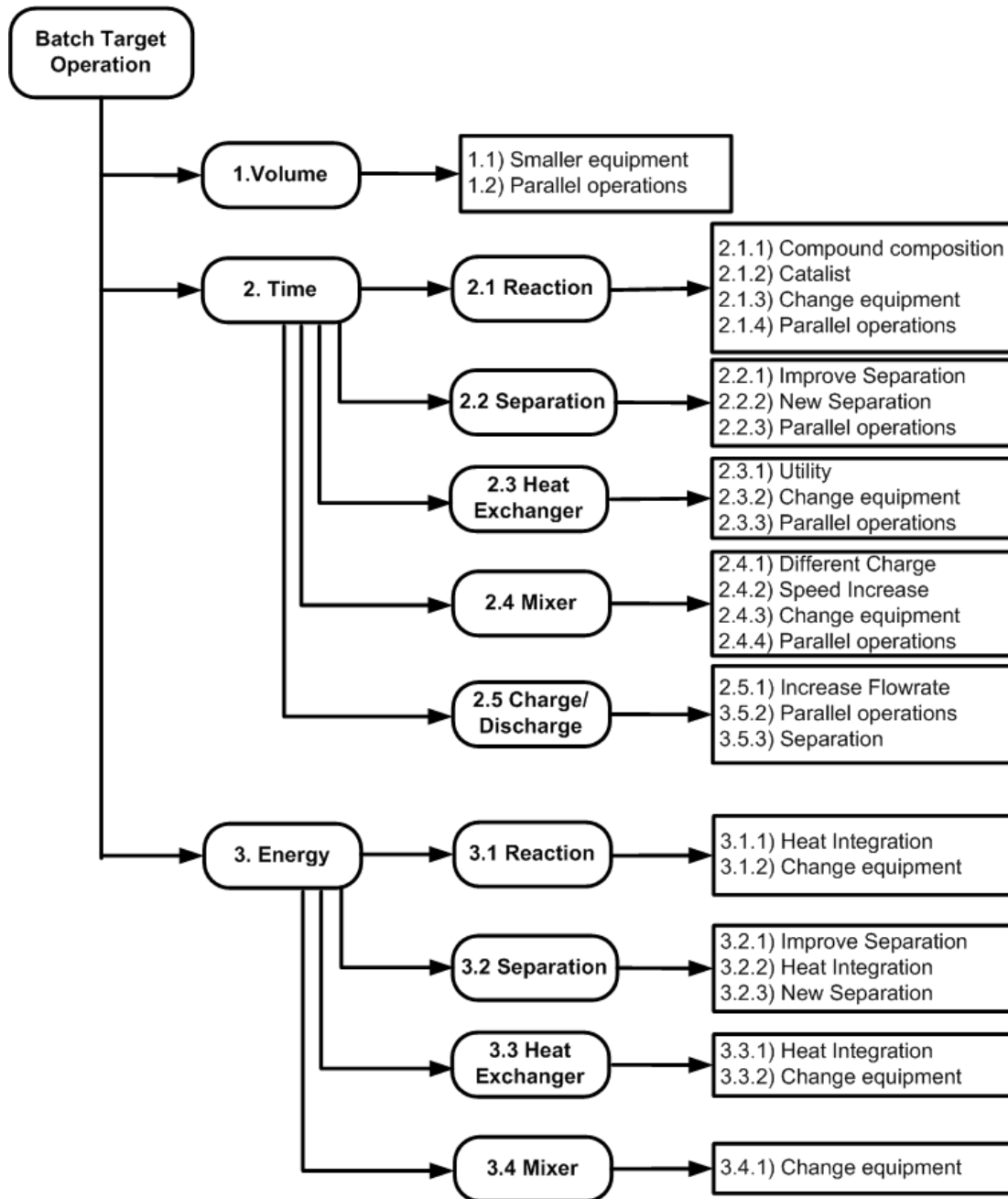


Figure 3.37: Workflow for generation of alternatives using batch indicators

## 3.5 Illustration of the methodology for batch processes – Laundry Case Study

### 3.5.1 Process description

This case study is based on data provided by a laundry in Frederiksborg, Denmark (Wulff et al., 2007). In this laundry they have three types of washing machines: washing tunnel, three small batch machines and three Milnors. The washing tunnel had already been optimized and the small batch machines do not use external water during the operation sequence. Consequently, the study presented here is based on the Milnor machines. In each Milnor process there is a sequence of 5 operations: Pre-Wash, Principal Wash, Cooling, Rinse and Last Rinse.

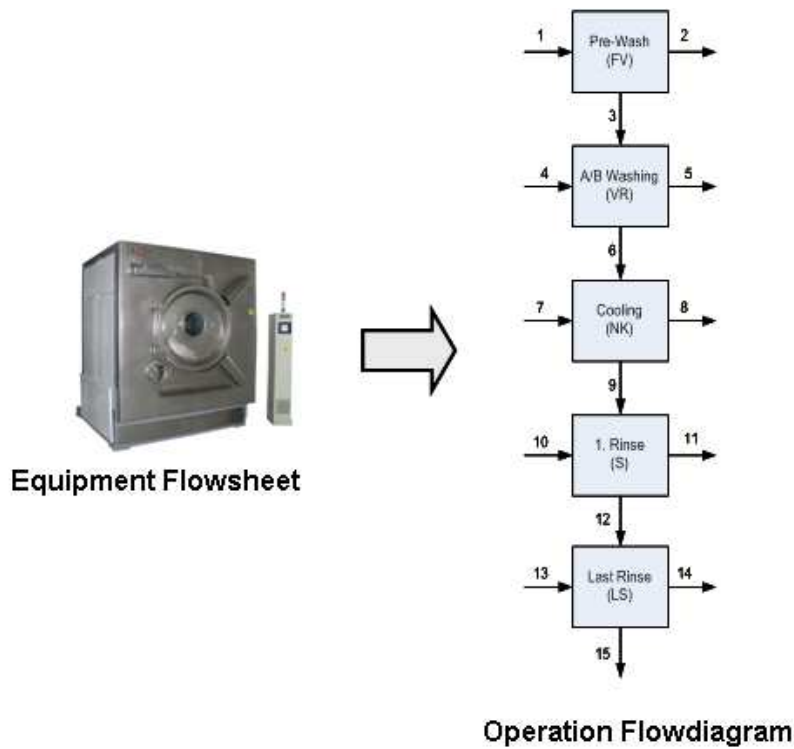
### 3.5.2 Methodology Results

#### ***Step 1: Data Collection***

The required detailed process data for the laundry process given by Wulff et al., 2007 has been used. All the data needed for the indicator calculation, such as prices, has also been taken from Wulff et al., 2007. The required data to apply *SustainPro* to the Laundry case study can be found in Appendix A2.

#### ***Step 1A: Transform equipment flowsheet in an operational flowdiagram***

Using the rules presented in section 3.4.2 the equipment flowsheet has been transformed in the operational flowdiagram. The equipment flowsheet consists of only one unit, the Milnor washing machine. However, it operates in a sequence of five operations and consequently the operational flowdiagram is the sequence of those operations (see Figure 3.38).



**Figure 3.38:** Equipment Flowsheet and operational flowdiagram- Laundry case study

**Step 2: Flowsheet decomposition**

Within the five operations there are 20 streams and 1 compound, water. For this case study the flowsheet decomposition generated 0 mass closed-paths, 20 mass open-paths, 0 energy closed-paths 11 energy open-paths and 5 accumulation-paths (see Table 3.31, Table 3.32 and Table 3.33).

**Table 3.31: Mass Open-paths- Laundry Case Study**

Open path	Compound	OP streams						Flow-rate (kg/h)
OP 1	H2O	S1	S2					3.41
OP 2	H2O	S1	S3	S5				0.61
OP 3	H2O	S1	S3	S6	S8			0.01
OP 4	H2O	S1	S3	S6	S9	S11		0.00
OP 5	H2O	S1	S3	S6	S9	S12	S14	0.00
OP 6	H2O	S1	S3	S6	S9	S12	S15	0.00
OP 7	H2O	S4	S5					34.39
OP 8	H2O	S4	S6	S8				0.58
OP 9	H2O	S4	S6	S9	S11			0.03
OP 10	H2O	S4	S6	S9	S12	S14		0.00
OP 11	H2O	S4	S6	S9	S12	S15		0.00
OP 12	H2O	S7	S8					8.77
OP 13	H2O	S7	S9	S11				0.51
OP 14	H2O	S7	S9	S12	S14			0.07
OP 15	H2O	S7	S9	S12	S15			0.01
OP 16	H2O	S10	S11					3.49
OP 17	H2O	S10	S12	S14				0.47
OP 18	H2O	S10	S12	S15				0.07
OP 19	H2O	S13	S14					3.49
OP 20	H2O	S13	S15					0.54

**Table 3.32: Energy Open-paths - Laundry Case Study**

Open-path	EOP streams			Flow-rate (GJ/h)
OP 1	S1	S2		$4.96 \times 10^{-5}$
OP 2	S1	S3	S5	$9.09 \times 10^{-6}$
OP 3	S4	S5		$-7.29 \times 10^{-4}$
OP 4	S4	S6	S8	$-1.43 \times 10^{-5}$
OP 5	S7	S8		$-1.17 \times 10^{-5}$
OP 6	S13	S14		$-8.03 \times 10^{-5}$
OP 7	S13	S15		$-1.25 \times 10^{-5}$
OP 8	H FV	S2		$4.98 \times 10^{-5}$
OP 9	H FV	S3	S5	$9.13 \times 10^{-6}$
OP 10	H VR	S5		$7.60 \times 10^{-3}$
OP 11	H VR	S6	S8	$1.49 \times 10^{-4}$

**Table 3.33: Accumulation-paths - Laundry Case Study**

AP	Operation	Compound	Flow(Kg/s)
1	FV	H2O	0.006
2	VR	H2O	0.022
3	NK	H2O	0.014
4	S	H2O	0.007
5	LS	H2O	0.007



**Step 3.1: Calculate mass, energy and batch indicators**

For the entire set of flow-paths, the full-set of indicators have been calculated. In Table 3.34 the mass indicators values are listed. The energy indicators are not listed here because they did not show any significant potential for improvement. The batch indicators are presented in Table 3.35.

**Table 3.34: Mass Indicators - Laundry Case Study**

OP	Path	Compound	Flowrate (kg/h)	MVA (10 <sup>3</sup> \$/yr)	EWC (10 <sup>3</sup> \$/yr)	TVA (10 <sup>3</sup> \$/yr)
OP 1	S1-S2	H2O	3.41	-182.50	0.00	-182.50
OP 2	S1-S5	H2O	0.61	-32.86	0.40	-33.27
OP 3	S1-S8	H2O	0.01	-0.55	0.01	-0.56
OP 4	S1-S11	H2O	0.00	-0.03	0.00	-0.03
OP 5	S1-S14	H2O	0.00	0.00	0.00	0.00
OP 6	S1-S15	H2O	0.00	0.00	0.00	0.00
OP 7	S4-S5	H2O	34.39	-1840.34	0.00	-1840.34
OP 8	S4-S8	H2O	0.58	-30.81	0.00	-30.81
OP 9	S4-S11	H2O	0.03	-1.78	0.00	-1.78
OP 10	S4-S14	H2O	0.00	-0.24	0.00	-0.24
OP 11	S4-S15	H2O	0.00	-0.04	0.00	-0.04
OP 12	S7-S8	H2O	8.77	-469.59	0.00	-469.59
OP 13	S7-S11	H2O	0.51	-27.15	0.00	-27.15
OP 14	S7-S14	H2O	0.07	-3.64	0.00	-3.64
OP 15	S7-S15	H2O	0.01	-0.57	0.00	-0.57
OP 16	S10-S11	H2O	3.49	-186.73	0.00	-186.73
OP 17	S10-S14	H2O	0.47	-25.07	0.00	-25.07
OP 18	S10-S15	H2O	0.07	-3.89	0.00	-3.89
OP 19	S13-S14	H2O	3.49	-186.73	0.00	-186.73
OP 20	S13-S15	H2O	0.54	-28.96	0.00	-28.96

**Table 3.35: Batch Indicators - Laundry Case Study**

AP	Operation	Compound	Flow(kg/s)	TFVF	OTF	OEF
1	FV	H2O	0.67	0.98	0.156	0.013
2	VR	H2O	2.50	0.86	0.364	0.855
3	NK	H2O	1.87	0.96	0.169	0.132
4	S	H2O	0.67	0.98	0.156	0
5	LS	H2O	0.67	0.98	0.156	0

Since there is only water in the process, the batch compound indicators were not applied for this case study. No further information will be given with the compound

indicators calculation, because the only compound responsible for the bottlenecks presented by the operational indicators is the water.

**Step 3.2 and Step 3.3 Calculate Safety Indices and Sustainability Metrics**

The sustainability metrics as well as the safety index were also calculated and their values are presented in Table 3.37, after step 6 (for further details see Appendix A2).

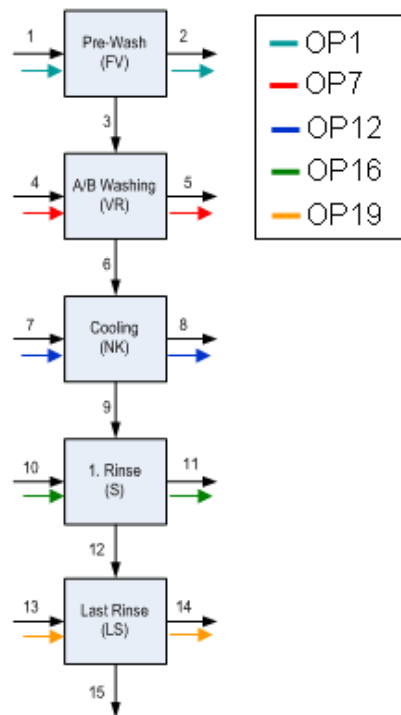
**Step 4: Indicator Sensitivity Analysis (ISA)**

For this case study the indicators selected as possible target indicators were the MVA for OP 1, 7, 12, 16 and 19. They presented very negative values, which means that a lot of money has been spent with the entrance and the exit of the water. In order to determine the indicators which present higher influence on the process cost, the ISA algorithm has been applied. In Table 3.36 the scores, obtained through the ISA algorithm for each indicator are given. Regarding the batch indicators, it can be seen that operations VR and NK have very high OTF values when compared to the other operations in the process. Consequently, they are the most sensitive indicators. The high OTF value indicates that these two operations are spending too much time in their execution, and consequently, their operational time should be reduced. The OTF for AP2 and AP3 are the target indicators.

**Table 3.36:** ISA algorithm results - Laundry Case Study

Path	Indicator	Scores
OP 7	MVA	12
OP 1	MVA	8
OP 12	MVA	3
OP 16	MVA	2
OP 19	MVA	1

Figure 3.39 shows the representation of the selected indicators in the respective open-paths.



**Figure 3.39:** Selected paths for the Laundry case study

**Step 5: Design Sensitivity Analysis**

Through a sensitivity analysis the operational parameters influencing the target indicators were analyzed and it has been found that the flowrates of OP 1, 7, 12, 16 and 19 are the most significant parameters. For the batch target indicators the most sensitive parameter has been found to be the temperature of the cooling water used in NK operation. Due to operational constrains, it was found that the operational parameters that influence OTF in VR operation cannot be improved because they are already optimized.

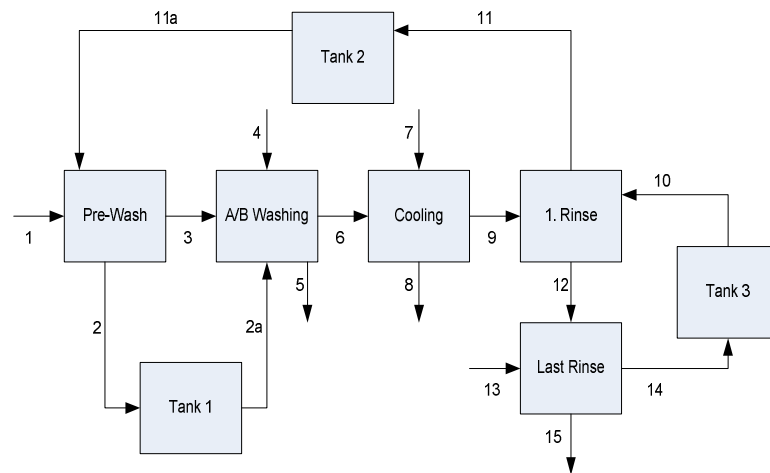
**Step 6: Generation and Evaluation of new design alternatives**

To generate new sustainable design alternative it is necessary to verify in which category the operational parameters are included (see section 3.2.6 and section 3.4.7). In this case, the operational parameters (flowrates of OP 1, 7, 12, 16 and 19) are in the category of reducing an open-path flowrate. This indicates that a recycle of water needs

to be considered. Due to some operational constraints described in Wullf et al., 2007, the flowrate of water coming from OP7 and OP12 cannot be recycled. All the other open-paths flowrates were recycled and consequently reduced.

Regarding the batch operation indicators, the OTF for NK can be improved changing the utility reducing the temperature of the water coming into the operation (decrease to 283K). The operation time decreases with this modification and consequently the OTF is reduced.

The new sustainable design alternative consists of recycling three streams as well as using colder water for the cooling operation. This new design alternative can be seen in the new operational flowdiagram presented in Figure 3.40.



**Figure 3.40:** Operational flowdiagram with the new design alternative-Laundry case study

The new alternative shows the reduction of the operational costs by 42% and the improvement of the water metrics by 21%. All the other parameters remain constant (see Table 3.37). The target indicators have been improved by 100% and the batch indicators are improved by 5% (see Table 3.38).

**Table 3.37:** Comparison of the performance criteria between the base case and the new sustainable design alternative - Laundry Case Study

Metrics	Initial	Final	Improvement
Total Net Primary Energy Usage rate (GJ/y)	77.26	77.26	0%
% Total Net Primary Energy sourced from renewable	1%	1%	0%
Net water consumed (kg)	56.46	44.39	21%
WAR	0	0	0%
Safety Index	9	9	0%
Costs (\$/yr)	-2912770	-1701015	42%

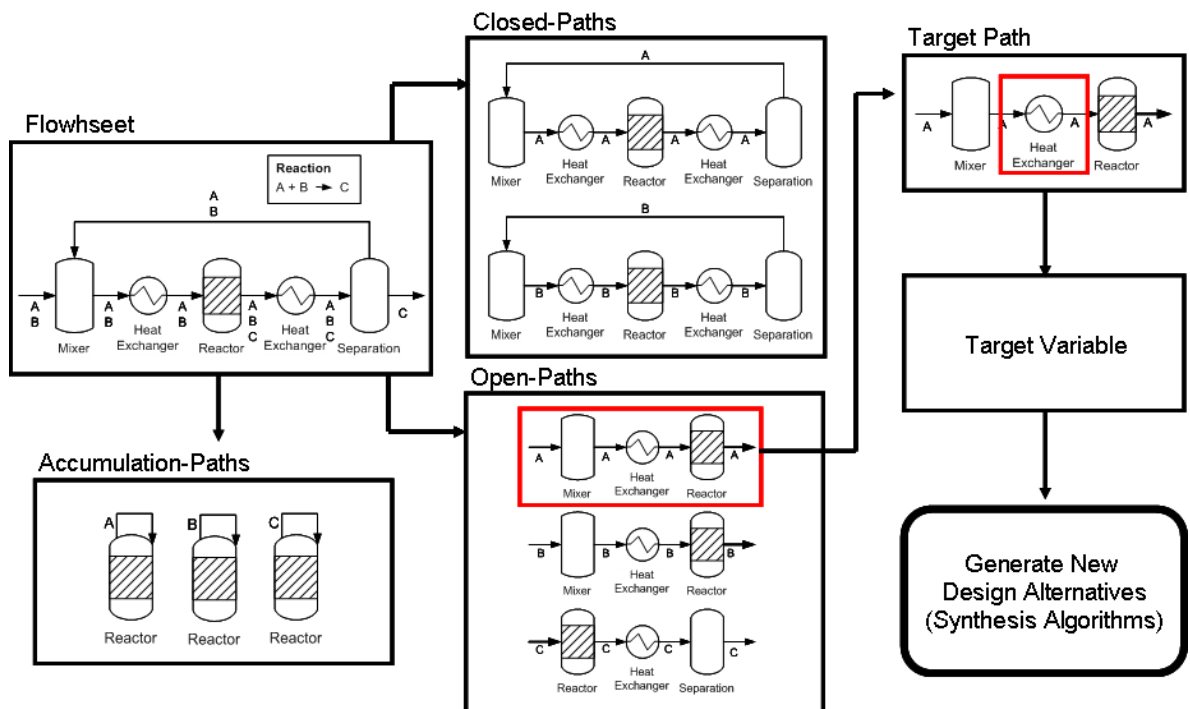
**Table 3.38:** Improvements in target indicators - Laundry Case Study

Target Indicator	Initial	Final
MVA – OP1	-1.82 x 10 <sup>5</sup> \$/y	0 \$/y
MVA – OP16	-1.86 x 10 <sup>5</sup> \$/y	0 \$/y
MVA – OP19	-1.86 x 10 <sup>5</sup> \$/y	0 \$/y
OTF – AP 3	0.17	0.16

### 3.6 Conclusions

A generic methodology for sustainable process design has been presented. The proposed methodology is able to deal with any type of process, operating in continuous, batch and/or semi-continuous mode. The methodology has been illustrated with two case studies (MTBE production- continuous process and Laundry- batch process).

Figure 3.41 presents a summary of the methodology presented in this chapter.

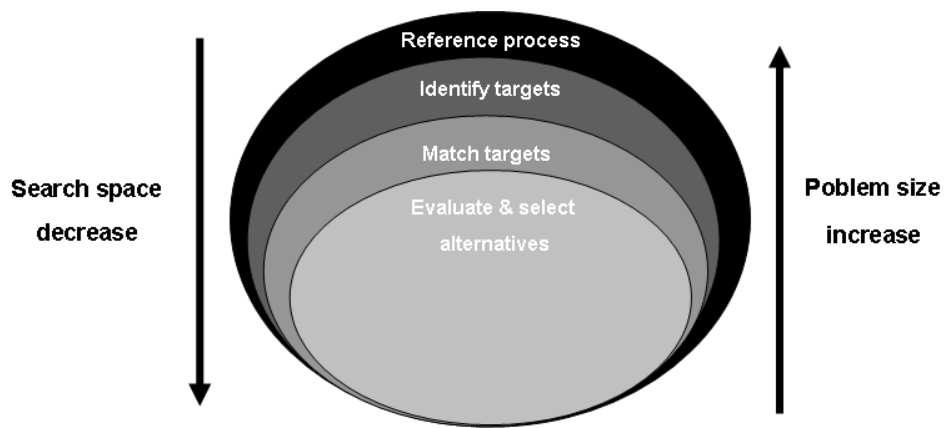


**Figure 3.41:** Summary of the methodology for sustainable process design

The methodology starts with a base case, with the respective flowsheet. Then the flowsheet decomposition takes place and consequently the initial flowsheet is broken down in smaller areas (open-, closed- and accumulation-paths), which correspond to a given compound. To those areas, a set of indicators is applied. Comparing their values the ones presenting the highest potential for improvement are selected. At this point only a fraction of the initial flowsheet is still being studied. A design sensitivity

analysis is performed which allows the determination of a target variable. Finally a new alternative can be generated to improve the selected target variable.

The methodology breaks down the process moving towards the critical point, reducing the search space and decreasing the problem size. Through this procedure the process is screen, analyzed and the critical points are identified. This methodology allows to manage the complexity, in a generic and systematic manner, making the retrofit problem an easier and accurate task (see Figure 3.42).



**Figure 3.42:** Managing the complexity- Methodology for sustainable process design

## 4. Software - *SustainPro*

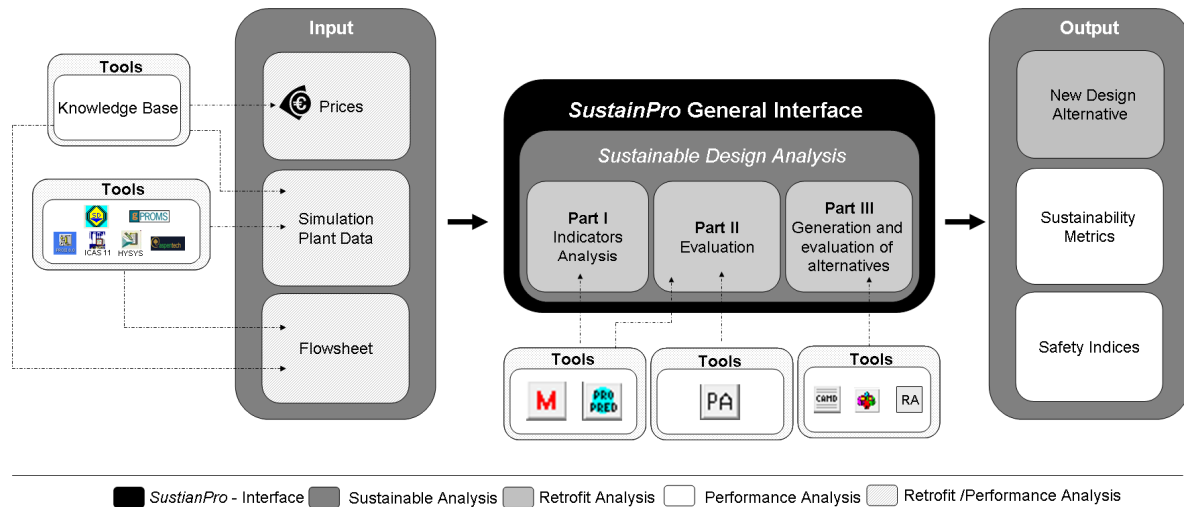
### 4.1 Introduction

A software, which applies the methodology presented in chapter 3 has been developed. In this chapter the implementation of the software (section 4.2), the architecture (section 4.3), the supporting tools (section 4.4) and the main features of the software (section 4.5) are described and discussed. A simple case study about acetone-chloroform separation is presented to illustrate the application of the software (section 4.6). General conclusions are presented in the end of the chapter (section 4.7).

### 4.2 *SustainPro* Implementation

*SustainPro* is an *Excel* based software, divided into 21 different *Excel* sheets, where two of the *Excel* sheets are Principal Menus, one with options for importing and exporting data and another to guide the user through the methodology steps (see architecture section). The remaining *Excel* sheets represent the different steps and sub-steps of the methodology presented in chapter 3. Figure 4.1 gives an overview about the methodology implementation in *SustainPro*.





**Figure 4.1:** Implementation of the methodology in a software

As shown in Figure 4.1 the basis of the software is the general interface presented in an Excel format. *SustainPro* receives information coming from the input data (Prices, Simulations results or Plant Data and the process flowsheet), performs the design sustainability analysis and finishes giving the results (output). The sustainability analysis has been divided in three parts, Part I – Indicator analysis, Part II – Evaluation and Part III- Generation and comparison of new alternative. Some supporting tools are used in each part of the analysis, such as properties database, (CAPEC Database, Nielsen *et. al.*, (2001)), properties prediction tools (ProPred, Marrero and Gani, (2001)) and tools for process synthesis (ProCAMD, Harper and Gani, (2000) and CAPSS, Jacksland *et al.*, (1995)). PA-WAR tool is used to apply the WAR algorithm analysis. In *SustainPro* implementation, the external tools use information provided by *SustainPro*, giving, after their application, important information back to *SustainPro*.

### ***Code Implementation***

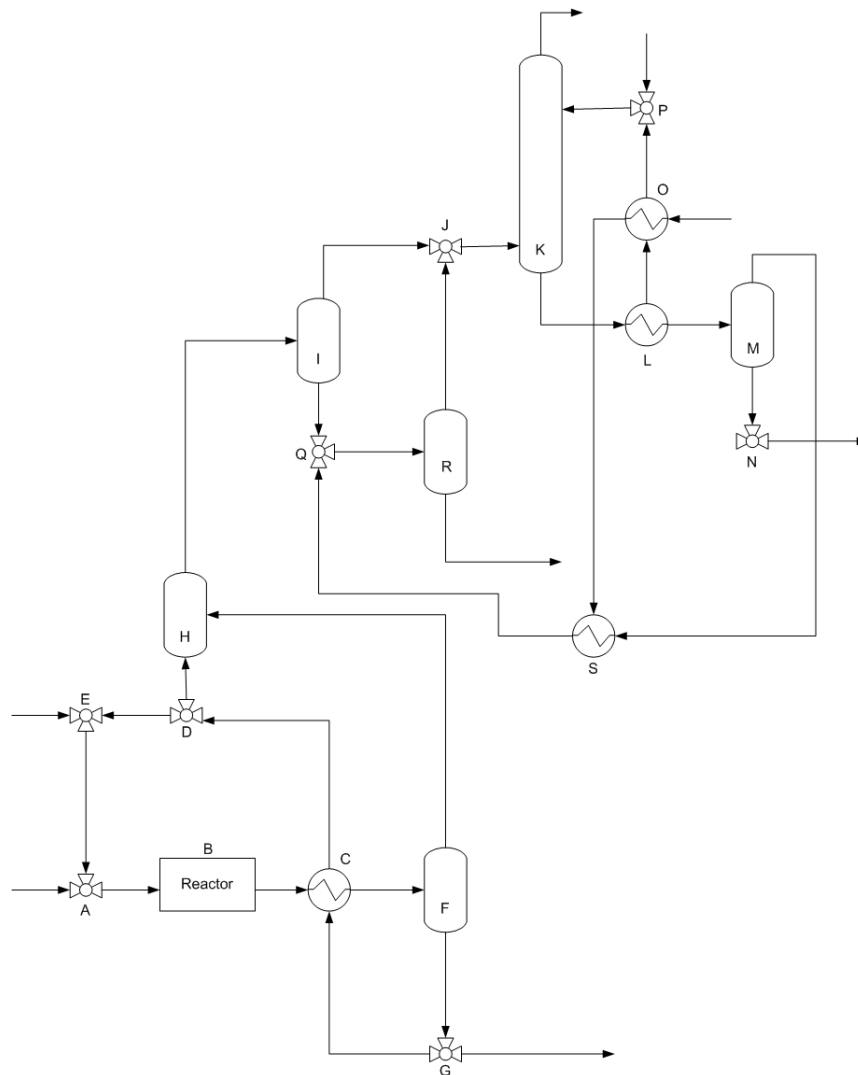
The methodology has been implemented in Visual Basic 6.0 (VB). This program has been selected because it can use *Excel* interface.

The first step to implement this algorithm in VB was to create a code to represent the process flowsheet. The program needs to have information about the connections

between the units in a given flowsheet. *SustainPro* code uses a design structure matrix (DSM) (Yassin, A., 2006) to translate the flowsheet information. This matrix is a binary matrix (the values are only 0 and 1). The number 1 in this matrix represents the edges between the units and 0 represents the independence between units.

For a better understanding of this implementation an example is given for the partitions determination based on the algorithm described in Figure 3.6.

The flowsheet used to exemplify the implementation is presented in Figure 4.2.



**Figure 4.2:** Flowsheet of the example for the partition determination– *SustainPro* implementation

The representation of the flowsheet presented in Figure 4.2 using a DSM matrix is shown in Figure 4.3.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
A	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
B	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
D	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
E	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0
G	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
I	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0
J	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
K	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
L	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0
M	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1
N	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1
P	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
Q	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
R	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0

**Figure 4.3:** DSM matrix describing the flowsheet presented in Figure 4.2

Through this matrix, *SustainPro* has the information about the connections between the units and consequently it is able to determine the partitions involved in the process. The code used to determine the partitions within the flowsheets follows the algorithm described in Figure 3.6. It manipulates the matrixes in such a way that all the partitions can be obtained.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
A	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
B	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
D	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
E	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0
G	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
I	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0
J	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
K	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
L	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0
M	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1
N	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1
P	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
Q	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
R	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0

Figure 4.4: First DSM matrix to the partition determination

Following the algorithm described in Figure 3.6, the first node needs to be selected, in this case unit A (first row Figure 4.4). The algorithm searches for connections of that unit with other units. It can be seen that in the first row a connection between unit A and B is available (1 in the matrix). Then B should be analysed to verify if any connection is available. To search connections of unit B with other units, second row should be followed. It is possible to see that B has a connection with C (1 in the matrix). Row three has to be studied now to verify if C has any other connection. This procedure should be taken until a unit that has already been searched appears again. From the previous matrix it is possible to see that E has a connection with A, which was the first element to be studied. Consequently there is a loop and a partition has been found. These rows and columns should be agglomerated in one partition and a new matrix should be defined. Therefore, *SustainPro* determines the new matrix to continue the analysis (see Figure 4.5).

	P1	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
P1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0
F	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0
G	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
I	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0
J	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
K	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
L	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0
M	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1
N	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
O	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1
P	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
Q	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
R	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0

Figure 4.5: Second DSM matrix to the partition determination

That partition should be analysed to verify if there are still units to be included on it. Row 1 is again analysed and it can be seen that partition 1 (P1) has a connection with unit F. Again, row two is analysed, following the procedure already described. It can be verified that unit G has a connection with P1, which means that units G and F should be included in P1 and a new matrix has to be defined (see Figure 4.6).

	P1	H	I	J	K	L	M	N	O	P	Q	R	S
P1	0	1	0	0	0	0	0	0	0	0	0	0	0
H	0	0	1	0	0	0	0	0	0	0	0	0	0
I	0	0	0	1	0	0	0	0	0	0	1	0	0
J	0	0	0	0	1	0	0	0	0	0	0	0	0
K	0	0	0	0	0	1	0	0	0	0	0	0	0
L	0	0	0	0	0	0	1	0	1	0	0	0	0
M	0	0	0	0	0	0	0	1	0	0	0	0	1
N	0	0	0	0	0	1	0	0	0	0	0	0	0
O	0	0	0	0	0	0	0	0	0	1	0	0	1
P	0	0	0	0	1	0	0	0	0	0	0	0	0
Q	0	0	0	0	0	0	0	0	0	0	0	1	0
R	0	0	0	1	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	1	0	0

Figure 4.6: Third DSM matrix to the partition determination

The same analysis is done. This time a new partition has been found between L, M and N units (see Figure 4.6). Again, *SustainPro* generates a new matrix with the new partition P2 (see Figure 4.7).

	P1	H	I	J	K	P2	O	P	Q	R	S
P1	0	1	0	0	0	0	0	0	0	0	0
H	0	0	1	0	0	0	0	0	0	0	0
I	0	0	0	1	0	0	0	0	1	0	0
J	0	0	0	0	1	0	0	0	0	0	0
K	0	0	0	0	0	1	0	0	0	0	0
P2	0	0	0	0	0	0	1	0	0	0	1
O	0	0	0	0	0	0	0	1	0	0	1
P	0	0	0	0	1	0	0	0	0	0	0
Q	0	0	0	0	0	0	0	0	0	1	0
R	0	0	0	1	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	1	0	0

**Figure 4.7:** Fourth DSM matrix to the partition determination

Following the already described procedures the matrices are determined until finding the entire set of partitions (see Figure 4.8 and Figure 4.9).

	P1	H	I	J	P2	Q	R	S
P1	0	1	0	0	0	0	0	0
H	0	0	1	0	0	0	0	0
I	0	0	0	1	0	1	0	0
J	0	0	0	0	1	0	0	0
P2	0	0	0	0	0	0	0	1
Q	0	0	0	0	0	0	1	0
R	0	0	0	1	0	0	0	0
S	0	0	0	0	0	1	0	0

**Figure 4.8:** Fifth DSM matrix to the partition determination

	P1	H	I	P2
P1	0	1	0	0
H	0	0	1	0
I	0	0	0	1
P2	0	0	0	0

**Figure 4.9:** Sixth DSM matrix to the partition determination

When no connection is found the row is eliminated and that unit defines a partition by itself.

*SustainPro* presents as an output of all these intermediate steps a matrix with the units belonging to each partition (see Figure 4.10).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
P1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
P2	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1
P3	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
P4	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
P5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

**Figure 4.10:** Partition matrix

Summarizing, it is possible to see that the code behind *SustainPro* is a complex structure of matrices manipulation. The partition determination has been given as an example of part of the code, but the remaining algorithms to determine the closed-

paths, open-paths, and the other parts of the methodology are also performed through manipulation of DMS matrices.



### 4.3 *SustainPro* Architecture

*SustainPro* is based on the methodology described in chapter 3 and consequently its architecture has been based on the methodology activity-flow (see Figure 4.11).

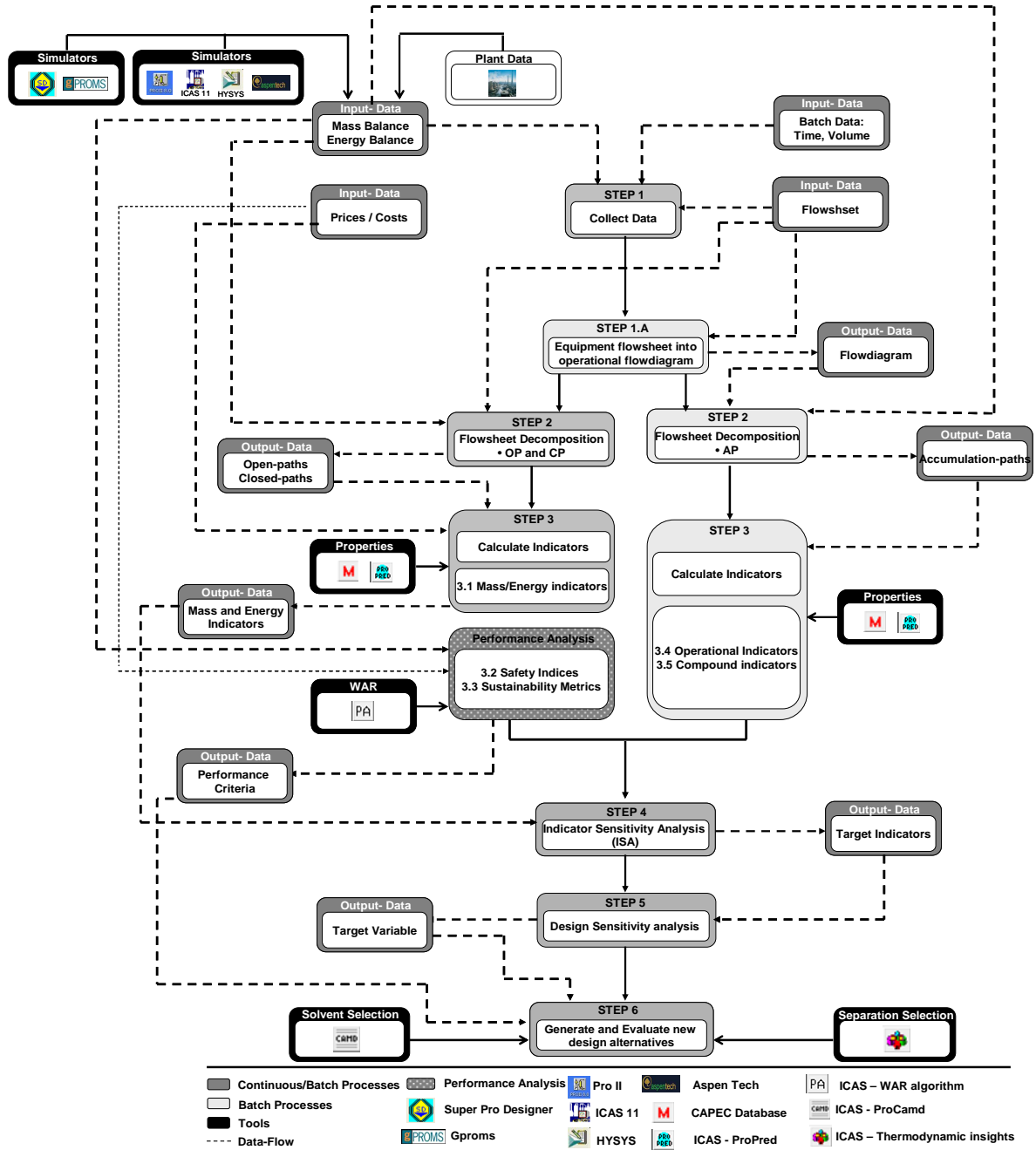
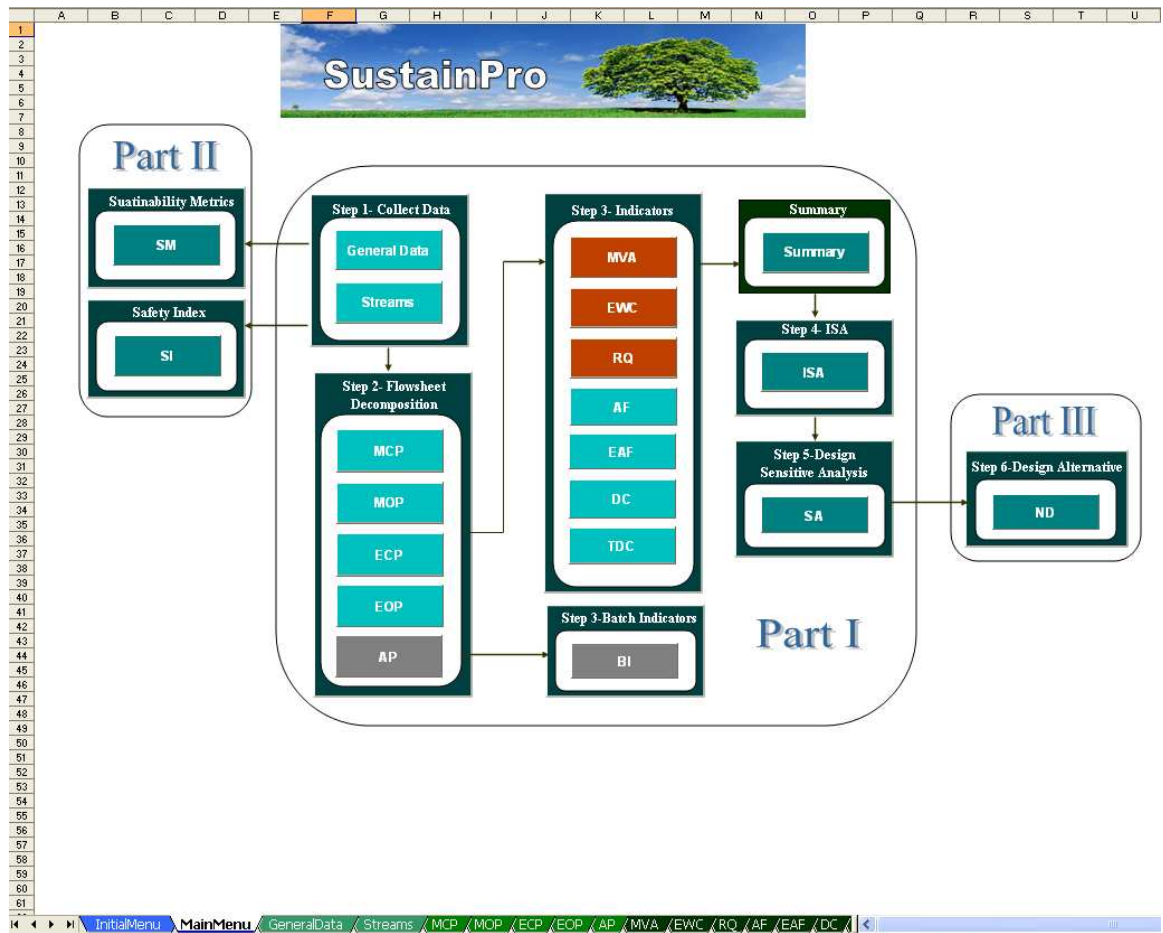


Figure 4.11: Activity-flow of the indicator-based methodology in *SustainPro*

In Figure 4.11 the solid lines represent the workflow of the methodology while the dashed-lines represent the activity-flow. In the activity-flow diagram the boxes designated as *Input-Data* are the overall input for the software. The boxes defined as *Output-Data* are results obtained by the application of the software. Note, however, that these output data can also serve as input to downstream calculation. The software uses some auxiliary tools, which are represented in the diagram with black (dark) boxes. An explanation about the tools and the respective interaction with the software is given in the supporting tools section (see section 4.4).

A Main Menu (see Figure 4.12) has been created to be the general interface of the software. The Main Menu performs the activities as outlined in Figure 4.11.



**Figure 4.12:** General interface of *SustainPro* (architecture)

The Main Menu is divided into three parts: Part I – Indicator analysis, Part II – Evaluation and Part III- Generation and comparison of new alternative. To solve a *Sustainable Design* problem (which means the methodology described in chapter 3), the user needs to perform sequentially, Part I, Part II and Part III. The built-in color code system guides the user through the different steps of the activity-flow (see Figure 4.11). The user must follow the button highlighted in “orange”, which is the next step to be followed. The light blue colour button represents the already performed steps and the dark blue buttons indicate the steps that have not yet been calculated.

If the user only wants to generate a new design alternative, Part I and Part III need to be executed. Part I and Part III combined form the *Retrofit Analysis*. Part II alone calculates the sustainability metrics and the safety indices. Part II is the performance analysis. Part III alone is used to generate new design alternatives for a specific problem.

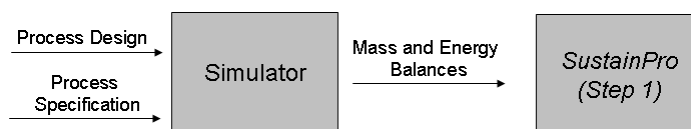
## 4.4 *SustainPro* Supporting tools

The tools shown in Figure 4.1 and Figure 4.11 are briefly described here.

### 4.4.1 Simulators

Process simulators provide mass and the energy balance related data for *SustainPro*. In principal any process simulator such as, *Pro II*, *AspenTech*, *HYSYS*, *ICAS-Simulator* (Gani *et al.*, 1997), *gPROMS* and *SuperPro Designer* can be used for this purpose. The inputs for the simulators are the process design and the process specifications. As output these tools give the mass and the energy balances (see Figure 4.13). The simulators may also be used to validate the generated design alternatives suggested by *SustainPro*. The user-interface of *SustainPro* is able to process the mass and the energy balances data from an *Excel* file generated by the simulators, thereby making the transfer of data from process simulators or from real plants relatively simple and easy.

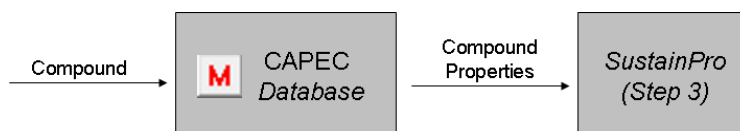
Figure 4.13 summarizes the integration of the simulators with *SustainPro*.



**Figure 4.13:** Integration of commercial simulators as a tool for *SustainPro*

#### 4.4.2 CAPEC Database

The *CAPEC database*, (Nielsen *et. al*, 2001), contains pure compound data for nearly 13000 chemicals and mixture properties data for mainly binary (organic) mixtures and some ternary mixtures. To calculate the mass and energy indicators, as well as the batch indicators, compound properties, such as heat capacity, density, heat of vaporization, etc, are needed. To retrieve data from *CAPEC database* it is necessary to search the compound in the database, then from all the known properties that are displayed, the needed ones are copied to *SustainPro* in order to calculate the indicators (see Figure 4.14).



**Figure 4.14:** Integration of *CAPEC Database* as a tool for *SustainPro*

#### 4.4.3 ProPred

*ProPred* (Marrero and Gani, 2001) is a toolbox for estimation of pure compound properties of organic compounds. When data is not available in *CAPEC database*, *ProPred* might be used to estimate the missing data. *ProPred* has an *Excel* interface, which is shown in Figure 4.15. The smiles of the molecules are given as input to

*ProPred* and the estimated properties for that compound are displayed in the *ProPred* interface (see Figure 4.15). The *ProPred* output is imported to *SustainPro* in step 3 (see Figure 4.16). With the data obtained from *ProPred* it is possible now to calculate the indicators and the safety indices.

Compound Property Data Sheet										
2	Name									
3	SMILES									
4	CAS			Formula				RI		1,65
5	MW	Tc (K)		Tm (K)		vm (cm <sup>3</sup> /mol)		LogKow		
6	Zc	Pc (bar)		Tb (K)		Hf (kJ/mol)		Gf (kJ/mol)		-625,93
7	ω	Vc (cm <sup>3</sup> /mol)		SolP (Mpa%)		Hfus (kJ/mol)		Dipole (D)		1,59
8	Low Temp (K)		298		ProPred		Plot		Print	
9	High Temp (K)		373		Copy				08-05-2007	
10	Step (K)		5						11:25:27 PM	
11					Save as		Reset		Help	
12	R. Gani et al., Computer Aided Process-Product Engineering Center									
13	Email: rsg@kt.dtu.dk      www.capec.kt.dtu.dk									
14	T	k (Thermal)	D (in Water)	Density (Liq.)	ΔHvap	VP	μ (Liq)	Cp (Gas)	Cp (Liq.)	
15	K	(W/m.K)	(1e-5cm <sup>2</sup> /s)	(g/cm <sup>3</sup> )	(kJ/mol)	(bar)	(cP)	(J/mol.K)	(J/mol.K)	
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Figure 4.15: *ProPred* Excel Interface

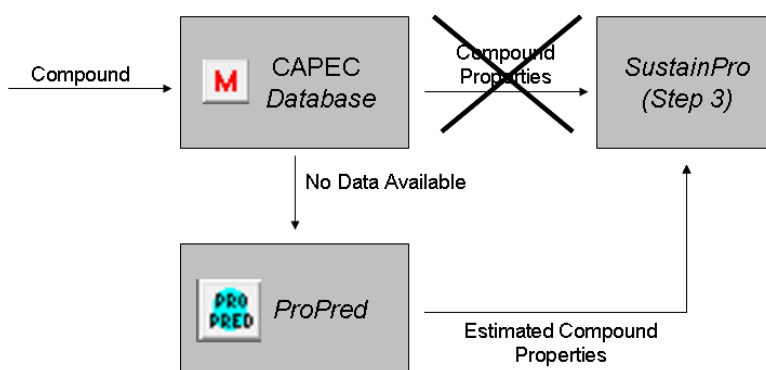
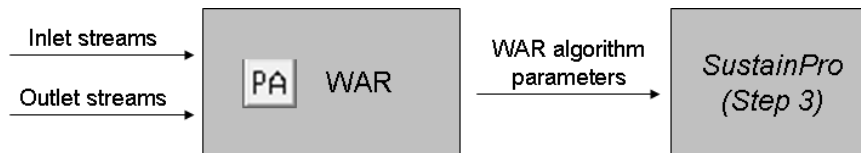


Figure 4.16: Integration of *ProPred* as a tool for *SustainPro*

#### 4.4.4 PA- WAR Algorithm

In *ICAS* software there is a tool called *PA-WAR*, which calculates the parameters involved in the WAR algorithm (Young and Cabezas, (1999)). The WAR algorithm parameters are used to substitute some of environmental metrics defined by *ICChemE*. Figure 4.17 shows that the input to calculate the WAR algorithm using *PA-WAR* tool is the data related to all inlet and outlet streams. The output of the *PA-WAR* is shown in Figure 4.18, and it can be imported directly to *SustainPro* as the result of the environmental metrics.



**Figure 4.17:** Integration of *PA –WAR* as a tool for *SustainPro*

	A	B	C	D	E	F	G	H	I	J	K	L
1												
2												
3												
4		WAR										
5												
6		<b>Stream No</b>	<b>Total PEI</b>	<b>HTPI</b>	<b>HTPE</b>	<b>ATP</b>	<b>TTP</b>	<b>GWP</b>	<b>ODP</b>	<b>PCOP</b>	<b>AP</b>	
7		Input 1	3369.4	555.819	10.0908	0.272979	555.819	0	0	2247.39	0	
8		Input 2	74460	14165.3	3.83617	1893.9	14165.3	0	0	44231.6	0	
9		Input 3	0	0	0	0	0	0	0	0	0	
10		Input sum	77829.4	14721.2	13.9269	1894.17	14721.2	0	0	46479	0	
11												
12		Output 1	4387.66	2151.92	50.1143	32.8405	2151.92	0	0	0.858464	0	
13		Output 2	44478.2	9528.27	3.8369	1814.95	9528.27	0	0	23602.9	0	
14		Output 3	1.16871	0.25199	0.000	0.0580768	0.25199	0	0	0.606479	0	
15		Output sum	48867	11680.4	53.9513	1847.85	11680.4	0	0	23604.4	0	
16												
17		<b>Impact generated</b>	<b>-28962.4</b>	<b>-3040.72</b>	<b>40.0244</b>	<b>-46.3203</b>	<b>-3040.72</b>	<b>0</b>	<b>0</b>	<b>-22874.7</b>	<b>0</b>	
18												

**Figure 4.18:** *PA-WAR* algorithm output

#### 4.4.5 ProCAMD

*ProCAMD* is based on the hybrid methodology for Computer Aided Molecular Design developed by (Harper and Gani, 2000). The output of step 5 of the methodology (see Figure 4.11) is the target variable that must be improved with the new alternative. When the improvement is related to the reduction of the flowrate of a solvent, the use of another solvent should be the design alternative. *ProCAMD* is used to find a suitable replacement solvent that improves sustainability. The input for *ProCAMD* tool is the operational conditions that the new solvent should match in order to be a better solvent. Figure 4.19 shows the list of solvents generated by *ProCAMD* given as an output. The list of solvents is imported to *SustainPro* and it is given as a new design alternative (Step 6 of the methodology).



**Figure 4.19:** Integration of *ProCAMD* as a tool for *SustainPro*

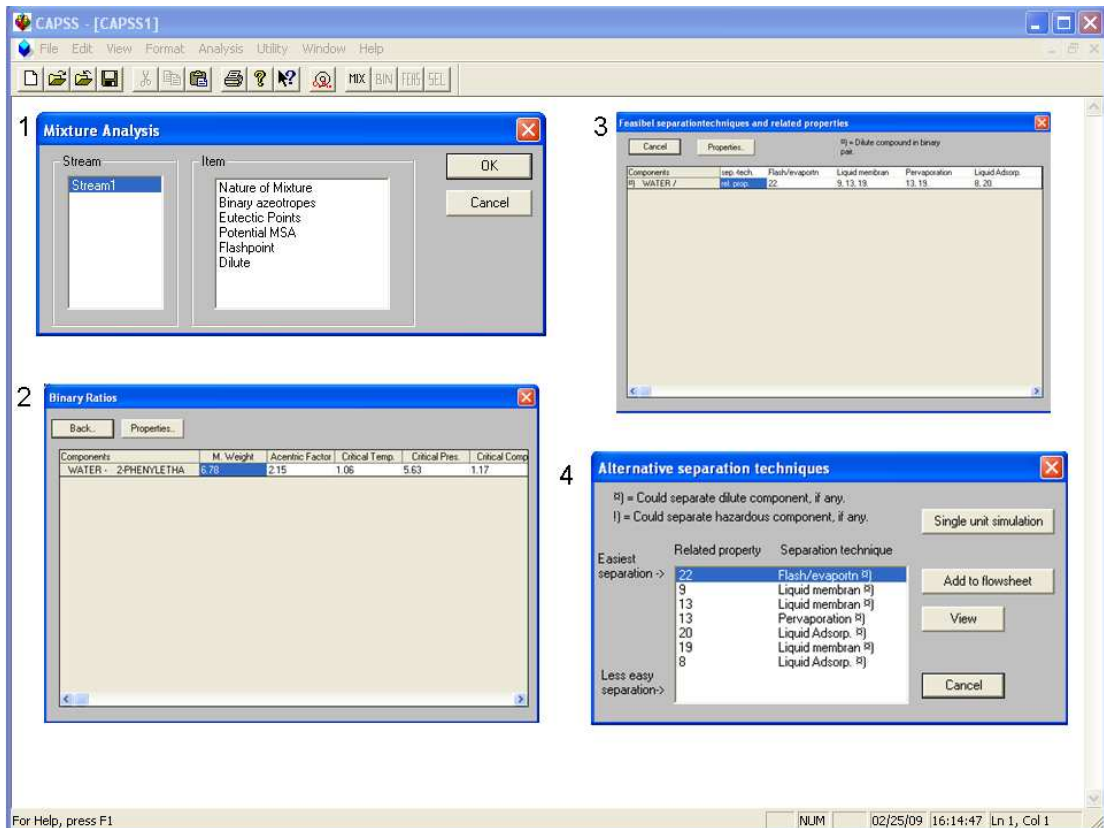
#### 4.4.6 CAPSS

The *CAPSS* tool is based on the methodology developed by Jaksland *et al.*, 1995, which employs physicochemical properties and their relationships to separation techniques for design and synthesis of separation processes. This tool is available in ICAS and is used to generate new design alternatives after *SustainPro* retrofitting analysis. From step 5, it is known that a new separation unit needs to be inserted, so the desired operational conditions to perform that separation are the input for the *CAPSS* tool (see Figure 4.20). The output of *CAPSS* tool is a list of possible separations techniques for the specified operational conditions.



**Figure 4.20:** Integration of CAPSS as a tool for *SustainPro*

The interface of this tool is shown in Figure 4.21.



**Figure 4.21:** CAPSS tool Interface

In Figure 4.21, window 1, it is specified the mixture nature, then, in windows 2 and 3 the parameters to evaluate the feasibility of separations are displayed. Finally the output



of CAPSS analysis is presented as a list of separation processes that can be seen in Figure 4.21, window 4.

Table 4.1 presents a summary of the interaction of *SustainPro* and the supporting tools.

**Table 4.1:** Summary of the interaction of *SustainPro* with the supporting tools

Tools	Purpose	Interaction with <i>SustainPro</i>
Simulators	Generate Mass and Energy Balances	
CAPEC Database	Compound Properties	
ProPred	Property prediction	
PA-WAR algorithm	Environmental Parameters	
ProCamd	Solvent Selection	
CAPSS	Separation Technique Selection	

#### 4.4.7 *SustainPro* – Knowledge Base

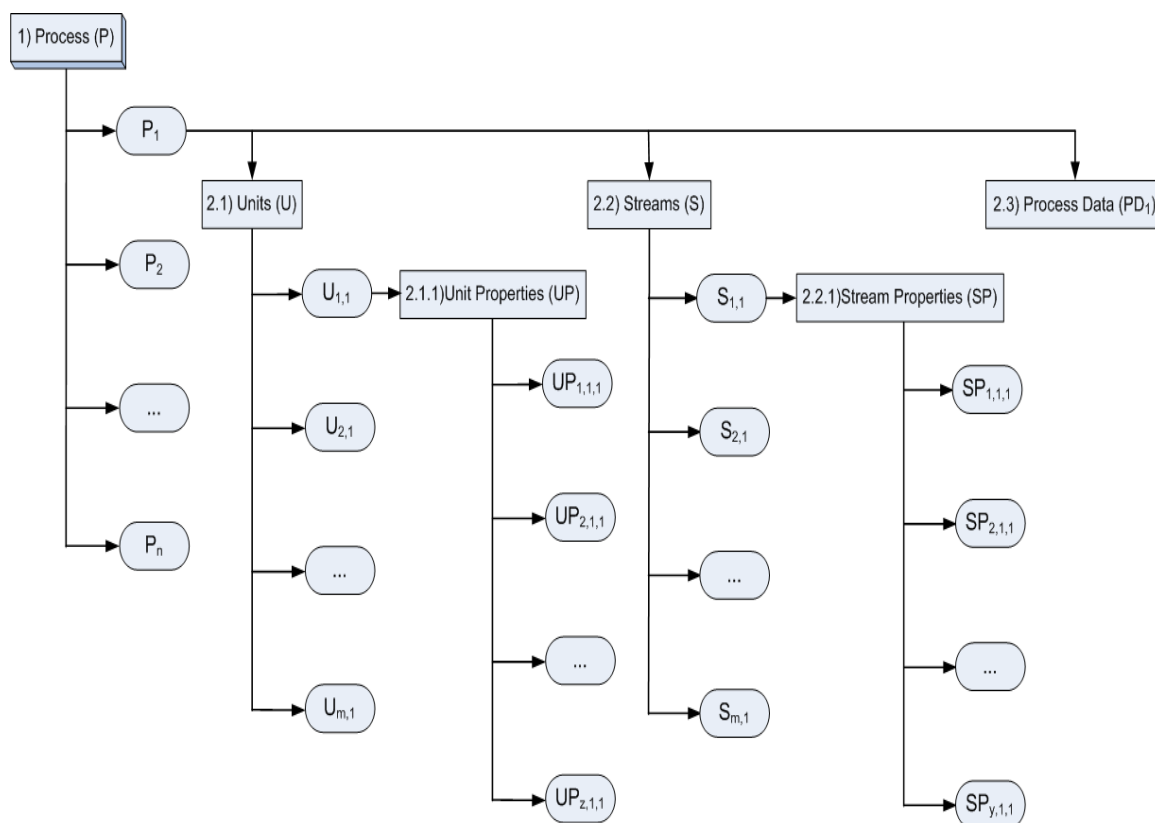
The objective of the knowledge base is to store data of processes / compounds that have been studied previously. The advantage of creating a knowledge base is that it provides the user the opportunity to modify an analysis that has already been done without having to start as a new problem. Therefore, less time is consumed searching for properties that were already determined before for other analysis

The current knowledge base contains saved data corresponding to several previously solved problems, such as, VCM production, MTBE production, HDA production, ammonia production, biodiesel production, etc, that were already studied through the methodology. The structure of the database is such that users are able to create and update their own versions of the knowledge base. The knowledge base is divided into two levels of information. The first level contains information about the process while the second level contains data about the compounds.

##### *First Level Knowledge base*

The process name, the process units, the unit properties, the process streams, the streams properties and the process data are the main categories of data in the first level of the knowledge base (see Figure 4.22). The processes are listed as the first category. The independent processes are the objects of this category (e.g. VCM production, MTBE production, HDA production, etc). For each process (e.g. the object of the first category) the next (second) category of data, is divided into three sub-categories: units (category 2.1), streams (category 2.2) and process data (category 2.3). In category 2.1, all the units involved in the process are listed. For each process there is a connection with the units present in that process. A third category, 2.1.1, is introduced in order to store the properties related to each process unit. Here, the type of unit is specified, the heat exchanged in each unit, the reactions taking place in the unit, the type of utility used by that unit (when required) and the utility price are stored. In category 2.2, the

streams within the process are listed. In the third category, 2.2.1, the properties related to each stream are stored. Pressure, temperature, compounds and the respective flowrates are specified in this third category. In category 2.3, the general information related to each process is listed such as working hours per year, layout description, construction material of the equipment, etc.

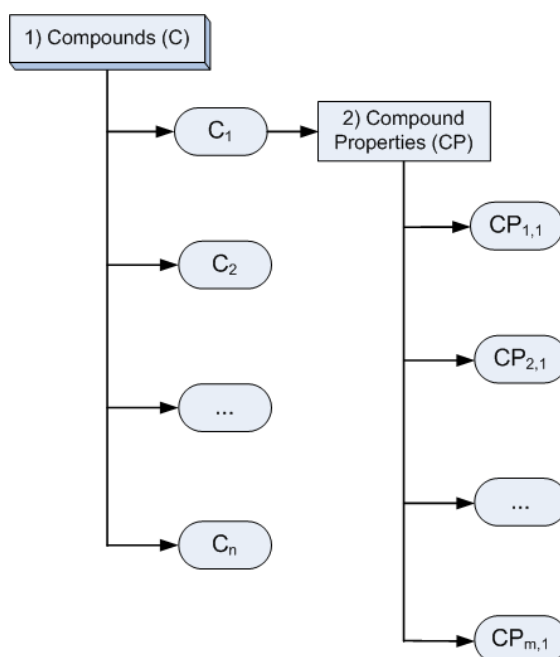


**Figure 4.22:** Structure of knowledge base (level 1)

### *Second Level Knowledge base*

The compounds are the first category of the second knowledge base level and the properties of the compounds are the second category of this knowledge base level (see Figure 4.23). For each compound listed in the first category, a set of properties, such as, molecular weight, heat capacity, density, enthalpy of vaporization, price, flash point, boiling point, upper explosive limit, lower explosive limit and toxic limit are stored. The knowledge base allows the storage of compounds and their properties even if a

process in study does not use them or vice-versa. Therefore, when the user applies the methodology to a process, which was not analysed before (means not available in the knowledge base), the user is still able to import information related to the compounds that make part of the new process and that are available in the knowledge base. This avoids extra work, on finding properties of compounds that are already saved in the knowledge base.



**Figure 4.23:** Structure of knowledge base (level 2)

## 4.5 Additional Features

A Start Menu has been created to give some extra options to the user. The Start Menu (see Figure 4.24) is divided in four areas. *SustainPro* File, Process Type, Knowledge Base – Import Data and Knowledge Base – Export Data.

### *SustainPro* File section

The user has the possibility to open a previously saved file containing the results for a problem already solved before or to start a new problem (see Figure 4.24). This gives the user the possibility to analyze the previous results and/or to modify the problem if necessary. The user has also the possibility of start a new *SustainPro* Analysis (see Figure 4.24 - *New SustainPro* Analysis button).



Figure 4.24: Start Menu interface - *SustainPro*

#### Process Type

The user needs to select “batch” or “continuous” so that *SustainPro* knows which indicators to calculate and what type of flowdiagrams for different paths need to be generated. This is because the analysis steps are different for batch and continuous processes.

#### Knowledge Base – Import Data

The user has the option to load previously saved knowledge base and also import available knowledge of a process or chemicals into *SustainPro* from the knowledge base.

#### Knowledge Base – Export Data

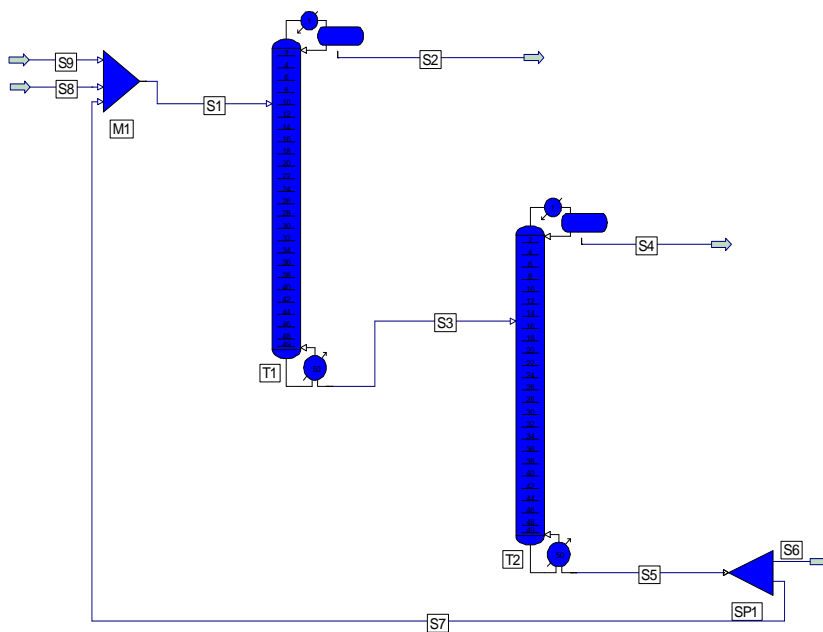
The user has the option to export new process or chemicals data into the knowledge base creating a users personal knowledge base.

## 4.6 Illustration of *SustainPro* application – Acetone-Chloroform Separation Case Study

### 4.6.1 Process description

In this case study, a benzene stream and an equimolar mixture of acetone and chloroform, which form an azeotrope, are mixed with recycled liquid benzene and fed to the first distillation column at 350K and 1atm; acetone ( $C_3H_6O$ ) goes out from the top of the unit and benzene ( $C_6H_6$ ) and chloroform ( $CHCl_3$ ) from the bottom as liquid. This bottom stream goes to a second distillation column where benzene and chloroform are separated. A purge stream is added to prevent the build-up of acetone in the system- this however means a loss of solvent.

The flowsheet of the process is shown in Figure 4.25.



**Figure 4.25:** Flowsheet of acetone-chloroform separation process

The objective of this example is to illustrate the main steps of each part of the sustainable design analysis performed in *SustainPro*.

Part I: Analyze the benzene-based separation scheme, determine the bottlenecks of the process through the use of the mass and energy indicators. Find targets for improvements through sensitivity analysis;

Part II: Check sustainability metrics and safety indices to evaluate the process;

Part III: Generate new design alternative to find more sustainable alternatives to the benzene-based separation. Compare the final design with the base case using sustainability metrics and safety indices to evaluate the process.

#### 4.6.2 Application of *SustainPro*

##### ***Part I: Indicators Calculation and Analysis***

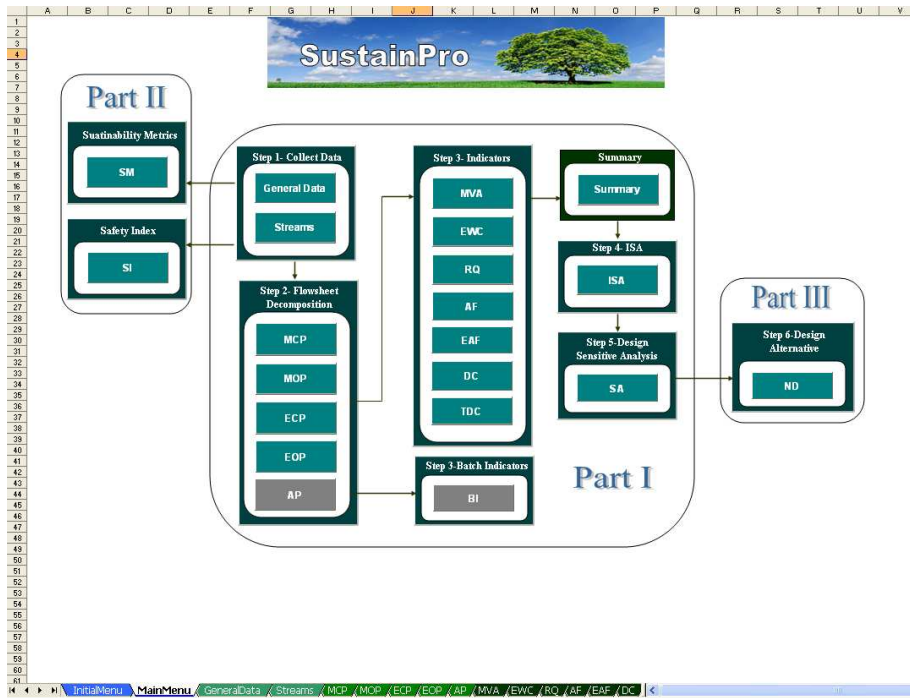
For the given process design indicators will be calculated and analyzed in this part.

##### *Step 1: Generate /Collect Data*

Steady state simulation at the reference design has been done in *PRO/II* with data from (Coll, N, 2003). Two Excel file reports have been generated using the *PRO/II* simulation (Mass Balance and Energy Balance). Cost data has been collected (Coll, N, 2003). The needed data could have also been obtained from the knowledge base in *SustainPro*.

After opening *SustainPro* the start menu presented in Figure 4.24 is displayed. Using the Start Menu (Figure 4.24), the user should select the type of process in study (Continuous or Batch process) and then click *Go to Main Menu* button. After pressing the button the screen shot below comes up, which shows the steps that needs to be followed sequentially (see Figure 4.26).





**Figure 4.26:** Main Menu interface - *SustainPro*

It is important to note that the colors will change in the main menu interface. “Orange” means next step to perform, “Light blue” means step already performed, “Dark blue” means step to be performed later and “Grey” means deactivated button for steps not involved in the respective analysis.

The user should click *General Data* button. General Data interface is displayed (see Figure 4.27).

**General Data**

Number of Units: 4    Accept Data    Number of reactions: 0  
 Number of streams: 9    Clear Data    Operation time per year (h): 8000  
 Number of components: 3

Units				
Name	M1	Col1	Col2	S1
Type		Column	Column	
Operation				

Components			
Name	ACETONE	BENZENE	CHLOROFM
Molecular weight (g/mol)	58	78	119
Hazardous		Yes	Yes
Type	P	S	P

ProII file directory (mass): C:\Documents and Settings\lac\My Documents\Doutoramento    Accept file  
 ProII file directory (energy): C:\Documents and Settings\lac\My Documents\Doutorarr    Accept file

**Figure 4.27:** General Data interface- Acetone-chloroform interface

The required data should be typed using PRO/II file information as seen in Figure 4.27. The directory where the generated Excel files were saved should be typed respectively in the *PRO/II file directory (mass)* and *PRO/II file directory (energy)* sections (see Figure 4.27). The user should click *Accept File* button for importing *PRO/II* data. Finally the user must click “*Go to Main Menu*” to return to the menu displayed in Figure 4.26.

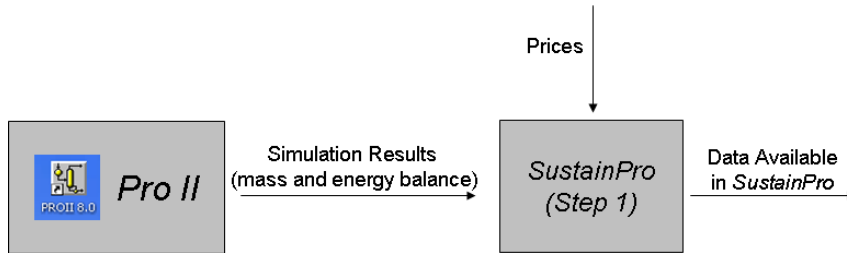
On the main menu the user must click on *Streams* button (see Figure 4.26). The user must fill out the initial and the final unit for each stream, as showed in Figure 4.28. The user should return again to the main menu clicking on *Go to Main Menu Button*.

**Streams**    Reactive units    Go to Main Menu

Stream Name	S1	S2	S3	S4	S5	S6	S7	S8	S9
Initial Unit	M1	Col1	Col1	Col2	Col2	S1	S1	0	0
Final Unit	Col1	0	Col2	0	S1	0	M1	M1	M1
Components (kg/h)									
ACETONE	5800,00	5771,00	29,00	29,00	0,00	0,00	0,00	0,00	5800,00
BENZENE	54379,24	378,46	54000,79	54,00	53946,79	2373,66	51573,12	2808,00	0,00
CHLOROFM	14695,79	73,47	14622,32	11697,86	2924,46	128,68	2795,79	0,00	11900,00
<b>Total Mass Flow(kg/h)</b>	<b>74875,04</b>	<b>6222,93</b>	<b>68652,11</b>	<b>11780,86</b>	<b>56871,25</b>	<b>2502,34</b>	<b>54368,91</b>	<b>2808,00</b>	<b>17700,00</b>
Temperature (°C)	67,73	56,77	77,70	61,44	79,72	79,72	79,72	27,00	27,00
Pressure (atm)	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00
Enthalpy Flow (GJ/h)	8,36	0,76	8,61	0,70	7,94	0,35	7,59	0,13	0,64

**Figure 4.28:** Streams interface-Acetone-chloroform interface

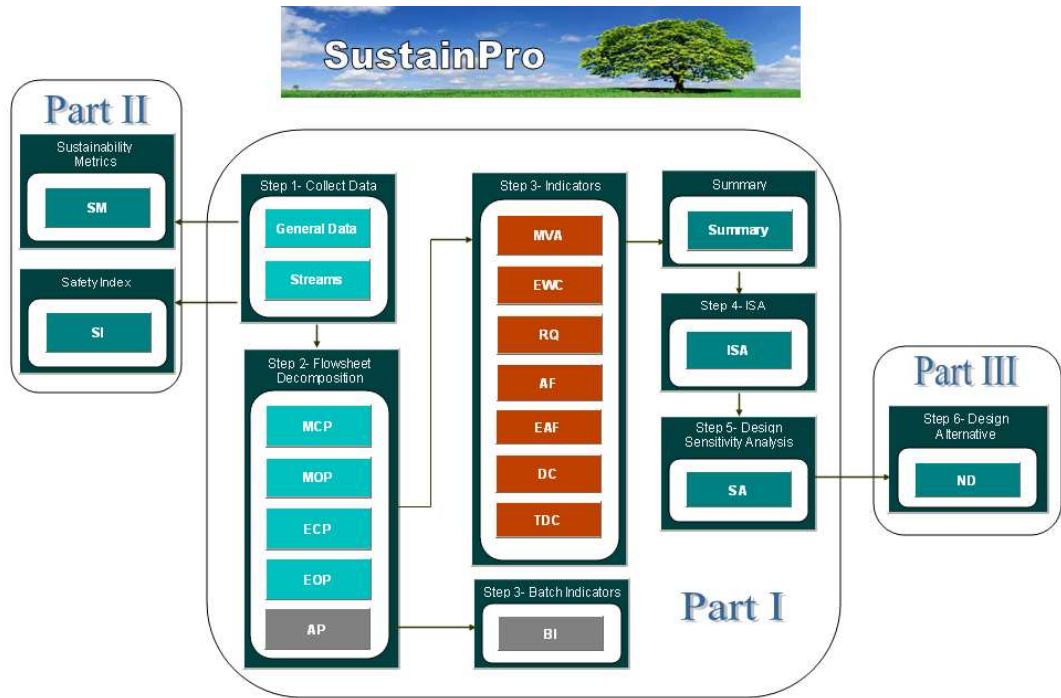
At this point, the first step of the methodology is completed. Figure 4.29 summarizes the data-flow executed in step 1 by *SustainPro*.



**Figure 4.29:** Data-flow for step 1 in *SustainPro*

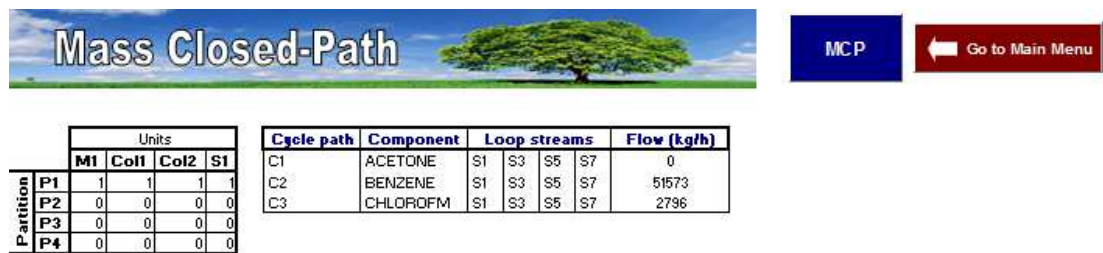
### *Step 2: Flowsheet Decomposition*

The user should click on “*Step 2: Flowsheet Decomposition*” (see Figure 4.26). *SustainPro* will perform decomposition of the process/operation flowdiagram in terms of: MCP (mass closed-path); MOP (mass opened-path); ECP (energy closed-path); and EOP (energy open-path). For batch processes, the following AP (accumulation-paths) will also appear. The user is able to see the details of any of these, clicking on the respective “light blue boxes” (see Figure 4.30).



**Figure 4.30:** Main Menu interface after flowsheet decomposition

The screen shots for the MCP, MOP, ECP and EOP results are displayed in Figure 4.31, Figure 4.32, Figure 4.33, and Figure 4.34 respectively.



**Figure 4.31:** Mass closed-paths interface- Acetone-chloroform interface



Open path	Component	OP streams								Flow-rate (kg/h)
OP 1	ACETONE	S9	S1	S2						5771
OP 2	ACETONE	S9	S1	S3	S4					29
OP 3	ACETONE	S9	S1	S3	S5	S6				0
OP 4	BENZENE	S8	S1	S2						379
OP 5	BENZENE	S8	S1	S3	S4					54
OP 6	BENZENE	S8	S1	S3	S5	S6				2375
OP 7	CHLOROFORM	S9	S1	S2						73
OP 8	CHLOROFORM	S9	S1	S3	S4					11698
OP 9	CHLOROFORM	S9	S1	S3	S5	S6				129

Figure 4.32: Mass open-paths interface- Acetone-chloroform interface



		Units				Closed-path	Loop streams	Flow (GJ/h)
		M1	Col1	Col2	S1	C1	S1 S3 S5 S7	7.59
Partition	P1	1	1	1	1			
	P2	0	0	0	0			
	P3	0	0	0	0			
	P4	0	0	0	0			

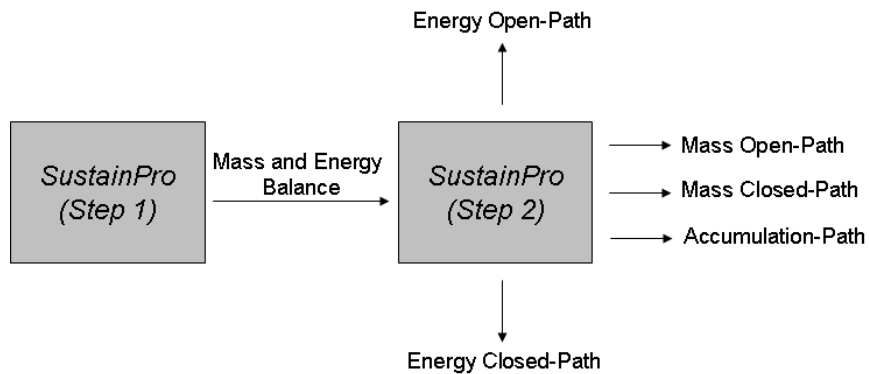
Figure 4.33: Energy closed-paths interface- Acetone-chloroform interface



Open path	EOP streams								Flow-rate (GJ/h)
OP 1	S8	S1	C Col1						0.1
OP 2	S9	S1	S2	S4					0.0
OP 3	S9	S1	S3	C Col2	S6				0.0
OP 4	S9	S1	C Col1						0.6
OP 5	H Col1	S2	S3	S4					0.7
OP 6	H Col1	S3	S4	S5	S6				0.0
OP 7	H Col1	S3	S5	S6					0.0
OP 8	H Col1	S3	C Col2						1.0
OP 9	H Col1	C Col1							28.3
OP 10	H Col2	S4							0.7
OP 11	H Col2	S5	S6						0.3
OP 12	H Col2	C Col2							40.0

Figure 4.34: Energy open-paths interface- Acetone-chloroform interface

At this point, the second step of the methodology is completed. Figure 4.35 summarizes the data-flow executed in step 2 by *SustainPro*.



**Figure 4.35:** Summary of data-flow for step 2

### *Step 3: Calculation of Indicators*

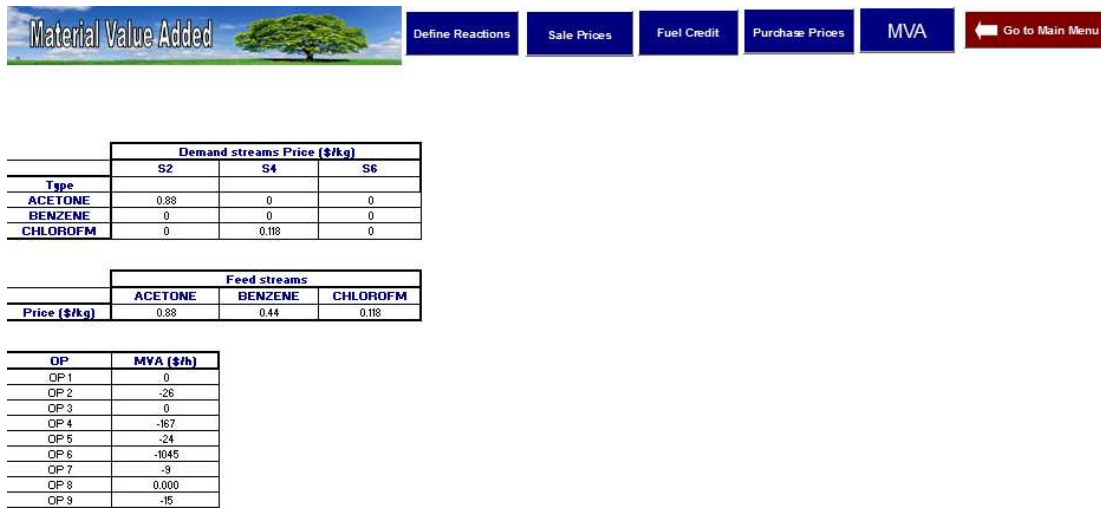
The user should click on “*Step 3: Indicators*” to start the indicator calculations (see Figure 4.30).

- The following indicator will be calculated without further addition of data, AF (Accumulation Factor).
- The following indicators will need additional data to calculate them, MVA (Material Value Added), EWC (Energy Waste Cost) and RQ (Reaction Quality). The user should click on the respective “orange” box for each indicator. The user-interface will ask for additional data.
- The following indicators, EAF (Energy Accumulation Factor), DC (Demand Cost) and TDC (Total Demand Cost), need the data from EWC. They are calculated automatically after the calculations of EWC.

The screen shots for the AF, MVA, EWC, EAF, DC and TDC results are displayed in Figure 4.36, Figure 4.37, Figure 4.38, Figure 4.39, Figure 4.40 and Figure 4.41 respectively



**Figure 4.36:** Accumulation Factor (AF) interface with the results - Acetone-chloroform interface



**Figure 4.37:** Material Value Added (MVA) interface with the results - Acetone-chloroform interface

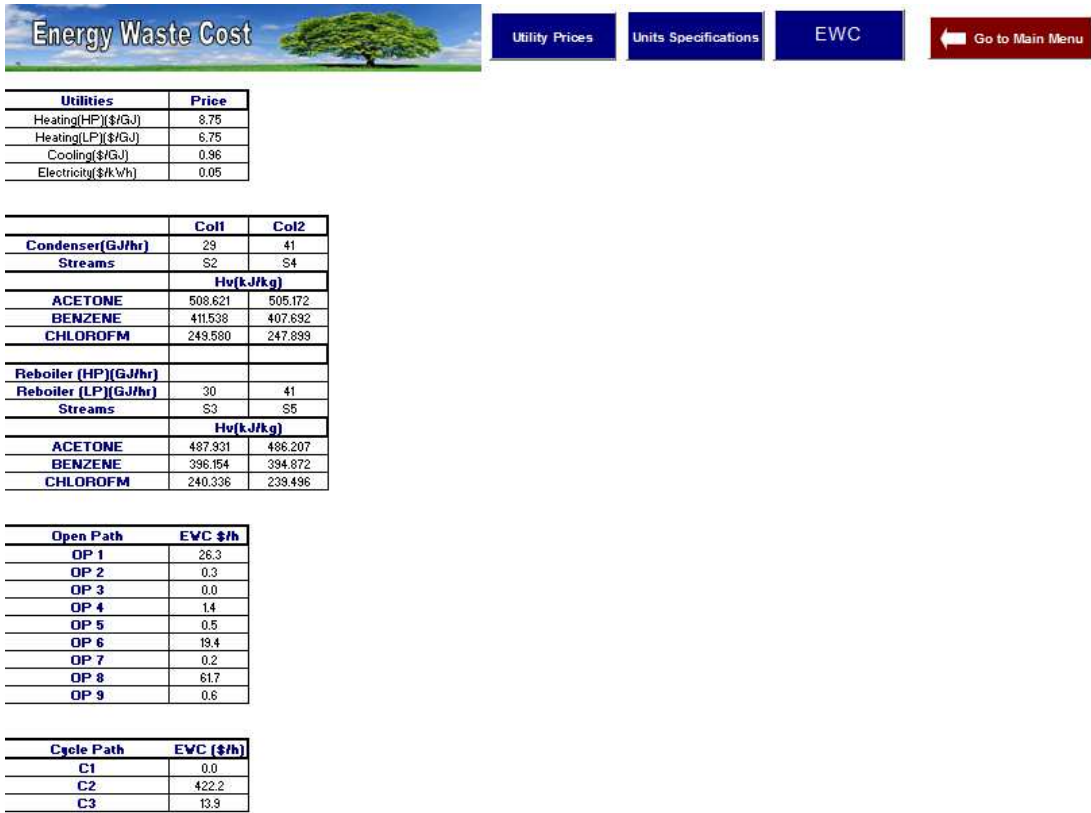


Figure 4.38: Energy and Waste Cost (EWC) interface with the results- Acetone-chloroform interface



Figure 4.39: Energy Accumulation Factor (EAF) interface with the results- Acetone-chloroform interface





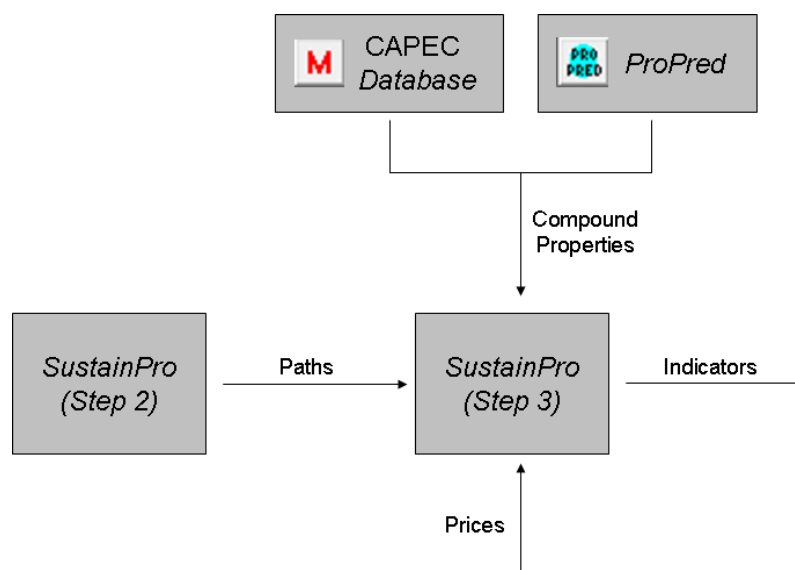
**Figure 4.40:** Demand Cost (DC) interface with the results- Acetone-chloroform interface



**Figure 4.41:** Total Demand Cost (TDC) interface with the results- Acetone-chloroform interface

It is important to note that RQ is not necessary for this example, because there is no reaction in this case study.

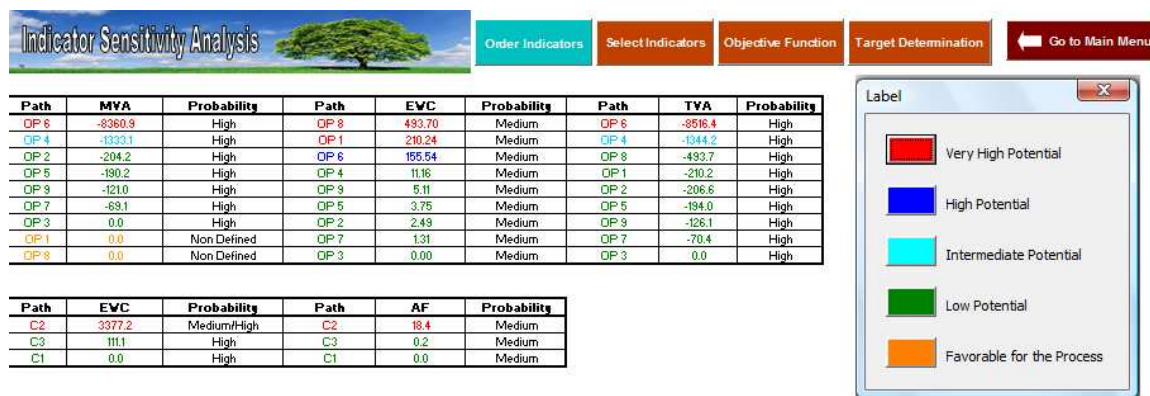
At this point, the third step of the methodology is completed. Figure 4.42 summarizes the data-flow executed in step 3 by *SustainPro*.



**Figure 4.42:** Summary of data-flow for step 3

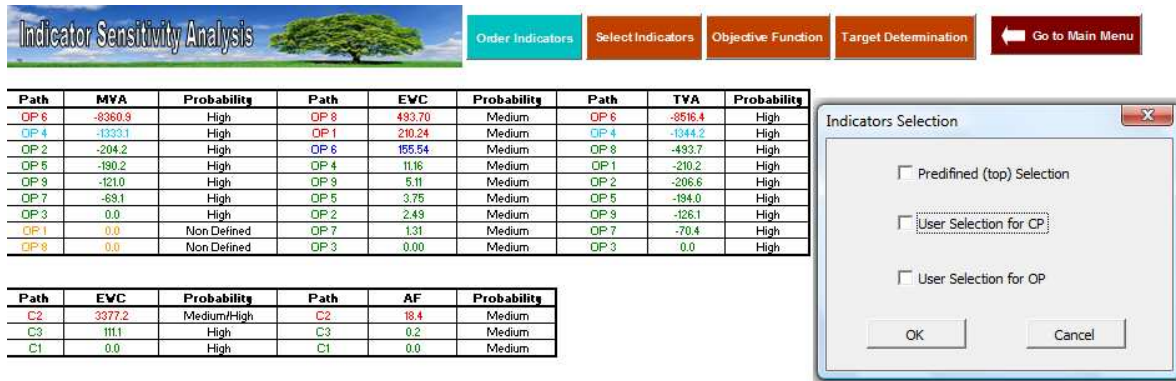
#### *Step 4: Indicator Sensitivity Analysis Algorithm*

The user should click on “*Step 4: ISA*” for indicator sensitivity analysis on the main-menu page (see Figure 4.30). The following screen comes up (see Figure 4.43).



**Figure 4.43:** Indicator Sensitivity Analysis Algorithm (ISA) interface - Acetone-chloroform interface

*SustianPro* has already ordered the indicators according to their values; the user needs to select the indicator by clicking on “*Select Indicators*”. The following screen comes up (see Figure 4.44).



**Figure 4.44:** Select indicators interface - Acetone-chloroform interface

For this case study the top one (Predefined (top) Selection) for each type of path (open and closed) has been selected.

After the selection has been made, *SustainPro* determines the “Objective Function” and “Target Indicators Scores”. The following screen-shot shows the variables influencing the objective function and target indicator scores (see Figure 4.45).

Path	Indicator	Streams Flowrates		Heat exchanged in units				Scores
		S8	S9	Cond Col1	Cond Col2	Reb Col1	Reb Col2	
OP 6	MVA	X				X	X	15
OP 8	EVC		X		X	X	X	14
OP 6	TVA	X				X	X	15

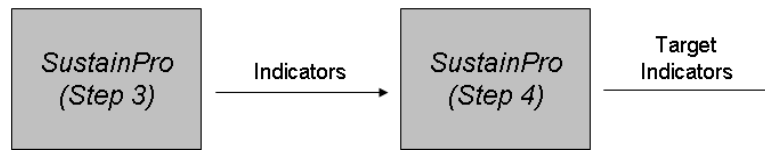
  

Path	Indicator	S8	S9	Cond Col1	Cond Col2	Reb Col1	Reb Col2	Scores
		C2	EVC					X
C2	AF					X	X	8

**Figure 4.45:** Indicator Sensitivity Analysis Algorithm (ISA) with target indicators - Acetone-chloroform interface

From Figure 4.45 it is possible to see that in terms of open-paths the target indicators are MVA and TVA for OP6. For the closed-paths EVC and AF for CP2 are the target indicators.

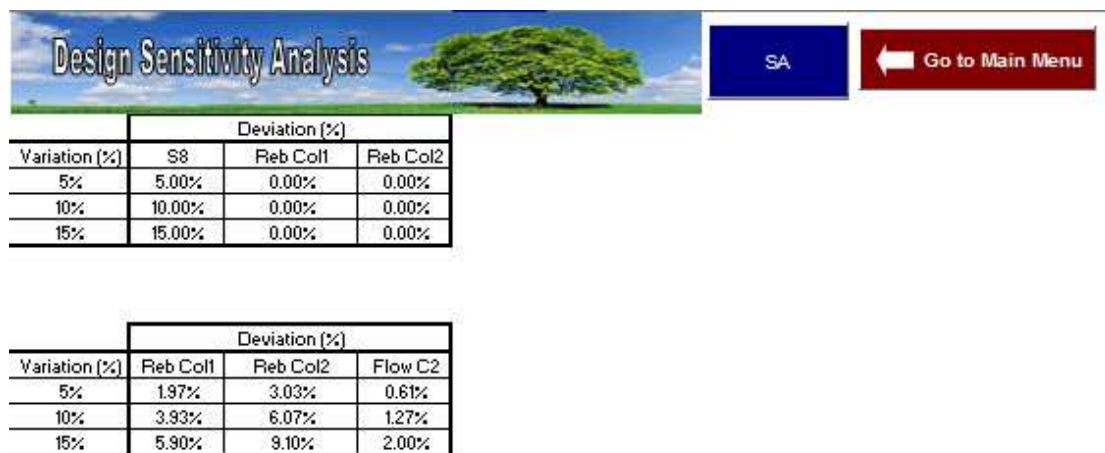
At this point, the fourth step of the methodology is completed. Figure 4.46 summarizes the data-flow executed in step 4 by *SustainPro*.



**Figure 4.46:** Summary of data-flow for step 4

#### *Step 5: Design Sensitivity Analysis*

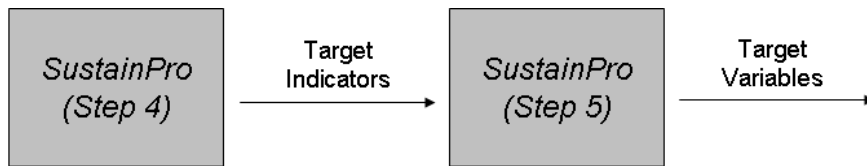
The user should click on “*Step 5: Design Sensitivity Analysis*” on the main-menu page (see Figure 4.30). The design sensitivity analysis is performed and the following screen-shot will appear (see Figure 4.47).



**Figure 4.47:** Design Sensitivity Analysis interface - Acetone-chloroform interface

Figure 4.47 presents the sensitivity analysis for MVA for OP6 and EWC for CP2. The highest improvements in the MVA are achieved with the S8 flowrate reduction and for EWC to be improved the best option is to change the heat in the reboiler of Col2.

At this point, the fifth step of the methodology is completed. Figure 4.48 summarizes the data-flow executed in step 5 by *SustainPro*.




**Figure 4.48:** Summary of data-flow for step 5

### ***Part II: Calculation of Performance Measures***

In this part, for the given process design, the performance measures (sustainability metrics and safety indices) is performed.

#### *Sustainability Metrics*

In the *SustainPro* main-menu (see Figure 4.30) the user should click on “*Sustainability Metrics*” to generate values for the metrics. Based on the available data supplied to *SustainPro*, the metrics will be calculated, as shown in the screen-shot (see Figure 4.49).



SM
Go to Main Menu

**Energy**

Total Net Primary Energy Usage rate (GJ/y)	700000	CF
% Total Net Primary Energy sourced from renewables	1	
Total Net Primary Energy Usage per Kg product (kJ/kg)	14060,9	Import
Total Net Primary Energy Usage per unit value added (kJ/\$)	-8,51301	

**Material (excluding fuel and water)**

Total raw materials used per kg product (kg/kg)	3,29555
Total raw materials used per unit value added	-0,002
Fraction of raw materials recycled within company	2,65111
Fraction of raw materials recycled from consumers	0
Hazardous raw material per kg product	2,36352

**Water**

Net water consumed per unit mass of product (kg/kg)	86,7396
Net water consumed per unit value added	-0,05252

RMC

TW (°C)

Water Type	0
Tinlet (°C)	25
Toutlet(°C)	27

Units

Unit	Col1	Col2
Water Type	0	0

**Land**

Total land occupied-affected for value added	
Rate of land restoration (restored per year total)	

**Emissions, effluents and waste (WAR Algorithm)**

Stream Ilo	Total PEI	HTPI	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
Input 1	12273,9	4977,59	15	84	4977,59	94,7408	0	2124,41	0
Input 2	2,05E+03	299,249	259	103,179	299,249	0	0	1,09E+03	0
<b>Input sum</b>	14327,030	5276,839	274,687	187,351	5276,839	94,741	0,000	3216,570	0,000
Output 1	3151,07	419,385	35,734	15,0582	419,385	0,58455	0	2,261	0
Output 2	9,34E+03	4554,18	19,4149	84,0934	4554,18	93,1302	0	3,16E+01	0
Output 3	1,838	303	219,35	88	303	1,02415	0	923	0
<b>Output sum</b>	1,43E+04	5,28E+03	2,74E+02	1,87E+02	5,28E+03	9,47E+01	0,00E+00	3,22E+03	0,00E+00
<b>Impact generated</b>	-2	0	0	0	0	0	0	-1	0

**Economic indicators**

**Profit, value and tax**

Value added	-10278386,79
-------------	--------------

**Figure 4.49:** Sustainability Metrics interface with the calculated values- Acetone-chloroform interface

It is important to note that a blank metric value means that this metric could not be calculated (because of missing data and/or it is not needed). In addition, it is necessary to take into consideration that the environmental indicators need to be calculated separately using the WAR algorithm, which is available as a toolbox in ICAS (see section 4.4.4).

## Safety Indices

From the main-menu of *SustainPro* (see Figure 4.30) the user should click on “*Safety Index*” to get these values (see Figure 4.50). Some data is needed to calculate these indices. This data can be obtained in MSDS sheets (<http://www.msds.com/>).

**Safety Indices**

Buttons: Data, SI, Go to Main Menu

**Reaction heat for the main reaction**

Heat of reaction (J/h)	0
Total mass (g/h)	0

**Reaction heat for the side reaction**

Heat of reaction (J/h)	0
Total reaction mass	0

**Chemical Interaction**

Chemical Interaction	Put ges
Heat Formation	
Fire	
Formation of harmless, nonflammable gas	
Formation of toxic gas	
Formation of flammable gas	
Explosion	Yes
Rapid polymerization	
Soluble toxic chemicals	

**Corrosiveness**

Construction material	
Stainless steel	

**Equipment Safety for ISBL**

Equipment items	Put ges
Equipment handling nonflammable, nontoxic materials	
Heat exchangers, pumps, ovens, drums	Yes
Air coolers, reactors, high hazard pumps	
Compressors, high hazard reactors	
Furnaces, fire heaters	

**Process structure**

Safety level of process structure	Put ges
Recommended (safety ec. Standard)	
Sound engineering practice	
No data or neutral	Yes
Probably unsafe	
Minor accidents	
Major accidents	

**Equipment Safety for OSBL**

Equipment items	Put ges
Equipment handling nonflammable, nontoxic materials	
Atmospheric storage tanks, pumps	Yes
Cooling towers, compressors, blowdown systems, pressurised or refrigerated storage tanks	
Flares, boilers, furnaces	

**Flamability, explosiveness and toxicity**

Components	Flash Point(°C)	Boiling Point(°C)	UEL(%vol)	LEL(%vol)	Toxic limit(ppm)
ACETONE	-18	56	13	2.2	750
BENZENE	-11	80	8	1.2	10
CHLOROFORM	No	61	Non-explosive	Non-explosive	10

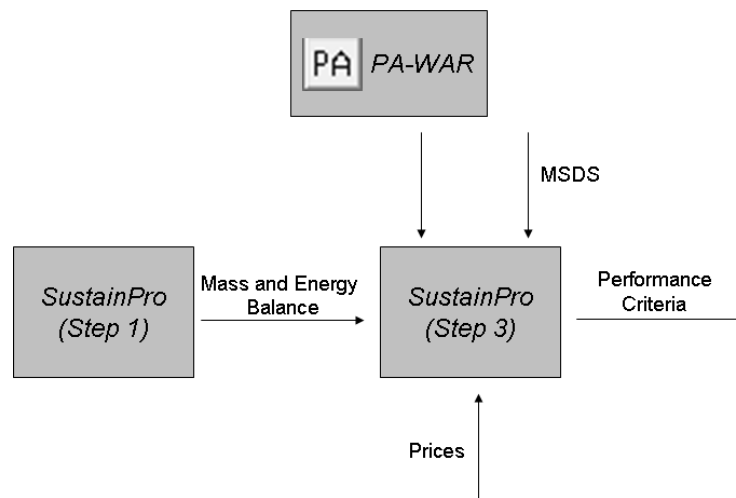
**Total inherent safety index (ISI)**

Chemical inherent safety index, ICI	Score	Process inherent safety index, IPI	Score
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, I <sub>rm</sub>	0	Inventories, I <sub>i</sub>	4
Heat of the side reactions, I <sub>rs</sub>	0	Process temperature, I <sub>t</sub>	1
Chemical interaction, I <sub>ci</sub>	4	Process pressure, I <sub>p</sub>	0
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, I <sub>f</sub>	4	Equipment, I <sub>eq</sub>	
Explosiveness, I <sub>ex</sub>	1	ISBL	1
Toxicity, I <sub>toe</sub>	4	OSBL	1
Corrosivity, I <sub>cor</sub>	1	Process structure, I <sub>st</sub>	2
<b>ICI</b>	<b>14</b>	<b>IPI</b>	<b>9</b>

ISI = 23

**Figure 4.50:** Safety Indices interface with the calculated values- Acetone-chloroform interface

At this point, the performance criteria have been calculated. Figure 4.51 summarizes the data-flow executed in the performance criteria calculated by *SustainPro*.



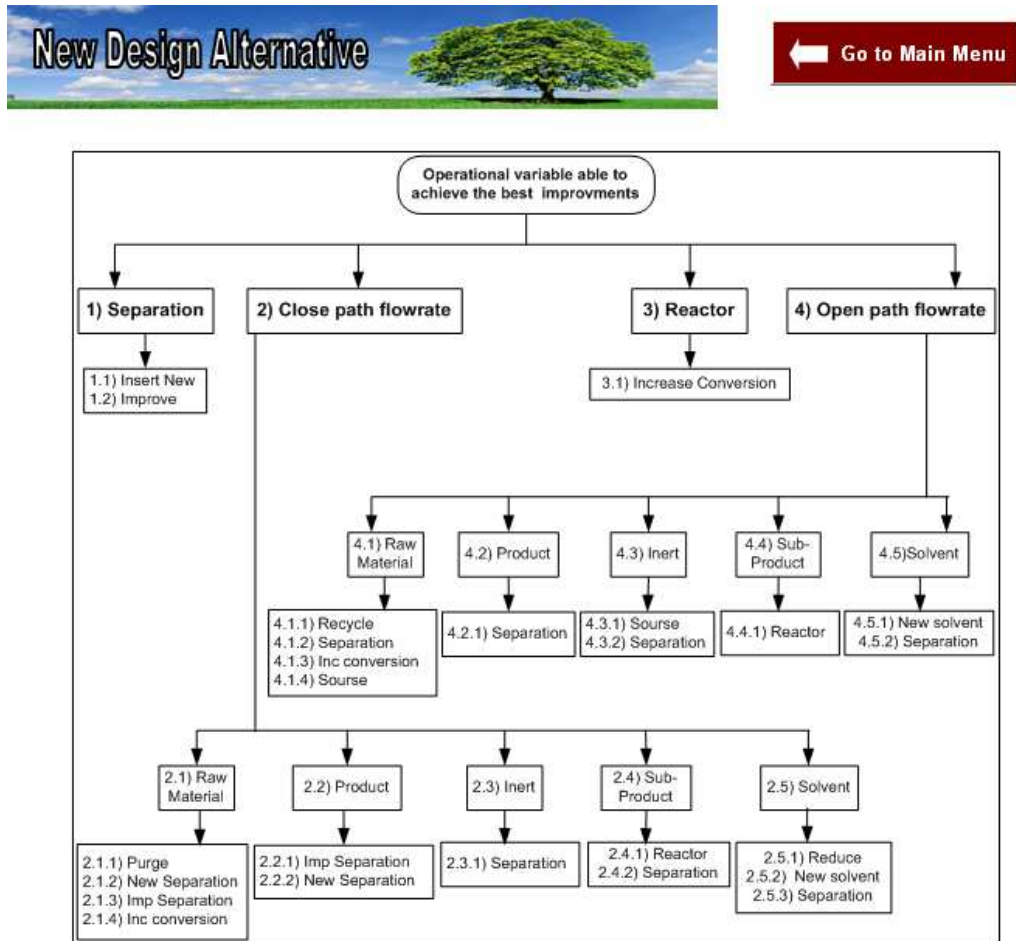
**Figure 4.51:** Summary of data-flow for performance criteria

### ***Part III: Generation and Comparison of New Alternatives***

The objective of this part is to generate new design alternatives that match the established targets for improvements (see Part I).

From the main menu of *SustainPro*, the user should click on “*Step 6: Design alternative*” (see Figure 4.30). The following screen-shot tells the user how to generate new alternatives (see Figure 4.52).





**Figure 4.52:** Design Alternative interface - Acetone-chloroform interface

For this case study, the following procedure has been done in order to improve the closed-path target indicator:

- 1) The target variables were related to improvements in separations. However using this solvent it was not possible to improve the respective separation. Consequently the reduction of the flowrate is the only variable that can be used to match the desired targets.
- 2) Since the flowrate of CP2 has to be reduced and that path is related to a solvent, suggestion of section 2.5 in Figure 4.52 should be considered. The objective here is to reduce the cost but at the same time to reduce the environmental

impact, so suggestion 2.5.2 has been considered. The new design alternative consists on finding new solvents and the corresponding flowsheets. The new solvent has been found through ProCAMD, which is available in ICAS. For this process methyl-n-pentyl ether has been selected as an alternative solvent. Steady state simulation for new design has been performed in *PRO/II*.

- 3) Parts I and II have been performed again for the new design alternative.
- 4) Compare new sustainability metrics and safety indices (performance criteria) with the values obtained for the base case.

For the new sustainable design alternative, which consists of using methyl-n-pentyl ether as a solvent, the following improvements were achieved. The costs decreased by 51%, the water and the energy metrics per kg of final product improved by 47%. The material metrics improved by 13%. The environmental impact output has been improved by 14%. The safety of the process has been improved by 13%. The rest of the performance criteria parameters have remained constant. The values for the performance criteria are listed in Table 4.2. The target indicators improved by 51% ( $EWC_{initial}=402\$/h$ ;  $EWC_{final}=206\$/h$ ).

**Table 4.2:** Comparison of the performance criteria between the base case and the new sustainable design alternative – Acetone-Chloroform Separation Case Study

	Base Case	New Design	Improvements
Total Net Primary Energy Usage rate (GJ/y)	700000.0	348000.0	50%
% Total Net Primary Energy sourced from renewables	1.0	1.0	0%
Total Net Primary Energy Usage per Kg product (kJ/kg)	14060.9	7443.1	47%
Total raw materials used per kg product (kg/kg)	3.3	3.0	8%
Fraction of raw materials recycled within company	2.7	2.3	13%
Hazardous raw material per kg product	2.4	2.1	13%
Net water consumed per unit mass of product (kg/kg)	86.7	46.3	47%
WAR	14325	12281	14%
Safety	23	20	13%
Costs (\$/y)	4371600	2141088	51%

These results show that a more sustainable design alternative has been presented.

## 4.7 Conclusions

In this chapter, a software called *SustainPro* has been presented. *SustainPro* performs the whole methodology described in Chapter 3, guiding the user through the methodology steps. This software allows an easy and fast analyze of the processes, making the methodology a reproducible study.

*SustainPro* is connected to a set of supporting tools that complement the missing data in the software. A knowledge base has been developed in order to provide the user the opportunity to modify an analysis that has already been done without having to start as a new problem. Therefore, less time is consumed searching for properties that were already determined before for other analysis.

The application of the software has been highlighted through a simple case study (Acetone-Chloroform Separation).

## 5. Case Studies

### 5.1 Introduction

In this chapter two sections of case studies will be presented. The first section (section 5.2) presents the main results for the application of the methodology using *SustainPro* to the Vinyl Chloride Monomer Production, Ammonia Production, Biodiesel Production and Copper Extraction Process. These processes operate in a continuous mode. In the second section (section 5.3) the processes operating in batch are studied, such as Insulin production and  $\beta$ -Gal production. In the end of the chapter general conclusions are presented.

### 5.2 Continuous Processes

#### 5.2.1 VCM (Vinyl Chloride Monomer) Production

The production of Vinyl Chloride Monomer has been selected as case study because it is not simple, has industrial significance and provides interesting challenges for *SustainPro*. The VCM plant comprises of 31 unit operations, which include 4 distillation columns and 3 reactor systems, 6 recycle streams, 52 streams and 35 compounds.

### 5.2.1.1 Process flowsheet

The VCM process flowsheet (PRO/II Casebook, 1992) can be divided into five sections as shown in Figure 5.1.

#### **Section 1: Direct Chlorination**

Here it takes place the direct chlorination of ethylene. Part of 1,2- dichloroethane (EDC), which is the raw material used to produce VCM, is obtained by the reaction of ethylene with chlorine.

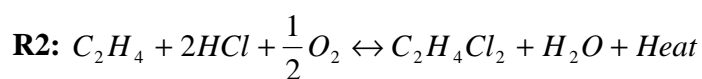


Where  $C_2H_4$  is the Ethylene,  $Cl_2$  is the Chlorine and  $C_2H_4Cl_2$  is the EDC.

The heat of the reaction is removed by circulating cooling water. In most commercial processes ferric chloride is used as a catalyst. The reactions are often run with a small excess of ethylene to maintain the vent gases fuel-rich for incineration. Conversion of the lean compound is usually 100% with selectivity greater than 99%.

#### **Section 2: Oxychlorination**

The remaining EDC, used in the process, is produced in this section by oxychlorination of ethylene with the recycled HCL and  $O_2$ .



Where  $C_2H_4$  is the Ethylene,  $HCl$  is the Hydrochloric acid,  $O_2$  is the Oxygen and  $C_2H_4Cl_2$  is the EDC.

The Hydrochloric acid is mainly produced from the thermal cracking of EDC and consequently is recovered and used in this section. This operation presents a conversion of 93-97% of ethylene and 93-96% of EDC selectivity.

**Section 3: Purification of EDC**

EDC, produced in sections 1 and 2 and recovered from the process, presents around 20 compounds as impurities that should be removed, so in this section it takes place the purification of EDC. The EDC purity should be at least 99%. Two distillation columns are used to remove the impurities, the first distillation column is to remove the light compounds and the second to remove the heavy compounds.

**Section 4: Production of VCM**

Pure EDC is preheated and vaporized before being fed to the cracking furnace, where it is thermally cracked at about 500°C and 200 psig by the following reaction.

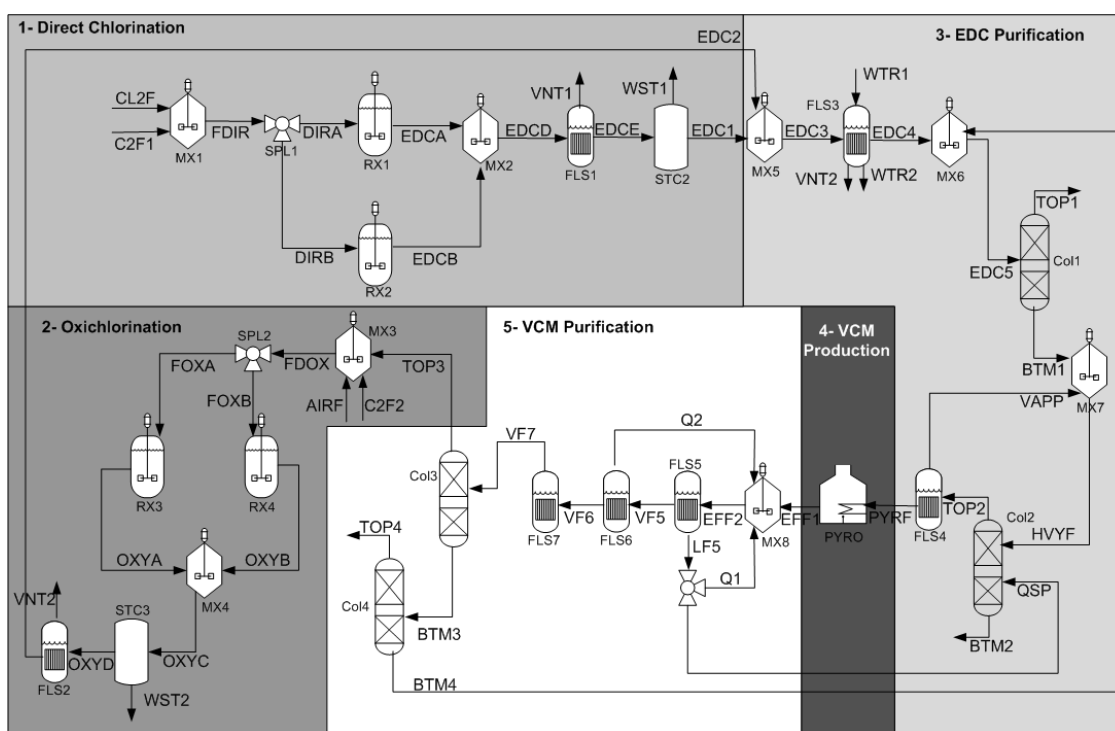


Where,  $C_2H_4Cl_2$  is the EDC,  $C_2H_3Cl$  is the Vinyl Chloride Monomer (VCM) and  $HCl$  is the Hydrochloric acid.

About half of the EDC entering the furnace is reacted. The product stream then contains roughly equimolar proportions of EDC, VCM and HCL.

**Section 5: Purification of VCM**

Finally, in this last section, the VCM's purification takes place, allowing the HCL's recover to the oxychlorination reactor. The unreacted EDC is also recycled to EDC purification system.



**Figure 5.1:** Flowsheet of VCM production

### 5.2.1.2 SustainPro and methodology application

#### **Step 1: Data Collection**

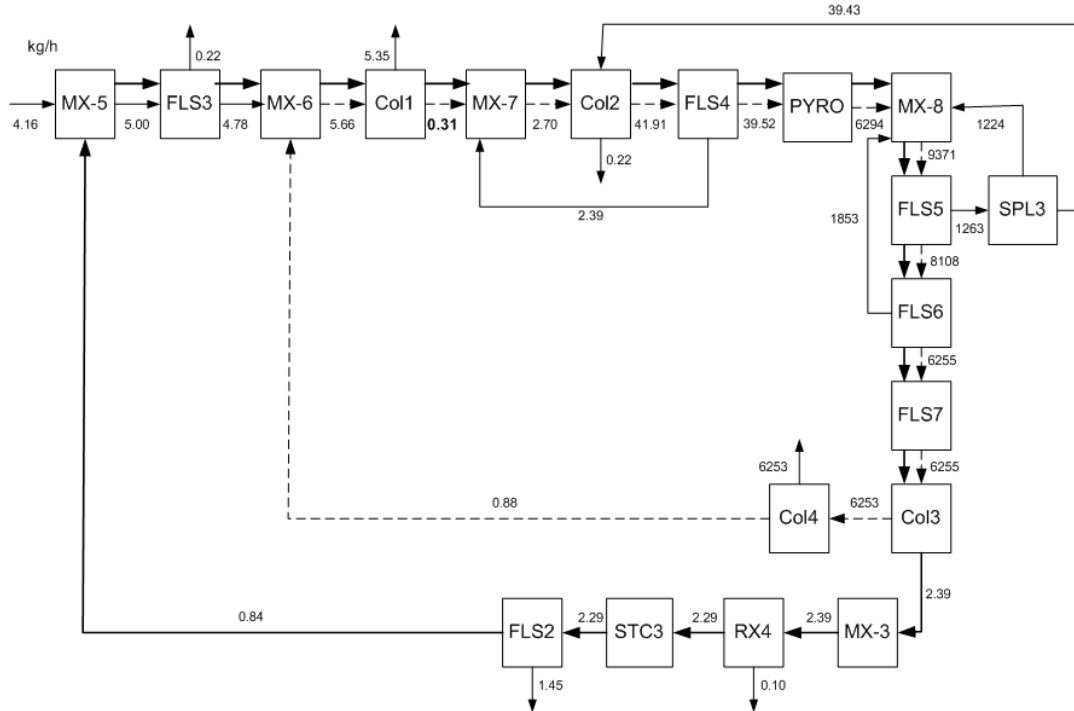
The required detailed process data for the VCM plant is given as a sample PRO/II (version 8) files (PRO/II Casebook, 1992). The steady state operational data has been generated through PRO/II. The input data required for this case study can be found in Appendix A3.

#### **Step 2: Flowsheet decomposition**

The flowsheet decomposition of this case study generated 8 different partitions with 252 mass closed-paths, 7 energy closed-paths, 575 mass open-paths and 52 energy open-paths.

Since in the MTBE example (see section 3.3) did not present nested loops, the flowsheet decomposition for the VCM production will be explained in a bit more detail to exemplify the flowsheet decomposition with nested loops. Figure 5.2 presents the decomposed

flowsheet, for VCM (compound selected) with the flowrates in the respective streams. Two closed-paths (nested loops) are highlighted by bold and dashed lines.



**Figure 5.2:** Flowrates of VCM in the nested loops of VCM process flowsheet

Eq(3.1) is used to calculate the fraction of the flowrate of VCM in each of the two closed-paths, as shown below.

$$fr_{C_{Dash\ line}}^{(VCM)} = \frac{m_{C_{Dash\ line}, S_{Bold}}^{(VCM)}}{\sum_{cp=0}^2 m_{cpj, si}^{(A)}} = \frac{0.88}{0.88 + 0.84} = 0.51$$

$$fr_{C_{Bold}}^{(VCM)} = \frac{m_{C_{Bold}, S_{Bold}}^{(VCM)}}{\sum_{cp=0}^2 m_{cpj, si}^{(A)}} = \frac{0.84}{0.88 + 0.84} = 0.49$$



Eq(3.2) is used to calculate the flowrates of VCM in each of the two closed-loops as follows:

$$m_{C_{Dash\ line}}^{(VCM)} = m_{Bold}^{(VCM),C_{Dash\ line}} \times x_{C_{Dash\ line}}^{(VCM)} = 0.31 \times 0.51 = 0.159$$

$$m_{C_{Bold}}^{(VCM)} = m_{Bold}^{(VCM),C_{Bold}} \times x_{C_{Bold}}^{(VCM)} = 0.31 \times 0.49 = 0.151$$

Here it is a good example to show the new flowsheet decomposition technique. In this way, it is possible to quantify the real accumulation for each closed-path. Repeating this procedure, the corresponding values for all other compounds are obtained. Also using the calculation steps outlined in Figure 3.11, the flowrates for all open- and closed-paths are obtained.

### ***Step 3.1: Calculate mass and energy indicators***

*SustainPro* determined the values of the indicators for all the open- and closed-paths. The indicators will be analysed and discussed in step 4. The top 10 indicators for mass open-paths and mass closed-paths as well as the energy indicators can be found in Appendix A3.

### ***Step 3.2: Calculate Safety Indices***

The value of each sub-index has been determined through the utilization of the process and compounds parameters and using the ranges available for each sub-index in Heikkilä, 1999. The Safety index has a score of 39. The scores for each sub-index can be found in Appendix A3.

### ***Step 3.3: Calculate Sustainability Metrics***

The sustainability metrics have also been determined and their values are listed in Table 5.8 (see step 6). The entire set of parameters determined in the WAR algorithm can be found in Appendix A3.

**Step 4: Indicator Sensitivity Analysis (ISA)**

Based on the algorithms described in section 3.2.4 the indicators showing the highest potential for improvements were selected. Comparing the values obtained for all the indicators and their corresponding paths, those that have the most negative values of MVA, RQ and TVA and the highest values of AF and EWC were identified and listed in Table 5.1 (for mass open-paths) and Table 5.2 (for mass closed-paths).

**Table 5.1:** Mass indicators of the most sensitive mass open-paths -VCM case study

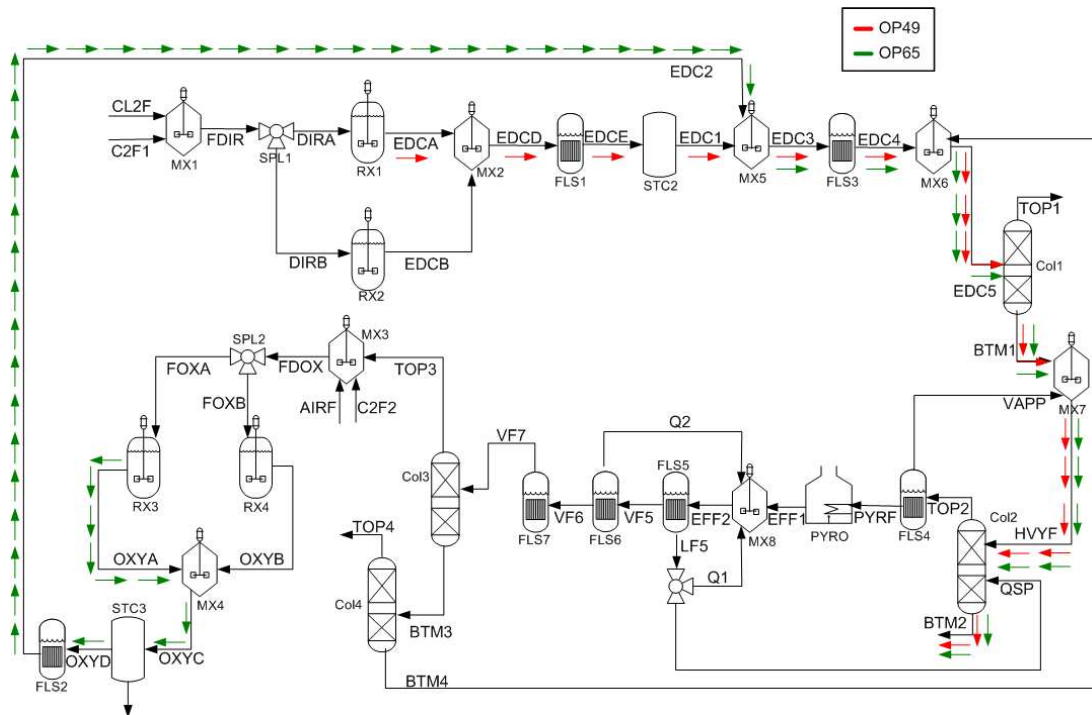
Open path	Compound	MVA ( $10^3$ \$/y)	EWC ( $10^3$ \$/y)	TVA ( $10^3$ \$/y)
OP49	EDC	99	277	-177
OP65	EDC	69	192	-122

**Table 5.2:** Mass indicators values of the most sensitive mass closed-paths -VCM case study

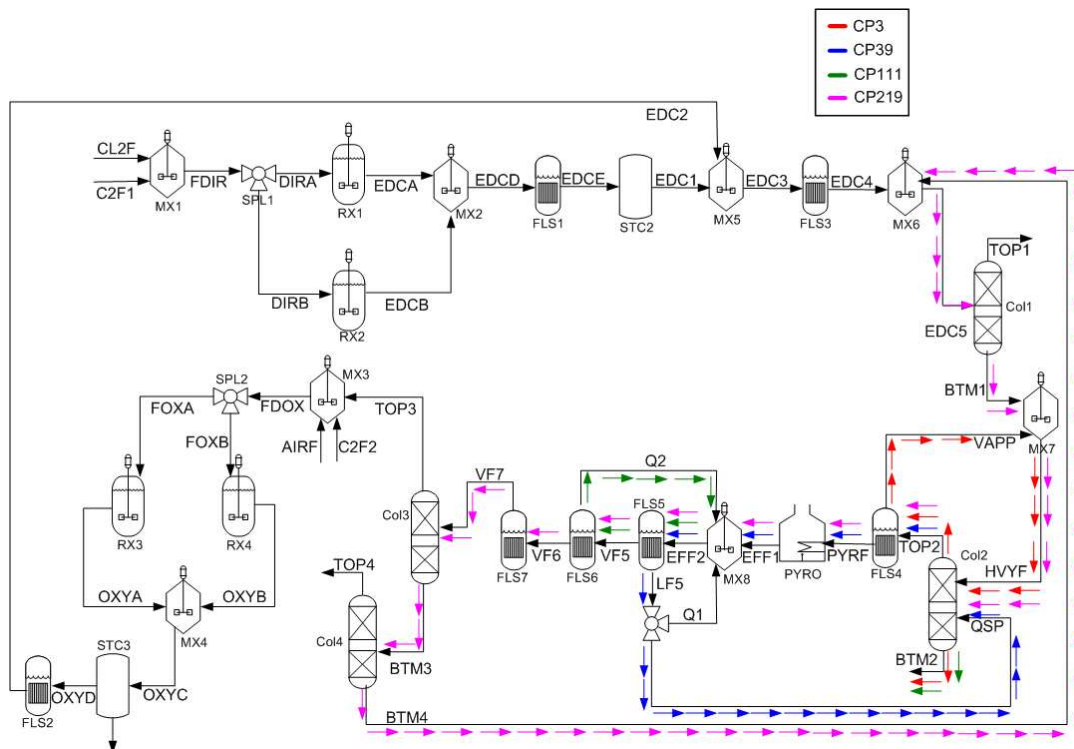
Closed path	Compound	EWC( $10^3$ \$/y)
CP3	EDC	84
CP39	EDC	43
CP111	EDC	42
CP219	EDC	755

The selected indicators correspond to different paths, which are highlighted in Figure 5.3 and Figure 5.4 respectively for open- and closed-paths.

## 5. Case Studies



**Figure 5.3:** Flowsheet highlighting the selected open-paths -VCM case study



**Figure 5.4:** Flowsheet highlighting the selected closed-paths -VCM case study

From Table 5.1 (mass open-paths), it is possible to see that all sensitive open-paths are related to EDC. The negative values of TVA (Total Value Added) demonstrate that a very high potential for improvements exist for these paths. The reason why these open-paths have very negative TVA values is due to their very high values of EWC, which indicates that these paths are consuming a lot of energy comparing with the remaining paths and consequently they should be reduced.

The closed-path indicators show high values corresponding to EWC, which means a big consumption of energy with the recovery of the raw material in all the places where it is being recovered. These values demonstrate that the utilization of EDC is not the optimal within the process.

At this point, 6 paths are available as potential target indicators; they are OP 19, OP 28, CP 3, CP 39, CP 111 and CP 219. Then the objective function has been specified as the gross-profit. The ISA algorithm has been performed and the scores for the selected indicators have been determined (see Table 5.3 and Table 5.4).

**Table 5.3:** ISA algorithm results for open-paths -VCM Case Study

Path	Indicator	Scores
OP 49	EWC	20
OP 65	EWC	19

**Table 5.4:** ISA algorithm results for closed-paths -VCM Case Study

Path	Indicator	Scores
C3	EWC	11
C39	EWC	15
C111	EWC	4
C219	EWC	43

The most sensitive indicators, which are the ones presenting the highest scores have been selected as targets for improvements. For this case study EWC of OP49 and EWC of CP219 are the target indicators. To illustrate the rest of the methodology (new design alternative) the closed-paths analysis has been selected and consequently EWC for CP219, is the target indicator. The results presented in step 5 and 6 are related to this indicator.

**Step 5: Design sensitivity analysis**

The operational variables that influence the value of EWC in the closed-path CP 219 are the following:

- **Reboiler heat duty:** Units COL1, COL3 and COL4
- **Condenser heat duty:** Unit COL2
- **Heat exchange duty:** Units FLS4, FLS5, FLS6, FLS7 and PYRO
- **Flowrates:** CP 219 flowrate

Variations of 5, 10 and 15% on the reference (design) values for all the identified operational variables. The improvements on the target indicator (EWC CP219) are listed for the variations of each variable. Table 5.5 gives a summary of the influence in the target indicator from the changes in the operational variables.

**Table 5.5:** Summary of the sensitivity analysis to measure the influence of operational variables in EWC of closed-path CP219—VCM case study

$\Delta OPV$	Target Indicator Improvement (%)									
	FLS4	PYRO	FLS5	FLS6	FLS7	Cond COL2	Reb COL1	Reb COL3	Reb COL4	Flowrate CP219
5%	0.73%	1.56%	0.00%	0.10%	0.22%	0.17%	0.55%	0.63%	1.04%	2.58%
10%	1.47%	3.12%	0.01%	0.20%	0.43%	0.35%	1.09%	1.26%	2.08%	5.25%
15%	2.20%	4.68%	0.01%	0.30%	0.65%	0.52%	1.64%	1.89%	3.12%	8.01%

Analyzing the results it is possible to conclude that the flowrate of closed-path CP219 is the most sensitive variable for the target indicator and consequently this is the target variable.

**Step 6: Generation and Evaluation of new design alternatives**

Step 5 identified the operational variable to achieve an improvement in the target indicator as the flowrate of a raw material (EDC) in a closed-path (CP 219). From Figure 3.24 it can be noted that the improvement category for this variable is the category 3.1.

To improve the variables of category 3.1 there are four alternatives available:

- Insert a Purge
- Improve the already existent separation units
- Insert a new separation process
- Improve the conversion

- **Insert a Purge**

This alternative is feasible if the raw material is recycled with small amounts of impurities that are becoming accumulated in the system. This alternative also involves practically no investment costs. However even though the target indicator is improved due to the reduction in the EDC flowrate reduction, the value added metric become worse by 9%, which is more than 1-2%, thereby not satisfying the criterion used to define a more sustainable alternative. The reason for this is that the loss of the raw material (7%) in the purge did not compensate for the reduction in the production of the profit. A simulation of process flowsheet with this alternative confirmed the above analysis.

- **Improve the already existent separation units**

The VCM process employs two distillation columns to purify the EDC before the production of VCM. The operational design of these two distillation columns has been studied to identify the design corresponding to a reduction of the flowrate in CP 219. Again, simulation of process flowsheet with this alternative has been performed, however it has not been possible to achieve better results which means that those separations were already optimized.

- **Insert a new separation process**

Inserting a new operation technique (equipment) in closed-path CP 219 becomes an interesting option if the flowrate of CP 219 can be reduced without reducing production rate.

To determine the best unit to separate the impurities present in the EDC recycle loop, the methodology of Jaksland *et al.*, 1996 has been used. Following this methodology, four

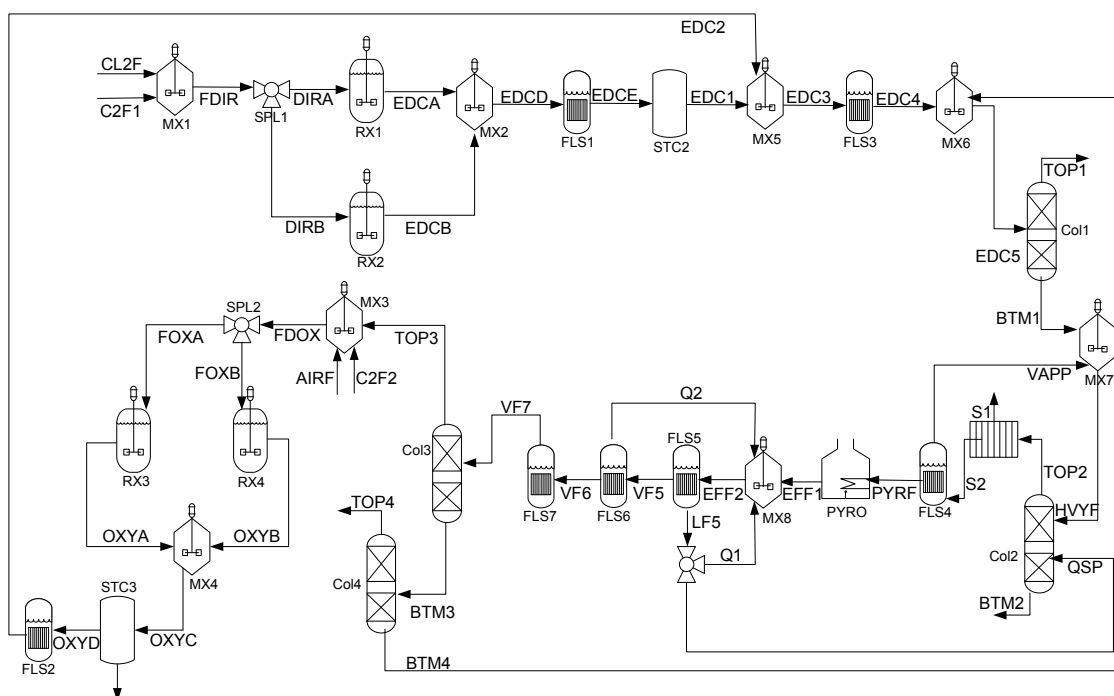
types of separation units were suggested to all pairs of compounds present in the recycle stream. The separation processes suggestions are listed in Table 5.6.

**Table 5.6:** List of feasible separation processes available for EDC purification -VCM Case Study

New Separation
Gas Adsorption
Liquid Adsorption
Liquid Membrane
Pervaporation

Since stream TOP2 that is going to be separated has very small flowrates of the impurities and it is in the liquid phase, pervaporation appeared to be a promising alternative.

The new design flowsheet is presented in Figure 5.5.



**Figure 5.5:** New design flowsheet -VCM case study

The simulation to validate this new approach has been done in PRO/II simulator and the target indicator, EWC of CP 219, has been improved in 1.23% (see Table 5.7).

**Table 5.7:** Improvements in target indicators - VCM production Case Study

Target Indicator	Initial	Final
EWC – CP 219	$7.55 \times 10^3$ \$/y	$7.46 \times 10^3$ \$/y

At the same time, all the performance criteria remained undisturbed while others actually improved. This means that this alternative respects the conditions (constraints) for being classified as a sustainable alternative. Further simulations reveal that the process is now more sustainable as the energy metrics per kg of final product and per value added decreased by 1% and 2% respectively, the water metrics per kg of final product and per value added decreased by 0.9% and 2% respectively. The profit improved by 0.25%, while all the other metrics and indices remained constant (see Table 5.8).

**Table 5.8:** Comparison of the performance criteria between the base case and the new sustainable design alternative - VCM Production Case Study

Sustainability Metrics	Base Case	New Design	Improvement
Total Net Primary Energy Usage rate (GJ/y)	379043	371263	2%
% Total Net Primary Energy sourced from renewables	1.00	1.00	0%
Total Net Primary Energy Usage per kg product (kJ/kg)	7539.10	7440.62	1%
Total Net Primary Energy Usage per unit value added (kJ/\$)	1.50	1.47	2%
Total raw materials used per kg product (kg/kg)	1.52	1.52	0%
Total raw materials used per unit value added (kg/\$)	0.00	0.00	0%
Fraction of raw materials recycled within company	0.00	0.00	0%
Fraction of raw materials recycled from consumers	0.00	0.00	0%
Hazardous raw material per kg product (kg/kg)	0.00	0.00	0%
Net water consumed per unit mass of product (kg/kg)	45.20	44.80	0.9%
Net water consumed per unit value added (kg/\$)	0,0090	0,0088	2%
Safety index	39	39	0%
WAR	-36201	-36201	0%
Profit (\$/y)	28893283	28965311	0.25%



- **Improve the conversion**

This alternative has not been tested, as there was not sufficient data available about the reaction kinetics. In addition, it is known that big changes in the reaction mean many changes in the down stream separation processes and therefore possible high investment costs.

## 5.2.2 Ammonia Production

Over 100 million tons of ammonia are produced each year. The rewards for reducing costs, increasing efficiency and improving the profitability of ammonia plants are enormous. Consequently, the production of Ammonia has been selected as case study.

### *5.2.2.1 Process flowsheet*

A PRO/II simulation model of ammonia synthesis plant is presented here. The entire plant is modelled, from the reforming of the hydrocarbon feedstream to synthesis gas through its purification to its conversion to ammonia in a synthesis reactor.

There are four principal licensors of ammonia synthesis processes: Braun, ICI, Kellogg and Haldor Topsoe. The Kellogg process has been installed in more ammonia plants than any other process and the reason is the lower energy usage. Therefore, Kellogg process as described in PRO/II Casebook is analysed through the process design methodology.

The Ammonia process flowsheet (PRO/II Casebook, 1992) can be divided into four sections as shown in Figure 5.6 and it involves 57 streams, 42 units and 14 compounds.

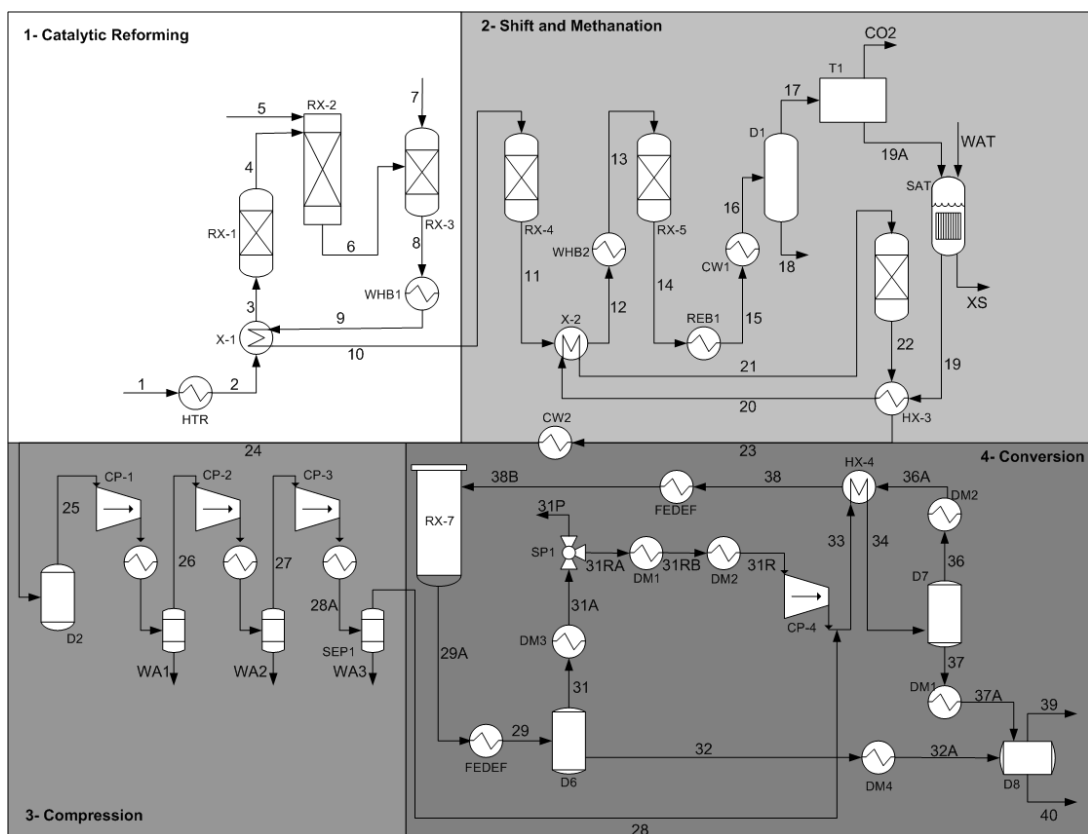


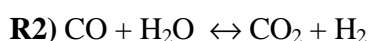
Figure 5.6: Flowsheet of Ammonia production

The ammonia process is a single train process and is divided into four stages which operate sequentially:

### Section 1: Catalytic Reforming

In this section the natural gas undergoes catalytic reforming to produce hydrogen from methane and steam. First, if any sulphur is contaminating the natural gas feed, it should be removed. Then the primary steam reformer converts about 70 % of the hydrocarbon feed into raw synthesis gas in the presence of steam using a nickel catalyst.

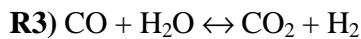
The main reforming reactions are:



In the secondary reformer, air is introduced to supply the nitrogen. The heat of combustion of the partially reformed gas raises the temperature and supplies the energy to reform most of the remaining hydrocarbon feed.

### ***Section 2: Shift and Methanation***

In this section, the resulting syngas is purified by the removal of carbon monoxide and carbon dioxide. The shift conversion is carried out in two stages. The first stage uses a high temperature catalyst and the second stage uses a low temperature one. In the shift converters the carbon monoxide produced in the reforming stage is removed by converting it to carbon dioxide. This reaction also creates additional hydrogen for the ammonia synthesis:



Shift reactor effluent is cooled and the condensed water is separated. Then the gas is passed to the purification section where carbon dioxide is removed from the synthesis gas. It can be removed in systems such as hot carbonate, MEA, Selexol, etc.

After the purification stage, the last traces of carbon monoxide and carbon dioxide are removed in the methanator.

### ***Section 3: Compression***

In this stage the purified gas is firstly cooled down and the condensed water is removed. Then the syngas is compressed, in a three stage unit, up to the pressure required in order to remove the rest of the water.

### ***Section 4: Conversion***

In this section the ammonia synthesis reaction takes place. The first step consists of drying the compressed synthesis gas. Then, the dry gas is mixed with a recycle stream and introduced into the synthesis loop. The gas mixture is chilled and liquid ammonia is removed from the secondary separator. The vapor is heated and passed to the ammonia converter.

The ammonia synthesis reaction is:



Very high pressures ( $\geq 300$  atm) are required in order to obtain a reasonable conversion. The conversion of hydrogen per pass is still less than 30% and so a large recycle of unreacted gases is necessary.

#### *5.2.2.2 SustainPro and methodology application*

##### ***Step 1: Data Collection***

The required detailed process data for the ammonia process plant is given as a sample PRO/II (version 8) files (PRO/II Casebook, (1992)). The steady state operational data has been generated through PRO/II. The input data required for this case study can be found in Appendix A4.

##### ***Step 2: Flowsheet Decomposition***

The flowsheet decomposition of this case study generated 29 different partitions with 14 mass closed-paths, 6 energy closed-paths, 891 mass open-paths and 87 energy open-paths.

##### ***Step 3.1: Calculate mass and energy indicators***

*SustainPro* determined the values of the indicators for all the open- and closed-paths. The indicators will be analysed and discussed in step 4. The top 10 indicators for mass open-paths and the top 5 mass closed-paths as well as the remaining energy indicators can be found in Appendix A4.

##### ***Step 3.2: Calculate Safety Indices***

The value of each sub-index has been determined through the utilization of the process and compounds parameters and using the ranges available for each sub-index in Heikkilä, 1999. The Safety index has a score of 38. The scores for each sub-index can be found in Appendix A4.

**Step 3.3: Calculate Sustainability Metrics**

The sustainability metrics have also been determined and their values are listed in Table 5.18 (see step 6). The entire set of parameters determined in the WAR algorithm can be found in Appendix A4.

**Step 4: Perform Indicator Sensitivity Analysis (ISA)**

Based on the algorithms described in section 3.4.5 the indicators showing the highest potential for improvements were selected. Comparing the values obtained for all the indicators and their corresponding paths, those that have the most negative values of MVA, RQ and TVA and the highest values of AF and EWC were identified and listed in Table 5.9 (for mass open-paths), Table 5.10 (for mass closed-paths) and Table 5.11 (for energy open-paths).

**Table 5.9:** Mass indicators values of the most sensitive open-paths -Ammonia case study

Open path	Compound	MVA ( $10^3$ \$/y)	EWC ( $10^3$ \$/y)	TVA ( $10^3$ \$/y)
OP 17	Water	-65	0	-65
OP 107	Water	-169	175	-345

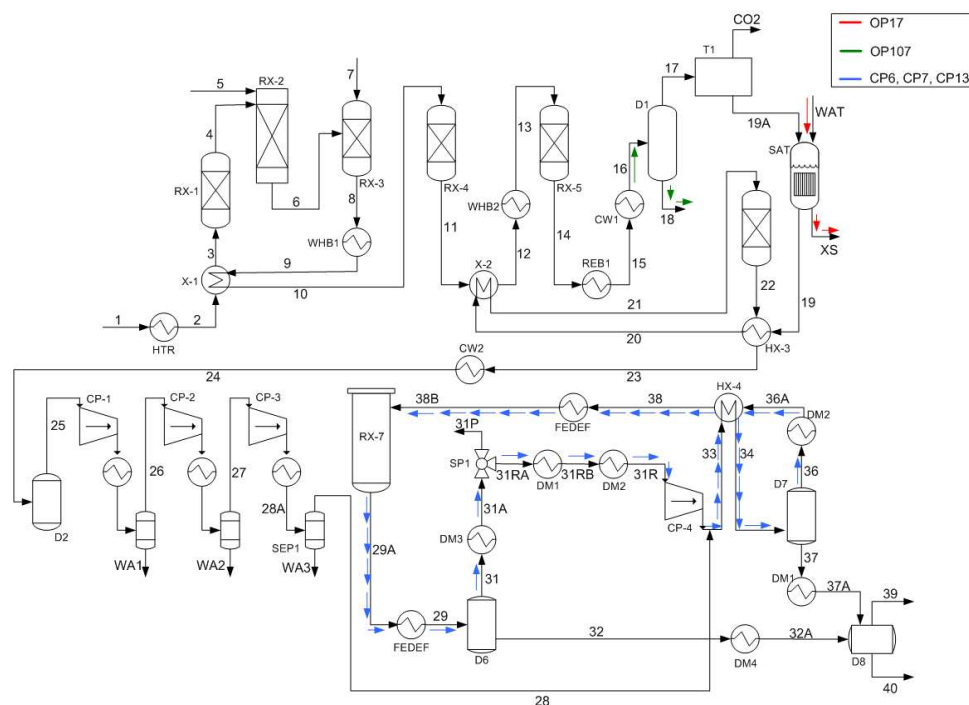
**Table 5.10:** Mass indicators values of the most sensitive closed-paths -Ammonia case study

Closed path	Compound	EWC( $10^3$ \$/y)	AF
CP6	Nitrogen	48	2.5
CP7	Argon	35	77
CP13	Ammonia	109	0.3

**Table 5.11:** Energy indicators values of the most sensitive energy indicators -Ammonia case study

Demand	TDC (\$/h)
C D-6	$2.12 \times 10^4$
C REB1	$1.73 \times 10^4$
XS	$9.67 \times 10^3$
C WHB1	$9.35 \times 10^3$

The selected indicators correspond to different paths, which are highlighted in Figure 5.7.



**Figure 5.7:** Flowsheet highlighting the selected open- and closed-paths -Ammonia Case Study

From Table 5.9 (mass open-paths), it is possible to see that the selected open-paths are related to Water. The negative values of TVA (Total Value Added) demonstrate that a very high potential for improvements exist for these paths. OP7 has very negative TVA value because of its very negative value of MVA, which indicates that money is being lost across the entrance and the exit of the water in the process. OP107 presents very negative value of TVA due to two factors. First, the very negative value of MVA, which indicates that money is being lost across the entrance and the exit of the water in the process and second the high value of EWC which means that this path is consuming a lot of energy comparing with the remaining paths and consequently it should be reduced.

From Table 5.10 (mass closed-paths), it is possible to see that these indicators show high values corresponding to EWC, which means a big consumption of energy with the recovery of the respective compounds. Also high values of AF are presented for CP6 and CP7, which means that these compounds are highly accumulated in the process.

In Appendix A4 it is possible to see that for open-path, the selected indicators are included in top indicators, however there are some indicators showing even worse results. The reason to select these indicators instead of the other ones is that the other indicators are related to products and by-products, which means that to improve those indicators major changes must be done in the reactional mechanism and that means high investment costs and deep analysis to the process, which is not the objective of these studies.

Regarding the energy indicators, it is possible to see from Table 5.11 that all the indicators present high values of TDC, which indicates high values of energy being released (wasted) in D-6, WBH1, REB1 and XS. Consequently, there is a high potential for energy integration with these units.

At this point, 5 paths are available as potential target indicators; they are OP 7 (MVA), OP 107 (MVA and EXC), CP6 (EWC), CP 7 (AF) and CP 13 (EWC). The objective function has been specified as the gross-profit. The ISA algorithm has been performed and the scores for the selected indicators have been determined (see Table 5.12 and Table 5.13).

**Table 5.12:** ISA algorithm results for open-paths -Ammonia Case Study

Path	Indicator	Scores
OP 17	MVA	2
OP 107	MVA	10
OP 107	EWC	10

**Table 5.13:** ISA algorithm results for closed-paths- Ammonia Case Study

Path	Indicator	Scores
CP6	EWC	17
CP7	AF	13
CP13	EWC	12

The most sensitive indicators, which are the ones presenting the highest scores have been selected as targets for improvements. For this case study, MVA and EWC of OP107 and EWC of CP6 are the possible target indicators. To generate the new design alternative MVA and EWC of OP107 have been selected as target indicators to illustrate the following steps of the methodology and consequently the results presented in step 5 and 6 are related to this indicator.



**Step 5: Design sensitivity analysis**

The operational variables that influence the value of MVA in the open-path OP107 is the following:

- **Flowrates:** OP107 flowrate

The operational variables that influence the value of EWC in the open-path OP107 are the following:

- **Heat exchange duty:** Units CW
- **Flowrates:** OP107 flowrate

Variations of 5, 10 and 15% on the reference (design) values for all the identified operational variables. The improvements on the target indicators (MVA and EWC OP107) are listed for the variations of each variable. Table 5.14 and Table 5.15 give a summary of the influence in the target indicators from the changes in the operational variables.

**Table 5.14:** Summary of the sensitivity analysis to measure the influence of operational variables in MVA of open-path OP107—Ammonia case study

$\Delta OPV$	Target Indicator Improvement (%)	
	Flowrate OP107	
5%	5%	
10%	10%	
15%	15%	

**Table 5.15:** Summary of the sensitivity analysis to measure the influence of operational variables in EWC of open-path OP107—Ammonia case study

$\Delta OPV$	Target Indicator Improvement (%)	
	Flowrate OP107	CW
5%	0.63%	5%
10%	1.31%	10%
15%	2.07%	15%

Analyzing the results it is possible to conclude that the flowrate of open-path OP107 is the most sensitive variable for MVA target indicator and CW is the most sensitive for EWC.

However since the flowrate influence both indicators this variable has been selected as target variable.

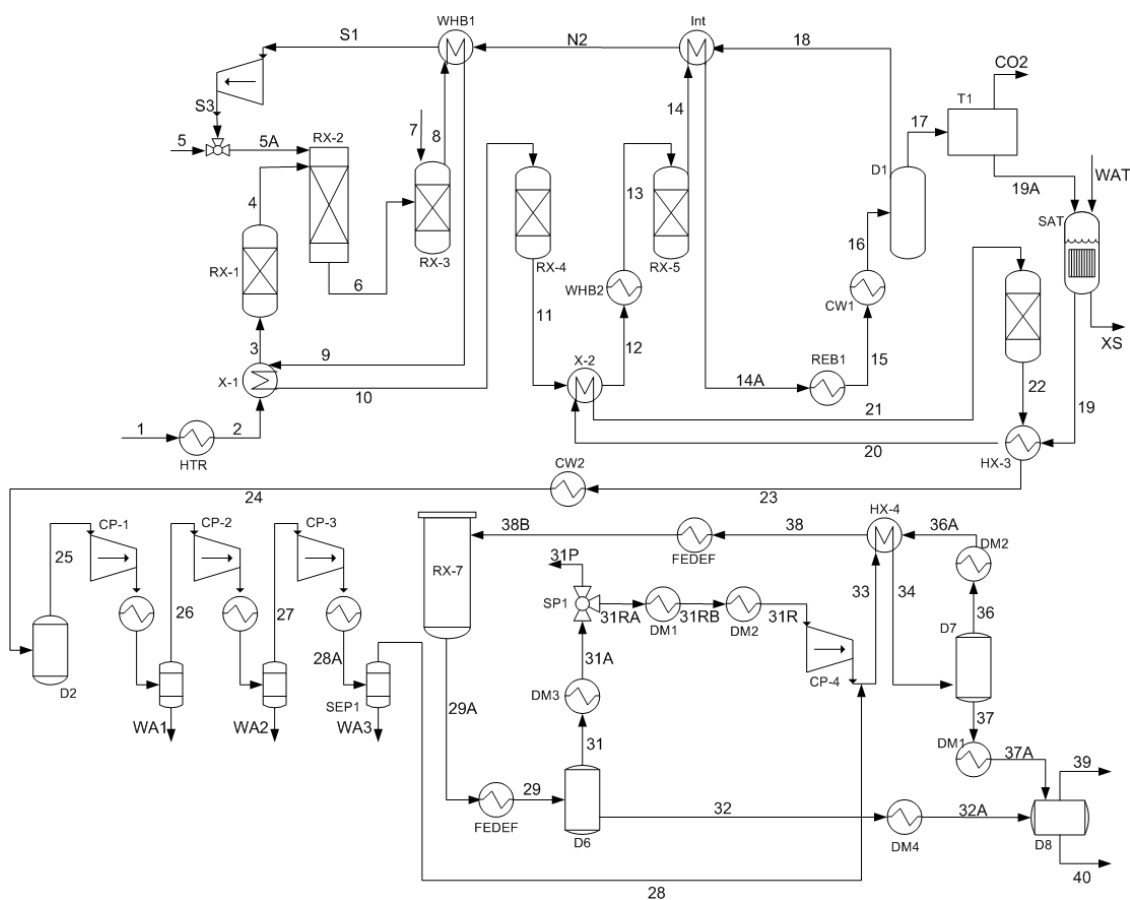
***Step 6: Generation and Evaluation of new design alternatives***

Step 5 identified the operational variable to achieve an improvement in the target indicator as the flowrate of a raw material (Water) in an open-path (OP107). From Figure 3.24 it can be noted that the improvement category for this variable is the category 4.1. To improve the variables of category 4.1 there are four alternatives available:

- Recycle
- Improve Separation
- Increase Conversion
- Source

- **Recycle**

In order to reduce the flowrate in OP107, a recycle of water should be considered. This water is pure and consequently can be completely recycled to the first reactor as steam. This water can be either recycle to stream 5 as steam or to WAT as water. Since steam is more expensive than water this water will be recycle as steam to stream 5. To produce steam it is necessary energy to vaporize the water. From the energy indicators it has been verified that a lot of energy has been wasted and consequently that energy can be used to obtain the steam. Despite of unit D-6, and stream XS releasing a lot of energy, their temperatures do not allow heat integration to produce vapor. Consequently, stream 18 (recovered water) will pass through Int (new heat exchanger that uses part of the energy consumed by utilities in REB1) and then pass through WHB1 (high TDC value) and use all its energy, being completely vaporized. After the vaporization a compressor is then used to adjust the pressure. The flowsheet for the new design alternative is presented in Figure 5.8.



**Figure 5.8:** New design flowsheet -Ammonia Case Study

The simulation to validate this new approach has been done and the target indicator, MVA and EWC of OP107, have been improved by 100%, since the water has been totally recycled (see Table 5.16). The energy indicators have also been improved (see Table 5.17). TDC for the WHB1 is zero since the energy exchanged in this unit has been completely integrated. The energy used in REB1 has been reduced with the partial integration that has been introduced.

**Table 5.16:** Improvements in target indicators - Ammonia production Case Study

Target Indicator	Initial	Final
MVA – OP107	-169	0
EWC – OP107	175	0

**Table 5.17:** Improvements in energy indicators - Ammonia production Case Study

Demand	TDC <sub>Initial</sub> (\$/GJ)	TDC <sub>Final</sub> (\$/GJ)
C WHB1	$9.35 \times 10^3$	0
C REB1	$1.73 \times 10^4$	2025

The sustainability metrics and the safety index are listed for the base case and for the new design alternative in Table 5.18.

**Table 5.18:** Comparison of the performance criteria between the base case and the new sustainable design alternative - Ammonia Production Case Study

Sustainability Metrics	Base Case	New Design	Improvement
Total Net Primary Energy Usage rate (GJ/y)	862693	876316	-1.6%
% Total Net Primary Energy sourced from renewables	0.99	0.98	1.6%
Total Net Primary Energy Usage per kg product (kJ/kg)	9045	9188	-1.6%
Total Net Primary Energy Usage per unit value added (kJ/\$)	6.7	5.2	22.8%
Total raw materials used per kg product (kg/kg)	1.6	1.6	0.0%
Total raw materials used per unit value added (kg/\$)	0.0012	0.0009	24.0%
Fraction of raw materials recycled within company	2.4	2.4	0.0%
Fraction of raw materials recycled from consumers	0.00	0.00	0.0%
Hazardous raw material per kg product (kg/kg)	0.49	0.49	0.0%
Net water consumed per unit mass of product (kg/kg)	41.4	37.6	9.2%
Net water consumed per unit value added (kg/\$)	0.03	0.02	31.0%
Safety index	38	38	0.0%
WAR	788947	788947	0.0%
Profit (\$/y)	8632877	14057457	62.8%

From Table 5.18, it is possible to see that the water metrics decreased by 9% and 31% respectively. The profit increased by 63% since the costs were reduced considerably. All the remaining performance criteria remained unchanged except the energy metrics. The energy metric per kg of final product increased by 1.6% due to the energy consumed in the new compressor, however, the energy metric per value added improved 23% due to the increase in the profit. Consequently, taking into consideration the sustainable process

criteria it can be seen that the energy metric that becomes worse is still in the limits of sustainability and also the energy metric per value added has been improved. The process with the alternative of recycled water can therefore be considered more sustainable.

For this case study the investment costs related to the heat exchangers and the compressor have been calculated. The same analysis would be done in the other case studies to evaluate the applicability of the new suggested designs.

The investment cost has been calculated using prices estimation based on the area of the heat exchangers (<http://matche.com/EquipCost/Exchanger.htm>) and based on the compressor power to the compressor (<http://matche.com/EquipCost/Compressor.htm>). The costs were updated to December 2008, using the cost indexes. The total investment cost has been calculated using the equipments cost multiplied by the lang factor (lang factor=6, Peters *et al.*, 2003). Table 5.19 lists the parameters for the new equipment and the respective investment cost.

**Table 5.19:** Investment costs to the new equipment required in the new design alternative – Ammonia Case Study

	Investment (\$)	U (W/m <sup>2</sup> ) *	Q (W)	T <sub>in</sub>	A (m <sup>2</sup> )	Power (kW)
Compressor (C1)	180365	-	-	-	-	473
Heat Exchanger (Int)	18579	2750	4.44 x 10 <sup>6</sup>	52	31	-
Heat Exchanger (WHB1)	10125	2750	1.56 x 10 <sup>7</sup>	294	19	-
Heat Exchanger (REB1)	4801	2750	3.61 x 10 <sup>6</sup>	117	11	-
Total Investment (\$)					1283218	

\* Values taken from Coulson and Richardson, 1989

Table 5.20 shows the economic comparison between the base case and the improved alternative. It is possible to see that the investment cost will be paid within one year.

**Table 5.20:** Evaluation of the new design alternative– Ammonia Case Study

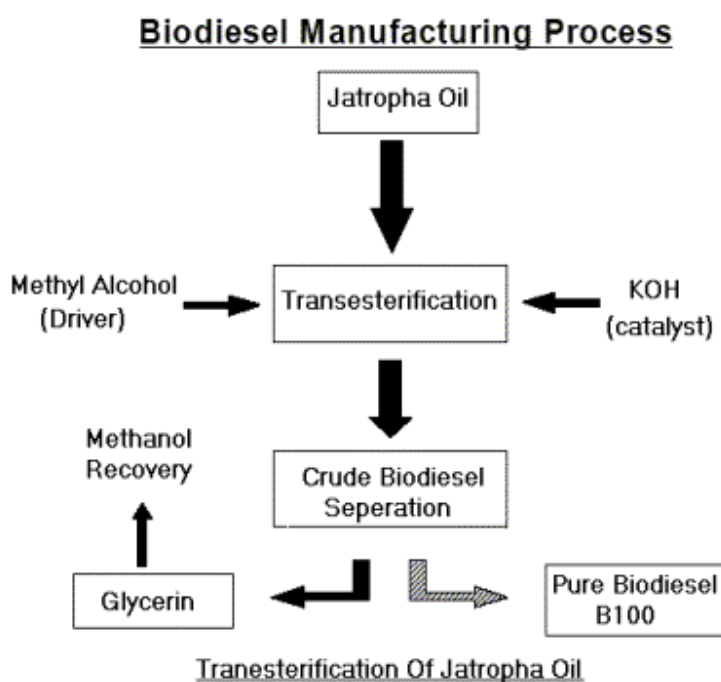
	<b>Base Case</b>	<b>Improved Alternative</b>
<b>Revenues (\$/year)</b>	$2.33 \times 10^7$	$2.33 \times 10^7$
<b>Variable Costs (\$/year)</b>	$7.38 \times 10^6$	$7.01 \times 10^6$
<b>Raw Material Costs (\$/year)</b>	$7.12 \times 10^6$	$2.07 \times 10^6$
<b>Waste Treatment Costs (\$/year)</b>	$1.73 \times 10^5$	$1.73 \times 10^5$
<b>Profit (\$/year)</b>	$8.63 \times 10^6$	$1.41 \times 10^7$

### 5.2.3 Biodiesel Production

#### 5.2.3.1 Process flowsheet

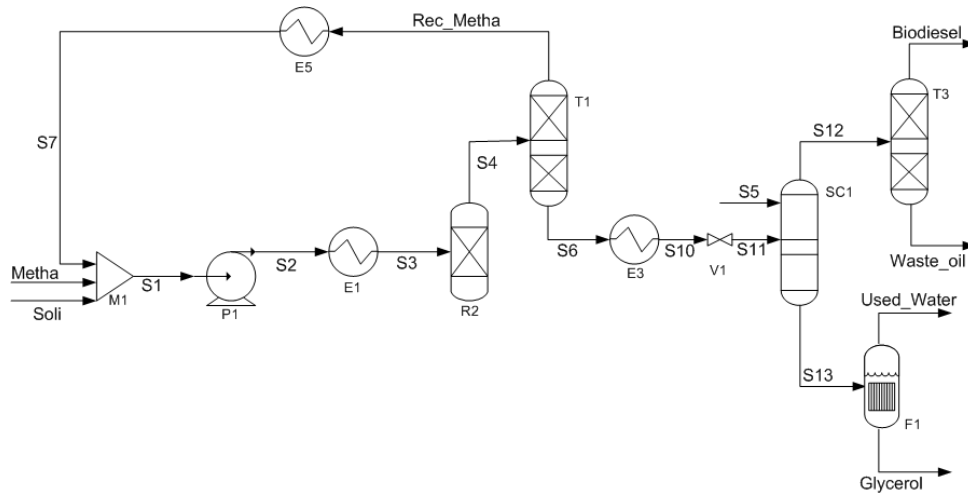
Jatropha oil is a vegetable oil produced from the seeds of a plant called, Jatropha Curcas. Jatropha seeds can be crushed, resulting jatropha oil, which can be processed to produce a high-quality biodiesel.

The process of biodiesel production from Jatropha oil is summarized in Figure 5.9. This process basically consists in the transesterification of the oil into biodiesel in the presence of methanol and a catalyst. A separation takes place to purify the biodiesel.



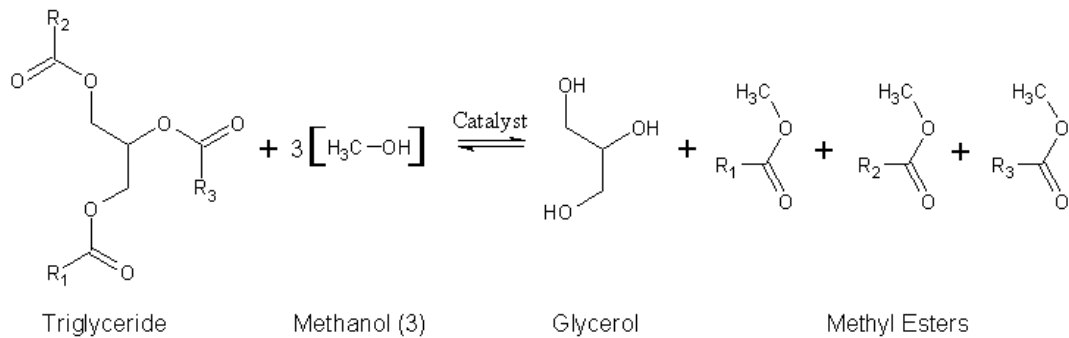
**Figure 5.9:** Scheme of biodiesel production from Jatropha oil (<http://www.geocities.com/biodieselindia/transesterification.htm>)

The flowsheet used for the biodiesel production is represented in Figure 5.10.



**Figure 5.10:** Flowsheet for biodiesel production from Jatropha oil

The feedstock (Jatropha oil with methanol) is first pre-heated before entering the reactor (R2). The transesterification reaction that takes place in the reactor is represented in Figure 5.11.



**Figure 5.11:** General equation of the transesterification of the oil to the biodiesel

The unreacted methanol is recovered with a distillation column (T1). The biodiesel with the glycerol pass through a liquid-liquid extractor (SC1). Glycerol is recovered as the heavy phase, and the biodiesel is the light phase. Finally, both products are purified in distillation columns (T3 and F1).



### *5.2.3.2 SustainPro and methodology application*

#### ***Step 1: Data Collection***

The required detailed process data for the biodiesel production plant has been taken from a simulation of the process in PRO/II (Geraldo, 2009). The steady state operational data has been generated through PRO/II. The input data required for this case study can be found in Appendix A5.

#### ***Step 2: Flowsheet decomposition***

The flowsheet decomposition of this case study generated 6 different partitions with 7 mass closed-paths, 1 energy closed-paths, 34 mass open-paths and 18 energy open-paths.

#### ***Step 3.1: Calculate mass and energy indicators***

*SustainPro* determined the values of the indicators for all the open- and closed-paths. The indicators will be analysed and discussed in step 4. The top 10 indicators for mass open-paths and the top 5 mass closed-paths as well as the remaining energy indicators can be found in Appendix A5.

#### ***Step 3.2: Calculate Safety Indices***

The value of each sub-index has been determined through the utilization of the process and compounds parameters and using the ranges available for each sub-index in Heikkilä, 1999. The Safety index has a score of 25. The scores for each sub-index can be found in Appendix A5.

#### ***Step 3.3: Calculate Sustainability Metrics***

The sustainability metrics have also been determined and their values are listed in Table 5.27 (see step 6). The entire set of parameters determined in the WAR algorithm can be found in Appendix A5.

**Step 4: Indicator Sensitivity Analysis (ISA)**

Based on the algorithms described in section 3.2.4 the indicators showing the highest potential for improvements were selected. Comparing the values obtained for all the indicators and their corresponding paths, those that have the most negative values of MVA, RQ and TVA and the highest values of AF and EWC were identified and listed in Table 5.21 (for mass open-paths) and Table 5.22 (for mass closed-paths). The most significant energy indicators are listed in Table 5.23.

**Table 5.21:** Mass indicators values of the most sensitive mass open-paths -Biodiesel case study

Open path	Compound	MVA ( $10^3$ \$/y)	EWC ( $10^3$ \$/y)	TVA ( $10^3$ \$/y)
OP2	Jatropha oil	-70	0.99	-71
OP12	Methyl linoleate	-276	5	-271
OP16	Methyl oleate	1422	27	1394
OP28	Glycerol	-269	24	-294

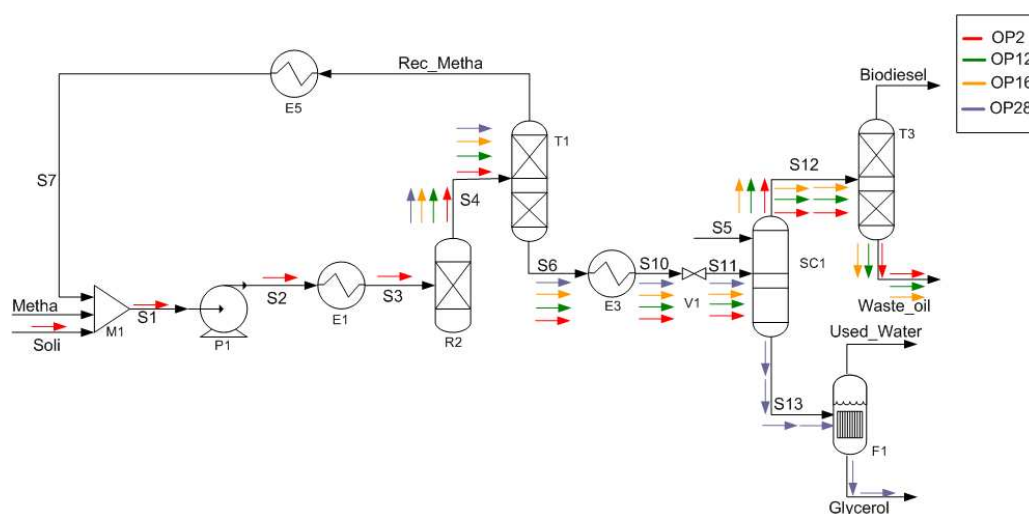
**Table 5.22:** Mass indicators values of the most sensitive mass closed-paths -Biodiesel case study

Closed path	Compound	AF	EWC( $10^3$ \$/y)
CP5	Methanol	1.03	4

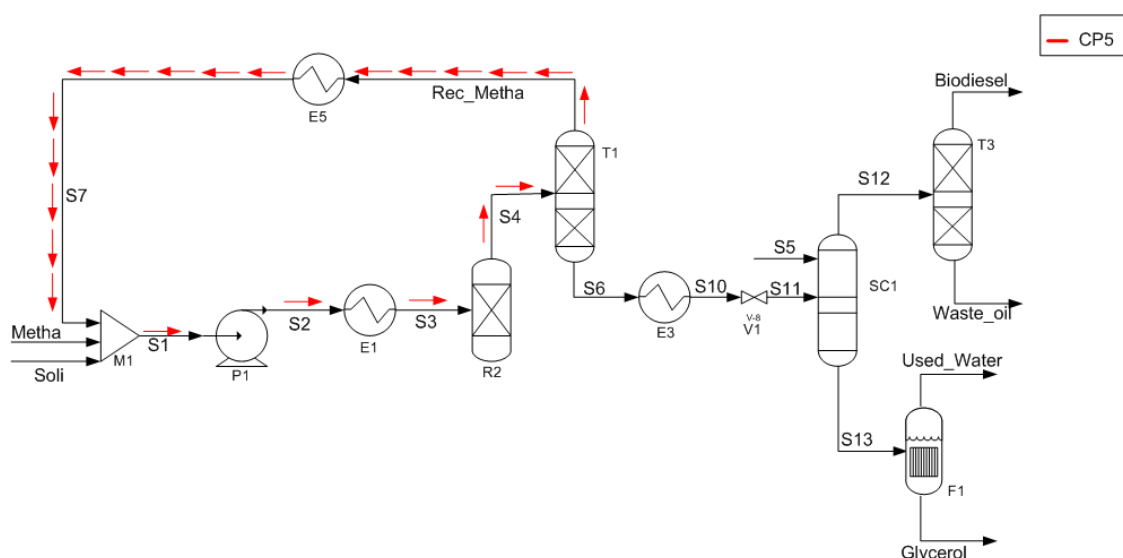
**Table 5.23:** Energy indicators values of the most sensitive energy open-paths -Biodiesel case study

Demand	TDC (\$/GJ)
BIODIESEL	63
GLYCEROL	62
WASTE_OIL	35
C T3	9
C E3	6

The selected indicators correspond to different paths, which are highlighted in Figure 5.12 for open-paths and in Figure 5.13 for closed-paths.



**Figure 5.12:** Flowsheet highlighting the selected open-paths -Biodiesel Case Study



**Figure 5.13:** Flowsheet highlighting the selected closed-paths -Biodiesel Case Study

For this case study the most sensitive indicators are the MVA, for the open-paths OP28, OP12 and OP2. They have very negative values, which means that a lot of money is wasted from the time the material (compound) enters to system to the time they exit the system. OP16, OP28 and CP5 show high EWC values and consequently high energy consumption that should be reduced.

Regarding the energy indicators, it is possible to see from Table 5.23 that biodiesel stream, glycerol stream, waste oil stream and the heat released in unit E3 and T3 present high

values of TDC. This indicates that high values of energy being released (wasted) in the respective demands. Consequently, there is a high potential for energy integration with these demand streams.

At this point, 6 paths are available as potential target indicators; they are MVA for OP28, OP12 and OP2, EWC for OP 16, OP28 and CP5. Then the objective function has been specified as the gross-profit. The ISA algorithm has been performed and the scores for the selected indicators have been determined (see Table 5.24 and Table 5.25).

**Table 5.24:** ISA algorithm results for open-paths -Biodiesel Case Study

Path	Indicator	Scores
OP 28	MVA	21
OP 12	MVA	21
<b>OP 2</b>	<b>MVA</b>	<b>29</b>
OP 16	EWC	14
OP 28	EWC	21

**Table 5.25:** ISA algorithm results for closed-paths -Biodiesel Case Study

Path	Indicator	Scores
CP5	EWC	18
CP5	AF	18

From Table 5.24 it is seen that from the selected indicators, the MVA indicator related to OP2 for the Jatropha oil is the most sensitive (highest score) for open-paths and EWC and AF for CP5 are the most sensitivity indicators for the closed-paths. Steps 5 and 6 are going to be highlighted using the MVA of open-path OP2.

#### ***Step 5: Design sensitivity Analysis***

The operational variables that influence the value of MVA in the open-path OP2 is the following:

- **Flowrates:** SOLI stream flowrate

Variations of 5, 10 and 15% on the reference (design) values for all the identified operational variables. The improvements on the target indicators (MVA OP2) are listed for the variations of each variable. Table 5.26 give a summary of the influence in the target indicators from the changes in the operational variables.

**Table 5.26:** Summary of the sensitivity analysis to measure the influence of operational variables in MVA of open-path OP2—Biodiesel case study

$\Delta OPV$	Target Indicator Improvement (%)
	SOLI
5%	5%
10%	10%
15%	15%

From a sensitivity analysis of the operational parameters influencing the target indicators (MVA- OP 2) it was found that the most significant operational variables is the flowrates of the respective open-paths.

***Step 6: Generation and Evaluation of new design alternatives***

Step 5 identified the operational variable to achieve an improvement in the target indicator as the flowrate of a raw material (Soli) in an open-path (OP2). From Figure 3.24 it can be noted that the improvement category for this variable is the category 4.1. To improve the variables of category 4.1 there are four alternatives available:

- Recycle
- Improve Separation
- Increase Conversion
- Source

• **Recycle**

For OP2, it was found that the operational variable is related to the reduction of an open-path flowrate of a raw material. This pointed to a reduction of the OP 2 flowrate by considering, the recycle of the Jatropha oil. To recycle Jatropha oil, a purge has been considered to avoid the build-up of undesired compounds.

Energy integration has been considered. Biodiesel stream presented a very high TDC value and consequently has been used to heat the stream entering the distillation column (T3). Energy has been saved with this approach. Waste oil stream has been recycled and this stream presented also very high TDC. Consequently, using the energy of the wasted oil, the

feed stream is warmed up and the heat exchanger, E5 can be removed (not required). Finally, the bottom stream coming from distillation column T1 can be used to heat the distillation column inlet stream, and consequently the heat exchanger E3 can be removed. Using this information the process has been simulated again with all the suggested improvements in order to validate the new design alternative.

The flowsheet for the new design alternative is presented in Figure 5.14.

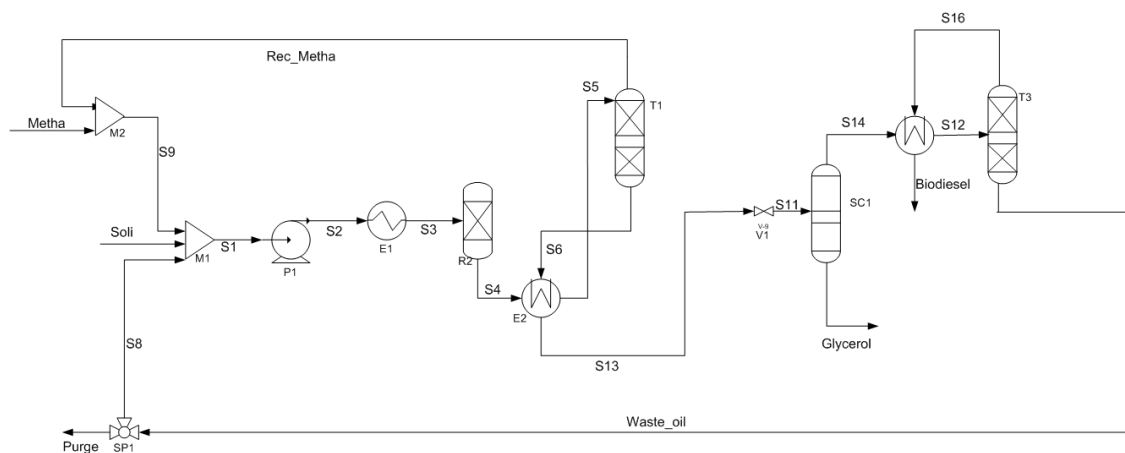


Figure 5.14: New Design Flowsheet -Biodiesel Case Study

For the new sustainable design alternative, which consists of the recycling of Jatropha oil, and the heat integration. The profit increased by 27%. The water metrics per kg of final product and per value added were improved by 39% and 44% respectively. The energy metrics per kg of final product and per value added improved by 71% and 74% respectively. The material metrics per kg of final product and per value added improved by 10% and 17% respectively. The environmental impact improved by 11%. The rest of the performance criteria parameters have remained constant. All the values for the performance criteria are listed in Table 5.27. These results show that a more sustainable design alternative is presented.

The improvements in the target indicators are listed in Table 5.28 and Table 5.29.

**Table 5.27:** Comparison of the performance criteria between the base case and the new sustainable design alternative - Biodiesel Production Case Study

<b>Sustainability Metrics</b>	<b>Base Case</b>	<b>New Design</b>	<b>Improvement</b>
Total Net Primary Energy Usage rate (GJ/y)	31281	9991	68%
% Total Net Primary Energy sourced from renewables	0.9999	0.9997	0.02%
Total Net Primary Energy Usage per kg product (kJ/kg)	1459	417	71%
Total Net Primary Energy Usage per unit value added (kJ/\$)	1.2	0.3	74%
Total raw materials used per kg product (kg/kg)	0.41	0.37	10%
Total raw materials used per unit value added (kg/\$)	0.00034	0.00028	17%
Fraction of raw materials recycled within company	0.1	0.1	0%
Fraction of raw materials recycled from consumers	0	0	0%
Hazardous raw material per kg product (kg/kg)	0	0	0%
Net water consumed per unit mass of product (kg/kg)	1.7	1.0	39%
Net water consumed per unit value added (kg/\$)	0.0014	0.0008	44%
Safety index	22	22	0%
WAR	114	102	11%
Profit (\$/y)	3005427	3827084	27%

**Table 5.28:** Mass Target Indicators improvements - Biodiesel Production Case Study

<b>MVA (\$/h)</b>	<b>Base-Case</b>	<b>New Design</b>	<b>Improvements</b>
OP 2	-8.7	-1.8	79%

**Table 5.29:** Energy Indicators improvements - Biodiesel Production Case Study

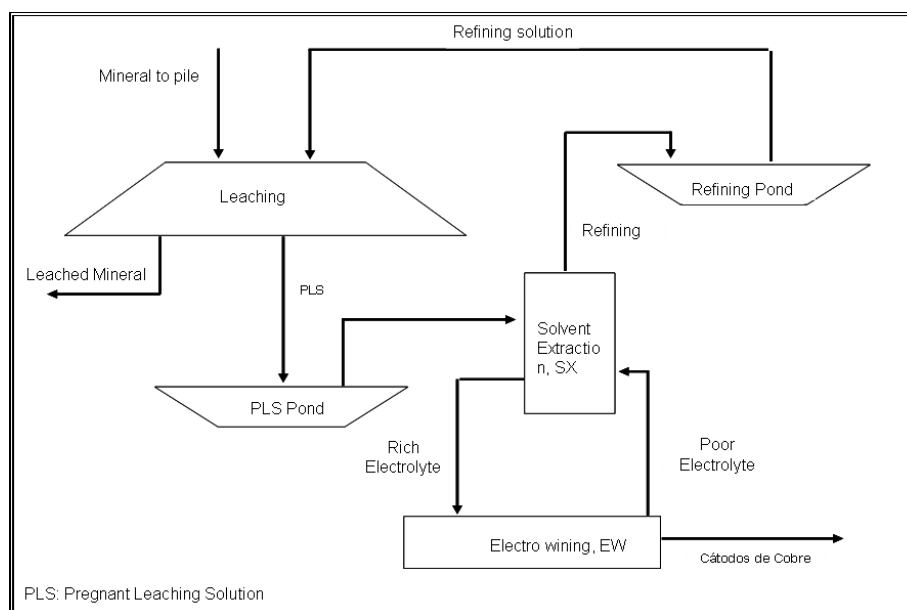
	<b>TDC<sub>Initial</sub> (\$/GJ)</b>	<b>TDC<sub>Final</sub> (\$/GJ)</b>
BIODIESEL	63	11
GLYCEROL	62	0
WASTE_OIL	35	0
C T3	9	5
C E3	6	0

### 5.2.4 Copper Extraction

Copper mining has long been one of the major outcomes to Chile. Codelco Norte, which is the Chilean State owned copper mining company, is currently the second largest copper producing company in the world producing more than 1.66 million tons of refined copper. Codelco also has the largest copper reserves in the world, representing around 20% of the total in the planet. Codelco Norte gave the required data to apply *SustainPro* in order to obtain design suggestions for a more sustainable process.

#### 5.2.4.1 Process flowsheet

The general process for copper recovery can be represented as follows.



**Figure 5.15:** General Hydrometallurgical Process Flowsheet

The process showed in Figure 5.15 consists of one leaching step (heap leaching) using the refining solution from the solvent extraction step. The pregnant leaching solution (PLS)



from the leached ore piles is sent to the solvent extraction circuit (SX), where the solution is purified and concentrated using an organic solution. From the SX step a rich electrolyte solution is sent to the electrowining, where the copper is precipitated. The poor electrolyte solution is sent back to the SX step.

A more specific flowsheet has been designed in order to represent the real cooper extraction process. The flowsheet is represented in Figure 5.16.

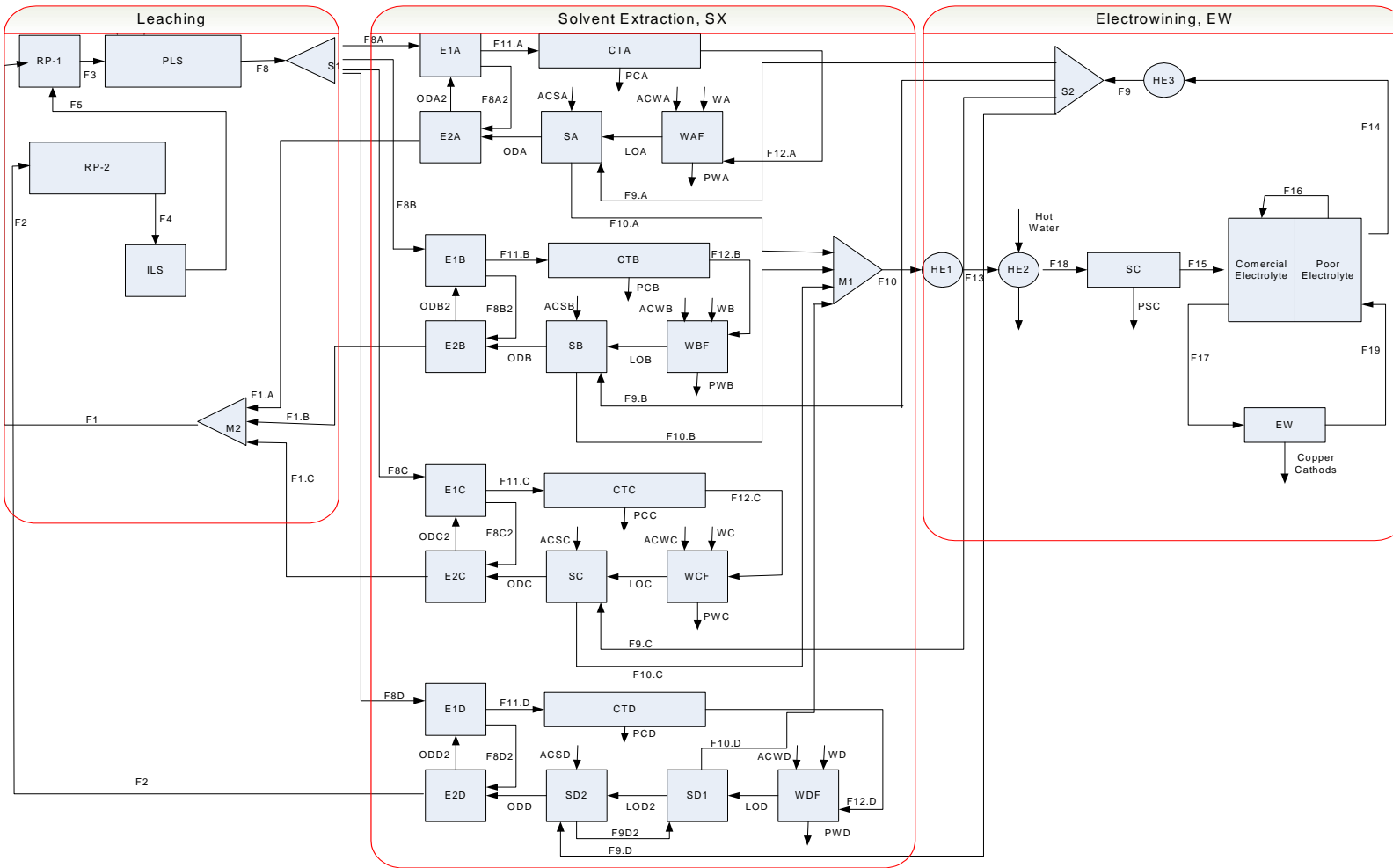


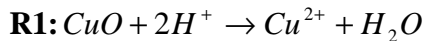
Figure 5.16: Cooper Extraction Flowsheet

The copper extraction process can be divided in three main sections

- Section 1: Leaching process
- Section 2: Solvent Extraction
- Section 3: Electrowining

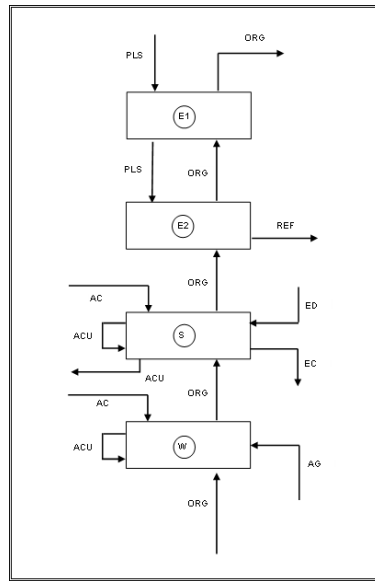
### ***Section 1: Leaching Process***

In this section the mineral is leaching with sulfuric acid. There are several reactions in this section, but once it is difficult to identify all of them it has been considered that the main reaction is



### ***Section 2: Solvent Extraction***

The pregnant leaching solution (PLS) from the leached ore piles is mixed in a first mixer–settler unit with an organic phase carrying an extracting for copper. The aqueous and organic phases are then allowed to separate in the settler. The discharged aqueous solution of the first extraction stage feeds a second extraction mixer–settler where it is allowed to contact a stripped organic solution. The organic and aqueous phases are separated again in another settler. The loaded organic phase flows into the first extraction stage while the discharged aqueous solution or refining (refine) is pumped back to the leach ore pads. The organic solution, from the first extraction stage, feeds the stripping mixer–settler where it is mixed with a poor electrolyte that reverses the extraction process and regenerates the extractant in the organic phase by releasing the extracted copper into the aqueous phase. The aqueous phase, or rich electrolyte, produced by the stripping unit feeds the electrowining circuit while the organic is returned to the second extraction stage. The copper in the rich electrolyte is plated onto cathodes in the EW circuit and the discharged solution or spent electrolyte returns to the stripping mixer–settler. Figure 5.17 shows the extraction process.

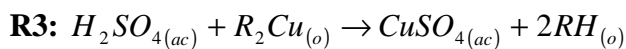
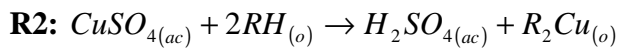


**Figure 5.17:** Extraction process

The organic solvent used in this process contains 80-84% of kerosene and 16-20% of the extractant. The extractant used can be LIX (Cognis) or ACORGA (Cytec). In order to determine some properties needed to apply the methodology it has been considered that LIX solvent is used as an extractant. This organic extractant has the following composition:

- 55% - 5T-Nonyl-2-Hydroxyacetophenone
- 29% - Light Petroleum Distillates
- 6% - 4-Nonylphenol Branched
- 10% - 5- Dodecylsalicylaldoxime

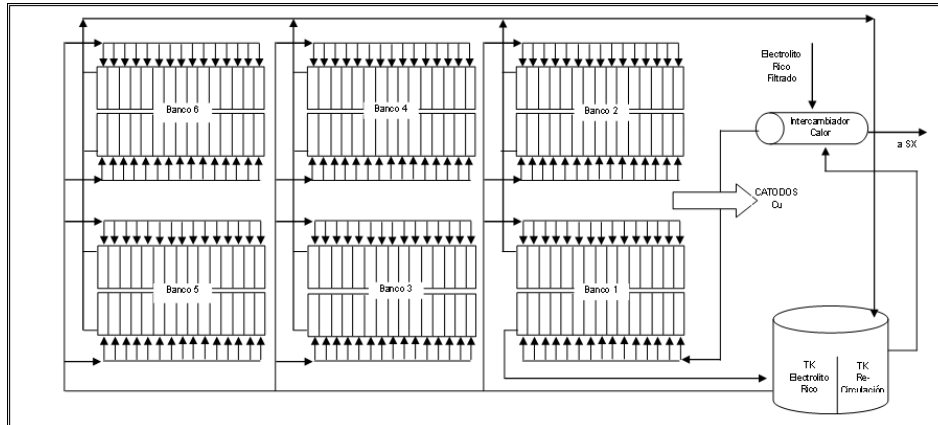
In this section, the following reactions are taking place:



Where *ac* represents the aqueous phase and *o* represents the organic phase.

### Section 3: Electrowining

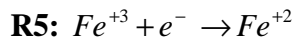
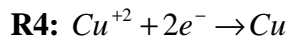
In this section the copper in the rich electrolyte is plated onto cathodes in the electrowining circuit (see Figure 5.18).



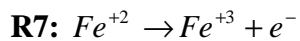
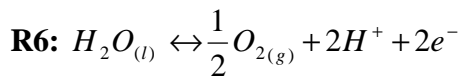
**Figure 5.18:** Electrowining process

In this section the following reactions take place.

Main reduction reactions at the cathode



Main oxidation reactions at the anode



#### *5.2.4.2 SustainPro and methodology application*

##### ***Step 1: Data Collection***

Coldelco Norte has given the required detailed process data for the copper extraction process plant. The input data required for this case study can be found in Appendix A6.

##### ***Step 2: Flowsheet Decomposition***

The flowsheet decomposition of this case study generated 1 partition with 440 mass closed-paths and 288 mass open-paths. No energy data has been given and consequently the energy open- and closed-paths have not been determined.

##### ***Step 3.1: Calculate mass and energy indicators***

*SustainPro* determined the values of the indicators for all the open- and closed-paths. The indicators will be analysed and discussed in step 4. The top 10 indicators for mass open-paths and mass closed-paths can be found in Appendix A6.

##### ***Step 3.2: Calculate Safety Indices***

The value of each sub-index has been determined through the utilization of the process and compounds parameters and using the ranges available for each sub-index in Heikkilä, 1999. The Safety index has a score of 16. The scores for each sub-index can be found in Appendix A6.

##### ***Step 3.3: Calculate Sustainability Metrics***

The sustainability metrics have also been determined and their values are listed in Table 5.36 (see step 6). The entire set of parameters determined in the WAR algorithm can be found in Appendix A6.

**Step 4: Indicator Sensitivity Analysis (ISA)**

Based on the algorithms described in section 3.2.4 the indicators showing the highest potential for improvements were selected. Comparing the values obtained for all the indicators and their corresponding paths, those that have the most negative values of MVA, RQ and TVA and the highest values of AF and EWC were identified and listed in Table 5.30 (for mass open-paths) and Table 5.31 (for mass closed-paths).

**Table 5.30:** Mass indicator values of the most sensitive open-paths -Copper Extraction case study

Open path	Compound	MVA ( $10^3$ \$/y)	EWC ( $10^3$ \$/y)	TVA ( $10^3$ \$/y)
OP 5	H <sub>2</sub> SO <sub>4</sub>	-636	0	-636
OP 12	H <sub>2</sub> SO <sub>4</sub>	-1357	0	-1357
OP 14	H <sub>2</sub> SO <sub>4</sub>	-1100	0	-1100
OP 16	H <sub>2</sub> SO <sub>4</sub>	-856	0	-856
OP 152	H <sub>2</sub> O	-667	0	-667
OP 173	H <sub>2</sub> O	-17	120	-138
OP 217	CuSO <sub>4</sub>	Non Defined	38	-38
OP 221	CuSO <sub>4</sub>	Non Defined	38	-38
OP 225	CuSO <sub>4</sub>	Non Defined	40	-40
OP 229	CuSO <sub>4</sub>	Non Defined	21	-21
OP 233	CuSO <sub>4</sub>	Non Defined	18	-18
OP 287	Cu	1003739	19	1003720

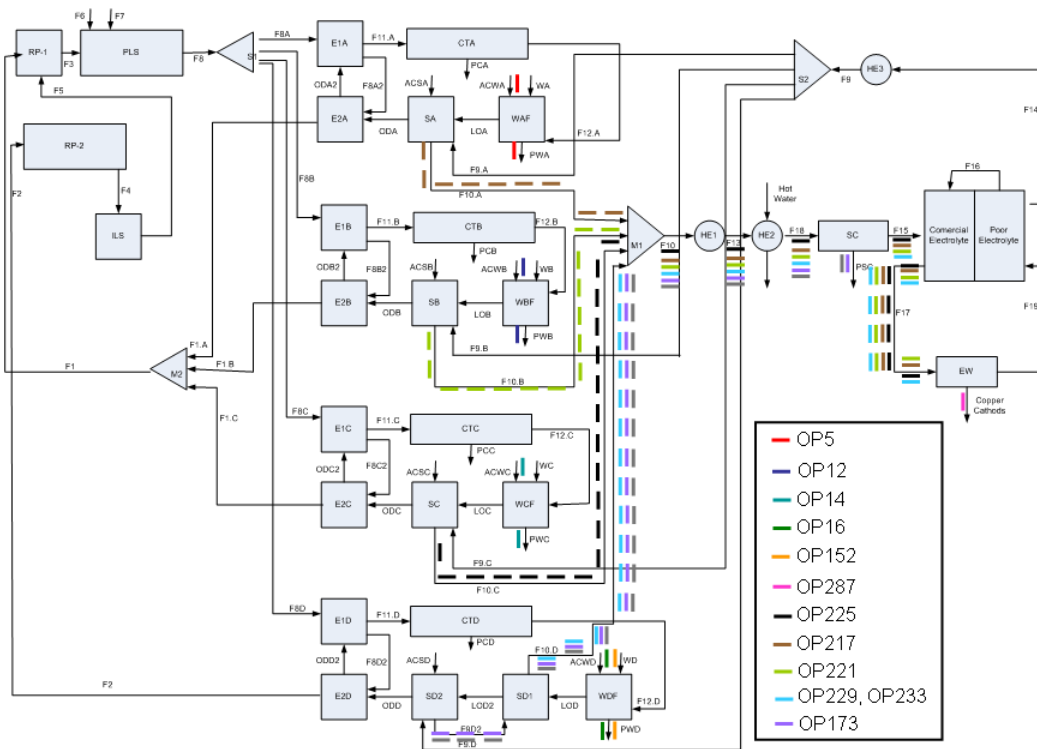
**Table 5.31:** Mass indicator values of the most sensitive closed-paths -Cooper Extraction case study

Closed path	Compound	AF	EWC( $10^3$ \$/y)
C33	H <sub>2</sub> SO <sub>4</sub>	0.018	1826
C36	H <sub>2</sub> O	0.020	23048
C41	H <sub>2</sub> SO <sub>4</sub>	0.018	1798
C44	H <sub>2</sub> O	0.020	22735
C73	H <sub>2</sub> SO <sub>4</sub>	0.018	1788
C76	H <sub>2</sub> O	0.020	22773
C145	H <sub>2</sub> SO <sub>4</sub>	0.021	2026
C148	H <sub>2</sub> O	0.022	25384
C161	H <sub>2</sub> SO <sub>4</sub>	0.028	1924
C164	H <sub>2</sub> O	0.031	24292
C169	H <sub>2</sub> SO <sub>4</sub>	0.028	1895
C172	H <sub>2</sub> O	0.031	23962
C185	H <sub>2</sub> SO <sub>4</sub>	0.027	1884
C188	H <sub>2</sub> O	0.031	24003
C217	H <sub>2</sub> SO <sub>4</sub>	0.031	2136
C220	H <sub>2</sub> O	0.034	26755
C225	H <sub>2</sub> SO <sub>4</sub>	0.735	1309
C228	H <sub>2</sub> O	0.733	14910

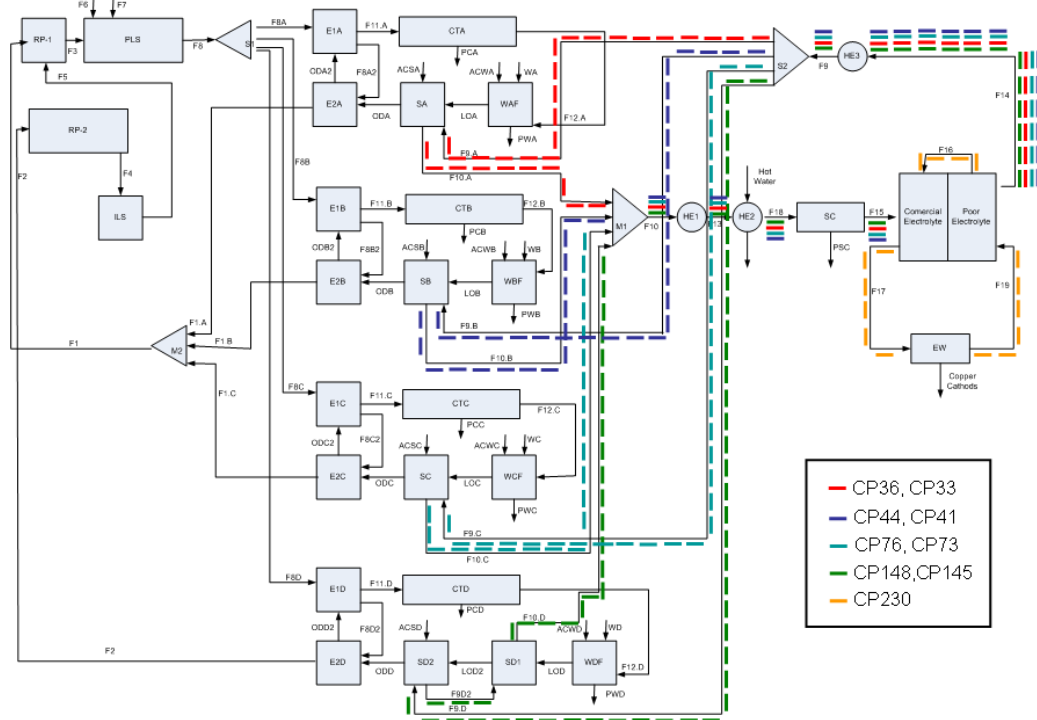
In Table 5.30 and Table 5.31 it is possible to identify the open- and closed-paths related to the most critical points. Figure 5.19 and Figure 5.20 highlight the selected open- and closed-paths.



## 5. Case Studies



**Figure 5.19:** Flowsheet highlighting the selected open-paths -Copper Extraction Case Study



**Figure 5.20:** Flowsheet highlighting the selected closed-paths -Copper Extraction Case Study

In Figure 5.20 some of the closed-paths are not represented, since it is too much information. However, the paths which are not represented are equal to some of the paths highlighted in the figure, the only difference is that instead of going from stream F15 directly to F14, they pass through F17 and F19 (CP220=CP148, CP164=CP36, CP188=CP76, CP172=CP44, CP217=CP145, CP161=CP33, CP169=41, CP185=CP73).

For this case study the most sensitive indicators are the MVA, for the open-paths listed in Table 5.30. They have very negative values, which points out to a big waste of acid in open-paths OP5, OP12, OP14 and OP16. From Table 5.30 it is also possible to see that some paths present high EWC, which means that high energy consumption is being carried out. However, all the open-paths listed for EWC in Table 5.30, except OP173, are related to the cooper recovery process in the electrowining section. This means that the high energy consumption cannot be decreased since that will also decrease the cooper recovery.

The indicators presented in Table 5.31 show very high values of EWC, which means very high energy consumption. These paths are all related to the acid and water recycles.

For the open-paths the ones presenting problems in the MVA were selected since the other related to the electrowinning process and that is a difficult area to improve. For the closed-paths the entire set of EWC indicators presented in Table 5.31 have been selected. The objective function has been specified as the gross-profit. The ISA algorithm has been performed and the scores for the selected indicators have been determined (see Table 5.32 and Table 5.33).

**Table 5.32:** ISA algorithm results for open-paths- Copper Extraction Case Study

Path	Indicator	Scores
OP 12	MVA	9
OP 14	MVA	7
OP 16	MVA	4
OP 5	MVA	6
OP 152	MVA	6

**Table 5.33:** ISA algorithm results for closed-paths -Copper Extraction Case Study

Path	Indicator	Scores
C220	EWC	16
C148	EWC	14
C164	EWC	14
C188	EWC	14
C172	EWC	14
C36	EWC	12
C76	EWC	12
C44	EWC	12
C228	EWC	3
C217	EWC	13
C145	EWC	11
C161	EWC	11
C169	EWC	11
C185	EWC	11
C33	EWC	9
C41	EWC	9
C73	EWC	9
C225	EWC	2

The most sensitive indicators, which are the ones presenting the highest scores have been selected as targets for improvements. For this case study, MVA of OP12 and EWC of CP220 are the possible target indicators. To generate the new design alternative all MVA indicators presented in Table 5.32 have been selected as target indicator, because they are all related to the same units and compounds, the only difference is the part of the process. Consequently analyzing one of them the new design alternative will be the same for the others.

***Step 5: Design sensitivity analysis***

This step will be illustrated to MVA of OP12, since this was the indicator presenting the highest score. For the other indicators the conclusions are the same.

The operational variable that influence the value of MVA in the open-path OP12 is the following:

- **Flowrates:** ACWB flowrate (Flowrate of open-path)

Variations of 5, 10 and 15% on the reference (design) values for all the identified operational variables. The improvements on the target indicator (MVA OP12) are listed for the variations of each variable. Table 5.34 gives a summary of the influence in the target indicators from the changes in the operational variables.

**Table 5.34:** Summary of the sensitivity analysis to measure the influence of operational variables in MVA of open-path OP12—Copper Extraction case study

$\Delta OPV$	<b>Target Indicator Improvement (%)</b>
	ACWB flowrate
5%	5%
10%	10%
15%	15%

Analyzing the results it is possible to conclude that the flowrate of open-path OP12 is the most sensitive variable for both target indicator and consequently this is the target variable.

#### ***Step 6: Generation and Evaluation of new design alternatives***

Step 5 identified the operational variable to achieve an improvement in the target indicator as the flowrate of a raw material (Sulfuric Acid) in an open-path (OP12). From Figure 3.24 it can be noted that the improvement category for this variable is the category 4.1.

To improve the variables of category 4.1 there are four alternatives available:

- Recycle
- Improve Separation
- Increase Conversion
- Source

- **Recycle**

The conclusions taken about recycling the acid and water are the same for OP5, OP14, OP16 and OP152. This means that recycling streams PWA, PWB, PWC and PWD will reduce the costs in the process as well as to reduce the demand of sulfuric acid and water. All these indicators will be improved with this design alternative and consequently the sustainability of the process will also be improved. These streams can be recycled directly back to the unit. The target indicator, MVA of OP12, has been improved by 100%, since the water has been completely recycled. The same happened with the other indicators (see Table 5.35).

**Table 5.35:** Improvements in target indicators - Copper Extraction production Case Study

Target Indicator	Initial	Final
MVA OP 5	$-6.36 \times 10^5$ \$/y	0
MVA OP 12	$-1.36 \times 10^6$ \$/y	0
MVA OP 14	$-1.10 \times 10^6$ \$/y	0
MVA OP 16	$-8.56 \times 10^5$ \$/y	0
MVA OP 152	$-6.67 \times 10^5$ \$/y	0

The sustainability metrics and the safety index are listed for the base case and for the new design alternative in Table 5.36.

**Table 5.36:** Comparison of the performance criteria between the base case and the new sustainable design alternative -Copper Extraction Production Case Study

<b>Sustainability Metrics</b>	<b>Base Case</b>	<b>New Design</b>	<b>Improvement</b>
Total Net Primary Energy Usage rate (GJ/y)	$1.35 \times 10^7$	$1.35 \times 10^7$	0%
% Total Net Primary Energy sourced from renewables	0.8	0.8	0%
Total Net Primary Energy Usage per kg product (kJ/kg)	45116	45116	0%
Total Net Primary Energy Usage per unit value added (kJ/\$)	4.39	4.31	2%
Total raw materials used per kg product (kg/kg)	1.8	1.6	9%
Total raw materials used per unit value added (kg/\$)	$1.7 \times 10^{-4}$	$1.5 \times 10^{-4}$	11%
Fraction of raw materials recycled within company	22	24	11%
Fraction of raw materials recycled from consumers	0	0	0%
Hazardous raw material per kg product (kg/kg)	0.8	0.6	22%
Net water consumed per unit mass of product (kg/kg)	19	14	24%
Net water consumed per unit value added (kg/\$)	$1.8 \times 10^{-4}$	$1.4 \times 10^{-4}$	26%
Safety index	16	16	0,00%
WAR	17600	13766	22%
Profit (\$/y)	$1.45 \times 10^8$	$1.51 \times 10^8$	4%

From Table 5.36, it is possible to see that the water metrics per kg of final product and per value added decreased by 24% and 26% respectively. The energy metric per value added improved 2% and the material metrics per kg of final product and per value added improved by 9% and 11% respectively. The profit increased by 4.42% since the costs were reduced considerably. The environmental impact decrease by 22%.

## 5.3 Batch Processes

### 5.3.1 Insulin Production

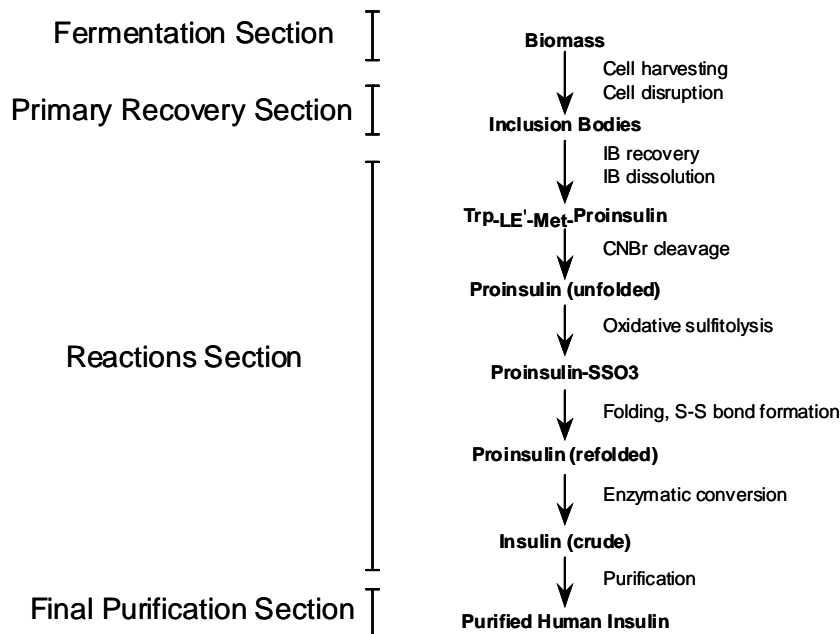
#### 5.3.1.1 Process flowsheet

The insulin process, Petrides, *et al.* (1995), is divided into four sections:

**Fermentation:** Here the *E. coli* cells are used to produce the Trp-LE'-MET-proinsulin precursor of insulin, which is retained in the cellular biomass. Fermentation takes place in order to achieve the desired biomass.

**Primary Recovery:** In this section it is used a high pressure homogenizer to break the cells and release the inclusion bodies. Then with a set of centrifuges and solvents the inclusion bodies are recovered with a higher purity.

**Reactions:** In this part of the process there is a sequence of reactions until the production of insulin. For a better understanding see Figure 5.21.



**Figure 5.21:** Human insulin from proinsulin fusion protein (Adapted from Petrides *et al.*, 1996)

**Final Purification:** Finally, a purification sequence based on multimodal chromatography, which exploits differences in molecular charge, size, and hydrophobicity, is used to isolate biosynthetic human insulin. The crystallization of insulin is the last step of the process.

The flowsheet for the insulin production process is shown in Figure 5.22.

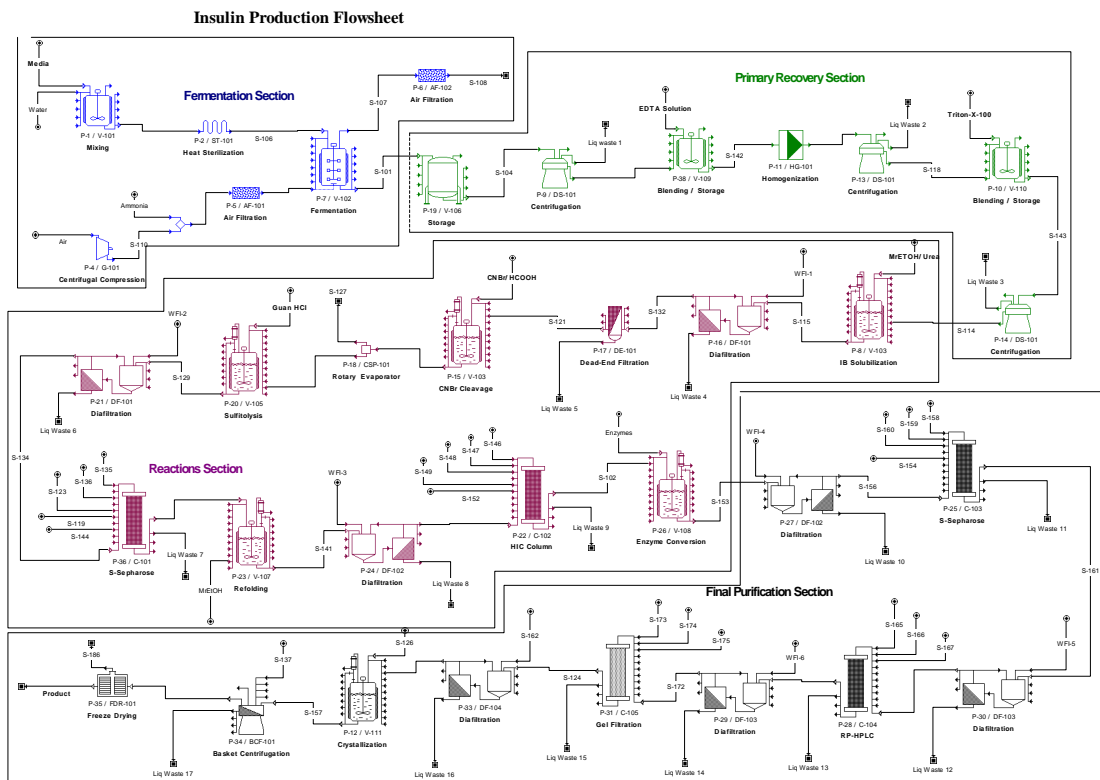


Figure 5.22: Equipment flowsheet for insulin production process



### *5.3.1.2 SustainPro and methodology application*

#### ***Step 1: Data Collection***

The required detailed process data for the insulin synthesis plant was taken from a simulation available on SuperPro Designer, 2008 software package. The prices and costs were taken from Petrides *et al.*, 1995, where the insulin production simulation is described in detail. The input data required for this case study can be found in Appendix A7.

#### ***Step 1-A: Transform equipment flowsheet in an operational flowsheet***

The equipment flowsheet consists of 31 units, which can be seen in Figure 5.22 (some equipments are represented more than once in the flowsheet; they have however, the same name). Taking into account the sequence of operations, the operational flowdiagram is determined (see Figure 5.23). The operational flowdiagram has 92 operations, 169 streams and 38 compounds.

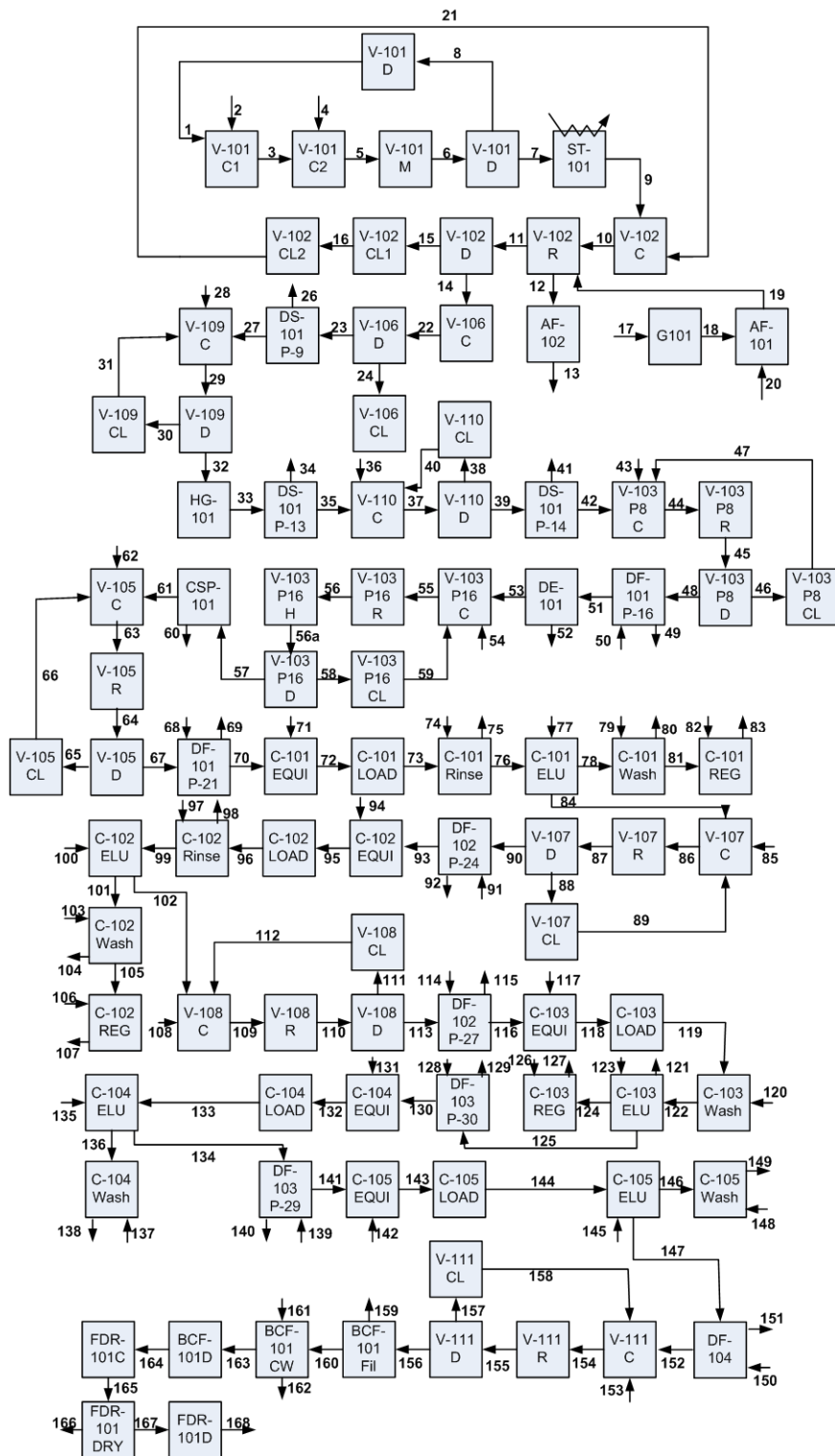
#### ***Step 2: Flowsheet decomposition***

For this case study the operations flowdiagram decomposition generated 68 partitions with 418 mass closed-paths, 11 energy closed-paths, 1022 mass open-paths, 12 energy open-paths and 3344 accumulation-paths.

#### ***Step 3.1: Calculate mass and energy indicators***

For the entire set of flow-paths, the full-set of indicators was calculated, except for some batch compound indicators whose data were not available. The indicators will be analysed in step 4. The top 10 indicators for mass open-paths the mass closed-paths as well as the energy indicators can be found in Appendix A7.

## 5. Case Studies



**Figure 5.23:** Operational flowdiagram -Insulin production process

***Step 3.2: Calculate Safety Indices***

The value of each sub-index has been determined through the utilization of the process and compounds parameters and using the ranges available for each sub-index in Heikkilä, 1999. The Safety index has a score of 18. The scores for each sub-index can be found in Appendix A7.

***Step 3.3: Calculate Sustainability Metrics***

The sustainability metrics have also been determined and their values are listed in Table 5.42 (see step 6). The entire set of parameters determined in the WAR algorithm can be found in Appendix A7.

***Step 4: Indicator Sensitivity Analysis (ISA)***

Based on the algorithms described in section 3.2.4 the indicators showing the highest potential for improvements were selected. Comparing the values obtained for all the indicators and their corresponding paths, those that have the most negative values of MVA, RQ and TVA and the highest values of AF and EWC were identified and listed in Table 5.37 (for mass open-paths) and Table 5.38 (for batch indicators).

**Table 5.37:** Mass indicator values of the most sensitive open-paths - Insulin Production Case Study

Section	OP	Path	Compound	Flowrate (kg/h)	MVA (10 <sup>3</sup> \$/yr)	EWC (10 <sup>3</sup> \$/yr)	TVA (10 <sup>3</sup> \$/yr)
Fermentation	OP 37	S4-S26	Water	25881.8	-22560	68.90	-22629
Primary Recovery	OP 552	S28-S34	TRIS	251.1	-11934	1.14	-11935
Reactions	OP 620	S79-S80	Urea	10399.9	-205917	0.00	-205917
	OP 591	S54-S60	Formic Acid	10837.6	-137334	0.34	-137334
	OP 613	S77-S80	Urea	4564.4	-90375	0.00	-90375
	OP 657	S62-S69	HCL	2987.9	-74542	0.01	-74542
	OP 659	S62-S80	HCL	2047.1	-51070	0.01	-51070
	OP 598	S43-S49	Urea	2199.6	-43552	0.01	-43552
	OP 615	S77-S92	Urea	1913.4	-37885	0.02	-37885
	OP 316	S85-S92	H <sub>2</sub> O Process	27170.1	-21519	17.82	-21537
	OP 313	S79-S80	H <sub>2</sub> O Process	25009.5	-19808	0.00	-19808
	OP 173	S50-S49	H <sub>2</sub> O Process	22301.8	-17663	0.00	-17663
	OP 403	S103-S104	H <sub>2</sub> O Process	20616.6	-16328	0.00	-16328
	OP 335	S91-S92	H <sub>2</sub> O Process	16596.3	-13144	0.00	-13144
	OP 292	S77-S80	H <sub>2</sub> O Process	13334.5	-10561	0.00	-10561
OP 721	S103-S104	NaCl	1204.4	-12210	0.00	-12210	
Final Purification	OP 1016	R V108-S138	Insulin	1.6	-639591	0.00	-639591
	OP 1009	R V108-S149	Insulin	1.4	-564122	0.00	-564122
	OP 1011	R V108-S159	Insulin	1.3	-507708	0.00	-507708
	OP 1005	R V108-S121	Insulin	0.9	-343498	0.00	-343498
	OP 822	S137-S138	Acetonitrile	2905.0	-80527	0.00	-80527
	OP 804	S148-S149	Acetic acid	6117.1	-169566	0.00	-169566
	OP 797	S145-S149	Acetic acid	3738.3	-103624	0.00	-103624
	OP 790	S142-S149	Acetic acid	1869.1	-51812	0.00	-51812
	OP 789	S137-S138	Acetic acid	1756.8	-48698	0.00	-48698
	OP 521	S148-S149	H <sub>2</sub> O Process	55053.9	-43603	0.00	-43603
	OP 821	S135-S138	Acetonitrile	1325.3	-36736	0.00	-36736
	OP 514	S145-S149	H <sub>2</sub> O Process	33670.7	-26667	0.00	-26667
OP 507	S142-S149	H <sub>2</sub> O Process	16835.3	-13334	0.00	-13334	

For this case study the most sensitive indicators are the MVA, for the open-paths listed in Table 5.37. They have very negative values, which means that a lot of money is wasted from the time the material (compound) enters to system to the time they exit the system. The energy consumption, as well as, the recycles in the process do not allow very high potential for improvements when compared with the

very high values of MVA (see also the EWC values in Table 5.37). The most sensitive batch indicators were selected and they are listed for each section in Table 5.38.

Operations V-102R, V-103(P8)R, V-105R and V-111R present high values of OTF when compared with the other operations, which means that these operations are spending too much time to execute their respective process operation. V-102R and DS-101(P9) have high values of OEF when compared with the other operations. This indicates that these two operations have high energy consumption. These indicators show high potential for improvements and their values should be reduced.

The options for improvements in each section are analysed below.

Fermentation: In this section the most critical points are related to the waste water. This water is produced as a by-product in the main reaction which means that the chances for reducing this by-product are not too big. Consequently this is not the best choice for a process improvement. Regarding the batch indicators it can be seen that a very high value of OTF has been calculated for the fermentation operation (V-102R). Analyzing the compound indicators for this operation it is seen that ammonia is the compound which is limiting the operation time. Consequently, to improve the fermentation process it would be necessary to take into consideration the ammonia concentration and the related parameters, which influence the rate of the reaction (this point is further discussed in steps 5 and 6).

**Table 5.38:** Batch Indicators values of the most sensitive accumulation-paths - Insulin Production Case Study

Section	Operation	TFVF	OTF	OEF	AP	Compound	Flow(kg/s)	TF	EF
Fermentation	V-102R	0.829	0.065	0.332	230	Oxygen	$6.84 \times 10^{-2}$	27058	0.06
					231	Glucose	$4.95 \times 10^{-2}$	9884	0.07
					232	Salts	$5.16 \times 10^{-3}$	63021	0.00
					233	Water	$5.30 \times 10^{-1}$	66039	3.06
					234	Biomass	$8.66 \times 10^{-3}$	Non-Defined	Non-Defined
					235	Ammonia	$5.14 \times 10^{-3}$	66244	0.00
					236	CO2	$1.79 \times 10^{-2}$	44668	0.10
Primary Recovery	DS-101(P9)	0.387	0.022	0.205	497	Glucose	$3.93 \times 10^{-2}$	$5.48 \times 10^{-6}$	0.01
					498	Salts	$5.74 \times 10^{-3}$	$1.65 \times 10^{-6}$	0.00
					499	Water	$9.98 \times 10^{-1}$	$3.27 \times 10^{-3}$	0.18
					500	Biomass	$5.14 \times 10^{-2}$	Non-Defined	0.009884671
Reaction	V-103(P8) R	0.869	0.029	0.013	943	Cont Proteins	$9.36 \times 10^{-4}$	20410.07	Not Available
					944	IBs	$3.85 \times 10^{-3}$	90061.83	Not Available
					945	Trp-Proinsulin	$2.79 \times 10^{-3}$	Non-Defined	Not Available
	V-105 R	0.737	0.043	0.002	1388	NaSO3	$6.97 \times 10^{-3}$	23.49	Not Available
					1389	Na2O6S4	$3.48 \times 10^{-3}$	100.90	Not Available
					1402	Denatured Proin	$5.62 \times 10^{-4}$	660080.16	Not Available
					1403	Proinsulin-SSO3	$5.41 \times 10^{-4}$	Non-Defined	Not Available
Final Purification	V-111 R	0.987	0.043	0.001	3039	Insulin	$1.63 \times 10^{-4}$	1513336.07	Not Available
					3040	Insulin Crystal	$1.34 \times 10^{-4}$	Non-Defined	Not Available

Primary Recovery: Here the most critical points are related to the Tris base waste. This solvent is used as a buffer to facilitate the separation of the cell debris particles from the inclusion bodies. Tris base has been used without being recycled. Purifying this compound will allow its recycle to the process and consequently reduce the money wasted with this solvent (MVA will consequently decrease). In this section the separation operation DS-101(P9), indicates a high OEF, which means that compared with the other operations this operation is having high utilities consumption. The compound which is mainly responsible for this high value is the water (it can be seen from in EF value in Table 5.38). To reduce OEF and EF indicators, the separation operation needs to be improved or a new separation technique, which makes the separation easier, may be used.

Reactions: This section involves many solvents (Urea, WFI, Formic acid, HCL, NaCl) which are also not recovered and recycled within the process. The best option to improve these indicators, and consequently, the process is to recover the solvents and recycle. For some of them it might not be economically feasible. Some waste solvents, however, may be sold to other users. For example, urea can be further processed and utilized as nitrogen fertilizer (Petrides, *et al.* (1995)). Here, two operations, V-103 R and V-105 R, indicate high values of OTF, which point out that their operation time should be reduced. Regarding the compound indicators for these two operations, it is possible to see from Table 5.38 that IB and denatured proteins, are respectively, the compounds causing the high time consumption. In order to decrease the time factor, it is necessary to analyze the rate of reaction conditions.

Final Purification: In this last section the insulin purification indicates some problems. The paths listed in Table 5.37, for insulin, have very low flowrates, although, their MVA values are very negatives. This happens because the insulin price is very high. These very negative values for MVA indicate that even very small losses of insulin imply very high loss in revenue. To improve the purification operations two options could be considered, to improve the existent separation process and/or add new

separation operation that can achieve higher insulin recovery. In this section, also, there are solvents (Acetonitrile, Acetic acid and WFI) that are being wasted. As mentioned above, these solvents might be purified and recycled or they may be sold to other users (Acetonitrile, Petrides, *et al.*, 1995). In this section V-111R is the operation which indicates the biggest potential for improvements, due to the high OTF value. Considering the TF values, it is possible to visualize that Insulin is the limiting compound. As in the previous section, the operational variables involved in the rate of the reactions needs to be investigated in order to reduce the reaction time, and consequently, this indicator.

Due to the large size of the flowsheet it is not be possible to present or discuss all the modifications to improve the whole process. Therefore, in the remaining steps, only section 1 and section 3 are highlighted with respect to improvement of their mass indicators and batch indicators.

To apply the ISA algorithm the indicators listed in Table 5.37 for section 3 were selected as possible target indicators. After applying the ISA algorithm it is seen that from the selected indicators, the MVA indicator related to OP591 for Formic acid is the most sensitive. Consequently, this indicator is considered the target indicator for improvements (see Table 5.39, row highlighted with bold letters). For batch indicators, the most sensitive indicator in section 1 is the TF of ammonia in the fermentation operation (V-102R).



**Table 5.39:** ISA algorithm results for the open-paths - Insulin Production Case Study

Path	Indicator	Compounds	Scores
OP 721	MVA	NaCl	2
OP 620	MVA	Urea	3
OP 613	MVA	Urea	2
OP 403	MVA	WFI	2
OP 335	MVA	WFI	8
OP 313	MVA	WFI	5
OP 292	MVA	WFI	3
OP 173	MVA	WFI	4
OP 316	MVA	WFI	10
<b>OP 591</b>	<b>MVA</b>	<b>Formic Acid</b>	<b>15</b>
OP 615	MVA	Urea	10
OP 598	MVA	Urea	11
OP 657	MVA	HCL	7
OP 659	MVA	HCL	6

The most sensitive indicators, which are the ones presenting the highest scores have been selected as targets for improvements. For this case study, MVA of OP591 and is the most promising target indicators.

#### **Step 5: Design sensitivity analysis**

The operational variables that influence the value of MVA in the open-path OP591 is the following:

- **Flowrates:** S54 flowrate (inlet stream same as open-path flowrate)

Variations of 5, 10 and 15% on the reference (design) values for all the identified operational variables. The improvements on the target indicator (MVA OP591) are listed for the variations of each variable. Table 5.40 gives a summary of the influence in the target indicators from the changes in the operational variables.

**Table 5.40:** Summary of the sensitivity analysis to measure the influence of operational variables in MVA of open-path OP591—Insulin case study

$\Delta OPV$	Target Indicator Improvement (%)
	S54 flowrate
5%	5%
10%	10%
15%	15%

From the sensitivity analysis of the operational parameters influencing the target indicator (MVA - OP591) it was found that the most significant operational parameter is the flowrate of OP591 (S4 flowrate reduction).

The fermentation process time is mainly dependent on the specific cell growth rate, which is represented by the following equation (Singh *et al.*, 2008)

$$\mu_g = \mu_{g \max} \frac{C_{O_{Glucose}}}{(k_{Glucose} + C_{O_{Glucose}})} \frac{C_{O_2}}{(k_{O_2} + C_{O_2})} \frac{C_{NH_3}}{(k_{NH_3} + C_{NH_3})} \frac{C_{H_3PO_4}}{(k_{H_3PO_4} + C_{H_3PO_4})} \quad \text{Eq (5.1)}$$

In the previous equation,  $\mu_g$  is the specific cell growth rate,  $\mu_{g \max}$  is the maximum specific cell growth rate,  $k_1$  is the monod constant for each compound and  $C_o$  is the concentration.

To analyze the operational parameters that influence the batch target indicator (TF), Eq (5.1) was used and it was possible to verify that the ammonia ( $NH_3$ ) concentration is the most significant parameter in order to reduce the time of the reaction.

#### ***Step 6: Generation and Evaluation of new design alternatives***

Step 5 identified the operational variable to achieve an improvement in the target indicator as the flowrate of a solvent (Formic acid) in an open-path (OP591). From Figure 3.24 it can be noted that the improvement category for this variable is the category 4.5.

To improve the variables of category 4.5 there are four alternatives available:

- Recycle
- Improve separation
- New Separation
- New solvent

- **Recycle**

To recycle formic acid, a separation operation needs to be inserted in order to purify/recover this compound. Applying the process separation algorithm of Jaksland and Gani, 1996, a set of feasible separation techniques for the recovery of formic acid coming from stream S60 has been identified and they are listed in Table 5.41.

**Table 5.41:** List of feasible separation processes available for formic acid purification- Insulin Production Case Study

New Separation
Distillation
Liquid Membrane
Liquid Adsorption
Gas Adsorption
Pervaporation

From Table 5.41, the pervaporation is selected as the separation operation, because it involves lower operational costs when compared with the other separation techniques and it does not need external compounds for the separation. In the literature, Nakatani *et al.*, 1994, found that membranes such as aromatic imide polymer asymmetric, are available to purify/recover formic acid from water (which is the mainly impurity compound in S60). To estimate the selectivity of the membrane, it is assumed that this system (membrane to separate) have the same behavior as the behavior of a similar mixture considered by Huang *et al.*, 1998. Using this information the new design alternative has been presented.

The flowsheet for the new design is presented in Figure 5.24.

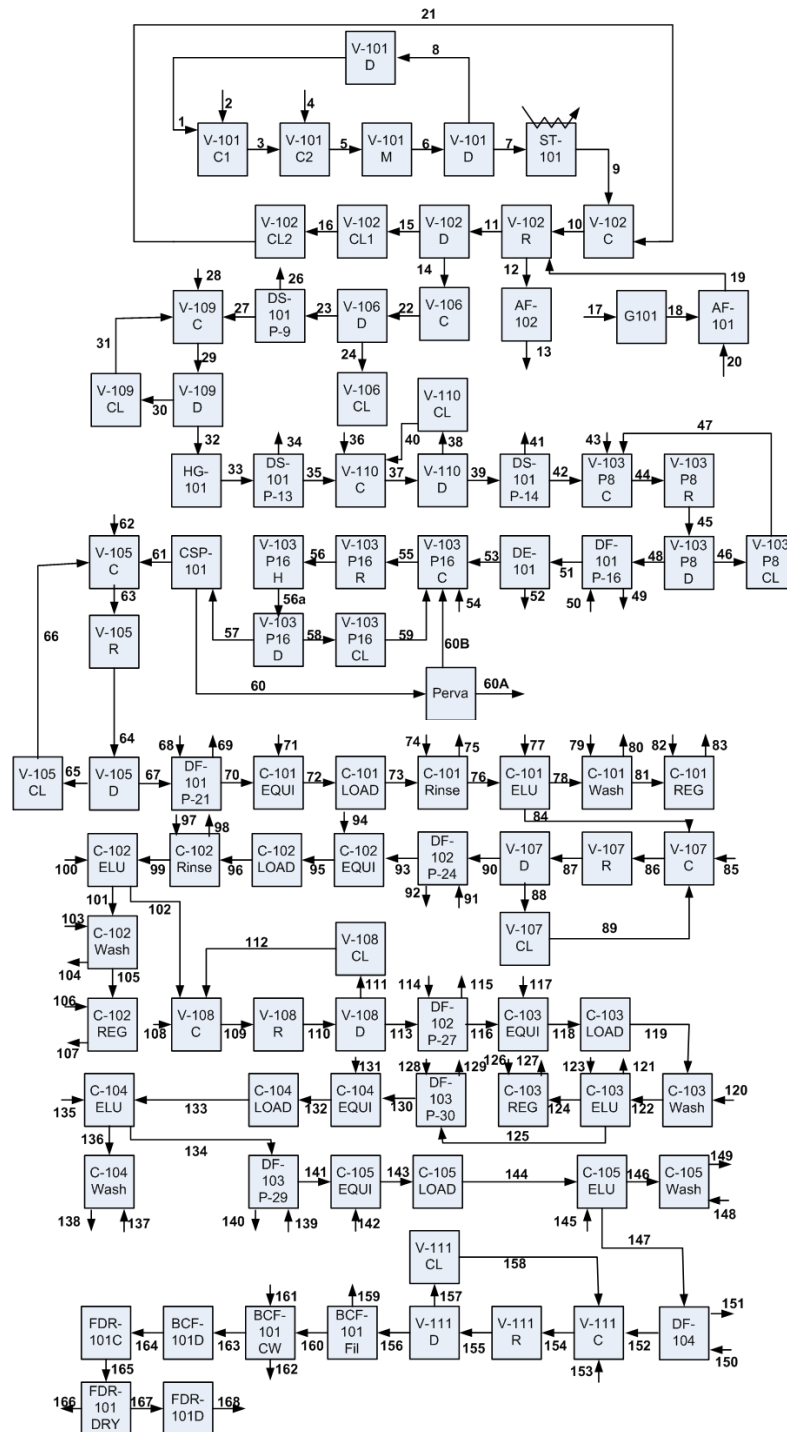


Figure 5.24: New design flowdiagram -Insulin Production Case Study

To reduce the fermentation time the concentration of ammonia needs to be increased. The concentration has been increased by 2% and 0.2% of fermentation time reduction was achieved. This is not a significant improvement. This fact indicates that the fermentation process is already optimized and nothing could be done in order to improve it. Also, the fermentation operation has more constraints that cannot be violated without changing the enzyme.

For the new sustainable design alternative, which consists of the recycling of formic acid, the following improvements were achieved. The profit increased by 2%, the water and the energy metrics per value added improved by 2%. The material metrics improved by 2% and 4% respectively per kg of final product and per value added. Finally, the environmental impact output was improved by 32%. The rest of the performance criteria parameters have remained constant. All the values for the performance criteria are listed in Table 5.42. The target indicator improved by 99.9% (see Table 5.43). These results show that a more sustainable design alternative is presented.

**Table 5.42:** Comparison of the performance criteria between the base case and the new sustainable design alternative - Insulin Production Case Study

Metrics	Initial	Final	Improvement
Total Net Primary Energy Usage rate (GJ/y)	26832	26832	0%
% Total Net Primary Energy sourced from renewables	0,720	0,72	0%
Total Net Primary Energy Usage per Kg product (kJ/kg)	293551	293551	0%
Total Net Primary Energy Usage per unit value added (kJ/\$)	0,000457	0,000447	2%
Total raw materials used per kg product (kg/kg)	40128	39182	2%
Total raw materials used per unit value added (kg/\$)	$6,24 \times 10^{-5}$	$5,98 \times 10^{-5}$	4%
Fraction of raw materials recycled within company	0,0006	0,02	3855%
Fraction of raw materials recycled from consumers	0	0	0%
Hazardous raw material per kg product (kg/kg)	4932	3986	19%
Net water consumed per unit mass of product (kg/kg)	10135	10135	0%
Net water consumed per unit value added (kg/\$)	$1,58 \times 10^{-5}$	$1,55 \times 10^{-5}$	2%
Safety index	18	18	0%
WAR	23709	16188	32%
Profit (\$/y)	7416586097	7563540066	2%

**Table 5.43:** Improvements in target indicators - Insulin Production Case Study

Target Indicator	Initial	Final
MVA – OP591	$-1,37 \times 10^{-8}$ \$/y	$-1,69 \times 10^{-5}$ \$/y

### 5.3.2 $\beta$ -Gal Production

$\beta$ -Gal is mainly used in the utilization of cheese whey. Another application of  $\beta$ -Gal is in the treatment of milk products. A significant number of people are lactose intolerant and cannot digest milk or milk products. Production of lactose-free milk products (using  $\beta$ -Gal reactors) allows those people to digest them. Due to the importance  $\beta$ -Gal in the society this case study has been selected as a case study.

#### 5.3.2.1 *Process flowsheet*

This case study presents the process production of  $\beta$ -galactosidase ( $\beta$ -Gal), an intracellular enzyme produced by *Escherichia coli* (E. coli). This enzyme is normally produced by E. coli up to 1-2% of total cell however using genetic engineering; the level can go up to 20-25% of total protein.

The flowsheet for the  $\beta$ -galactosidase production process is shown in Figure 5.25.

The  $\beta$ -galactosidase production flowsheet can be divided into three sections: 1) Fermentation, 2) Primary Recovery, and 3) Purification (see Figure 5.25).

#### ***Section 1: Fermentation Section***

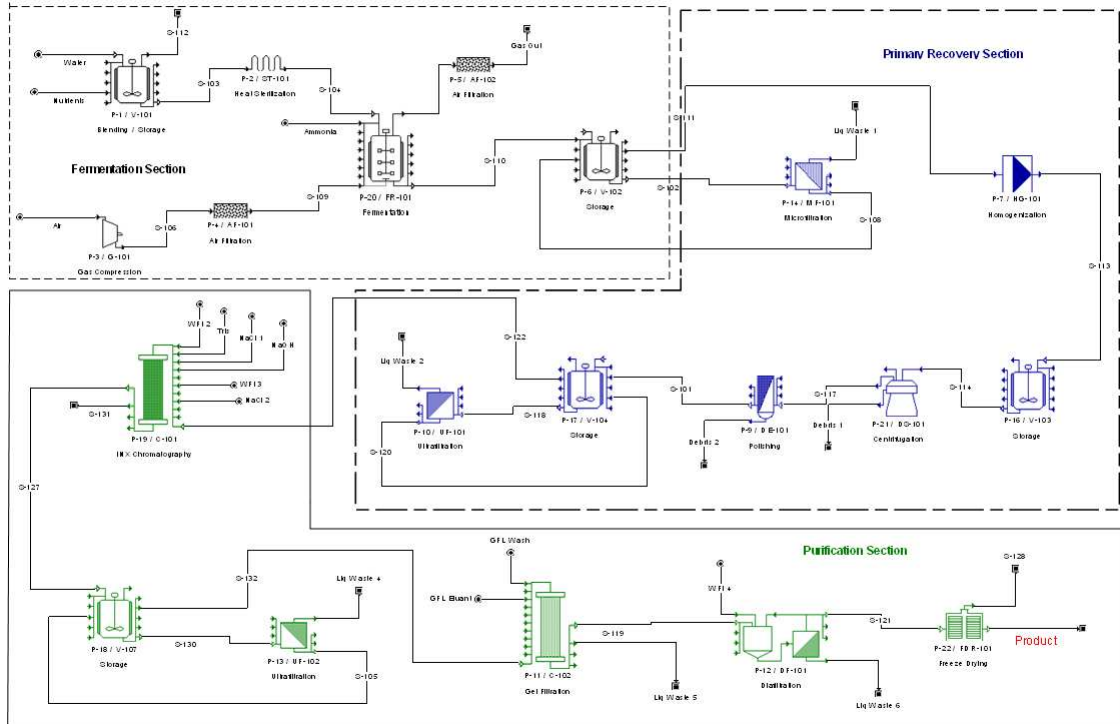
Here the *Escherichia coli*. cells are used to produce the  $\beta$ -galactosidase ( $\beta$ -Gal), through a fermentation process. The fermentation process consists in four operations, the charge, the reaction, the discharge and the clean.

#### ***Section 2: Primary Recovery Section***

The first step of the primary recovery section is cell harvesting to reduce the volume of the broth and to remove extracellular impurities. Since  $\beta$ -galactosidase is an intracellular product, the next step is cell disruption, performed in a high-pressure homogenizer. After homogenization, a centrifuge is used to remove most of the cell

debris. A dead-end polishing filter removes the remaining cell debris. The resulting protein solution is concentrated by an ultrafilter.

**Beta-Galactosidase Process Flowsheet**



**Figure 5.25:** Flowsheet of  $\beta$ -galactosidase production process

**Section 3: Purification Section**

Next the product stream is purified by an ion exchange chromatography column. Then it is concentrated by a second ultrafiltration unit and polished by a gel filtration unit.



### *5.3.2.2 SustainPro and methodology application*

#### ***Step 1: Data Collection***

The required detailed process data for the  $\beta$ -Gal production is given as a sample of *SuperPro Designer*. The mass and energy balances were taken from the simulation results obtained from *SuperPro Designer*, 2009 library, which used the information from Mominuddin, 2003. All the prices necessary to the indicators calculation were also obtained from Mominuddin, 2003. The input data required for this case study can be found in Appendix A8.

#### ***Step 1A: Transform equipment flowsheet in an operational flowsheet***

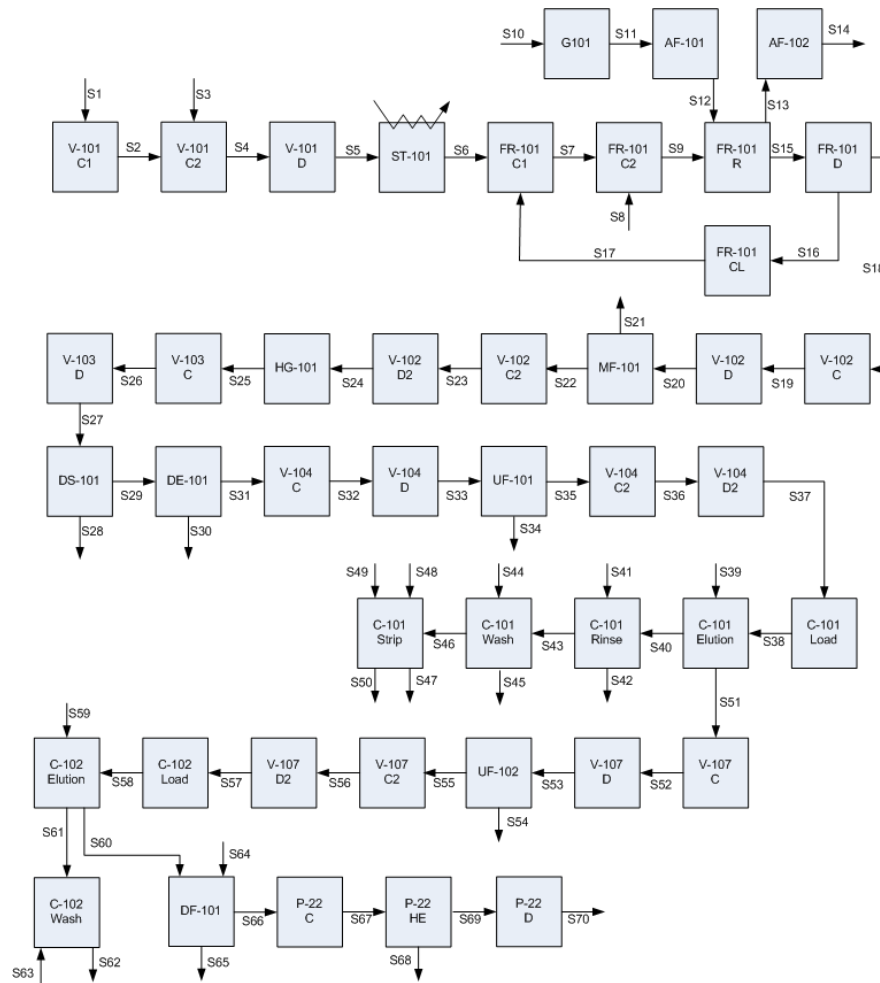
The equipment flowsheet consists of 20 units, as shown in Figure 5.25. To apply the algorithm, the flowsheet needs to be connected to an operational flowdiagram (see Figure 5.26). The operational flowdiagram has 44 operations, 70 streams and 17 compounds.

#### ***Step 2: Flowsheet decomposition***

For the  $\beta$ -Gal production the operations flowdiagram decomposition generated a total of 41 partitions, 17 mass closed-paths, 251 mass open-paths, 1 energy closed-paths, 36 energy open-paths and 663 accumulation-paths.

#### ***Step 3.1: Calculate mass and energy indicators***

For the entire set of flow-paths, the full-set of indicators was calculated, except for some batch compound indicators whose data were not available. The indicators will be analysed in step 4. The top 10 indicators for mass open-paths the top 5 mass closed-paths as well as the energy indicators can be found in Appendix A8.



**Figure 5.26:** Operational flowdiagram of  $\beta$ -galactosidase production process

**Step 3.2: Calculate Safety Indices**

The value of each sub-index has been determined through the utilization of the process and compounds parameters and using the ranges available for each sub-index in Heikkilä, 1999. The Safety index has a score of 28. The scores for each sub-index can be found in Appendix A8.

**Step 3.3: Calculate Sustainability Metrics**

The sustainability metrics have also been determined and their values are listed in Table 5.51 (see step 6). The entire set of parameters determined in the WAR algorithm can be found in Appendix A8.

**Step 4: Indicator Sensitivity Analysis (ISA)**

Based on the algorithms described in section 3.2.4 the indicators showing the highest potential for improvements were selected. Comparing the values obtained for all the indicators and their corresponding paths, those that have the most negative values of MVA, RQ and TVA and the highest values of AF and EWC were identified and listed in Table 5.44 (for mass open-paths) and Table 5.49 (for batch indicators).

**Table 5.44:** Mass indicator values of the most sensitive open-paths - $\beta$ -Gal Production

OP	Path	Compound	Flowrate (kg/h)	MVA ( $10^3$ \$/yr)	EWC ( $10^3$ \$/yr)	TVA ( $10^3$ \$/yr)
OP 31	S1-S21	H <sub>2</sub> O	33158	-55177	69	-55246
OP 34	S1-S34	H <sub>2</sub> O	15295	-25451	37	-25488
OP 37	S1-S47	WFI	14472	-22939	35	-22973
OP 114	S41-S42	WFI	95438	-75367	0	-75367
OP 118	S44-S45	WFI	155349	-122679	0	-122679
OP 121	S63-S62	WFI	72043	-62582	0	-122679
OP 125	S10-S14	N <sub>2</sub>	33684	0	67	-67

**Table 5.45:** Batch Indicators values of the most sensitive operations-  $\beta$ -Gal Production

Operation	OTF	OEF
DS-101	0.043	0.84
V-104 D2	0.088	0
V-107 C	0.088	0
V-107 D2	0.088	0

From Table 5.44 it can be seen that OP31, OP34, OP37, OP114, OP118 and OP121 present very negative values of MVA (Material Value Added). This means that money is being lost across the entrance and the exit of those compounds in the process. It can be also seen that OP125 shows high value of EWC, which means high energy

consumption through that open-path. The EWC value should be reduced in order to improve the process.

For the batch processes (see Table 5.45) it can be seen that the operational bottlenecks regarding to time are operation V-104 D2, V-107 C and V-107 D2 (high value of OTF). For this set of operations, the operational times are not influenced by any of the compounds once these operations are related to equipments charges and discharges. Consequently, the compound indicators are not necessary for these operations and only operational indicators are calculated to them. It is also possible to see from Table 5.45 that operation DS-101 presents high energy consumption (high value of OEF).

To apply the ISA algorithm the indicators listed in Table 5.44 have been selected as possible target indicators. After applying the ISA algorithm it is seen that from the selected indicators, the MVA indicator related to OP34 and OP37 are the most sensitive. Consequently, this indicator is considered the target indicator for improvements (see Table 5.46, row highlighted with bold letters). For batch indicators, OTF of unit V-104 D2 has been selected as the batch target indicators.

**Table 5.46:** ISA algorithm results –  $\beta$ -Gal Production

Path	Indicator	Scores
OP 31	MVA	12
<b>OP 34</b>	<b>MVA</b>	<b>20</b>
<b>OP 37</b>	<b>MVA</b>	<b>20</b>
OP 114	MVA	4
OP 118	MVA	6
OP 121	MVA	4
OP 125	EWC	6

The most sensitive indicators, which are the ones presenting the highest scores have been selected as targets for improvements. For this case study, MVA of OP34 and OP37 are the most promising target indicators.

Regarding the batch indicators OTF for V-104 D2, V-107 C and V-107 D2 presented equal potential for improvements with respect to time reduction. To illustrate the

application of the methodology OTF for V-104 D2 as been selected as batch target indicator.

**Step 5: Design Sensitivity Analysis**

The operational variables that influence the value of MVA in the open-path OP34 and OP37 are the following:

- **Flowrates:** S1 flowrate for both open-paths (inlet stream same as open-path flowrate)

Variations of 5, 10 and 15% on the reference (design) values for all the identified operational variables. The improvements on the target indicators (MVA OP34 and OP37) are listed for the variations of each variable. Table 5.47 and Table 5.48 give a summary of the influence in the target indicators from the changes in the operational variables.

**Table 5.47:** Summary of the sensitivity analysis to measure the influence of operational variables in MVA of open-path OP34— $\beta$ -Gal case study

	<b>Target Indicator Improvement (%)</b>
$\Delta OPV$	S1 flowrate
5%	5%
10%	10%
15%	15%

**Table 5.48:** Summary of the sensitivity analysis to measure the influence of operational variables in MVA of open-path OP37— $\beta$ -Gal case study

	<b>Target Indicator Improvement (%)</b>
$\Delta OPV$	S1 flowrate
5%	5%
10%	10%
15%	15%

From the sensitivity analysis of the operational parameters influencing the target indicators (MVA – OP34 and OP37) it was found that the most significant operational parameter is the flowrate of the respective open-paths (S1 flowrate reduction).

For the batch indicators the flowrate of the accumulation-path is the most sensitivity variable, and consequently for a decrease on the operation time an increase on the operational flowrate should be considered.

***Step 6: Generation and Evaluation of new design alternatives***

Step 5 identified the operational variable to achieve an improvement in the target indicator as the flowrate of a raw material (Water) in an open-path (OP34 and OP37). From Figure 3.24 it can be noted that the improvement category for this variable is the category 4.1. To improve the variables of category 4.1 there are four alternatives available:

- Recycle
- Improve/New separation
- Increase Conversion
- Source

• **Recycle**

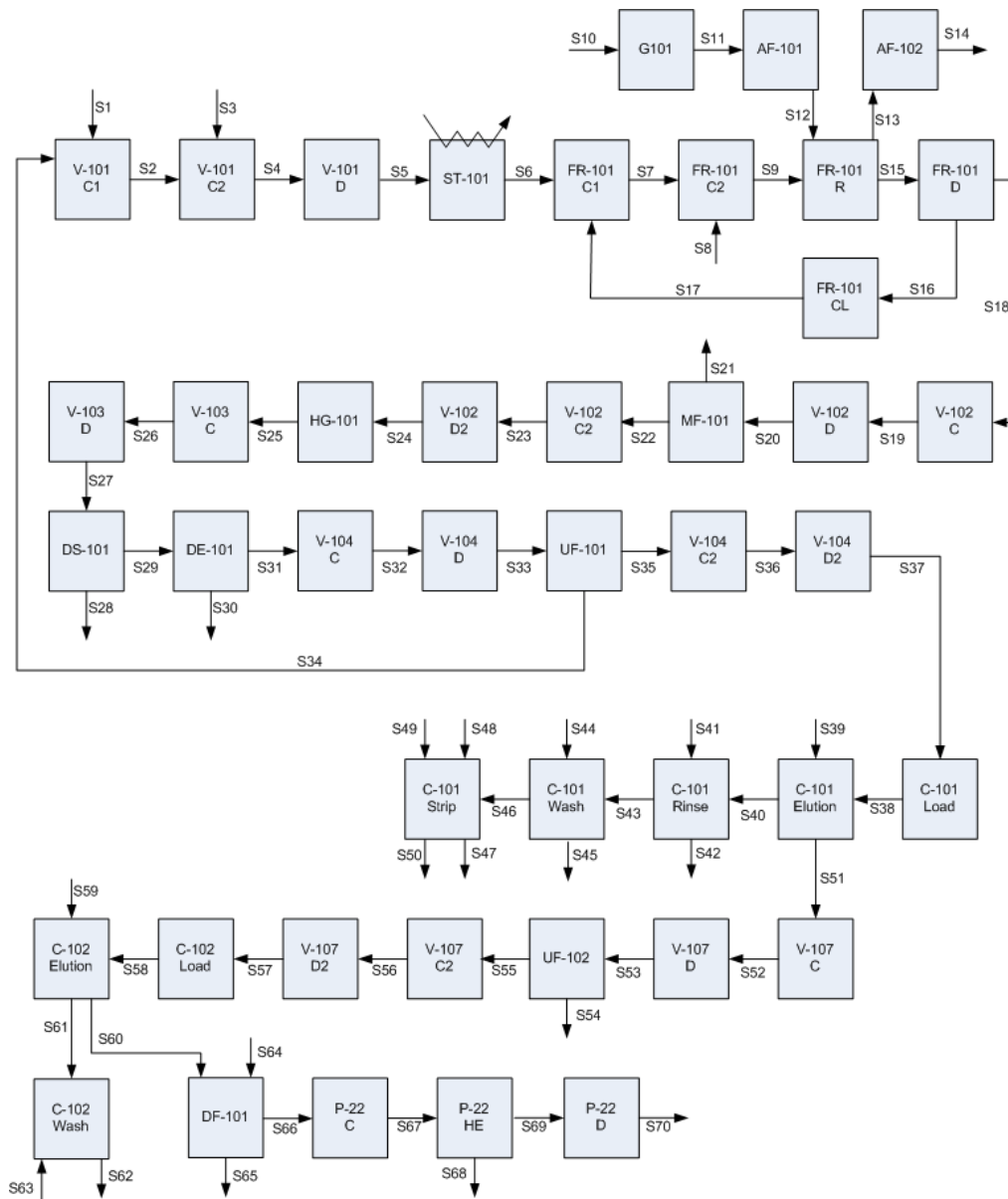
To reduce the flowrate of open-path OP34 and OP37 the recycle of water must be considered. The water coming from OP34 can be recycled directly to the initial operation (V-101C). However, looking at OP37 it is possible to see that the water exiting in this path contains proteins. These proteins require difficult separation processes in order to purify the water. This means that would not be economically viable to purify this water and recycle it. Therefore, water of OP37 will be sent for treatment.

To improve the batch target indicator (OTF), the discharge flowrate of V-104 D2 operation should be increased. This flowrate depends on the chromatographic column specifications. The catalog for chromatographic columns, Tosoh Bioscience, 2008, includes data for an ion exchanged chromatographic column for  $\beta$ -galactosidase

purification. The biggest chromatographic column presented in the catalogue shows approximately the same dimensions as the chromatographic column simulated in *Super Pro Designer* ( $D_{\text{Catalogue}} = 60\text{cm}$ ,  $L_{\text{Catalogue}} = 40\text{cm}$ ;  $D_{\text{Catalogue}} = 53\text{cm}$ ,  $L_{\text{Catalogue}} = 33\text{cm}$ ) and therefore the operational data can be taken from here (for further details see Appendix C). This chromatographic column presents a maximum flowrate of 1600 ml/min. The flowrate of the discharged operation has been increased up to 75% of the maximum flowrate of the chromatographic column, reducing in this way the operational time.

Summarizing, the new design alternative consists in recycle the water coming from OP34 and reducing the time in operation V-104 D2.

The flowsheet for the new design is presented Figure 5.27.



**Figure 5.27:** New Design flowdiagram - $\beta$ -Gal production

With the water recycling, the target indicator improved 100%, since it is possible to recycle completely the water. Increasing the flowrate in the discharge operation, the batch target indicator improved 74%. Table 5.49 and Table 5.50 show the initial and the final value of the target indicators.



**Table 5.49:** Improvements in target indicators -  $\beta$ -Gal Production

Target Indicator	Initial	Final
MVA – OP34	-25451 \$/y	0 \$/y

**Table 5.50:** Improvements in batch target indicator -  $\beta$ -Gal Production

Target Indicator	Initial	Final
OTF – V-104 D2	0,088 %	0,03%

Table 5.51 shows that the new design alternative is more sustainable. For the new sustainable design alternative, which consists of the recycling water, the following improvements were achieved, the energy per value added improved 0.09%, the profit increased by 0.1%, the water metrics improved by 32%. The rest of the performance criteria parameters have remained constant. The time of discharge has been reduced by 74%.

**Table 5.51:** Comparison of the performance criteria between the base case and the new sustainable design alternative -  $\beta$ -Gal Production

Metrics	Base Case	New Design	Improvement
Total Net Primary Energy Usage rate (GJ/y)	28703	28703	0%
% Total Net Primary Energy sourced from renewables	0,7	0,7	0%
Total Net Primary Energy Usage per Kg product (kJ/kg)	29802	29802	0%
Total Net Primary Energy Usage per unit value added (kJ/\$)	$5.692 \times 10^4$	$5.687 \times 10^4$	0,09%
Total raw materials used per kg product (kg/kg)	5364,8	5364,8	0%
Total raw materials used per unit value added (kg/\$)	$1,025 \times 10^{-4}$	$1,023 \times 10^{-4}$	0%
Fraction of raw materials recycled within company	0	0	0%
Fraction of raw materials recycled from consumers	0	0	0%
Hazardous raw material per kg product (kg/kg)	16,6	16,6	0%
Net water consumed per unit mass of product (kg/kg)	885	599	32%
Net water consumed per unit value added (kg/\$)	$1,69 \times 10^5$	$1,14 \times 10^5$	32%
Safety index	28	28	0%
WAR	15890	15890	0%
Profit (\$/y)	$6,38 \times 10^9$	$6,39 \times 10^9$	0,1%

## 5.4 Conclusions

Six case studies have been presented and new sustainable alternatives have been suggested to all of them. Therefore,  $F_{obj}$  has been improved, to all of them, without any trade-off in the sense that something improved at the expense of others.

For the VCM case study, the insertion of a new membrane-based pervaporation unit appears to be a promising alternative to achieve improved sustainability of the process. In this (design) alternative, none of the performance criteria became worse compared to their reference values, except for those that were improved. In this case study the new flowsheet decomposition technique has been highlighted.

In the ammonia case study, heat integration has been considered to recover water as steam. For this new design alternative, the investment costs related to the new design alternative have been evaluated. This analysis has been done to illustrate the following steps that must be performed after the application of the sustainable design methodology. The investment costs have to be verified by the companies. If the investment cost is not satisfactory a new alternative must be suggested. In this (design) alternative, the total energy became worse compared to their reference values in 1.5%, however the energy metric per value added has been improved by 23%. The remaining performance criteria improved or became constant. The profit increase (63%) ensures that the investment can be payed in one year.

For biodiesel case study, the raw material has been recycled and heat integration has been considered. This new alternative improved profit, environmental impact and reduced the utilities consumption.

The copper extraction case study, which used data from Codelco Norte company has been improved. The water and acid were recovered decreasing the raw material depletion and the environmental impact. The profit has also been improved. The

company is satisfied with the results and is now thinking to apply the software to other parts of the process.

Insulin production process has been improved with the formic acid recovery. The sustainability of the process has been improved with the environmental impact reduction, with the profit increase and with the decrease of raw materials consumption.

$\beta$ -Gal production has been improved with the water recycle. The operation time has also been reduced improving the performance of a cromathography column. The profit and the water consumption have been improved in this case study.

## 6. Integrated Framework –*SustainPro* & *ENVOPExpert*

### 6.1 Introduction

In this chapter, an integrated framework for sustainability assessment of chemical process plants, which comprises two computer aided systems, *ENVOPExpert* and *SustainPro*, is presented. In section 6.2, a summary about *ENVOPExpert* is presented. The integrated framework is presented in section 6.3. The application of the framework is illustrated through the ammonia and the acetone production case studies (section 6.4). Conclusions are presented in section 6.5.

### 6.2 *ENVOPExpert*

An intelligent decision support system, called *ENVOPExpert*, has been developed to assist in sustainability assessment of chemical processes (Halim and Srinivasan, 2002; Halim and Srinivasan, 2008). It has been successfully tested on a number of industrial-scale processes including hydrocarbons separation, alcohol washing process, hydrodealkylation (HDA) of toluene to benzene, chemical intermediate manufacturing process, and a biodiesel production and found to generate results comparable to the analysis by human experts. *ENVOPExpert* has been implemented in an object-oriented framework using Gensym's G2 expert system shell with the following task: *Given a flow diagram and chemistry of a chemical process plant, identify alternatives, which*

*simultaneously minimize waste generated in the plant and improve the economic.* *ENVOPEExpert* performs this task using the methodologies that have been embedded into its knowledge base including material flow representation, waste source diagnosis, heuristic qualitative alternative generation, environmental and economic analysis and multi-objective optimization.

*ENVOPEExpert* methodology can be divided into five main tasks:

- 1) The first task consists on process data collection. This information can be easily obtained from the plant operational data or, if available, process simulation results in the forms of flowsheet, reaction chemistry, and material and energy balances. In addition to these, other data needed includes the classification of material compounds (raw material, utility, waste or product), status of each material compound in output streams (desirable or detrimental), environmental impact factors of the different materials and economic data.
- 2) Step 2 consists on representing the process through a P-graph – a special directed bipartite graph for representing process structure suitable for the synthesis problem (Friedler *et al.*, 1994). In the P-graph model, a circle represents a material stream and a bar represents a unit operation. Connecting the stream and the operating unit nodes are arcs, which define the precedence of units. The P-graph representation of a process provides a convenient framework for diagnosing the origins of waste in the process and for deriving waste minimization alternatives. Starting from each waste stream and tracing each material in the waste stream upstream using the P-graph model, sources of waste, such as impurities in inlet stream, excessive feed of materials, low conversion of materials, waste byproducts and ineffective separation of useful materials, can be identified.
- 3) The subsequent step after diagnosing the waste sources is to derive waste minimization alternatives to the sources. For this, a set of design heuristics, which have been compiled from Douglas, 1992 and Smith, 1995, is applied for generating design alternatives. These heuristics are implemented in *ENVOPEExpert* through IF-THEN rules, which mention the modification required in the process unit or

material stream to minimize waste generation and recover the valuable material from the waste stream.

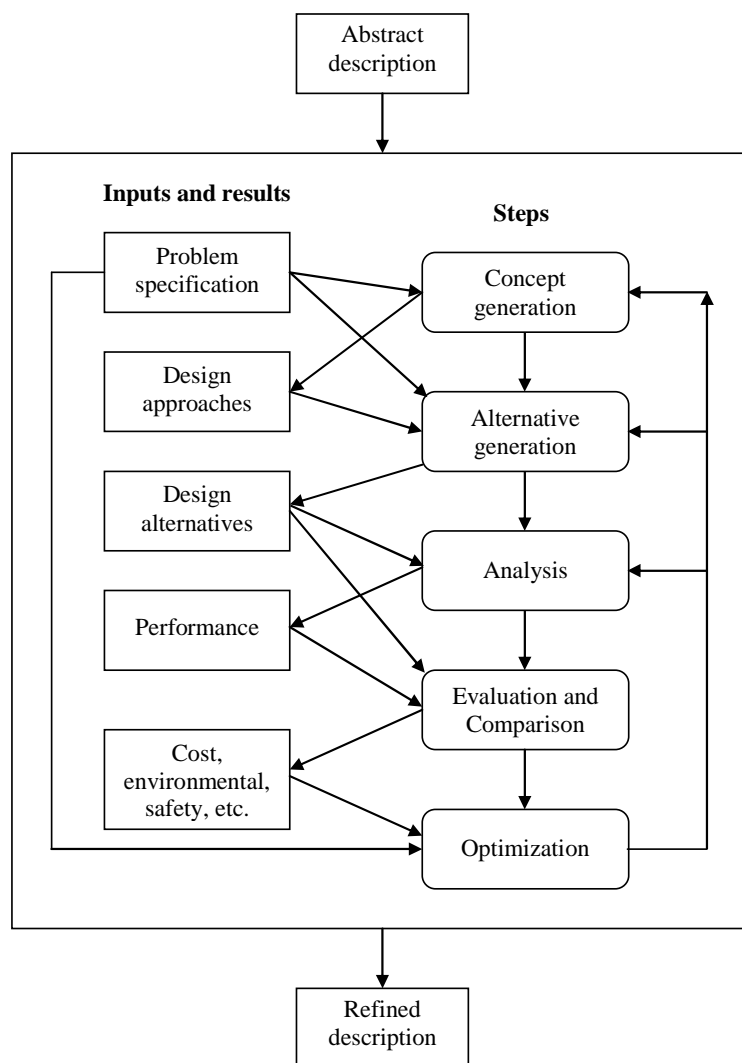
- 4) The objective of step 4 is to identify the functional variables. The analysis based on P-graph model provides only a broad level perspective of the various design modifications to improve the sustainability of the process. It is not capable of specifically determining the variables that should be manipulated (i.e. detailed alternatives) and the extent of the manipulation in order to achieve the desired waste reduction. To identify the variables that should be chased in the alternatives, functional modeling of the process is used. In functional modeling, each unit operation of the process is represented by its functions and the functional variables that characterize that unit. Each of these functional variables can be impacted by the functional variables of other unit connected upstream. For example, the function of a reactor is material transformation and its functional variables are pressure, temperature and concentration. A heater that is connected upstream of the reactor would then affect the material transformation in the reactor as the functional variable of the heater (i.e., temperature) interacts with the functional variable of the reactor. Thus, given a P-graph model of a material in a waste stream, the entire chain of functional interactions between the process units can be identified. To determine the extent of variable modification, the cause-and-effect interactions among variables need to be known. This can be obtained from signed digraph model in the case of limited information and knowledge of the process. Such model captures the cause-and-effect relations between the variables and phenomena within a process unit in a qualitative way. In digraph modeling, each process variable of the process units is represented as a node and interaction between two variables is captured using a directed edge. Process variable nodes can take the values increase or decrease and the arcs connecting the nodes can have the values directly proportional (+) or inversely proportional (–) indicating the direction of influence of one variable on another. Digraph models of common unit operations such as compressor, absorption column, reactor, distillation column and heat exchanger have been built in the knowledge base of *ENVOPExpert*. Alternatively, the

response of the process from changes made to one or more variables can be determined through process simulation. For this, a bridge between G2 and HYSYS simulator has been developed using G2-ActiveXLink and the HYSYS-Browser compounds. This two-way connection is used to send the values of decision variables to HYSYS, which simulates their effects and returns the results back to G2.

- 5) With the functional variables identified and connection with process simulator established, the last step would be to measure the feasibility of the proposed alternatives in terms of economic and environmental implications. The former can be quantified in term of profit or operating cost. For the later, Waste Reduction (WAR) algorithm (Cabezas *et al.*, 1999) is used to calculate the environmental impact of the alternative. Subsequently, the environmental and economic impact evaluation can be carried out by modifying these variables. At the same time, optimization of these variables can also be performed. As conflicting effects between environmental and economic factors are commonly encountered, multi-objective optimization may be employed to identify solution strategies that concurrently satisfy the different objectives. *ENVOPExpert* is capable of performing such task through a simulated annealing algorithm that has been embedded in its library. The result from the simulation-optimization approach is a Pareto optimal plot involving the functional variables

## 6.3 Framework

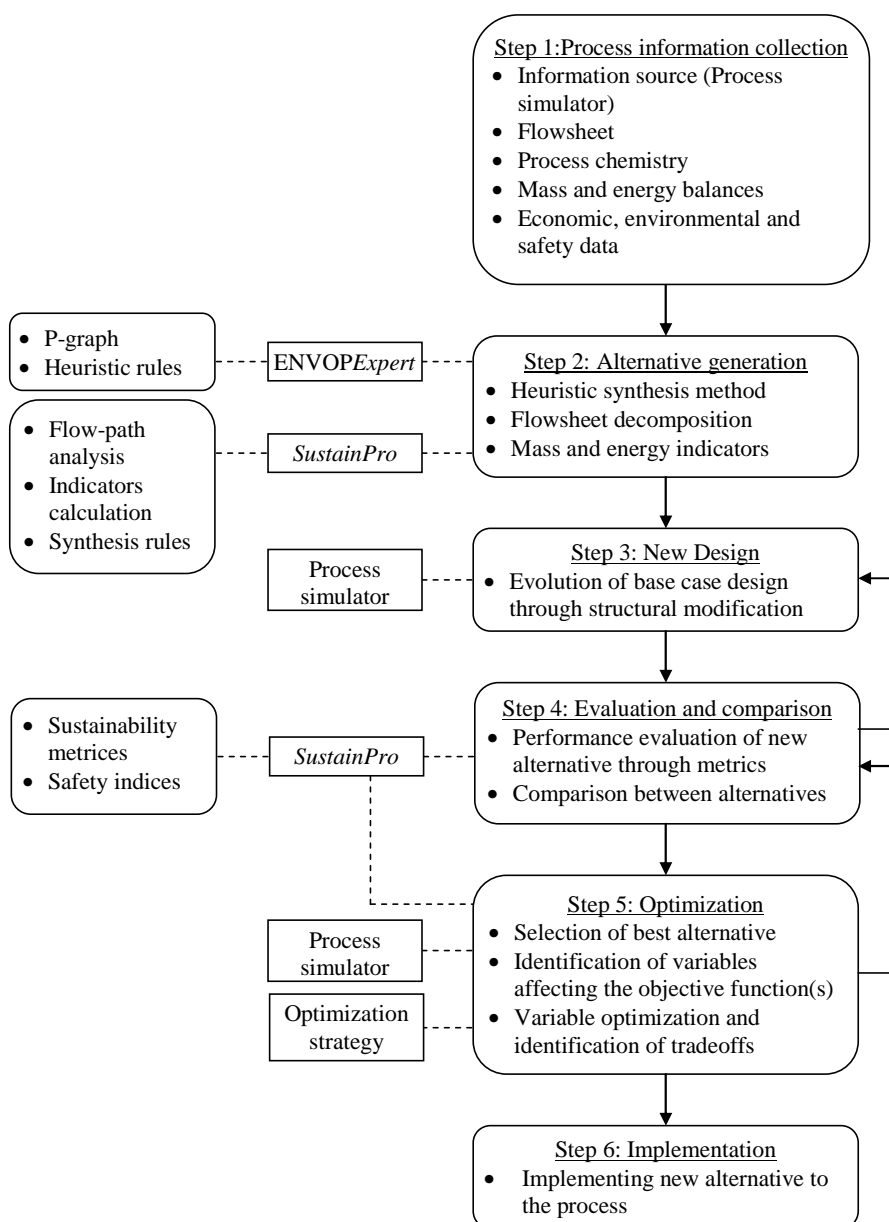
A systematic methodology that exploits the features of *ENVOPExpert* and *SustainPro* for generating and evaluating design alternatives for sustainable chemical processes has been developed. The methodology has been developed following the sequence of steps proposed by Biegler *et al.*, 1999 to identify the structural as well as operational changes suitable to the process (see Figure 6.1).



**Figure 6.1:** Design synthesis activity (Biegler et al., 1999)



As such, the methodology is applicable to different stages of the process design life-cycle from conceptual design to retrofitting. The two computer aided systems have been integrated according to the framework (Carvalho et.al., 2009<sup>2</sup>) shown in Figure 6.2, which shows the steps employed in the methodology.



**Figure 6.2:** Integrated framework of *ENVOPEExpert* and *SustainPro*

First, structural modifications to the flowsheet design are explored following the suggestions given by *ENVOPExpert* and *SustainPro*. Next, interactions between key process variables are identified and changes to these variables are simulated. This is followed by optimization of the variables using stochastic algorithm to find the process optima (local or global). All these sequential steps are described in details below.

These two tools have been integrated since they present strong points that complement each other analysis. The join framework can easily identify critical points in the process and suggest new design alternatives to improve those bottlenecks (*SustainPro* and *ENVOPExpert*), it can also generate new design alternatives to improve the identified bottlenecks (*SustainPro*). The new design is tested and in the new framework an optimization of the new design alternative is performed (*ENVOPExpert*). The new framework will also perform a selection on the optimization variables that lead to better improvements, giving the respective operational ranges for the optimization variables (*SustainPro*), therefore reducing the optimization search space (reduction on optimization time).

This joint framework is going to be explained step by step.

### ***Step 1 – Process information collection***

The framework starts with collecting information about the base process including the flowsheet and the mass and energy balances. In HYSYS, such information can be easily extracted in the form of XML data (Hyprotech, 2003). This HYSYS-XML data, which consists of the building block of the process, contains the list of materials, list of unit operations, stream and unit operation connections and positions, reaction kinetics, thermodynamic model, and user-specified values of the operating variables and process parameters. In addition, other data needed by *ENVOPExpert* are material and stream classification, chemical environmental impact (WAR algorithm) and economic data. Those information need to be specified explicitly in the library of *ENVOPExpert*. Once the required process data is available, it can then be used to construct the P-graph model of the process.

The required input to *SustainPro* is the mass and energy balances of the process. Such information is delivered by *ENVOPExpert* using a text file format that is cast into the following syntax: <stream-name> <vapor-fraction> <temperature> <pressure> <heat-flow> <array-of-compounds> <array-of-mass-of-compounds> <desired-modification> <from-unit> <from-subunit> <to-unit> <to-subunit> for the material stream and <stream-name> <connection-status> <connecting-unit> <heat-flow> for the energy stream.

*SustainPro* reads the text file importing the data. This information combined with the unit information and economic and environmental impact data are used by *SustainPro* to determine the flow path decomposition of the process and follow the rest of the analysis.

### ***Step 2 – Alternatives generation***

In this step, new design alternatives are identified using *ENVOPExpert* and *SustainPro*. Qualitative design modifications are identified by *ENVOPExpert* in two-step procedure: first, a P-graph analysis is performed to identify the root cause of waste generation, next the hierarchical design method is used to generate heuristic alternatives. In parallel, a set of mass and energy indicators is calculated in *SustainPro* to identify the critical points in the process with respect to material accumulation and process economics. The most significant indicators are next identified using a sensitivity analysis method to propose design modifications (changes in design variables that improve targeted indicators, which in turn, improve a corresponding subset of sustainability metrics). The next step is to generate sustainable design alternatives (those that match the target indicators). The *SustainPro*'s alternatives are in-line with the suggestions of *ENVOPExpert*. However, the alternatives of *SustainPro* are more specific. For instance, using the material accumulation indicator, a high build-up of certain materials in a recycle stream can be diagnosed and hence suggestions for reducing this material recycle can be proposed. Such specific suggestion cannot be inferred by *ENVOPExpert* as its analysis is purely based on qualitative reasoning.

### ***Step 3 – New process design***

The suggested new design alternatives are implemented to the base process. This is done by modifying the flowsheet of the simulator (HYSYS) followed by simulation of the new flowsheet to generate mass and energy balance data.

### ***Step 4 – Evaluation and comparison***

In this step, the sustainability of the modified process is evaluated using *SustainPro* for comparison with the base case. This is done by calculating a set of performance metrics for the base and the modified process. In the proposed methodology, sustainability metrics from different sources including the sustainability metrics of Azapagic *et al.*, 2002, WAR algorithm (Cabezas *et al.*, 1999) and the safety indices (Heikkilä, 1999) are used as the measure of economic, environmental, and safety indices.

The new alternative is considered to be more sustainable if and only if it improves at least one of the metrics while ensuring negligible “negative” changes to all other metrics (in this case, the limit is set to be 1-2 %).

### ***Step 5 – Optimization***

The previous modification step considers only structural changes to the flowsheet to improve the sustainability of the process. In this step, operational changes in terms of variables modification are performed for process refinement. Thus, in this step, a list of process variables that can be manipulated is specified. *SustainPro* then screens these variables by prioritizing the ones that may significantly affect the process. The minimum and maximum ranges for optimizing these variables are also estimated based on reverse approach, which uses sustainability metrics and other operational constraints. First, a limit for sustainability metrics of the process is fixed. For instance, the new sustainability metrics (after the optimization) should be within 1% from the initial metrics. This means that a move to new variable values can only be allowed only if it does not worsen the metrics by more than 1%. Writing the equation of the variable

in study as a function of the new sustainability metric and using the reverse approach, the min-max range of the variables that correspond to those new metric values can be calculated.

To clarify this approach, consider the following example, which shows the steps for determining the maximum flowrate for a raw material stream.

### **Example 6.1**

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Consider the following expression for the value added sustainability metric, in a given process:

$$Va_{ini} = m_{pd}P_{pd} - m_{rm}P_{rm} - Q_S P_S \quad \text{Eq(6.1)}$$

where, Va is the value added, m is the flowrate and P is the price while the subscript pd, rm and S are for product, raw material and solvent, respectively.

In the optimization process, this metric cannot become worse more than 1%. This statement can be represented by the following equation:

$$Va_{new} = Va_{ini} \times 0.99 \quad \text{Eq(6.2)}$$

To determine the minimum flowrate of the raw material, Eq(6.1) can be written using the following form:

$$m_{RM} = \frac{-Va_{New} - m_S P_S}{P_{rm} - P_{pd} \times \%C} Va_{ini} \quad \text{Eq(6.3)}$$

The product flow can also be defined in term of raw material flow according to the following expression:

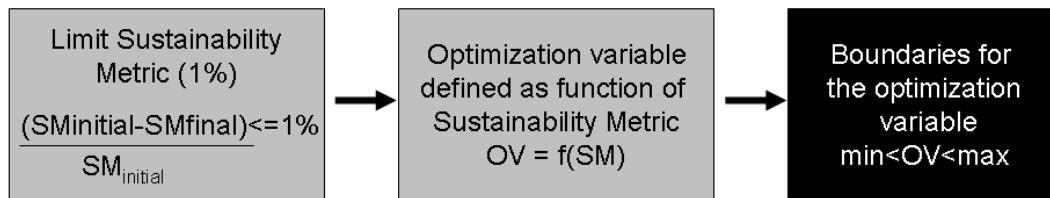
$$m_{pd} = m_{rm} \times \%C \quad \text{Eq(6.4)}$$

Where %C is the reaction conversion.

By substituting the relevant values to the right hand side of Eq(6.3), the maximum flowrate of the feed material can thus be specified.

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Figure 6.3 summarizes the reverse approach process to determine the boundaries for the optimization variable.



**Figure 6.3:** Reverse approach to determine the boundaries for the optimization variable– Joint framework

In Figure 6.3 SM is the sustainability metric and OV is the optimization variable.

Following the same procedure for all the variables, the maximum and minimum ranges can be determined. It is important to mention, that when the variable in study is influencing more than one sustainability metric, the reverse approach is applied to all the sustainability metrics. The boundaries that lead to a smaller range are selected.

With the minimum and maximum ranges of variables specified, the next step is to simulate the process within these variable ranges. This is to ensure that flowsheet convergence can be attained during the optimization run. This is particularly important as changes, even small ones, in these variables could lead to failed convergence, especially in the column operation. A single objective problem involving profit maximization is next performed to these variables using a simulated annealing algorithm. This is done by capitalizing the simulation-optimization capability of *ENVOPExpert* which uses *HYSYS* as the simulation engine.

### ***Step 6 – Implementation***

Here the new alternative should be implemented in the process. Investment cost should be analyzed.



Here, a series of plug flow reactors is used as a representation model for the multi-bed reactor unit. The economic data, material and stream classifications and chemical environmental impacts are listed in Table 6.1.

**Table 6.1:** Ammonia process information– Joint framework

Stream	Status	Value/Cost	Material	Purpose	Env. Impact (mass basis)
Feed-gas	Feed	\$ 0.13/kg	Methane	Impurity	0.0408
Purge-gas	Waste	\$ 0.005/kg	Water	Utility	0.0
Ammonia-product	Product	\$ 0.3/kg	Hydrogen	Raw material	0.0
Q-100	Energy	\$ 0.07/kWh	Nitrogen	Raw material	0.0
Q-101	Energy	\$ 0.006/kWh	Ammonia	Product	3.984
Q-103	Energy	\$ 0.1/kWh	Argon	Impurity	0.0

#### 6.4.1.2 Methodology application

##### **Step 1 – Process information collection**

Information about the process has been obtained from a HYSYS simulation model.

##### **Step 2 – Alternatives generation**

Table 6.2 lists some of the qualitative suggestions identified by *ENVOPExpert* and *SustainPro*. As seen from the table, the two sets of alternatives complement each other.

**Table 6.2:** Qualitative alternatives for the ammonia process- Joint framework

System	Qualitative Suggestions
<i>ENVOPExpert</i>	<ul style="list-style-type: none"> <li>Prevent excessive feed of materials in the feed-gas stream, remove impurities (methane and argon) from feed-gas</li> <li>Increase reactant conversion in the reactors</li> <li>Recycle or recovery-recycle useful materials (nitrogen, hydrogen and ammonia) from purge-gas stream</li> </ul>
<i>SustainPro</i>	<ul style="list-style-type: none"> <li>Separate methane in the feed-gas stream before entering the process</li> <li>Reduce the recycle of methane using a new separation process</li> </ul>

The suggestions presented in Table 6.2, by *SustainPro*, have been obtained using the mass and energy indicators. *SustainPro* identified the critical paths in the process by



performing a sensitivity analysis on the operational parameters related to these paths. This analysis pointed to the reduction of methane in the feed-gas stream as the most promising because of its effects on the targeted indicators. Following the methodology described in Jaksland et. al., 1996, one possible separation process to reduce this impurity is to use a membrane. A specific membrane for this type of mixtures is reported in Wang et al., 2002. Hence, this alternative is implemented in the HYSYS model of the base process and a new simulation was carried out.

### ***Step 3 – New process design***

The suggested new design alternatives have been implemented to the base process. The base case flowsheet has been changed and the new simulation has been performed in the simulator (HYSYS). The data about the new design has been obtained.

### ***Step 4 – Evaluation and comparison***

The new sustainability and safety metrics are calculated using the *SustainPro* and compared with the base case. Table 6.3 shows that the new alternative improves all the sustainability indicator metrics while maintaining the same safety index to their base values. Therefore, it is concluded that the new design is more sustainable.

**Table 6.3:** Selected sustainability metrics for the base and improved process for ammonia process case study— Joint framework

Metrics	Base	New	Improvement
Total Net Primary Energy Usage rate (GJ/y)	19336	18968	2%
% Total Net Primary Energy sourced from renewables	NA	NA	NA
Total Net Primary Energy Usage per Kg product (kJ/kg)	23.7	23.4	1%
Total Net Primary Energy Usage per unit value added (kJ/\$)	0.012	0.011	8%
Total raw materials used per kg product (kg/kg)	1.23	1.21	2%
Total raw materials used per unit value added	$6.14 \times 10^{-4}$	$5.80 \times 10^{-4}$	5%
Fraction of raw materials recycled within company	NA	NA	NA
Net water consumed per unit mass of product (kg/kg)	7.9	7.8	2%
Net water consumed per unit value added	$3.96 \times 10^{-3}$	$3.71 \times 10^{-3}$	6%
WAR per kg product (impact/kg)	0.154	0.152	1%
Safety Index	26	26	0%
Profit (\$/yr)	$1.13 \times 10^8$	$1.21 \times 10^8$	8%

**Step 5 – -Define the optimization problem**

Here, the feed stream and the purge flowrates have been decided as the decision variables (i.e., two degree of freedoms). Using the reverse approach combined with sensitivity analysis, *SustainPro* verifies that manipulating the feed flowrate offers the best improvement to the process. The minimum and maximum range for the feed flowrate is found to be  $1.22 \times 10^5 < \text{flowrate} < 4 \times 10^5$  kg/h. This range is obtained by considering the maximum allowable profit loss (1%) and the constraints of the reactor performance.

With the specified range, the feed flowrate is optimized using simulated annealing. A single objective problem involving profit maximization has been considered. Table 6.4 lists the sustainability and safety metrics for the optimized process. As seen from the table, the profit reaches a maximum when operating near the maximum feed-gas flow. The other sustainability and safety metrics are also shown to be constant or slightly improved at this maximum flow. The only metric that becomes worse is the total

energy used per year. However per kg of product, the energy consumption fraction is maintained constant, which means that to produce the same amount of product the energy spent is the same.

**Table 6.4:** Sustainability metrics for the optimized process for the ammonia process case study- Joint framework

Metrics	Base	New	Optimal (Feed-gas = $3.55 \times 10^5$ kg/h)
Total Net Primary Energy Usage rate (GJ/y)	19336	18968	18264
% Total Net Primary Energy sourced from renewables	NA	NA	NA
Total Net Primary Energy Usage per Kg product (kJ/kg)	23.7	23.4	23.4
Total Net Primary Energy Usage per unit value added (kJ/\$)	0.012	0.011	0.011
Total raw materials used per kg product (kg/kg)	1.23	1.21	1.21
Total raw materials used per unit value added	$6.14 \times 10^{-4}$	$5.80 \times 10^{-4}$	$5.81 \times 10^{-4}$
Fraction of raw materials recycled within company	NA	NA	NA
Net water consumed per unit mass of product (kg/kg)	7.9	7.8	7.7
Net water consumed per unit value added	$3.96 \times 10^{-3}$	$3.71 \times 10^{-3}$	$3.70 \times 10^{-3}$
WAR per kg product (impact/kg)	0.154	0.152	0.152
Safety Index	26	26	26
Profit (\$/yr)	$1.13 \times 10^8$	$1.21 \times 10^8$	$1.22 \times 10^8$

It is then concluded that a more sustainable process has been presented.

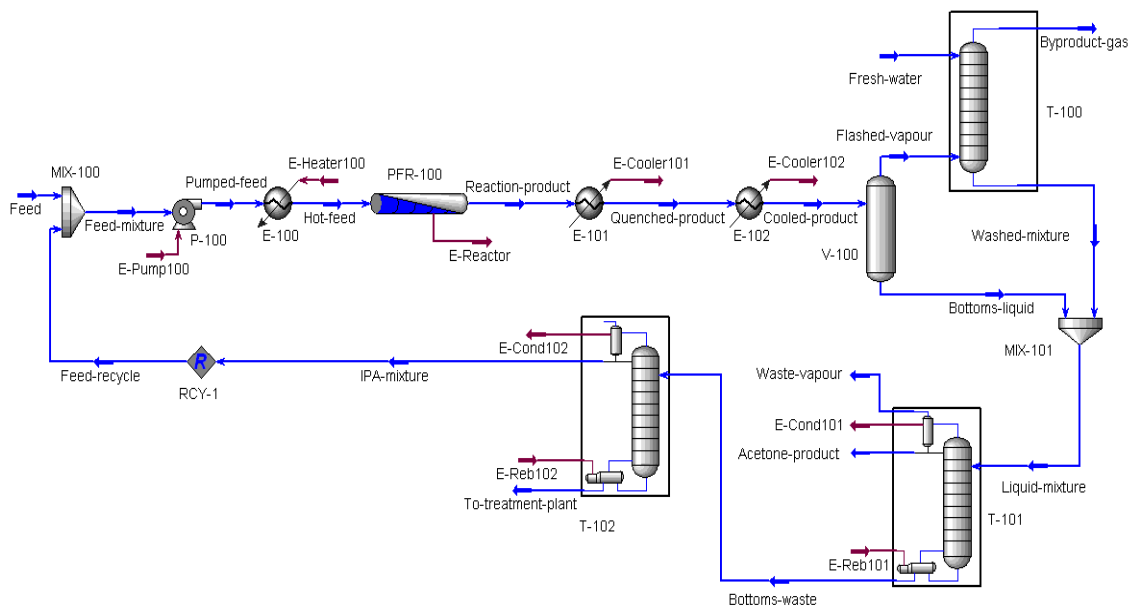
### ***Step 6 – Implementation***

The producers of the ammonia, who follow the simulated process, should further analyze the implementation of the new design alternative.

## 6.4.2 Acetone

### 6.4.2.1 Process flowsheet

One possible way for manufacturing of acetone is through dehydrogenation of isopropyl alcohol (IPA) or 2-propanol. The primary advantage of this process over the other routes is that the acetone produced is high in purity thereby makes it suitable for use as solvent in the pharmaceutical industry. Figure 6.5 shows the flowsheet of an acetone process (Turton *et al.*, 2003).



**Figure 6.5:** Flowsheet of acetone production – Joint framework

A feed stream comprising of an azeotropic mixture of IPA and water (88% mass of IPA) is initially mixed with a recycle stream containing IPA, water and acetone. The feed mixture is first vaporized using a high pressure steam before being passed to a reactor. The reaction is endothermic and proceeds according to the following reaction:  $\text{IPA} \rightarrow \text{Acetone} + \text{H}_2$ . The reaction kinetics are first order with respect to the concentration of IPA and can be expressed as follows:

$$\text{where } E_a = 72.38 \text{ MJ/kmol, } k_0 = 3.51 \times 10^5 \frac{m^3 \text{ gas}}{m^3 \text{ reactor} \cdot s} \text{ and } C_{o\text{IPA}} = \frac{\text{kmol}}{m^3 \text{ gas}}.$$

During the reaction, heat is supplied using a circulating molten salt. The reactor effluent, containing unreacted IPA, acetone, water and hydrogen byproduct is cooled in two heat exchangers prior to entering a phase separator. The vapor leaving the separator is scrubbed with water to recover the acetone. The liquid from the phase separator is next combined with the liquid from the bottom of the scrubber and sent to the separations section. Two distillation columns are used to separate the acetone product (99.9% mass) and to remove the excess water, which is then recycled back to the front end of the process as an azeotropic mixture. Table 6.5 shows the unit cost and environmental data for this process. There are two waste streams in this process – the vapor stream leaving the scrubber and the waste water from the second distillation column.

**Table 6.5:** Cost and environmental impact data for acetone process- Joint framework

Description	Value
Cost of raw material (\$/kg)	
Feed	0.63
Fresh-water	0.00004
Price of product (\$/kg)	
Acetone-product	0.88
Byproduct-gas	0.00124
Cost of waste stream (\$/kg)	
Waste-vapor	0.005
To-treatment-plant	0.001
Cost of energy (\$/kW h)	
E-Pump100	0.05
E-Heater100	0.011
E-Reactor	0.011
E-Cooler101	0.0006
E-Cooler102	0.008
E-Cond101	0.0006
E-Reb101	0.007
E-Cond102	0.0006
E-Reb102	0.007
Environmental impact (per kg)	
Hydrogen	0
Acetone	0.478
IPA	0.1401
Water	0

#### 6.4.2.2 Methodology application

##### **Step 1 – Process information collection**

Information about the process has been obtained from a HYSYS simulation model.

##### **Step 2 – Alternatives generation**

Table 6.6 lists some of the qualitative suggestions identified by *ENVOPExpert* and *SustainPro*.

**Table 6.6:** Qualitative alternatives for the acetone production- Joint framework

System	Qualitative Suggestions
<i>ENVOPExpert</i>	<ul style="list-style-type: none"> <li>• Waste of Raw material (IPA) – Prevent excessive feed of IPA and water in the stream or use alternative material in the stream</li> <li>• Waste of washing agent (Water) - Add separation unit to recover acetone, water, and hydrogen from becoming waste, optimize the operating condition of the distillation (T-101), direct-recycle or recovery-recycle of acetone, water, and hydrogen in the stream</li> </ul>
<i>SustainPro</i>	<ul style="list-style-type: none"> <li>• Waste of Raw material (IPA) - Improve or insert new separation to recycle the raw material</li> <li>• Waste of washing agent (Water) - Reduce the feed stream, improve or insert new separation to recycle the raw material</li> </ul>

The suggestions presented in Table 6.6, by *SustainPro*, have been obtained using the mass and energy indicators. *SustainPro* identified the critical paths in the process by performing a sensitivity analysis on the operational parameters related to these paths. This analysis pointed to the recovery of water and IPA as the most promising because of its effects on the targeted indicators.

The proposed design alternatives “reducing the feed flowrate” and “adding a new separation unit to recover-recycle IPA and water in the waste water stream” are implemented to the base process. To identify a suitable separation process for the recovery of IPA and water, the separation synthesis methodology of Jakobs and Gani, 1996 is used at this stage. This methodology evaluates the properties of the mixture to

be separated on the basis of its thermodynamic relations. The objective is to derive a set of feasible separation processes based on the equilibrium calculations and rank them in the order of preferences. Using the methodology, the list of possible separation technologies for IPA recovery can be identified as follows: liquid membrane, gas adsorption and pervaporation.

The use of pervaporation process for recovering alcohol compounds from water has been studied by many researchers. The process involves contacting a liquid stream containing two or more miscible compounds with one side of a non-porous polymeric membrane (such as polydimethyl siloxane (PDMS)) or a molecularly porous inorganic membrane (such as zeolite) while applying a vacuum or gas purge in the other side to draw the permeate liquid and evaporate it. A suitable operating condition for IPA separation from water has been reported to be less than 30°C for 5.5 wt% IPA (Vane, 2005). Such operating range is considered suitable for implementation to this process.

### ***Step 3 – New process design***

The suggested new design alternatives have been implemented to the base process. The base case flowsheet has been changed and the new simulation has been performed in the simulator (HYSYS). Figure 6.6 shows the new flowsheet incorporating pervaporator unit. In the flowsheet, the wastewater stream from column T-102 is cooled to 28°C before being passed to a pervaporator unit (modeled by compound splitter with a “dummy” energy stream). The vapor permeate (13 wt% IPA, 14 wt% acetone and 72 wt% water) is recovered and recycled to the feed stream. The liquid retentate obtained at 99 wt% water is recycled and mixed with fresh water as the washing liquid for T-100. To prevent a material build-up, a purge stream is provided.





**Table 6.7:** Sustainability metrics for the base and modified process for acetone production case study- Joint framework

	Base Case	Modified	% Improvement
Total Net Primary Energy Usage rate (GJ/y)	215844	218228	-1
% Total Net Primary Energy sourced from renewables	1	1	0
Total Net Primary Energy Usage per Kg product (kJ/kg)	7959	7980	-0.3
Total Net Primary Energy Usage per unit value added (kJ/\$)	6	5	21
Total raw materials used per kg product (kg/kg)	2	1	52
Total raw materials used per unit value added	0.002	0.0007	62
Fraction of raw materials recycled within company	0.01	0.02	100
Hazardous raw material per kg product	1.13	1.07	5
Net water consumed per unit mass of product (kg/kg)	38	30	21
Net water consumed per unit value added	0.03	0.02	33
Value added (\$)	4352296	5579857	28
WAR	43	23	48
Safety	28	28	0

**Step 5 – -Define the optimization problem**

To determine the key variables (degrees of freedom) of the modified acetone process the following expression, which describes the profit calculation, has been used:

$$\text{Profit} = \text{Product sales} - \text{Raw material costs} - \text{Treatment costs} - \text{Energy costs}$$

In this equation, there are 18 variables – feed flowrate, fresh-water flowrate, byproduct-gas, acetone product, to-treatment-plant, waste-vapor, E-Pump100, E-Heater100, E-Reactor, E-Cooler101, E-Cooler102, E-Cond101, E-Reb101, E-Cond102, E-Reb102, E-Pump101, E-Cooler103, and E-Comp100 – that affect the process profit.

*SustainPro* Identified among the variables that the most significant variables are E-Reb101, E-Cooler101, E-Cooler102 and E-Cooler103.

Using the reverse approach, *SustainPro* determined the bound for the selected variables. The minimum and maximum ranges are listed in Table 6.8. This range is obtained by considering the maximum allowable profit loss of 1%.

**Table 6.8:** Bounds of decision variables for optimizing the acetone process- Joint framework

Process variables	Minimum	Maximum
E-Reb101	3.3 GJ/h	11.45 GJ/h
E-Cooler101	4.2 GJ/h	7.2 GJ/h
E-Cooler102	0.63 GJ/h	0.93GJ/h
E-Cooler103	0.95 GJ/h	1.16 GJ/h

With the minimum and maximum ranges of variables specified, the next step is to simulate the process within these variable ranges. This is to ensure that flowsheet convergence can be attained during the optimization run. This is particularly important as changes, even small ones, in these variables could lead to failed convergence, especially in the column operation.

A single objective problem involving profit maximization is next performed to these variables using a simulated annealing algorithm. This is done by capitalizing the simulation-optimization capability of *ENVOPExpert* which uses *HYSYS* as the simulation engine. Table 6.9 compares the sustainability metrics for the modified and the optimized acetone process. The value added (profit) of the optimized process increases by small margin (0.04%). However, substantial improvement is observed in the environmental impact (37% decrease). Compared to the modified case, the amount of utilities of the optimized process also reduces. In this case, 2% reduction in the total energy consumption and 1% reduction in the total water usage can be observed. Overall, it can be concluded that the optimized process is more sustainable than the modified case.

**Table 6.9:** Comparison between the sustainability metrics for the modified and the optimized acetone process- Joint framework

	<b>Modified</b>	<b>Optimized</b>	<b>% Improvement</b>
Total Net Primary Energy Usage rate (GJ/y)	218228	214530	2
% Total Net Primary Energy sourced from renewables	1	1	0
Total Net Primary Energy Usage per Kg product (kJ/kg)	7980	7845	2
Total Net Primary Energy Usage per unit value added (kJ/\$)	4.9	4.8	2
Total raw materials used per kg product (kg/kg)	1.07	1.07	0
Total raw materials used per unit value added	0.00065	0.00065	0
Fraction of raw materials recycled within company	0.02	0.08	300
Hazardous raw material per kg product	1.07	1.07	0
Net water consumed per unit mass of product (kg/kg)	30.17	29.96	1
Net water consumed per unit value added	0.02	0.02	0
Value added (\$)	5579857	5581977	0.04
WAR	22	14	37
Safety	28	28	0

***Step 6 – Implementation***

The implementation of the new design alternative should be further analyzed by the producers of the ammonia, who follow the simulated process.

## 6.5 Conclusions

The presented framework is an important tool for sustainable process design. This framework diagnoses and then recommends specific alternatives to make significant improvement in sustainability. The new design alternatives are implemented and then an optimization is performed to the new design alternative. The combination of these two tools allows an easier and faster optimization problem (*ENVOPExpert*), due to the selection of the optimization and due to the constraints given to each optimization variable (*SustainPro*). It is also possible to conclude that the big improvement is achieved from the base case to the new design, the optimization process only “fine-tune” the new design alternative.

## 7. Conclusions

### 7.1 Achievements

In this work, a systematic and generic indicator-based methodology has been developed for process analysis and generation of new sustainable design alternatives. The methodology has been presented for processes operating in continuous, semi-continuous and batch mode. A software called *SustainPro*, which applies the described methodology has also been developed. The capabilities of the methodology as well as the use of the software have been presented and they were highlighted through non-trivial case studies.

The main achievements/advantages obtain from this work are analyzed below:

- This methodology is a step-by-step procedure, which allows a systematic analysis and consequently an easier application. The user of the methodology is guided from the collecting data to the generation of new sustainable design alternatives.
- This methodology is able to trace and then locate possible problems related to the compounds being handled in the process across the flowsheet (open- and closed-paths) and also for the operation time, energy consumption and volume occupancy (accumulation-path). The methodology identifies the bottlenecks of the process, pointing out the exactly location of the benefits, costs and accumulations in the process.

- Using some basic concepts developed by Uerdingen, 2002, a new methodology has been developed and presented (See Chapter 3.2). With this new approach, any type of chemical process can now be analyzed. Processes presenting nested loops could be accomplished and consequently the methodology can be applied to complex processes. The new sensitivity analysis (ISA algorithm) determines the target indicators. With this new analysis is then possible to verify by how much the process can be improved by a given indicator improvement. Therefore, the selected target indicators are those, which allow higher improvements.
- A new approach to study processes operating in semi-continuous and batch mode has been developed. With the additional set of batch indicators and the flowsheet decomposition technique for batch operations, it is possible to locate the bottlenecks in a batch operation and to trace the causes for the respective solution. The new set of indicators give a comparison between operations, which allow the identification of the most critical operations, taking in consideration factors such as time, energy and volume occupancy. The new set of indicators can also identify the compound that has the highest influence in the identified operational bottleneck.
- A software called *SustainPro* has been developed and is able to perform a systematic and generic retrofitting process analysis and at the same time calculate some evaluation parameters useful in the selection / comparison of different design alternatives/ processes. *SustainPro* retrofitting analysis for a given process needs to be performed only once. Any request of a further process improving uses the same analysis, but changing some new specific parameters. *SustainPro* allows a simple, accurate and faster analysis of any chemical process. In this way even the more complex and big flowsheets can be analysed through the methodologies described in Chapter 3, which would not be possible without the use of this computer aided tool. Other advantage of this tool, when compared with the other commercial tools is the fact that *SustainPro* joins two important analysis. It can be used as retrofitting software to generate new design alternatives and at the same time it can be used as

an evaluation tool. This makes this tool more powerful, with a wider applicability. *SustainPro* guides the user through the methodology, facilitating the users work (See Main Menu Chapter 4). A manual has also been developed in order to help the user in the software application (Carvalho *et al.*, 2009<sup>3</sup>). *SustainPro* allows the reproducibility of the methodology which extends the applicability of the methodology to any person and place.

- A supporting tool called *knowledge base* has been developed in order to make the *SustainPro* retrofitting analysis more generic and applicable. With this supporting tool duplicate work will be avoid and time will be saved. Many examples have been incorporated in the data base. The user has the possibility of importing process data from the knowledge base. In case the process has not been studied yet and it is not available in the knowledge base the user can select independent compounds in order to import their data. It is also given the possibility of actualizing the knowledge base with new process analysis, creating in this way a user's personal knowledge base that can be used later on.
- One important feature of this methodology is the possibility of identify sustainable design alternatives, avoiding tradeoffs in design decisions (if such opportunities exist). This is achieved, because improving the indicators, the sustainability metrics and the safety indices move in the same direction (improve/maintain constant).
- This methodology follows a sequence of steps, which reduce the search space of the process bottlenecks. The methodology starts with the whole flowsheet, than a flowsheet decomposition is done, which means that the flowsheet is divided in sub-areas. Those sub-areas are then related to each compound, which further reduce the search space. The indicators are calculated to each sub-area. Taking into account their values the most significant are selected. To finalize the operational sensitivity analysis is performed, which indicates exactly the unit/variable that should be improved in order to achieve the desired improvements.



- The methodology is generic in nature and any type of chemical and biochemical process can be studied, including those operating in mixed-mode of operations (continuous, semi-continuous and batch). As it can be seen from the case studies presented, any type of process can be studied with this methodology, chemical, pharmaceutical and biochemical. Moreover, this methodology could go further as shown with the laundry case study, which demonstrates that this methodology is generic enough to deal with the daily problems that can appear in any field.
- The methodology has been applied to nine case studies. As shown through the presented case studies, the size of the problem is not an issue as the objective is to locate the most sensitive indicators and their related variables, which are not that many. Data coming from plant can be used to apply the proposed methodology (Copper Extraction Case Study). For all the case studies a new sustainable design alternative as been presented. The performance parameters improved for each case study are listed in Table 7.1.
- A combined framework between *SustainPro* and *ENVOPExpert*, two computational tools, has been presented and tested. The proposed framework is able to generate and optimize new design sustainable alternatives. The new framework allowed a more efficient and faster optimization problem, since the search space has been reduced and limited. It is also possible to conclude that the big improvement is achieved from the base case to the new design, the optimization process only “fine-tune” the new design alternative.

**Table 7.1: Summary of the case study results**

Case Study	Improvements
MTBE Production	Energy Reduction Water Reduction Profit Increase
Laundry Case Study	Water Reduction Cost Decrease
Acetone-Chloroform Separation	Energy Reduction Water Reduction Environmental Impact Reduction Safety
VCM Production	Energy Reduction Water Reduction Profit Increase
Ammonia Production	Water Reduction Profit Increase
Biodiesel Production	Energy Reduction Raw Material Reduction Water Reduction Environmental Impact Reduction Profit Increase
Cooper Extraction	Raw Material Reduction Water Reduction Environmental Impact Reduction Profit Increase
Insulin Production	Raw Material Reduction Water Reduction Environmental Impact Reduction Profit Increase
B-Gal Production	Water Reduction Profit Increase

Some weak points in the presented methodology could be pointed out and can be considered as issues to deal in the future work.

- Data for the reference design is required and this could be obtained from Process Simulation or real industrial records; prices, costs and other data related to sustainability metrics, safety metrics and environmental impact are also required and that might be time consuming.
- There are some model assumptions (such as ideal mixing for volume, etc). These limitations may restrict the applications of the methodology to some operations.

## 7.2 Future Work

- The synthesis methods used for identification and generation of new sustainable design alternatives should be further developed. New methods can be added and a systematic algorithm for their application might be developed. Process intensification should be included.
- In order to help in the generation of the new alternatives a list with all the possible suggestion must be given. In that list it might be specified what can be done and the maximum benefits that can be achieved with that change. This can be done using the reverse approach method. It should also be analyzed the number of sustainability metrics and safety indices that go in the desired direction for the sustainable improvements. The design alternatives presenting the highest benefits should be the selected ones.
- Further work can be done in the batch processes. There can be a further investigation in the network of the tasks. The operation sequence can be revised. New indicators can be added in order to address the scheduling issues.
- The methodology can be further extended to handle uncertainties in the input data. There might be some studies in order to analyse the influence of the input data and quantify the influence of the data.
- The criteria to establish that a new design is more sustainable than the base case (performance criteria cannot get worsen more than 1-2%) can be further developed. This is an initial criteria, however a criteria based on statistical and/or comparison of the metrics could be an interesting option. A global indicator giving weights, to the

mass and energy indicators, sustainability metrics and safety indices, might be a good suggestion.

- The main interface of *SustainPro* might be connected with the commercial simulators (Aspen, PRO II, HYSYS, ICAS, gPROMS, Super Pro Designer, etc), importing the data automatically to the software.
- It might be created a connection with some commercial simulators / databases in order to fill out the compound properties automatically.
- The software can be transformed for real time analysis by receiving inputs automatically and analyze them. This will be helpful for permanent industry usage of *SustainPro*.
- For dynamic processes some software modifications should be performed and a statistical analysis could be implemented to allow the results obtained in the dynamic analysis. Some industrial operations are transient, that means different results can be achieved at different periods of analysis. With the statistical analysis, it will be possible to verify the most reliable results.
- An interactive flowsheet can be developed, in order to simplify the results analysis. This flowsheet might identify automatically the open-, closed- and accumulation paths when required by the user. The user should have also the opportunity of highlighting the target variables when necessary. This will allow an easy identification of the critical points (methodology results) in the process.
- Connect *SustainPro* with the synthesis algorithms tool that is used for the generation of the new alternatives. After the user select the desired synthesis algorithm to generate the new design alternative, *SustainPro* might call directly that tool and guide the user through its utilization.

- The knowledge base should be further developed, incorporating more chemical/biochemical processes operating in continuous and in batch mode. The further development of this tool will avoid duplicate work. Therefore, the time for collecting data process, which is one of the methodology consuming time steps, might be reduced.



# Appendixes

## A. Data for Case Studies

### A1. MTBE Production Case Study

#### *Streams Data*

**Table A1.1:** Input and output streams- MTBE Case Study

Stream Name	Inlet Streams			Outlet Streams		
	1	2	MKUP	8	11	15
<b>Flowrate (kg/h)</b>						
NC4	0.00	4446.49	0.00	0.01	4446.28	0.20
IC4	0.00	20256.21	0.00	0.00	20255.53	0.67
1BUTENE	0.00	3338.43	0.00	0.00	3338.42	0.01
BTC2	0.00	1907.67	0.00	0.03	1907.64	0.01
BTT2	0.00	2861.51	0.00	0.02	2861.49	0.00
IBTE	0.00	15738.29	0.00	0.00	126.36	0.00
MTBE	0.00	0.00	0.00	24448.48	0.39	0.00
MEOH	8891.66	0.00	0.00	3.40	0.12	0.03
TBA	0.00	0.00	0.00	13.95	0.00	0.00
Water	0.00	0.00	10.77	0.00	7.19	0.20
DIB	0.00	0.00	0.00	39.34	0.00	0.00
<b>Total Flowrate</b>	<b>8891.66</b>	<b>48548.60</b>	<b>10.77</b>	<b>24505.23</b>	<b>32943.41</b>	<b>1.12</b>
Temperature (°C)	16.00	16.00	38.00	89.26	38.16	99.10
Pressure (atm)	16.200	16.200	3.500	6.630	7.920	2.410
Enthalpy Flow (GJ/h)	-0.06	1.63	0.00	4.72	2.87	0.00

Note: Data obtained from PRO/II casebooks, 1992



*Prices*

**Table A1.2: Utility Prices- MTBE Case Study**

Utilities	
Heating (US\$/GJ) low pressure	8.75
Cooling (US\$/GJ)	0.96
Electricity (US\$/kWh)	0.05

Note: Data obtained from Coll, N., 2003

**Table A1.3: Purchase prices - MTBE Case Study**

Compound	Price (\$/kg)
NC4	0.353
IC4	0.353
1 Butene	0.353
BTC2	0.353
BTT2	0.353
IBTE	0.353
MTBE	0.514
MEOH	0.291
TBA	1.265
Water	0.001
DIB	0.353

Note: Data obtained from [www.che.cemr.wvu.edu/publications/projects/mtbe-a.pdf](http://www.che.cemr.wvu.edu/publications/projects/mtbe-a.pdf)

**Table A1.4: Demand stream prices – MTBE Case Study**

	<b>Demand streams Price (\$/kg)</b>		
	<b>8</b>	<b>11</b>	<b>15</b>
<b>NC4</b>	0	0.247	0
<b>IC4</b>	0	0.247	0
<b>1BUTENE</b>	0	0.247	0
<b>BTC2</b>	0	0.247	0
<b>BTT2</b>	0	0.247	0
<b>IBTE</b>	0	0.247	0
<b>MTBE</b>	0.514	0	0
<b>MEOH</b>	0	0	0
<b>TBA</b>	0	0	0
<b>Water</b>	0	0	0
<b>DIB</b>	0	0	0

Note: Data obtained from [www.che.cemr.wvu.edu/publications/projects/mtbe-a.pdf](http://www.che.cemr.wvu.edu/publications/projects/mtbe-a.pdf)

*Paths*

**Table A1.5: Mass closed-paths- MTBE Case Study**

Closed-path	Compound	Loop streams													Flowrate (kg/h)
		20	3	4	5	6	6P	9	12	13	14	16	17	19	
CP1	NC4	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.1
CP2	IC4	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.2
CP3	1BUTENE	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP4	BTC2	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP5	BTT2	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP6	IBTE	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP7	MTBE	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP8	MEOH	20	3	4	5	6	6P	9	12	13	14	16	17	19	133.7
CP9	TBA	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP10	Water	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP11	DIB	20	3	4	5	6	6P	9	12	13	14	16	17	19	0.0
CP12	NC4	12	13	14	16	17	18	21	22	10					0.0
CP13	IC4	12	13	14	16	17	18	21	22	10					0.0
CP14	1BUTENE	12	13	14	16	17	18	21	22	10					0.0
CP15	BTC2	12	13	14	16	17	18	21	22	10					0.0
CP16	BTT2	12	13	14	16	17	18	21	22	10					0.0
CP17	IBTE	12	13	14	16	17	18	21	22	10					0.0
CP18	MTBE	12	13	14	16	17	18	21	22	10					0.0
CP19	MEOH	12	13	14	16	17	18	21	22	10					0.7
CP20	TBA	12	13	14	16	17	18	21	22	10					0.0
CP21	Water	12	13	14	16	17	18	21	22	10					6744.9
CP22	DIB	12	13	14	16	17	18	21	22	10					0.0

**Table A1.6: Energy closed-paths- MTBE Case Study**

Closed-path	Loop streams														Flowrate (GJ/h)
	5	7													
CP1	5	7													7.186
CP2	12	22	10												0.982
CP3	20	3	4	5	6	6P	9	12	13	14	16	17	19		0.004
CP4	13	14	16	17	18	21									2.746

**Table A1.7: Mass open-paths- MTBE Case Study**

Open path	Compound	OP streams													Flowrate (kg/h)
		2	3	4	5	6	6P	9	11						
OP 1	NC4	2	3	4	5	6	6P	9	11					4446	
OP 10	IC4	2	3	4	5	6	6P	9	11					20256	
OP 11	IC4	2	3	4	5	6	6P	9	12	13	14	15		1	
OP 19	1BUTENE	2	3	4	5	6	6P	9	11					3338	
OP 28	BTC2	2	3	4	5	6	6P	9	11					1908	
OP 37	BTT2	2	3	4	5	6	6P	9	11					2861	
OP 42	IBTE	2	3	4	5	6	6P	9	11					126	
OP 45	IBTE	2	3	4	5	R TH1								866	
OP 46	IBTE	2	3	R RX1										14746	
OP 49	MTBE	P RX1	4	5	7	8								23088	
OP 54	MTBE	P TH1	7	8										1360	
OP 58	MEOH	1	3	4	5	7	8							3	
OP 59	MEOH	1	3	4	5	R TH1								495	
OP 60	MEOH	1	3	R RX1										8394	
OP 63	TBA	P RX1	4	5	7	8								14	
OP 70	Water	MKUP	21	22	10	11								7	
OP 72	Water	MKUP	21	22	10	12	13	14	16	17	19	20	3	R RX1	3
OP 75	DIB	P RX1	4	5	7	8								39	

**Note:** Open-paths with flowrate approximate zero have been removed from the table

**Table A1.8:** Energy open-paths- MTBE Case Study

Open path	EOP streams								Flowrate (GJ/h)
OP 1	1	3	4	8					-0.01
OP 2	1	3	4	5	6	6P	9	11	-0.01
OP 3	1	3	4	5	C TH1				-0.01
OP 4	1	3	C RX1						-0.03
OP 5	2	3	4	8					0.29
OP 6	2	3	4	5	6	6P	9	11	0.13
OP 7	2	3	4	5	6	6P	C HX3		0.02
OP 8	2	3	4	5	C TH1				0.16
OP 9	2	3	C RX1						0.72
OP 10	P RX1	4	8						3.53
OP 11	P RX1	4	5	6	6P	9	11		1.62
OP 12	P RX1	4	5	6	6P	C HX3			0.25
OP 13	P RX1	4	5	C TH1					1.90
OP 14	P RX1	C RX1							8.72
OP 15	P TH1	6	6P	9	11				0.62
OP 16	P TH1	6	6P	C HX3					0.10
OP 17	P TH1	C TH1							0.72
OP 18	H HX1	3	4	8					0.91
OP 19	H HX1	3	4	5	6	6P	9	11	0.42
OP 20	H HX1	3	4	5	6	6P	C HX3		0.06
OP 21	H HX1	3	4	5	C TH1				0.49
OP 22	H HX1	3	C RX1						2.24
OP 23	E P1	6P	9	11					0.41
OP 24	E P1	6P	C HX3						0.06
OP 25	E P4	21	22	C HX5					3.97
OP 26	H T3	18	21	22	C HX5				0.44
OP 27	H T3	C T3							4.41

A2. Laundry Case Study

*Streams Data*

**Table A2.1:** Input and output streams- Laundry Case Study

Stream Name	Inlet Streams						Outlet Streams				
	S1	S4	S7	S10	S13	S2	S5	S8	S11	S14	S15
Flowrate (kg/h)											
Water	4.04	35.00	9.36	4.03	4.03	3.41	35.00	9.36	4.03	4.03	0.63
<b>Total Flowrate</b>	4.04	35.00	9.36	4.03	4.03	3.41	35.00	9.36	4.03	4.03	0.63
Temperature (°C)	32.00	20.00	22.00	20.00	20.00	32.00	77.00	55.00	25.90	20.35	20.35
Pressure (atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Enthalpy Flow (GJ/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00

Note: Data obtained from Wulff *et al.*, 2007

**Prices**

**Table A2.2: Utility Prices- Laundry Case Study**

Utilities	
Cooling (US\$/GJ)	0.96

Note: Data obtained from Coll, N., 2003

**Table A2.3: Purchase prices - Laundry Case Study**

Compound	Price (\$/kg)
Water	0.95

Note: Data obtained from Wullf *et al.*, 2007

**Table A2.4: Demand stream prices – Laundry Case Study**

Demand streams Price (\$/kg)						
	S2	S5	S8	S11	S14	S15
Water	-5.74	-5.74	-5.74	-5.74	-5.74	-5.74

Note: Data obtained from Wullf *et al.*, 2007

*Safety*

**Table A2.5:** Safety Indices –Laundry Case Study

<b>Total inherent safety index (ISI)</b>			
<b><i>Chemical inherent safety index, I<sub>ci</sub></i></b>	<b><i>Score</i></b>	<b><i>Process inherent safety index, I<sub>pi</sub></i></b>	<b><i>Score</i></b>
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, $I_{RM}$	0	Inventory, $I_I$	0
Heat of the side reactions, $I_{RS}$	0	Process temperature, $I_T$	1
Chemical Interaction, $I_{INT}$	1	Process pressure, $I_P$	0
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, $I_{FL}$	0	Equipment, $I_{EQ}$	
Explosiveness, $I_{EX}$	0	ISBL	0
Toxicity, $I_{TOX}$	0	OSBL	0
Corrosivity, $I_{COR}$	0	Process structure, $I_{ST}$	1
Maximum score $I_{CI}$	1	Maximum score $I_{PI}$	2
<b><math>I_{TI}</math></b>		<b>3</b>	



## A3. VCM Production Case Study

*Streams Data***Table A3.1:** Input and output flowrates - VCM production case study

Stream Name	Inlet					Outlet							
	C2F1	CL2F	C2F2	AIRF	WTR1	WST1	WST2	VNT2	VNT3	WTR2	TOP1	BTM2	TOP4
<b>Compound (kg/h)</b>													
<b>ET</b>	1814	0.00	1442	0.00	0.00	0.00	0.00	67.9	6.62	0.00	12.1	0.00	0.00
<b>CL2</b>	0.00	4540	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>EDC</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	377	20.3	0.00	17	669.8	0.15
<b>CCL4</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.02	0.00
<b>CF</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.04	0.05	0.01
<b>MC</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.94	0.24	0.00	4.23	0.00	0.03
<b>CH4</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>DM</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.07	0.00	0.14
<b>CO</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.65	0.00	0.00	0.00	0.00	0.00
<b>CO2</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.4	0.67	0.00	1.66	0.00	0.00
<b>TCE</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.69	0.00
<b>HCE</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.20	0.00
<b>T-CE</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.18	0.00
<b>PCE</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.64	0.00
<b>Ace</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.49	0.71	0.00	1.96	0.00	0.00
<b>T12</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.04	0.00	0.03
<b>11c2</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.32	0.00	0.52
<b>C12</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02	0.01	0.01
<b>1112C</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.11	0.00
<b>1122C</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.49	0.00
<b>VCM</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.45	0.22	0.00	5.35	0.02	6252
<b>112C</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.63	0.00
<b>111C</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.11	0.00
<b>11C</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.02	0.02	0.01
<b>DCL</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	1.76	0.00
<b>VAC</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	1.17	0.00	2.44
<b>CLE</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.04	0.74	0.00	10.2	0.00	23.6
<b>P2D</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>PE</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Chlo</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
<b>1,3B</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>BEN</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.81	0.00
<b>HCL</b>	0.00	0.00	0.00	0.00	0.00	4.17	116.5	0.00	0.00	0.00	0.00	0.00	0.00
<b>O2</b>	0.00	0.00	0.00	402	0.00	0.00	0.00	3	0.01	0.00	0.00	0.00	0.00
<b>N2</b>	0.00	0.00	0.00	1324	0.00	0.00	0.00	1322	2.04	0.00	0.31	0.00	0.00
<b>H2O</b>	0.00	0.00	0.00	0.00	453	0.00	0.00	26	1.96	1289	3.71	0.00	5.12
<b>Total Mass Flow</b>	<b>1814</b>	<b>4539</b>	<b>1442</b>	<b>1727</b>	<b>453</b>	<b>4</b>	<b>116</b>	<b>1848</b>	<b>33</b>	<b>1289</b>	<b>59</b>	<b>699</b>	<b>6284</b>

**Table A3.2:** Temperature, pressure and enthalphy of the input and output streams- VCM production case study

	Inlet Streams					Outlet Streams							
Stream Name	C2F1	CL2F	C2F2	AIRF	WTR1	WST1	WST2	VNT2	VNT3	WTR2	TOP1	BTM2	TOP4
Temperature (°C)	75	75	75	75	40	24.8	290	25.0	65.3	65.3	112	155	32.6
Pressure (atm)	1.05	1.05	7.35	7.35	0.84	0.91	6.30	4.20	0.77	0.77	12.9	5.25	4.55
Enthalpy Flow (GJ/h)	0.74	1.32	0.58	0.10	0.07	0.21	6.10	0.06	0.96	0.69	4.85	6.06	1.56

Note: Data of Table A3.1 and Table A3.2 obtained from PRO/II casebooks, 1992

*Prices*

**Table A3.3:** Utility Prices- VCM production Case Study

Utilities	
Heating (US\$/GJ) High pressure	8.75
Heating (US\$/GJ) Low pressure	6.75
Cooling (US\$/GJ)	0.96
Electricity (US\$/kWh)	0.05

Note: Data obtained from Coll, N., 2003

**Table A3.4:** Purchase prices- VCM production case study

Componet	Price (\$/kg)	Componet	Price (\$/kg)
ET	0.125	1112C	0.088
CL2	0.190	1122C	0.088
EDC	0.138	VCM	0.735
CCL4	0.088	112C	0.088
CF	0.088	111C	0.088
MC	0.088	11C	0.088
CH4	0.29	DCL	0.088
DM	0.088	VAC	0.088
CO	0.000	CLE	0.088
CO2	0.000	P2D	0.088
TCE	0.088	PE	0.088
HCE	0.088	Chlo	0.088
T-CE	0.088	1.3B	0.088
PCE	0.088	BEN	0.44
Ace	0.468	HCL	0.080
T12	0.088	O2	0.000
11c2	0.088	N2	0.000
C12	0.088	H2O	0.001

Note: Data obtained from <http://www.icispricing.com/>, <http://news.dow.com/prodbus/2005pricing/20050930c.htm>, <http://www.engage-tips.com/viewthread.cfm?qid=150369&page=5>, [www.che.cemr.wvu.edu/publications/projects/mtbe-a.pdf](http://www.che.cemr.wvu.edu/publications/projects/mtbe-a.pdf) and Coll, N., 2003.

**Table A3.5: Demand Stream prices - VCM production case study**

	Demand streams Price (\$/kg)								
	VNT1	WST1	WST2	VNT2	VNT3	WTR2	TOP1	BTM2	TOP4
ET	0.221	0	0	0	0.221	0	0	0	0
CL2	0.000	0	0	0	0.000	0	0	0	0
EDC	0.052	0	0	0	0.052	0	0	0,046	0
CCL4	0.008	0	0	0	0.008	0	0	0	0
CF	0.015	0	0	0	0.015	0	0	0	0
MC	0.063	0	0	0	0.063	0	0	0	0
CH4	0.234	0	0	0	0.234	0	0	0	0
DM	0.028	0	0	0	0.028	0	0	0	0
CO	0.000	0	0	0	0.000	0	0	0	0
CO2	0.000	0	0	0	0.000	0	0	0	0
TCE	0.021	0	0	0	0.021	0	0	0	0
HCE	0.011	0	0	0	0.011	0	0	0	0
T-CE	0.031	0	0	0	0.031	0	0	0	0
PCE	0.017	0	0	0	0.017	0	0	0	0
Ace	0.226	0	0	0	0.226	0	0	0	0
T12	0.048	0	0	0	0.048	0	0	0	0
11c2	0.053	0	0	0	0.053	0	0	0	0
C12	0.048	0	0	0	0.048	0	0	0	0
1112C	0.023	0	0	0	0.023	0	0	0	0
1122C	0.023	0	0	0	0.023	0	0	0	0
VCM	0.087	0	0	0	0.087	0	0	0	0,830
112C	0.034	0	0	0	0.034	0	0	0	0
111C	0.034	0	0	0	0.034	0	0	0	0
11C	0.053	0	0	0	0.053	0	0	0	0
DCL	0.021	0	0	0	0.021	0	0	0	0
VAC	0.221	0	0	0	0.221	0	0	0	0
CLE	0.093	0	0	0	0.093	0	0	0	0
P2D	0.217	0	0	0	0.217	0	0	0	0
PE	0.214	0	0	0	0.214	0	0	0	0
Chlo	0.118	0	0	0	0.118	0	0	0	0
1,3B	0.209	0	0	0	0.209	0	0	0	0
BEN	0.188	0	0	0	0.188	0	0	0	0
HCL	0.000	0	0,080	0	0.000	0	0	0	0
O2	0.000	0	0	0	0.000	0	0	0	0
N2	0.000	0	0	0	0.000	0	0	0	0
H2O	0.000	0	0	0	0.000	0,001	0	0	0

**Indicators**

**Table A3.6:** Top 10 indicators for open-paths -VCM production case study

Path	MVA (10 <sup>3</sup> \$/y)	Path	EWC (10 <sup>3</sup> \$/y)	Path	TVA (10 <sup>3</sup> \$/y)
OP 515	-74.93	OP 50	424.30	OP 50	-424.30
OP 63	-43.48	OP 363	327.80	OP 66	-272.75
OP 17	-41.98	OP 49	276.69	OP 49	-177.13
OP 25	-25.94	OP 66	272.75	OP 65	-122.09
OP 5	-11.72	OP 65	191.60	OP 513	-114.39
OP 257	-8.94	OP 513	114.39	OP 515	-79.15
OP 253	-6.85	OP 564	48.88	OP 564	-55.40
OP 564	-6.52	OP 8	24.77	OP 63	-45.20
OP 82	-5.03	OP 39	17.93	OP 17	-42.36
OP 350	-3.96	OP 24	12.08	OP 25	-26.35

**Table A3.7:** Top 10 indicators for closed-paths -VCM production case study

Path	EWC(10 <sup>3</sup> \$/y)	Path	AF
CP219	755.09	CP84	6.36
CP3	83.91	CP86	4.38
CP39	43.15	CP92	3.33
CP111	42.03	CP91	2.42
CP248	6.26	CP83	1.94
CP240	1.92	CP94	1.74
CP220	1.82	CP97	1.18
CP229	1.81	CP75	0.93
CP57	1.71	CP104	0.85
C2P21	1.61	CP95	0.79

**Table A3.8:** Energy closed-paths indicators-VCM production case study

Energy Path	EAF
CP1	0.00
CP2	0.00
CP3	0.88
CP4	0.07
CP5	0.00
CP6	0.00
CP7	0.00

**Table A3.9:** Energy open-paths indicators-VCM production case study

Supply	Demand	DC (\$/GJ)	TDC (\$/GJ)
C2F1	C RX1	200.8	7906.4
CL2F	C RX1	1567.0	
P RX1	C RX1	6138.6	
C2F1	VNT1	453.6	10043.7
CL2F	VNT1	2632.4	
P RX2	VNT1	6945.1	
P RX1	VNT1	12.6	
C2F1	C FLS1	680.4	11147.4
CL2F	C FLS1	3494.9	
P RX1	C FLS1	14.7	
P RX2	C FLS1	6957.4	
C2F1	C RX2	34.2	198.7
CL2F	C RX2	164.5	
WTR1	VNT3	4358.0	4547.2
P RX4	VNT3	189.3	
WTR1	WTR2	3607.3	3764.0
P RX4	WTR2	156.7	
P RX3	C FLS2	35.8	8004.0
P RX4	C FLS2	7968.2	
P RX3	WST2	43.5	8974.7
P RX4	WST2	8931.2	
P RX3	C RX3	6499.9	6499.9
P RX4	C RX4	2183.5	2183.5
H FLS4	TOP4	0.0	10.0
H PYRO	TOP4	0.1	
H COL3	TOP4	0.3	
H COL4	TOP4	9.6	
H FLS4	C COL4	0.1	18.3
H PYRO	C COL4	0.3	
H COL3	C COL4	0.5	
H COL4	C COL4	17.4	
H FLS4	C COL3	0.3	4.4
H PYRO	C COL3	1.4	
H COL3	C COL3	2.7	
H FLS4	C FLS7	2.2	11.5
H PYRO	C FLS7	9.3	
H FLS4	C FLS6	6.2	32.0
H PYRO	C FLS6	25.8	
H FLS4	C FLS5	1.2	6.0
H PYRO	C FLS5	4.8	
H FLS4	R PYRO	9.6	49.5
H PYRO	R PYRO	39.8	
H COL2	R PYRO	0.0	

Appendixes

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Supply	Demand	DC (\$/GJ)	TDC (\$/GJ)
H PYRO	TOP1	0.1	35.2
H COL1	TOP1	25.6	
H COL3	TOP1	0.3	
H COL4	TOP1	9.2	
H COL1	C COL1	5.8	7.9
H COL3	C COL1	0.1	
H COL4	C COL1	2.1	
H COL2	BTM2	40.9	40.9
H COL2	C COL2	58.7	58.7

**Safety**

**Table A3.10: Safety Indices-VCM production case study**

<b>Total inherent safety index (<math>I_{TI}</math>)</b>			
<b><i>Chemical inherent safety index, <math>I_{CI}</math></i></b>	<b><i>Score</i></b>	<b><i>Process inherent safety index, <math>I_{PI}</math></i></b>	<b><i>Score</i></b>
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, $I_{RM}$	3	Inventory, $I_I$	4
Heat of the side reactions, $I_{RS}$	3	Process temperature, $I_T$	3
Chemical Interaction, $I_{INT}$	4	Process pressure, $I_P$	1
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, $I_{FL}$	4	Equipment, $I_{EQ}$	
Explosiveness, $I_{EX}$	1	ISBL	4
Toxicity, $I_{TOX}$	6	OSBL	3
Corrosivity, $I_{COR}$	1	Process structure, $I_{ST}$	2
Maximum score $I_{CI}$	22	Maximum score $I_{PI}$	17
<b><math>I_{TI}</math></b>		<b>39</b>	

**Environment**

**Table A3.11: WAR algorithm- VCM production case study**

Stream No	Total PEI	HTPI	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
C2F1	3757	0	0	28	0	0	0	3729	0
CL2F	41425	0	447	40978	0	0	0	0	0
C2F2	2986	0	0	22	0	0	0	2964	0
AIRF	0	0	0	0	0	0	0	0	0
WTR1	0	0	0	0	0	0	0	0	0
Input sum	48085	0	446324	41008	0	0	0	6629	0
WST1	285	90	5	0	90	0	0	0	100
WST2	569	212	1	5	212	0	0	140	0
VNT1	0	0	0	0	0	0	0	0	0
VNT3	731	360	1	9	360	0	0	0	0
VNT2	10263	4417	1419	10	4417	0	0	0	0
TOP1	10	3	0	0	3	0	0	0	3
BTM2	37	11	0	0	11	0	0	14	0
TOP4	70	22	1	1	22	0	0	25	0
Output sum	11966	5116	1428	25	5116	0	0	178	104
Impact generated	-36201	5116	981	-41004	5116	0	0	-6514	104



**Compounds****Table A3.12:** Compound names- VCM production case study

Compound	Name in the tables
Ethylene	ET
Chlorine	CL2
1,2-Dichloroethane	EDC
Carbon tetrachloride	CCL4
Chloroform	CF
Methyl chloride	MC
Methane	CH4
Dichloromethane	DM
Carbon monoxide	CO
Carbon dioxide	CO2
Tetrachloroethylene	TCE
Hexachlorethane	HCE
Trichloroethylene	T-CE
Pentachlorethane	PCE
Acetylene	Ace
trans-1,2-Dichloroethene	T12
1,1-Dichloroethene	11c2
cis-1,2-Dichloroethene	C12
1,1,1,2-Tetrachloroethane	1112C
1,1,2,2-Tetrachloroethane	1122C
VCM	VCM
1,1,2-Trichloroethane	112C
1,1,1-Trichloroethane	111C
1,1-Dichloroethane	11C
2,2-Dichloroacetyl chloride	DCL
Acetic acid ethenyl ester	VAC
Ethyl chloride	CLE
1,2-Propadiene	P2D
Propene	PE
2-Chloropropene	Chlo
1,3-Butadiene	1,3B
Benzene	BEN
Hydrogen chloride	HCL
Oxygen	O2
Nitrogen	N2
Water	H2O

## A4. Ammonia Production Case Study

*Streams Data***Table A4.1:** Input and output flowrates- Ammonia production case study

Stream Name	Inlet Streams							Outlet Streams						
	1	5	7	WAT	31P	39	40	18	CO2	XS	24W	WA1	WA2	WA3
<b>Flowrate (kg/h)</b>														
<b>Water</b>	0.00	0.00	0.00	8171.46	0.00	0.00	0.00	23385.02	0.00	8188.57	40.31	64.78	19.41	11.01
<b>Oxygen</b>	0.00	0.00	3072.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Carbon monoxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Carbon dioxide</b>	387.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	15316.11	0.00	0.00	0.00	0.00	0.00
<b>Hydrogene</b>	0.00	0.00	0.00	0.00	36.62	19.31	1.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Nitrogen</b>	255.31	0.00	9996.24	0.00	170.33	75.23	5.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Argon</b>	0.00	0.00	173.51	0.00	88.28	74.90	10.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Methane</b>	3871.16	0.00	0.00	0.00	42.60	56.26	14.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ethane</b>	669.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Propane</b>	428.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Butane</b>	401.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Pentane</b>	51.74	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonia</b>	0.00	0.00	0.00	0.00	46.29	256.10	11891.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Steam</b>	0.00	32299.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	6065.07	32299.67	13242.02	8171.46	384.12	481.81	11922.32	23385.02	15316.11	8188.57	40.31	64.78	19.41	11.01
<b>Temperature (°C)</b>	15.56	510.00	165.56	37.78	29.44	26.32	26.32	37.78	-20.48	37.78	37.78	35.00	35.00	35.00
<b>Pressure (atm)</b>	24.46	24.04	20.94	19.70	322.31	25.14	25.14	19.35	19.35	18.53	18.25	48.93	135.12	342.65
<b>Enthalpy Flow</b>	1.44	112.47	1.63	1.31	0.11	0.37	1.14	3.74	3.68	1.31	0.01	0.01	0.00	0.00

Note: Data obtained from PRO/II casebooks, 1992

**Prices**

**Table A4.2: Utility prices - Ammonia production case study**

<b>Utilities</b>	
Heating (US\$/GJ) High pressure	8.75
Heating (US\$/GJ) Low pressure	6.75
Cooling (US\$/GJ)	0.96
Electricity (US\$/kWh)	0.05

Note: Data obtained from Coll, N., 2003

**Table A4.3: Purchase prices – Ammonia production Case Study**

<b>Compound</b>	<b>Price (\$/kg)</b>
<b>Water</b>	0.0010
<b>Oxygen</b>	0
<b>Carbon monoxide</b>	0
<b>Carbon dioxide</b>	0
<b>Hydrogene</b>	0
<b>Nitrogen</b>	0
<b>Argon</b>	0
<b>Methane</b>	0.0018
<b>Ethane</b>	0.0018
<b>Propane</b>	0.0018
<b>Butane</b>	0.0018
<b>Pentane</b>	0.0018
<b>Ammonia</b>	0.2450
<b>Steam</b>	0.027

Note: Data obtained from Vázquez, M.C., 2007

**Table A4.4:** Demand stream prices – Ammonia production Case Study

Compound	Demand streams Price (\$/kg)									
	31P	39	40	18	CO2	XS	24W	WA1	WA2	WA3
Water	-0.02	-0.02	0	0	0	0	0	0	0	0
Oxygen	-0.02	-0.02	0	0	0	0	0	0	0	0
Carbon monoxide	-0.02	-0.02	0	0	0	0	0	0	0	0
Carbon dioxide	-0.02	-0.02	0	0	0	0	0	0	0	0
Hydrogene	-0.02	-0.02	0	0	0	0	0	0	0	0
Nitrogen	-0.02	-0.02	0	0	0	0	0	0	0	0
Argon	-0.02	-0.02	0	0	0	0	0	0	0	0
Methane	-0.02	-0.02	0	0	0	0	0	0	0	0
Ethane	-0.02	-0.02	0	0	0	0	0	0	0	0
Propane	-0.02	-0.02	0	0	0	0	0	0	0	0
Butane	-0.02	-0.02	0	0	0	0	0	0	0	0
Pentane	-0.02	-0.02	0	0	0	0	0	0	0	0
Ammonia	-0.02	-0.02	0.25	0	0	0	0	0	0	0
Steam	-0.02	-0.02	0	0	0	0	0	0	0	0

Note: Data obtained from Vázquez, M.C., 2007

**Indicators**

**Table A4.5:** Top 10 indicators for open-paths -Ammonia production case study

Path	MVA (10 <sup>3</sup> \$/yr)	Path	EWC (10 <sup>3</sup> \$/yr)	Path	TVA(10 <sup>3</sup> \$/yr)
OP 107	-169.36	OP 429	1724.08	OP 429	-1724.08
OP 17	-65.37	OP 850	1058.45	OP 850	-1058.45
OP 822	-38.07	OP 299	608.31	OP 299	-608.31
OP 85	-17.72	OP 648	575.95	OP 648	-575.95
OP 600	-17.30	OP 846	543.41	OP 846	-543.41
OP 601	-12.74	OP 647	400.60	OP 647	-400.59
OP 820	-12.11	OP 823	190.25	OP 107	-345.75
OP 819	-9.07	OP 107	176.39	OP 690	-156.48
OP 604	-1.94	OP 690	156.48	OP 245	-148.96
OP 154	-0.52	OP 245	148.96	OP 154	-109.72

**Table A4.6:** Top 5 indicators for closed-paths -Ammonia production case study

Path	EWC (10 <sup>3</sup> \$/yr)	Path	AF
CP13	109.04	CP7	77.22
CP6	47.97	CP3	70.78
CP7	35.46	CP8	57.19
CP8	6.87	CP11	49.94
CP5	0.75	CP12	40.06

**Table A4.7:** Energy closed-paths indicators-Ammonia production case study

ECP	EAF
CP1	0.04
CP2	0.03
CP3	0.11
CP4	0.56
CP5	1.11
CP6	0.12

**Table A4.8:** Energy open-paths indicators-Ammonia production case study

Supply	Demand	DC (\$/GJ)	TDC (\$/GJ)
1	18	1.4	1338.7
5	18	82.7	
7	18	216.1	
P RX-3	18	221.4	
P RX-4	18	349.2	
P RX-5	18	458.1	
H HTR	18	0.4	
H RX-2	18	9.5	
P RX-7	39	121.4	121.5
H CP-3	39	0.1	
P RX-7	40	442.3	442.7
H CP-2	40	0.1	
H CP-3	40	0.2	
E CP-4	40	0.2	
P RX-7	31P	68.6	68.6
1	C CW1	11.8	9443.4
5	C CW1	672.2	
7	C CW1	1507.9	
P RX-3	C CW1	1550.8	
P RX-4	C CW1	2436.1	
P RX-5	C CW1	3195.9	
H HTR	C CW1	2.8	
H RX-2	C CW1	66.0	
1	C CW2	0.4	7392.0
5	C CW2	54.0	
7	C CW2	278.4	
P RX-3	C CW2	282.0	
P RX-4	C CW2	449.8	
P RX-6	C CW2	6314.6	
H HTR	C CW2	0.5	
H RX-2	C CW2	12.2	
P RX-7	C D-6	21203.5	21204.5
H CP-1	C D-6	0.1	
H CP-2	C D-6	0.2	
H CP-3	C D-6	0.4	
E CP-4	C D-6	0.4	
5	C D-7	1.3	288.8
P RX-3	C D-7	10.2	
P RX-4	C D-7	16.3	
P RX-6	C D-7	229.0	
H RX-2	C D-7	0.4	
H CP-1	C D-7	2.1	
H CP-2	C D-7	5.4	
H CP-3	C D-7	12.6	
E CP-4	C D-7	11.5	

Appendixes

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Supply	Demand	DC (\$/GJ)	TDC (\$/GJ)
1	C REB1	25.8	17373.9
5	C REB1	1396.1	
7	C REB1	2744.2	
P RX-3	C REB1	2833.1	
P RX-4	C REB1	4433.4	
P RX-5	C REB1	5816.2	
H HTR	C REB1	5.0	
H RX-2	C REB1	120.2	
5	C RX-1	0.4	7.1
P RX-3	C RX-1	6.4	
H RX-2	C RX-1	0.3	
1	C T-1	0.3	373.2
5	C T-1	19.5	
7	C T-1	60.9	
P RX-3	C T-1	62.2	
P RX-4	C T-1	98.4	
P RX-5	C T-1	129.1	
H HTR	C T-1	0.1	
H RX-2	C T-1	2.7	
5	C WHB1	2182.6	9349.2
7	C WHB1	3438.7	
P RX-3	C WHB1	3577.3	
H RX-2	C WHB1	150.6	
1	C WHB2	10.4	4045.0
5	C WHB2	540.3	
7	C WHB2	945.0	
P RX-3	C WHB2	979.4	
P RX-4	C WHB2	1526.8	
H HTR	C WHB2	1.7	
H RX-2	C WHB2	41.4	
1	CO2	0.7	1288.9
5	CO2	54.7	
7	CO2	212.8	
P RX-3	CO2	216.3	
P RX-4	CO2	343.8	
P RX-5	CO2	451.0	
H HTR	CO2	0.4	
H RX-2	CO2	9.3	
5	R RX-2	1966.3	2089.8
H RX-2	R RX-2	123.4	
H CP-1	WA1	0.0	0.0
WAT	XS	9669.5	9669.5

**Safety**

**Table A4.9: Safety Indices-Ammonia production case study**

<b>Total inherent safety index (I<sub>TI</sub>)</b>			
<b><i>Chemical inherent safety index, I<sub>CI</sub></i></b>	<b><i>Score</i></b>	<b><i>Process inherent safety index, I<sub>PI</sub></i></b>	<b><i>Score</i></b>
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, I <sub>RM</sub>	4	Inventory, I <sub>I</sub>	0
Heat of the side reactions, I <sub>RS</sub>	4	Process temperature, I <sub>T</sub>	4
Chemical Interaction, I <sub>INT</sub>	4	Process pressure, I <sub>P</sub>	4
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, I <sub>FL</sub>	3	Equipment, I <sub>EQ</sub>	
Explosiveness, I <sub>EX</sub>	1	ISBL	3
Toxicity, I <sub>TOX</sub>	6	OSBL	2
Corrosivity, I <sub>COR</sub>	1	Process structure, I <sub>ST</sub>	2
Maximum score I <sub>CI</sub>	23	Maximum score I <sub>PI</sub>	15
<b>I<sub>TI</sub></b>		<b>38</b>	

**Environment**

**Table A4.10: WAR algorithm- Ammonia production case study**

<b>Stream</b>	<b>Total PEI</b>	<b>HTPI</b>	<b>HTPE</b>	<b>ATP</b>	<b>TTP</b>	<b>GWP</b>	<b>ODP</b>	<b>PCOP</b>	<b>AP</b>
<b>1</b>	63406.60	7532.91	7.64	4817.57	7532.91	222.26	0	43293.3	0
<b>5</b>	0	0	0	0	0	0	0	0	0
<b>7</b>	0	0	0	0	0	0	0	0	0
<b>WAT</b>	0	0	0	0	0	0	0	0	0
<b>Input</b>	63406.6	7532.91	7.6397	4817.57	7532.91	222	0	43293.3	0
<b>31P</b>	3168.2	794.729	13.862	116.692	794.729	2.353	0	9.692	1436.14
<b>39</b>	17404.7	4386.280	40.586	583.082	4386.28	3.137	0	12.923	7992.43
<b>40</b>	806195	203561	1707.480	26118.1	203561	0.784	0	3.231	371242
<b>CO2</b>	25586.2	0	22.099	25350.1	0	213.98	0	0	0
<b>18</b>	0	0	0	0	0	0	0	0	0
<b>XS</b>	0	0	0	0	0	0	0	0	0
<b>24W</b>	0	0	0	0	0	0	0	0	0
<b>WA1</b>	0	0	0	0	0	0	0	0	0
<b>WA2</b>	0	0	0	0	0	0	0	0	0
<b>WA3</b>	0	0	0	0	0	0	0	0	0
<b>Output</b>	852354	208742	1784.03	52168	208742	220.25	0	25.846	380671
<b>Impact generated</b>	788947	201210	1776.39	47350.5	201210	-2.012	0	-43267.5	380671



## A5. Biodiesel Production Case Study

### *Streams Data*

**Table A5.1:** Input and output flowrates- Biodiesel production case study

Stream Name	Inlet Streams			Outlet Streams			
	METHALC	S5	SOLI	BIODIESEL	GLYCEROL	USED_WATER	WASTE_OIL
<b>Flowrate (kg/h)</b>							
<b>Jatropha oil</b>	0.00	0.00	1000.00	2.46	0.00	0.00	17.54
<b>Methyl stearate</b>	0.00	0.00	0.00	325.75	0.00	0.00	0.17
<b>Methyl linoleate</b>	0.00	0.00	0.00	236.69	0.00	0.00	93.70
<b>Methyl oleate</b>	0.00	0.00	0.00	328.16	0.00	0.00	0.00
<b>Methanol</b>	106.62	0.00	0.00	0.00	0.00	0.22	0.00
<b>Glycerol</b>	0.00	0.00	0.00	0.00	99.89	2.04	0.00
<b>Water</b>	0.00	20.00	0.00	0.00	10.24	9.76	0.00
<b>Total Flowrate</b>	106.62	20.00	1000.00	893.06	110.14	12.02	111.41
<b>Temperature (°C)</b>	25.00	25.00	25.00	364.65	202.82	202.82	440.01
<b>Pressure (kPa)</b>	101.32	101.32	101.32	101.00	101.32	101.32	101.00
<b>Enthalpy Flow (GJ/h)</b>	0.01	0.00	3.28	0.80	0.07	0.03	0.19

Note: Data obtained from Guillotin, G., 2009

### *Prices*

**Table A5.2:** Utility prices – Biodiesel production case study

Utilities	
Heating (US\$/GJ) High pressure	8.75
Heating (US\$/GJ) Low pressure	6.75
Cooling (US\$/GJ)	0.96
Electricity (US\$/kWh)	0.05

Note: Data obtained from Coll, N., 2003

**Table A5.3: Purchase prices – Biodiesel production Case Study**

<b>Compound</b>	<b>Price (\$/kg)</b>
<b>Jatropha oil</b>	0.500
<b>Methyl stearate</b>	0.900
<b>Methyl linoleate</b>	0.900
<b>Methyl oleate</b>	0.900
<b>Methanol</b>	0.180
<b>Glycerol</b>	1.200
<b>Water</b>	0.014

Note: Data obtained from Guillotin, G., 2009

**Table A5.4: Demand stream prices – Biodiesel production Case Study**

	<b>Demand streams Price (\$/kg)</b>			
	<b>BIODIESEL</b>	<b>GLYCEROL</b>	<b>USED_WATER</b>	<b>WASTE_OIL</b>
<b>Jatropha oil</b>	0.00	0.00	0.00	0.00
<b>Methyl stearate</b>	0.90	0.00	0.00	0.00
<b>Methyl linoleate</b>	0.90	0.00	0.00	0.00
<b>Methyl oleate</b>	0.90	0.00	0.00	0.00
<b>Methanol</b>	0.00	0.00	0.00	0.00
<b>Glycerol</b>	0.00	1.20	0.00	0.00
<b>Water</b>	0.00	0.00	0.00	0.00

Note: Data obtained from Guillotin, G., 2009

**Indicators**

**Table A5.5:** Top 10 indicators for open-paths -Biodiesel production case study

Path	MVA (10 <sup>3</sup> \$/yr)	Path	EWC (10 <sup>3</sup> \$/yr)	Path	TVA(10 <sup>3</sup> \$/yr)
OP 28	-269.27	OP 16	27.79	OP 28	-293.75
OP 12	-266.58	OP 28	24.48	OP 12	-271.63
OP 2	-71.15	OP 6	19.34	OP 2	-71.15
OP 29	-25.06	OP 11	13.95	OP 29	-25.56
OP 1	-9.84	OP 5	6.43	OP 1	-9.99
OP 33	-1.14	OP 12	5.04	OP 5	-6.43
OP 34	-1.09	OP 2	0.99	OP 33	-1.91
OP 7	-0.50	OP 33	0.78	OP 34	-1.09
OP 24	-0.31	OP 25	0.57	OP 25	-0.57
OP 17	-0.01	OP 29	0.50	OP 7	-0.51

**Table A5.6:** Top 5 indicators for closed-paths -Biodiesel production case study

Path	EWC (10 <sup>3</sup> \$/yr)	Path	AF
CP5	4.11E+00	CP5	1.04E+00
CP6	3.04E-06	CP6	9.47E-07
CP4	1.18E-06	CP4	2.58E-07
CP2	7.66E-07	CP2	2.13E-07
CP3	4.90E-07	CP3	1.32E-07

**Table A5.7:** Energy closed-paths indicators-Biodiesel production case study

ECP	EAF
CP1	0.009

**Table A5.8:** Energy open-paths indicators-Biodiesel production case study

Supply	Demand	DC (\$/GJ)	TDC (\$/GJ)
SOLI	BIODIESEL	1.63	62.97
SOLI	BIODIESEL	54.57	
H T1	BIODIESEL	0.50	
H T3	BIODIESEL	6.27	
SOLI	C T3	2.87	8.83
H T1	C T3	0.44	
H T3	C T3	5.52	
SOLI	WASTE_OIL	33.64	35.21
H T1	WASTE_OIL	0.12	
H T3	WASTE_OIL	1.46	
SOLI	GLYCEROL	61.90	62.33
H T1	GLYCEROL	0.08	
H F1	GLYCEROL	0.35	
H T1	USED_WATER	0.09	0.29
H T1	USED_WATER	0.04	
H F1	USED_WATER	0.16	
H T1	C E3	5.61	5.61
H T1	C T1	2.59	2.59

## Safety

**Table A5.9:** Safety Indices-Biodiesel production case study

Total inherent safety index ( $I_{TI}$ )			
<i>Chemical inherent safety index, <math>I_{CI}</math></i>	<i>Score</i>	<i>Process inherent safety index, <math>I_{PI}</math></i>	<i>Score</i>
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, $I_{RM}$	0	Inventory, $I_I$	1
Heat of the side reactions, $I_{RS}$	0	Process temperature, $I_T$	3
Chemical Interaction, $I_{INT}$	4	Process pressure, $I_P$	1
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, $I_{FL}$	1	Equipment, $I_{EQ}$	
Explosiveness, $I_{EX}$	1	ISBL	1
Toxicity, $I_{TOX}$	6	OSBL	1
Corrosivity, $I_{COR}$	1	Process structure, $I_{ST}$	2
Maximum score $I_{CI}$	13	Maximum score $I_{PI}$	9
<b><math>I_{TI}</math></b>		<b>22</b>	

## Environment

**Table A5.10:** WAR algorithm-Biodiesel production case study

Total generation rate of PEI (PEI/hr)								
HTPI	HTPE	TTP	ATP	GWP	ODP	PCOP	AP	TOTAL
14.9	4.8	14.9	0.0	0.0	0.0	78.9	0.0	114.0

Due to missing data in ICAS the war algorithm to the biodiesel case-study has been calculated using WAR algorithm tool developed by U.S. Environmental Protection Agency available in [http://www.epa.gov/nrmrl/std/cppb/war/sim\\_war.htm](http://www.epa.gov/nrmrl/std/cppb/war/sim_war.htm).

## A6. Copper Extraction Case Study

All data in this appendix as been given by Coldeco Norte.

**Table A6.1:** Input flowrates- Copper extraction case study

Stream Name	Inlet Stream															
	F6	WA	WB	WC	WD	F7	AcWA	AcWB	AcWC	AcWD	AcSA	AcSB	AcSC	AcSD	Mineral 1	Mineral 2
Flowrate (kg/h)																
Sulfuric Acid	0.00	0.00	0.00	0.00	0.00	10524.80	956.80	2042.40	1656.00	1288.00	2778.40	2741.60	2760.00	2741.60	0.00	0.00
Kerosene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Aldoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	518680.00	40630.00	40830.00	39730.00	45100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	34910.12	1492.39
CuSO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
R2Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flowrate	518680.00	40630.00	40830.00	39730.00	45100.00	10524.80	956.80	2042.40	1656.00	1288.00	2778.40	2741.60	2760.00	2741.60	34910.12	1492.39
Temperature (°C)	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Pressure (atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

**Table A6.2:** Output flowrates- Copper extraction case study

Stream Name	Outlet Stream								
	PCA	PCB	PCC	PCD	PWB	PWC	PWD	Cathodes	PSC
<b>Flowrate (kg/h)</b>									
<b>Sulfuric Acid</b>	1.06	1.05	1.06	1.07	2043.10	1656.71	1288.71	0.00	2042.05
<b>Kerosene</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Aldoxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Water</b>	83.68	82.92	82.24	83.78	40885.28	39784.83	45155.85	0.00	40802.36
<b>CuO</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>CuSO4</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>R2Cu</b>	0.37	0.37	0.35	0.37	0.25	0.24	0.25	0.00	-0.12
<b>Cu</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	36086.11	0.00
<b>Total Flowrate</b>	85.12	84.34	83.66	85.22	42928.63	41441.77	46444.81	36086.11	42844.29
<b>Temperature (°C)</b>	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
<b>Pressure (atm)</b>	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

*Prices*

**Table A6.3:** Utility prices – Copper Extraction case study

Utility	Price
Heating (Low pressure) (US\$/GJ)	22.70
Electricity (US\$/kWh)	0.04

**Table A6.4:** Purchase prices – Copper Extraction Case Study

Compound	Price	Units
Copper	1.52	US\$/Lb
Sulphuric Acid	80	US\$/Ton
Water	1.78	US\$/m3
Kerosene	0.8	US\$/l
LIX Solvent	8200	US\$/m3

**Table A6.5:** Demand stream prices – Copper Extraction Case Study

Compound	Demand streams Price (\$/kg)									
	PCA	PCB	PCC	PCD	PWA	PWB	PWC	PWD	Cathodes	PSC
Sulfuric Acid	0	0	0	0	0	0	0	0	0.00	0
Kerosene	0	0	0	0	0	0	0	0	0.00	0
Aldoxide	0	0	0	0	0	0	0	0	0.00	0
Water	0	0	0	0	0	0	0	0	0.00	0
CuO	0	0	0	0	0	0	0	0	0.00	0
CuSO4	0	0	0	0	0	0	0	0	0.00	0
R2Cu	0	0	0	0	0	0	0	0	0.00	0
Cu	0	0	0	0	0	0	0	0	3.35	0



*Indicators*

**Table A6.6:** Top 10 indicators for open-paths - Copper Extraction case study

Path	MVA (10 <sup>3</sup> \$/yr)	Path	EWC (10 <sup>3</sup> \$/yr)	Path	TVA(10 <sup>3</sup> \$/yr)
OP 12	-1356.62	OP 173	120.49	OP 12	-1356.62
OP 14	-1100.05	OP 225	40.26	OP 14	-1100.05
OP 16	-855.70	OP 217	38.14	OP 16	-855.70
OP 152	-667.13	OP 221	38.11	OP 152	-667.13
OP 5	-635.78	OP 73	23.30	OP 5	-635.78
OP 138	-604.04	OP 72	21.79	OP 138	-604.04
OP 135	-601.09	OP 71	21.74	OP 135	-601.09
OP 145	-587.78	OP 229	20.84	OP 145	-587.78
OP 173	-17.04	OP 287	18.81	OP 173	-137.53
OP 106	0.00	OP 233	17.91	OP 225	-40.26

**Table A6.7:** Top 10 indicators for closed-paths - Copper Extraction case study

Path	EWC (10 <sup>3</sup> \$/yr)	Path	AF
CP220	26755.28	CP18	165.64
CP148	25384.67	CP19	165.64
CP164	24292.21	CP59	164.32
CP188	24003.53	CP58	164.32
CP172	23962.59	CP122	163.49
CP36	23047.78	CP123	163.49
CP76	22773.89	CP90	154.18
CP44	22735.05	CP91	154.18
CP228	14909.95	CP23	0.90
CP217	2136.27	CP127	0.87

**Safety**

**Table A6.8: Safety Indices- Copper Extraction production case study**

<b>Total inherent safety index (<math>I_{TI}</math>)</b>			
<b><i>Chemical inherent safety index, <math>I_{CI}</math></i></b>	<b><i>Score</i></b>	<b><i>Process inherent safety index, <math>I_{PI}</math></i></b>	<b><i>Score</i></b>
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, $I_{RM}$	0	Inventory, $I_I$	0
Heat of the side reactions, $I_{RS}$	0	Process temperature, $I_T$	0
Chemical Interaction, $I_{INT}$	0	Process pressure, $I_P$	0
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, $I_{FL}$	4	Equipment, $I_{EQ}$	
Explosiveness, $I_{EX}$	1	ISBL	1
Toxicity, $I_{TOX}$	6	OSBL	1
Corrosivity, $I_{COR}$	1	Process structure, $I_{ST}$	2
Maximum score $I_{CI}$	12	Maximum score $I_{PI}$	4
<b><math>I_{TI}</math></b>		<b>16</b>	

**Environment**

**Table A6.9: WAR algorithm - Copper Extraction production case study**

Stream No	Total PEI	HTPI	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
Sum Input	17600	4515	8103	467	4514	0	0	0	0
Input sum	17600	4515	8103	467	4514	0	0	0	0
Sum Output	17600	4515	8103	467	4514	0	0	0	0
Output sum	17600	4515	8103	467	4514	0	0	0	0
Impact generated	0	0	0	0	0	0	0	0	0

## A7. Insulin Production Case Study

**Table A7.1:** Input flowrates- Insulin production case study

Stream Name	Inlet Streams							
	S2	S4	S20	S28	S36	S43	S50	S54
<b>Flowrate (kg/h)</b>								
<b>Nitrogen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Oxygen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Glucose</b>	4888.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Salts</b>	446.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Water</b>	0.00	33482.79	0.00	0.00	0.00	0.00	0.00	0.00
<b>Biomass</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonia</b>	0.00	0.00	450.83	0.00	0.00	0.00	0.00	0.00
<b>Carbon dioxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Process Water</b>	0.00	0.00	0.00	8975.06	2831.03	7027.80	26112.95	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Phosforic acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>TRIS solvent</b>	0.00	0.00	0.00	270.00	0.00	0.00	0.00	0.00
<b>EDTA solvent</b>	0.00	0.00	0.00	65.17	0.00	0.00	0.00	0.00
<b>Triton-X solvent</b>	0.00	0.00	0.00	0.00	18.97	0.00	0.00	0.00
<b>Cyanogen bromide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	95.43
<b>Formic Acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10947.03
<b>Urea</b>	0.00	0.00	0.00	0.00	0.00	2223.49	0.00	0.00
<b>2-Mercaptoethanol</b>	0.00	0.00	0.00	0.00	0.00	300.03	0.00	0.00
<b>Ammonium bicarbonate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Sulfite</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium tetrathionate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Hydrogen chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetic Acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Enzymes</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetonitrile</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonium acetate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Zinc dichloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cell Debris</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cont Proteins</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Inclusion Bodies</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Trp-Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Denatured Proin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin-SSO3</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin Crystal</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	5335.42	33482.79	450.83	9310.23	2850.00	9551.33	26112.95	11042.46
<b>Temperature (°C)</b>	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
<b>Pressure (atm)</b>	1	1	1	1	1	1	1	1
<b>Enthalpy Flow (GJ/h)</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendixes

Inlet Streams								
Stream Name	S62	S68	S71	S74	S77	S79	S82	S85
<b>Flowrate (kg/h)</b>								
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glucose	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Salts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonia	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	1116.10	15785.34	8260.63	8284.65	15616.95	25009.41	12100.15	29683.41
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phosphoric acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIS solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EDTA solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triton-X solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyanogen bromide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formic Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urea	0.00	0.00	0.00	0.00	6518.32	10399.87	0.00	0.00
2-Mercaptoethanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	316.59
Ammonium bicarbonate	34.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Sulfite	301.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium tetrathionate	150.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen chloride	5034.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	0.00	52.00	0.00	338.81	542.12	707.25	0.00
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Enzymes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetonitrile	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonium acetate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zinc dichloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cell Debris	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cont Proteins	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Inclusion Bodies	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Trp-Proinsulin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Denatured Proin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Proinsulin-SSO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Proinsulin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Insulin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Insulin Crystal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	<b>6638.73</b>	<b>15785.34</b>	<b>8312.62</b>	<b>8284.65</b>	<b>22474.07</b>	<b>35951.40</b>	<b>12807.41</b>	<b>30000.00</b>
<b>Temperature (°C)</b>	<b>25.0</b>	<b>25.00</b>	<b>25.00</b>	<b>25.00</b>	<b>25.00</b>	<b>25.00</b>	<b>25.00</b>	<b>25.00</b>
<b>Pressure (atm)</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>
<b>Enthalpy Flow (GJ/h)</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>

Appendixes

Stream Name	Inlet Streams							
	S91	S94	S97	S100	S103	S106	S108	S114
<b>Flowrate (kg/h)</b>								
<b>Nitrogen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Oxygen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Glucose</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Salts</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Water</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Biomass</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonia</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Carbon dioxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Process Water</b>	18131.48	8538.37	4312.06	12807.56	20616.64	6297.99	11.05	4353.85
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	824.56	0.00	0.00	0.00
<b>Phosforic acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>TRIS solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>EDTA solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Triton-X solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cyanogen bromide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Formic Acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Urea</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>2-Mercaptoethanol</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonium bicarbonate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Sulfit</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium tetrathionate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Hydrogen chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Chloride</b>	0.00	156.83	0.00	235.24	1204.40	368.12	0.00	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetic Acid</b>	0.00	13.94	0.00	20.90	0.00	0.00	0.00	0.00
<b>Enzymes</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
<b>Acetonitrile</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonium acetate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Zinc dichloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cell Debris</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cont Proteins</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Inclusion Bodies</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Trp-Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Denatured Proin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin-SSO3</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin Crystal</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	18131.48	8709.14	4312.06	13063.70	22645.60	6666.10	11.07	4353.85
<b>Temperature (°C)</b>	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
<b>Pressure (atm)</b>	1	1	1	1	1	1	1	1
<b>Enthalpy Flow (GJ/h)</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendixes

Inlet Streams								
Stream Name	S117	S120	S123	S126	S128	S131	S135	S137
<b>Flowrate (kg/h)</b>								
<b>Nitrogen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Oxygen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Glucose</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Salts</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Water</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Biomass</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonia</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Carbon dioxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Process Water</b>	2588.60	2222.01	8384.55	4427.15	1682.67	1051.18	4505.06	1171.20
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	35.92	0.00	0.00	0.00	0.00
<b>Phosphoric acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>TRIS solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>EDTA solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Triton-X solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cyanogen bromide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Formic Acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Urea</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>2-Mercaptoethanol</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonium bicarbonate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Sulfit</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium tetrathionate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Hydrogen chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Chloride</b>	168.37	0.00	1089.52	0.00	0.00	0.00	0.00	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetic Acid</b>	0.00	0.00	0.00	0.00	0.00	21.45	91.94	1756.80
<b>Enzymes</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetonitrile</b>	0.00	0.00	0.00	0.00	0.00	357.54	1532.33	2905.01
<b>Ammonium acetate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Zinc dichloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cell Debris</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cont Proteins</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Inclusion Bodies</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Trp-Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Denatured Proin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin-SSO3</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin Crystal</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	2756.97	2222.01	9474.07	4463.07	1682.67	1430.18	6129.34	5833.01
<b>Temperature (°C)</b>	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
<b>Pressure (atm)</b>	1	1	1	1	1	1	1	1
<b>Enthalpy Flow (GJ/h)</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendixes

	Inlet Streams							
Stream Name	S139	S142	S145	S148	S150	S153	S161	ST1
Flowrate (kg/h)								
<b>Nitrogen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	16666.60
<b>Oxygen</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5059.66
<b>Glucose</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Salts</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Water</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Biomass</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonia</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Carbon dioxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Process Water</b>	2208.70	18351.31	36702.62	55053.94	0.00	0.00	64.11	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Phosforic acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>TRIS solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>EDTA solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Triton-X solvent</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cyanogen bromide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Formic Acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Urea</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>2-Mercaptoethanol</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonium bicarbonate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Sulfit</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium tetrathionate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Hydrogen chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetic Acid</b>	0.00	2039.03	4078.07	6117.10	0.00	0.00	0.00	0.00
<b>Enzymes</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetonitrile</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonium acetate</b>	0.00	0.00	0.00	0.00	0.00	1.13	0.00	0.00
<b>Zinc dichloride</b>	0.00	0.00	0.00	0.00	0.00	2.00	0.00	0.00
<b>Cell Debris</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cont Proteins</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Inclusion Bodies</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Trp-Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Denatured Proin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin-SSO3</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin Crystal</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	2208.70	20390.35	40780.69	61171.04	0.00	3.13	64.11	21726.26
<b>Temperature (°C)</b>	25.00	25.00	25.00	25.00	25.00	25.00	5.00	26.00
<b>Pressure (atm)</b>	1	1	1	1	1	1	1	1
<b>Enthalpy Flow (GJ/h)</b>	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.02



**Table A7.2:** Output flowrates- Insulin production case study

Stream Name	Outlet Streams							
	S13	S26	S34	S41	S49	S52	S60	S69
<b>Flowrate (kg/h)</b>								
<b>Nitrogen</b>	16666.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Oxygen</b>	3780.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Glucose</b>	0.00	1344.47	165.28	8.70	3.69	0.00	0.00	0.02
<b>Salts</b>	0.00	196.06	24.10	1.27	0.54	0.00	0.00	0.00
<b>Water</b>	0.00	27165.67	7418.85	390.55	165.60	1.68	0.39	0.79
<b>Biomass</b>	0.00	22.45		0.00	0.00	0.42	0.00	0.00
<b>Ammonia</b>	215.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Carbon dioxide</b>	2323.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Process Water</b>	0.00	0.00	8347.69	2422.45	29188.71	11.59	1393.39	12306.62
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Phosforic acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>TRIS solvent</b>	0.00	0.00	251.13	13.22	5.61	0.00	0.00	0.04
<b>EDTA solvent</b>	0.00	0.00	60.61	3.19	1.35	0.00	0.00	0.01
<b>Triton-X solvent</b>	0.00	0.00	0.00	13.29	5.60	0.00	0.00	0.06
<b>Cyanogen bromide</b>	0.00	0.00	0.00	0.00	0.00	0.00	95.43	0.00
<b>Formic Acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	10837.56	81.09
<b>Urea</b>	0.00	0.00	0.00	0.00	2199.62	0.06	0.24	18.32
<b>2-Mercaptoethanol</b>	0.00	0.00	0.00	0.00	296.81	0.01	0.16	2.37
<b>Ammonium bicarbonate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	26.95
<b>Sodium Sulfit</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	222.66
<b>Sodium tetrathionate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	110.81
<b>Hydrogen chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2987.90
<b>Sodium Chloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetic Acid</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Enzymes</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Acetonitrile</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Ammonium acetate</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Zinc dichloride</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Cell Debris</b>	0.00	0.00	517.27	30.49	0.00	1.95	0.00	0.00
<b>Cont Proteins</b>	0.00	0.00	306.77	16.15	30.90	0.04	0.00	44.27
<b>Inclusion Bodies</b>	0.00	0.00	4.40	4.31	0.00	10.56	0.00	0.00
<b>Trp-Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.37	0.00	0.00
<b>Denatured Proin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin-SSO3</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Proinsulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Insulin Crystal</b>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	22985.13	28728.64	17096.11	2903.61	31898.43	26.67	12327.18	15801.91
<b>Temperature (°C)</b>	20.00	10.00	10.00	10.00	25.00	25.00	35.00	25.00
<b>Pressure (atm)</b>	1	1	1	1	1	1	1	1
<b>Enthalpy Flow (GJ/h)</b>	-0.12	-1.72	-0.99	-0.18	0.00	0.00	0.29	0.00

Appendixes

Stream Name	Outlet Streams							
	S75	S80	S83	S92	S98	S104	S107	S115
<b>Flowrate (kg/h)</b>								
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glucose	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Salts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.23	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonia	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	8284.65	52379.88	12100.00	48054.78	4312.06	42138.58	6297.99	7576.89
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	824.56	0.00	0.00
Phosforic acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIS solvent	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
EDTA solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triton-X solvent	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Cyanogen bromide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formic Acid	0.00	28.38	0.00	0.00	0.00	0.00	0.00	0.00
Urea	0.00	14967.95	0.00	1914.93	0.00	40.57	0.00	0.00
2-Mercaptoethanol	0.00	0.68	0.00	310.02	0.00	6.57	0.00	0.00
Ammonium bicarbonate	0.00	7.74	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Sulfit	0.00	77.92	0.00	0.00	0.00	0.00	0.00	0.00
Sodium tetrathionate	0.00	38.78	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen chloride	0.00	2047.06	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	831.54	707.00	99.53	0.00	1520.16	368.12	75.27
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	0.00	0.00	0.00	0.00	0.00	27.87	0.00	6.73
Enzymes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetonitrile	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonium acetate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zinc dichloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cell Debris	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cont Proteins	0.00	71.66	0.00	0.00	0.00	7.70	0.00	1.81
Inclusion Bodies	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Trp-Proinsulin	0.00	7.22	0.00	0.00	0.00	0.61	0.00	0.00
Denatured Proin	0.00	1.39	0.00	0.00	0.00	0.70	0.00	0.00
Proinsulin-SSO3	0.00	4.67	0.00	0.00	0.00	5.30	0.00	0.00
Proinsulin	0.00	0.00	0.00	0.00	0.00	3.39	0.00	0.00
Insulin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Insulin Crystal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	<b>8284.65</b>	<b>70465.14</b>	<b>12807.00</b>	<b>50379.27</b>	<b>4312.06</b>	<b>44576.01</b>	<b>6666.10</b>	<b>7660.71</b>
Temperature (°C)	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Pressure (atm)	1	1	1	1	1	1	1	1
Enthalpy Flow (GJ/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendixes

Outlet Streams								
Stream Name	S121	S127	S129	S138	S140	S149	S151	S159
<b>Flowrate (kg/h)</b>								
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glucose	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Salts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonia	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	12680.25	4427.15	92.82	6794.51	2476.64	106002.95	4129.05	453.65
Sodium Hydroxide	0.00	35.92	0.00	0.00	0.00	0.00	0.00	0.00
Phosphoric acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIS solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EDTA solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triton-X solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyanogen bromide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formic Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urea	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Mercaptoethanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonium bicarbonate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Sulfit	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium tetrathionate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen chloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	1056.74	0.00	7.18	15.82	0.00	0.00	0.00	0.00
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	0.24	0.00	0.00	1854.87	14.84	11724.93	458.78	50.98
Enzymes	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetonitrile	0.00	0.00	0.00	4539.50	247.41	7.98	0.00	0.00
Ammonium acetate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.13
Zinc dichloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.00
Cell Debris	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cont Proteins	9.43	0.00	0.00	0.33	0.00	0.01	0.00	0.00
Inclusion Bodies	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Trp-Proinsulin	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Denatured Proin	0.56	0.00	0.00	0.35	0.00	0.29	0.00	0.00
Proinsulin-SSO3	0.98	0.00	0.00	0.03	0.00	0.00	0.00	0.00
Proinsulin	1.48	0.00	0.00	0.05	0.00	0.00	0.00	0.00
Insulin	0.87	0.00	0.00	1.62	0.00	1.42	0.00	1.28
Insulin Crystal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	<b>13750.58</b>	<b>4463.07</b>	<b>100.00</b>	<b>13207.06</b>	<b>2738.89</b>	<b>117737.58</b>	<b>4587.83</b>	<b>509.05</b>
Temperature (°C)	25.00	25.00	25.00	25.00	25.00	25.00	25.00	5.01
Pressure (atm)	1	1	1	1	1	1	1	1
Enthalpy Flow (GJ/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.04

Appendixes

Stream Name	Outlet Streams		
	S163	S166	S168
<b>Flowrate (kg/h)</b>			
<b>Nitrogen</b>	0.00	0.00	0.00
<b>Oxygen</b>	0.00	0.00	0.00
<b>Glucose</b>	0.00	0.00	0.00
<b>Salts</b>	0.00	0.00	0.00
<b>Water</b>	0.00	0.00	0.00
<b>Biomass</b>	0.00	0.00	0.00
<b>Ammonia</b>	0.00	0.00	0.00
<b>Carbon dioxide</b>	0.00	0.00	0.00
<b>Process Water</b>	64.11	5.13	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00
<b>Phosforic acid</b>	0.00	0.00	0.00
<b>TRIS solvent</b>	0.00	0.00	0.00
<b>EDTA solvent</b>	0.00	0.00	0.00
<b>Triton-X solvent</b>	0.00	0.00	0.00
<b>Cyanogen bromide</b>	0.00	0.00	0.00
<b>Formic Acid</b>	0.00	0.00	0.00
<b>Urea</b>	0.00	0.00	0.00
<b>2-Mercaptoethanol</b>	0.00	0.00	0.00
<b>Ammonium bicarbonate</b>	0.00	0.00	0.00
<b>Sodium Sulfite</b>	0.00	0.00	0.00
<b>Sodium tetrathionate</b>	0.00	0.00	0.00
<b>Hydrogen chloride</b>	0.00	0.00	0.00
<b>Sodium Chloride</b>	0.00	0.00	0.00
<b>Sodium Hydroxide</b>	0.00	0.00	0.00
<b>Acetic Acid</b>	0.00	0.00	0.00
<b>Enzymes</b>	0.00	0.00	0.00
<b>Acetonitrile</b>	0.00	0.00	0.00
<b>Ammonium acetate</b>	0.00	0.00	0.00
<b>Zinc dichloride</b>	0.00	0.00	0.00
<b>Cell Debris</b>	0.00	0.00	0.00
<b>Cont Proteins</b>	0.00	0.00	0.00
<b>Inclusion Bodies</b>	0.00	0.00	0.00
<b>Trp-Proinsulin</b>	0.00	0.00	0.00
<b>Denatured Proin</b>	0.00	0.00	0.00
<b>Proinsulin-SSO3</b>	0.00	0.00	0.00
<b>Proinsulin</b>	0.00	0.00	0.00
<b>Insulin</b>	0.00	0.00	0.00
<b>Insulin Crystal</b>	0.00	0.00	11.54
<b>Total Flowrate</b>	64.11	5.13	11.54
<b>Temperature (°C)</b>	5.01	12.00	25.00
<b>Pressure (atm)</b>	1	1	1
<b>Enthalpy Flow (GJ/h)</b>	-0.01	0.00	0.00

Note: Data obtained from SuperProDesigner, 2008

*Prices***Table A7.3:** Utility prices – Insulin production case study

<b>Utilities</b>	
Heating (US\$/GJ) High pressure	8.75
Heating (US\$/GJ) Low pressure	6.75
Cooling (US\$/GJ)	0.96
Electricity (US\$/kWh)	0.05

Note: Data obtained from Coll, N., 2003

**Table A7.4:** Purchase prices – Insulin production Case Study

<b>Compound</b>	<b>Price (\$/kg)</b>	<b>Compound</b>	<b>Price (\$/kg)</b>	<b>Compound</b>	<b>Price (\$/kg)</b>
Nitrogen	0.00	Triton-X solvent	1.50	Acetonitrile	3.00
Oxygen	0.00	Cyanogen bromide	11.00	Ammonium acetate	15.00
Glucose	0.60	Formic Acid	1.60	Zinc dichloride	12.00
Salts	1.00	Urea	1.50	Cell Debris	0.62
Water	0.05	2-Mercaptoethanol	3.00	Cont Proteins	0.00
Biomass	0.61	Ammonium bicarbonate	1.00	Inclusion Bodies	0.62
Ammonia	0.70	Sodium Sulfite	0.40	Trp-Proinsulin	0.64
Carbon dioxide	0.00	Sodium tetrathionate	0.60	Denatured Proin	0.65
Process Water	0.10	Hydrogen chloride	2.15	Proinsulin-SSO3	0.66
Sodium Hydroxide	0.50	Sodium Chloride	1.23	Proinsulin	0.68
Phosforic acid	1.00	Sodium Hydroxide	3.50	Insulin	50000.00
TRIS solvent	6.00	Acetic Acid	2.50	Insulin Crystal	100000.00
EDTA solvent	18.50	Enzymes	500000.00		

Note: Data obtained from Petrides, *et al.* (1995)

**Table A7.5: Demand stream prices – Insulin production Case Study**

Compound	Demand streams Price (\$/kg)								
	S13	S26	S34	S41	S49	S52	S60	S69	S75
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glucose	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70
Salts	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Ammonia	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20
Carbon dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Hydroxide	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Phosforic acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIS solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EDTA solvent	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Triton-X solvent	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Cyanogen bromide	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00
Formic Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urea	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
2-Mercaptoethanol	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Ammonium bicarbonate	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Sodium Sulfite	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Sodium tetrathionate	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Hydrogen chloride	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Sodium Chloride	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Enzymes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetonitrile	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50
Ammonium acetate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zinc dichloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cell Debris	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Cont Proteins	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Inclusion Bodies	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Trp-Proinsulin	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Denatured Proin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Proinsulin-SSO3	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Proinsulin	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Insulin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Insulin Crystal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Note: Data obtained from Petrides, *et al.* (1995)

Appendixes

Compound	Demand streams Price (\$/kg)								
	S80	S83	S92	S98	S104	S107	S115	S121	S127
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glucose	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70
Salts	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Ammonia	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20
Carbon dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Hydroxide	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Phosphoric acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIS solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EDTA solvent	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Triton-X solvent	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Cyanogen bromide	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00
Formic Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urea	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
2-Mercaptoethanol	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Ammonium bicarbonate	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Sodium Sulfite	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Sodium tetrathionate	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Hydrogen chloride	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Sodium Chloride	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Enzymes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetonitrile	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50
Ammonium acetate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zinc dichloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cell Debris	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Cont Proteins	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Inclusion Bodies	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Trp-Proinsulin	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Denatured Proin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Proinsulin-SSO3	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Proinsulin	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
Insulin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Insulin Crystal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Note: Data obtained from Petrides, *et al.* (1995)

Appendixes

Compound	Demand streams Price (\$/kg)								
	S129	S138	S140	S149	S151	S159	S163	S166	S168
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glucose	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	-0.70	0.00
Salts	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Ammonia	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	0.00
Carbon dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Hydroxide	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	0.00
Phosphoric acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIS solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EDTA solvent	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Triton-X solvent	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Cyanogen bromide	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	-2.00	0.00
Formic Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urea	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
2-Mercaptoethanol	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Ammonium bicarbonate	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Sodium Sulfit	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Sodium tetrathionate	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Hydrogen chloride	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Sodium Chloride	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	0.00
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Enzymes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetonitrile	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	0.00
Ammonium acetate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zinc dichloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cell Debris	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Cont Proteins	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Inclusion Bodies	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Trp-Proinsulin	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Denatured Proin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Proinsulin-SSO3	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Proinsulin	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.00
Insulin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Insulin Crystal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100000.00

Note: Data obtained from Petrides, *et al.* (1995)



*Indicators*

**Table A7.6:** Top 10 indicators for open-paths -Insulin production case study

Path	MVA (10 <sup>3</sup> \$/yr)	Path	EWC (10 <sup>3</sup> \$/yr)	Path	TVA(10 <sup>3</sup> \$/yr)
OP 1016	-639591.48	OP 37	69.75	OP 1016	-639591.48
OP 1009	-564121.80	OP 38	36.47	OP 1009	-564121.80
OP 1011	-507707.64	OP 1	28.26	OP 1011	-507707.64
OP 1005	-343498.32	OP 82	20.57	OP 1005	-343498.32
OP 620	-205917.38	OP 316	17.82	OP 620	-205917.38
OP 804	-169566.12	OP 114	9.38	OP 804	-169566.12
OP 591	-137333.60	OP 3	6.38	OP 591	-137333.95
OP 797	-103624.48	OP 115	3.75	OP 797	-103624.48
OP 613	-90375.09	OP 39	3.68	OP 613	-90375.09
OP 822	-80526.88	OP 83	3.16	OP 822	-80526.88

**Table A7.7:** Top 10 indicators for closed-paths -Insulin production case study

Path	EWC (10 <sup>3</sup> \$/yr)	Path	AF
CP39	0.0030	CP382	Infinite
CP191	0.0013	CP381	Infinite
CP40	0.0008	CP344	Infinite
CP305	0.0004	CP343	Infinite
CP192	0.0003	CP306	Infinite
CP229	0.0002	CP305	Infinite
CP343	0.0001	CP268	Infinite
CP306	0.0001	CP267	Infinite
CP230	0.0001	CP230	Infinite
CP344	0.0000	CP229	Infinite

**Table A7.8:** Energy closed-paths indicators- Insulin production case study

ECP	EAF
CP1	0.0
CP2	0.0
CP3	0.0
CP4	1.0
CP5	1.0
CP6	-0.2
CP7	-0.5
CP8	0.0
CP9	1.0
CP10	1.0
CP11	1.0

**Table A7.9:** Energy open-paths indicators- Insulin production case study

<b>Supply</b>	<b>Demand</b>	<b>DC (\$/GJ)</b>	<b>TDC (\$/GJ)</b>
P V-102R	C DS-101(P9)	32.5	33.09841
H ST-101	C DS-101(P9)	0.4	
E G-101	C DS-101(P9)	0.2	
P HG-101	C HG-101	2790.0	2790.038
P V-102R	C V-102R	158.5	159.4307
H ST-101	C V-102R	0.7	
E G-101	C V-102R	0.3	
H V-103(P8) R	R V-103(P8) R	0.4	0.392211
P V-102R	S13	20.0	20.17572
H ST-101	S13	0.1	
E DS-101(P13)	S34	5.1	5.06472
H V-103(P8) R	C DF-101(P16)	0.1	0.086207

**Safety**

**Table A7.10: Safety Indices-Insulin production case study**

<b>Total inherent safety index (I<sub>TI</sub>)</b>			
<b><i>Chemical inherent safety index, I<sub>CI</sub></i></b>	<b><i>Score</i></b>	<b><i>Process inherent safety index, I<sub>PI</sub></i></b>	<b><i>Score</i></b>
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, I <sub>RM</sub>	0	Inventory, I <sub>I</sub>	4
Heat of the side reactions, I <sub>RS</sub>	0	Process temperature, I <sub>T</sub>	0
Chemical Interaction, I <sub>INT</sub>	1	Process pressure, I <sub>P</sub>	0
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, I <sub>FL</sub>	4	Equipment, I <sub>EQ</sub>	
Explosiveness, I <sub>EX</sub>	1	ISBL	2
Toxicity, I <sub>TOX</sub>	3	OSBL	1
Corrosivity, I <sub>COR</sub>	0	Process structure, I <sub>ST</sub>	2
Maximum score I <sub>CI</sub>	9	Maximum score I <sub>PI</sub>	9
<b>I<sub>TI</sub></b>		<b>18</b>	

**Environment**

**Table A7.11: WAR algorithm- Insulin production case study**

	TPEI	HTPI	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
Sum inlet	24720	10472	758	541	10472	0	0	0	2475
Sum Water	0	0	0	0	0	0	0	0	0
<b>Input</b>	<b>24720</b>	<b>10472</b>	<b>758</b>	<b>541</b>	<b>10472</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>2475</b>
Sum 25 and =	16047	6622	400	359	6622	1	0	0	2043
S60	7530	3468	356	239	3468	0	0	0	0
Sum 10 and =	120	60	0	0	60	0	0	0	0
Sum 5 and =	12	6	1	1	6	0	0	0	0
<b>Output</b>	<b>23710</b>	<b>10156</b>	<b>756</b>	<b>598</b>	<b>10156</b>	<b>1</b>	<b>0</b>	<b>0</b>	<b>2043</b>
<b>Total</b>	<b>-1010</b>	<b>-317</b>	<b>-2</b>	<b>57</b>	<b>-317</b>	<b>1</b>	<b>0</b>	<b>0</b>	<b>-432</b>

A8.  $\beta$ -Gal Production Case StudyTable A8.1: Input flowrates-  $\beta$ -Gal production case study

Inlet Streams												
Stream Name	S1	S3	S8	S39	S41	S44	S48	S49	S59	S63	S64	Sin
Initial Unit	0	0	0	0	0	0	0	0	0	0	0	0
Final Unit	V-101C1	V-101C2	FR-101C2	C-101 Elution	C-101 Rinse	C-101 Wash	C-101 Strip	C-101 Strip	C-102 Elution	C-102 Wash	DF-101	T1
<b>Flowrate (kg/h)</b>												
B-Gal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glucose	0.00	6143.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	64000.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Proteins	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Salts	0.00	1026.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	0.00	0.00	0.00	0.00	0.00	724.06	0.00	429.51	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	77643.40	81793.59	73054.35	0.00	0.00	0.00
Process water 2	0.00	0.00	0.00	21224.55	98055.39	158469.76	0.00	0.00	0.00	72043.00	4652.21	0.00
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	33683.89
Oxygen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10225.77
Ammonia	0.00	0.00	395.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nucleic Acids	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Debris	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1635.20	0.00	0.00	0.00	0.00
Tris Solvent	0.00	0.00	0.00	0.00	0.00	13127.17	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	<b>64000.00</b>	<b>7169.00</b>	<b>395.00</b>	<b>21224.55</b>	<b>98055.39</b>	<b>171596.93</b>	<b>78367.46</b>	<b>83428.79</b>	<b>73483.86</b>	<b>72043.00</b>	<b>4652.21</b>	<b>43909.66</b>
Temperature (°C)	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00	25.00
Pressure (atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00
Enthalpy Flow (GJ/h)	-6.68	-0.21	-0.01	-2.22	-10.24	-16.71	-8.13	-8.62	-7.64	-7.52	-0.49	0.00

Note: Data obtained from SuperProDesigner, 2008

Appendixes

**Table A8.2:** Output flowrates-  $\beta$ -Gal production case study

Outlet Streams														
Stream Name	S14	S21	S28	S30	S34	S42	S45	S47	S50	S54	S62	S65	S68	S70
Initial Unit	AF-102	MF-101	DS-101	DE-101	UF-101	C-101 Rinse	C-101 Wash	C-101 Strip	C-101 Strip	UF-102	C-102 Wash	DF-101	P22-HE	P22-D
Final Unit	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Flowrate (kg/h)														
B-Gal	0.00	0.00	1.55	1.20	0.00	0.00	0.00	11.48	0.00	0.00	9.82	0.00	0.00	85.72
Glucose	0.00	63.65	0.76	1.31	29.36	0.00	0.00	27.78	0.00	0.00	0.00	0.00	0.00	0.00
Process Water	0.00	34859.94	413.49	717.39	16079.88	0.00	0.00	15214.30	0.00	0.00	0.00	0.00	0.00	0.00
Proteins	0.00	0.00	14.73	57.03	140.74	0.00	0.00	918.07	0.00	0.00	33.23	0.34	0.00	0.00
Salts	0.00	94.91	1.13	1.95	43.78	0.00	0.00	41.42	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	673.91	0.00	34.32	413.13	32.18	0.00	0.04
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	75940.08	81793.59	1165.64	68112.95	5475.57	5.65	0.51
Process water 2	0.00	0.00	0.00	0.00	0.00	116096.26	158469.76	0.00	0.00	2178.71	73047.98	4265.00	351.50	35.71
Nitrogen	33765.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	7126.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonia	39.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biomass	0.00	0.00	13.23	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide	4491.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nucleic Acids	0.00	0.00	6.51	25.21	246.07	0.00	0.00	232.25	0.00	0.40	0.18	0.00	0.00	0.00
Debris	0.00	0.00	62.81	703.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1635.20	0.00	0.00	0.00	0.00	0.00
Tris Solvent	0.00	0.00	0.00	0.00	0.00	0.00	13127.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total Flowrate</b>	<b>45422.20</b>	<b>35018.50</b>	<b>514.19</b>	<b>1507.48</b>	<b>16539.83</b>	<b>116096.26</b>	<b>171596.93</b>	<b>93059.29</b>	<b>83428.79</b>	<b>3379.06</b>	<b>141617.29</b>	<b>9773.08</b>	<b>357.15</b>	<b>121.97</b>
Temperature (°C)	20.00	25.00	15.00	15.00	15.00	24.63	24.63	24.63	24.63	15.00	24.80	25.00	12.00	12.00
Pressure (atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Enthalpy Flow (GJ/h)	0.00	-3.64	-0.05	-0.15	-1.68	-12.13	-16.71	-9.56	-8.62	-0.35	-14.76	-1.02	-0.04	0.00

Note: Data obtained from SuperProDesigner, 2008

*Prices*

**Table A8.3:** Utility prices –  $\beta$ -Gal production case study

Utilities	
Heating (US\$/GJ) High pressure	8.75
Heating (US\$/GJ) Low pressure	6.75
Cooling (US\$/GJ)	0.96
Electricity (US\$/kWh)	0.05

Note: Data obtained from Coll, N., 2003

**Table A8.4:** Purchase prices –  $\beta$ -Gal production Case Study

Compound	Price (\$/kg)	Compound	Price (\$/kg)
B-Gal	10000	Oxygen	0
Glucose	1	Ammonia	1
Process Water	0	Biomass	1
Proteins	0	Carbon Dioxide	0
Salts	2	Nucleic Acids	0
Sodium Chloride	0.13	Debris	0
Water	0	Sodium Chloride	0.12
Process water 2	0	Tris Solvent	0
Nitrogen	0		

Note: Data obtained from SuperProDesigner, 2008

**Table A8.5: Demand stream prices –  $\beta$ -Gal Case Study**

Demand streams Price (\$/kg)							
	S14	S21	S28	S30	S34	S42	S45
<b>B-Gal</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Glucose</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Process Water</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Proteins</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Salts</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Sodium Chloride</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Water</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Process water 2</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Nitrogen</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Oxygen</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Ammonia</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Biomass</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Carbon Dioxide</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Nucleic Acids</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Debris</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Sodium Chloride</b>	0	-0.01	-0.01	-0.01	-0.01	0	0
<b>Tris Solvent</b>	0	-0.01	-0.01	-0.01	-0.01	0	0

Demand streams Price (\$/kg)							
	S47	S50	S54	S62	S65	S68	S70
B-Gal	0	0	-0.01	-0.01	-0.01	0	10000
Glucose	0	0	-0.01	-0.01	-0.01	0	0
Process Water	0	0	-0.01	-0.01	-0.01	0	0
Proteins	0	0	-0.01	-0.01	-0.01	0	0
Salts	0	0	-0.01	-0.01	-0.01	0	0
Sodium Chloride	0	0	-0.01	-0.01	-0.01	0	0
Water	0	0	-0.01	-0.01	-0.01	0	0
Process water 2	0	0	-0.01	-0.01	-0.01	0	0
Nitrogen	0	0	-0.01	-0.01	-0.01	0	0
Oxygen	0	0	-0.01	-0.01	-0.01	0	0
Ammonia	0	0	-0.01	-0.01	-0.01	0	0
Biomass	0	0	-0.01	-0.01	-0.01	0	0
Carbon Dioxide	0	0	-0.01	-0.01	-0.01	0	0
Nucleic Acids	0	0	-0.01	-0.01	-0.01	0	0
Debris	0	0	-0.01	-0.01	-0.01	0	0
Sodium Chloride	0	0	-0.01	-0.01	-0.01	0	0
Tris Solvent	0	0	-0.01	-0.01	-0.01	0	0

Note: Data obtained from SuperProDesigner, 2008

**Indicators**

**Table A8.6:** Top 10 indicators for open-paths -  $\beta$ -Gal Case Study

Path	MVA ( $10^3$ \$/yr)	Path	EWC ( $10^3$ \$/yr)	Path	TVA( $10^3$ \$/yr)
OP 118	-122678.93	OP 31	69.03	OP 118	-122678.93
OP 114	-75367.55	OP 125	67.06	OP 114	-75367.55
OP 121	-62581.59	OP 34	36.71	OP 121	-62581.59
OP 31	-55176.98	OP 37	34.74	OP 31	-55246.01
OP 34	-25451.54	OP 157	14.19	OP 34	-25488.25
OP 37	-22938.66	OP 172	6.17	OP 37	-22973.40
OP 105	-16313.66	OP 123	4.80	OP 105	-16313.66
OP 249	-15549.78	OP 29	3.58	OP 249	-15549.78
OP 104	-5339.58	OP 33	1.64	OP 104	-5339.58
OP 122	-3704.88	OP 203	1.29	OP 122	-3704.88

**Table A8.7:** Top 5 indicators for closed-paths -  $\beta$ -Gal Case Study

Path	EWC ( $10^3$ \$/yr)	Path	AF
CP9	$7.06 \times 10^{-13}$	CP10	0.0024
CP10	$2.14 \times 10^{-13}$	CP9	0.0024
CP2	0	CP2	0
CP1	0	CP1	0
CP3	0	CP3	0

**Table A8.8:** Energy closed-paths indicators-  $\beta$ -Gal Case Study

ECP	EAF
CP1	-0.11



**Table A8.9:** Energy open-paths indicators- β-Gal Case Study

Supply	Demand	DC (\$/GJ)	TDC (\$/GJ)
S1	C FR-101R	-44.0	8139
S3	C FR-101R	-578.9	
P FR-101R	C FR-101R	8760.6	
H ST-101	C FR-101R	1.0	
E G-101	C FR-101R	0.8	
P HG-101	S28	19728.0	19728
P HG-101	S30	109244.5	109245
P HG-101	S34	1815684.6	1815685
S39	S42	-9095.4	1933709
S41	S42	-28533.4	
P HG-101	S42	1971338.0	
S39	S45	-1562.8	271818
S41	S45	-5290.7	
S44	S45	-71982.3	
P HG-101	S45	350653.5	
S39	S47	-108.1	-124526
S41	S47	-385.0	
S44	S47	-5209.0	
S48	S47	-59337.8	
S49	S47	-59486.3	
S39	S50	-111.5	-113396
S41	S50	-411.9	
S44	S50	-5551.9	
S48	S50	-53569.9	
S49	S50	-53750.9	
S39	S54	-1746.4	310135
P HG-101	S54	311881.9	
S39	S62	-915.3	-77406
S59	S62	-108129.4	
S63	S62	-123904.6	
P HG-101	S62	155543.7	
S39	S65	-63.4	-127874
S59	S65	-8232.8	
S64	S65	-119577.7	
S59	S68	-301.7	-4698
S64	S68	-4396.4	

## Safety

**Table A8.10: Safety Indices-  $\beta$ -Gal production case study**

<b>Total inherent safety index (<math>I_{TI}</math>)</b>			
<b><i>Chemical inherent safety index, <math>I_{CI}</math></i></b>	<b><i>Score</i></b>	<b><i>Process inherent safety index, <math>I_{PI}</math></i></b>	<b><i>Score</i></b>
<b>Subindices for reactions hazards</b>		<b>Subindices for process conditions</b>	
Heat of the main reaction, $I_{RM}$	4	Inventory, $I_I$	4
Heat of the side reactions, $I_{RS}$	0	Process temperature, $I_T$	0
Chemical Interaction, $I_{INT}$	2	Process pressure, $I_P$	0
<b>Subindices for hazardous substances</b>		<b>Subindices for process system</b>	
Flammability, $I_{FL}$	4	Equipment, $I_{EQ}$	
Explosiveness, $I_{EX}$	1	ISBL	3
Toxicity, $I_{TOX}$	6	OSBL	1
Corrosivity, $I_{COR}$	1	Process structure, $I_{ST}$	2
Maximum score $I_{CI}$	18	Maximum score $I_{PI}$	10
<b><math>I_{TI}</math></b>		<b>28</b>	

## Environment

**Table A8.11: WAR algorithm-  $\beta$ -Gal production case study**

Stream No	Total PEI	HTPI	HTPE	ATP	TTP	GWP	ODP	PCOP	AP
Input 1	0	0	0	0	0	0	0	0	0
Input 2	30182	15091	0	0	15091	0	0	0	0
Input 3	26780	6761	567	867	6761	0	0	0	12332
Input 4	0	0	0	0	0	0	0	0	0
Input 5	0	0	0	0	0	0	0	0	0
Input 6	10367	5181	0	5	5181	0	0	0	0
Input sum	67329	27033	567	872	27033	0	0	0	12332
Output 1	10146	667	120	7518	667	627	0	0	1217
Output 2	309	154	0	0	154	0	0	0	0
Output 3	5434	2717	0	0	2717	0	0	0	0
Output sum	15889	3,538	120	7518	3,538	627	0	0	1217
Impact generated	-51440	-23,495	447	6,646	-23,495	627	0	0	-11115

## B. Separation Techniques

**Table B.1:** Separation techniques with separation properties

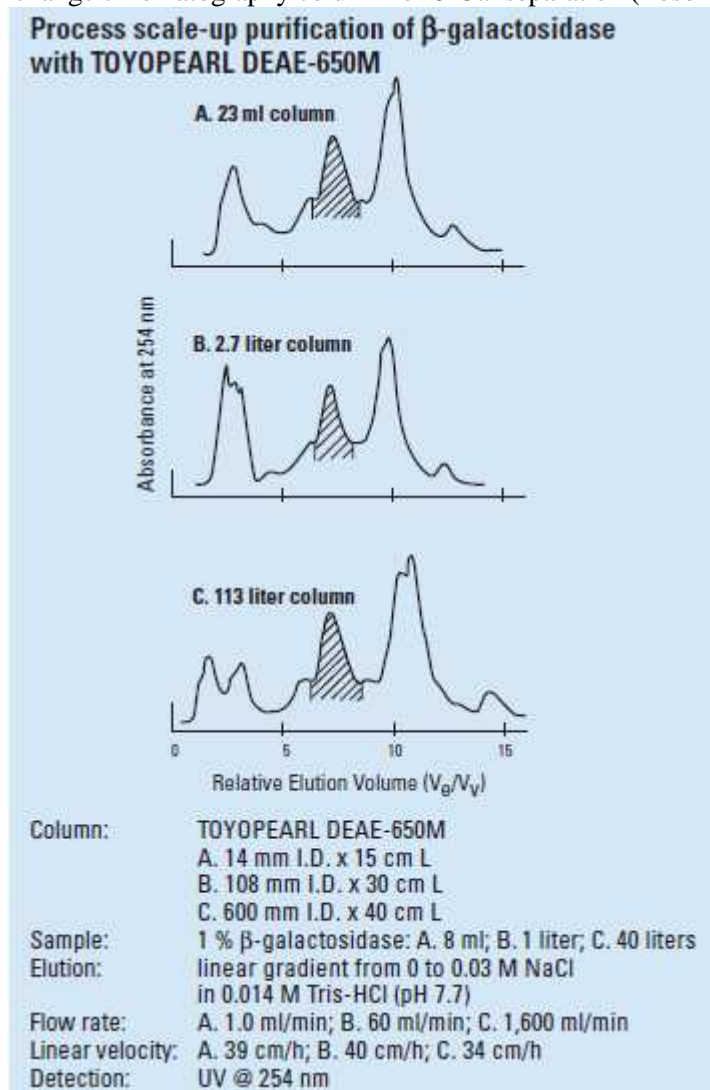
Separation technique	Feed phase	Separating agent	Phase equilibria	Products	Principle of separation (Differences in)
Absorption (physical)	gas	MSA	GLE	liquid + vapour	solubility parameter <sup>1</sup> , solubility
Adsorption (physical)	gas or liquid	EA	GSE LSE	gas/liquid + solid	kinetic diameter, van der Waals volume, polarisability, dipolemoment
Azeotropic distillation	vapour and/or liquid	MSA	VLE	liquid + vapour	vapour pressure, azeotropes, solubility parameter <sup>1</sup>
Condensation	vapour	ESA	VLE	liquid	boiling point
Cryogenic distillation	vapour	ESA	VLE	liquid + vapour	vapour pressure, heat of vaporization, boiling point
Crystallisation	liquid	ESA	SLE	liquid + solid	melting point, heat of fusion at melting point
Decanter	liquid	MSA	LLE	liquid + liquid	solubility parameter <sup>1</sup>
Desublimation	vapour	ESA	SVE	solid + vapour	triple point temperature and pressure
Distillation	vapour and/or liquid	ESA	VLE	liquid + vapour	vapour pressure, heat of vaporization, boiling point
Extractive distillation	vapour and/or liquid	MSA	VLE	liquid + vapour	vapour pressure, heat of vaporization, boiling point, solubility parameter <sup>1</sup>
Flash operation	vapour-liquid	ESA	VLE	liquid + vapour	vapour pressure, heat of vaporization, boiling point
Gas separation membranes	gas	EA	*	gas + gas	critical temperature, van der Waals volume
Ion exchange	liquid	EA	SLE	liquid+solid resin	ion charge
Liquid-liquid extraction	liquid	MSA	LLE	liquid + liquid	solubility parameter <sup>1</sup>

**Table B.2:** Separation techniques with separation properties – Cont.

Liquid membranes	liquid or gas	EA	*	liquid + liquid or gas + gas	solubility parameter <sup>1</sup> , molar volume, radius of gyration, affinity to carrier
Microfiltration	liquid	EA	*	liquid + liquid	size, molecular weight
Pervaporation	liquid	EA	*	liquid + vapour	molecular volume, solubility parameter <sup>1</sup> , dipolemoment
Stripping	liquid	ESA	GLE	liquid + gas	solubility parameter <sup>1</sup>
Sublimation	solid	ESA	SVE	solid + vapour	triple point pressure and temperature
Supercritical extraction	liquid	MSA	LLE	liquid + liquid	solubility parameter <sup>1</sup> , critical temperature, critical pressure
Ultrafiltration	liquid	EA	*	liquid + liquid	size, molecular weight

## C. Ion Exchange Chromatography Column

**Table C.1:** Ion exchange chromatography column for  $\beta$ -Gal separation (Tosoh Bioscience, 2009)



# Nomenclature

A	Allocation factor
AF	Accumulation Factor
AP	Accumulation-path
AP*	Acidification Potential
ATP	Aquatic Toxicity Potential
c	Compound
C	Total number of compounds
%C	Reaction Conversion
CA	Cost allocation factor
CAFD	Computer Aided Flowsheet Design
CAMD	Computer Aided Molecular Design
Cf	Coefficients in the $F_{obj}$
Co	Concentration
CP	Closed-path
$C_p$	Heat capacity
d	Mass flowrate leaving closed-paths in demand streams
DC	Demand Cost
E	Energy
Ea	Energy of activation
EAF	Energy Accumulation Factor
ebl	Energy base level
ECP	Energy Closed-Path
EF	Energy Factor
$E_H$	Parameter denoting the effect of a path compound on a reaction
EN	Total number of leaving streams from a closed-path excluding the demand streams

EOP	Energy Open-Path
es	Exit or Entering stream in a given unit
Es	Total number of exit stream or the entering streams in a given unit
EWC	Energy Waste Cost
f	Mass flowrate leaving closed-paths in internal streams
fr	Closed-path fraction relative to the other nested loops passing in a common stream $S_{NL}$
F	Flowrate
$FE_{cp}$	Faction of energy spent in the heat/cool in a reactor (not from the reaction)
$FE_{\Delta H_R}$	Faction of energy spent in the heat of the reaction
$F_{obj}$	Objective function
FP	Total number of desired products in the process
FVF	Free Volume Factor
g	Fraction of heat of formation of a reactant/product by the sum of all heat of formation of the reactants/ products
GWP	Global Warming Potential
H	Total number of compound pairs
HTPE	Human Toxicity Potential by Exposure both dermal and Inhalation
HTPI	Human Toxicity Potential by Ingestion
I	Indicator
IB	Inclusion Bodies
ICAS	Integrated Computer Aided System
$I_{CI}$	Chemical inherent safety index
$I_{COR}$	Corrosivity safety sub-index
IEP	Inherent Energy Properties
ISP	Inherently separation properties
$I_{EQ}$	Equipment safety sub-index
$I_{EX}$	Explosiveness safety sub-index
$I_{FL}$	Flammability safety sub-index
$I_I$	Inventory safety sub-index

In	Increment in the ISA scores scale
$I_{INT}$	Chemical interaction safety sub-index
$I_P$	Process pressure safety sub-index
$I_{PI}$	Process inherent safety sub-index
$I_{RM}$	Heat of the main reaction safety sub-index
$I_{RS}$	Heat of the side reactions safety sub-index
ISBL	Inside Battery Limit Area
$I_{ST}$	Process structure safety sub-index
$I_T$	Process temperature safety sub-index
$I_{TI}$	Total Inherently Safety Index
$I_{TOX}$	Toxicity safety sub-index
$I_V$	Total number of vertices in a closed-path
J	Total number of operations
k	Reaction Rate Constant
$k_0$	Reaction Rate Constant for the first order
$k_1$	Monod Constant
K	Total number of paths selected in ISA algorithm
$m$	Mass flowrate
M	Mass
MCP	Mass Closed-Path
MINLP	Mixed integer nonlinear programming
MM	Molar Flowrate
MOP	Mass Open-Path
$M_{React}$	Mass reacted
MSA	Mass Separation Agent
MVA	Material Value Added
MW	Molecular weight
n	Compound different from compound c
N	Total number of compounds, which are not compound c
NL	Number of closed-path, which pass through $S_{NL}$



OEF	Operational Energy Factor
ODP	Ozone Depletion Potential
OP	Open-paths
OPR	Operation
OPV	Operational Variable
OSBL	Offside Battery Limit Area
OTF	Operational Time Factor
OV	Optimization Variable
p	Pressure
P#	Path
PCOP	Photochemical Oxidation Potential
PD	Total number of products in the overall reaction
PrD	Utility/stream price in units of price/energy
PE	Utility price
PEI	Potential Environmental Impact
PP	Value outside the process boundaries
PR	Purchase price
Pr	Price of a given compound
PCOP	Photochemical Oxidation Potential
PD	Total number of products in the overall reaction
Q	Heat exchange in a given unit
R	Total number of reactive unit operations
RK	Total number of reactions
RQ	Reaction Quality
RM	Total number of raw materials involved in the overall reaction
S	Stream
S <sub>E</sub>	Stream belonging exclusively to on given closed-path, CP
S <sub>N</sub>	Stream common to nested loops
SM	Sustainability Metrics
SS	Total number of supplies

## Nomenclature

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t	Time
T	Temperature
TI	Target Indicator
$T_{Fob}$	Terms of the objective function
TDC	Total Demand Cost
TVA	Total Value Added
TF	Time Factor
TFVF	Total Free Volume Factor
TTP	Terrestrial Toxicity Potential
u	Unit
U	Total number of units
UEL	Upper Explosive Limit
UK	Total number of compound path flows in a sub-operation
V	Volume
Va	Value Added
VA	Total number of variables influencing $F_{obj}$
$V_I$	Variable that influence the indicators
$V_F$	Variable that influence the $i F_{obj}$
$V_T$	Variable that influence the objective function terms and the selected indicators
w	Distribution factor
WAR	Waste Reduction Algorithm
x	Fraction of the flowrate of path (k) by the total amount of a given variable
y	Fraction of a given term from the $F_{obj}$ in the sum of all the terms related to the selected variables in ISA
$y_1$	Binary variable to inert/solvents
$y_2$	Binary variable to reactants/products
$y_3$	Binary variable to Exothermic/Endothermic reactions
z	Fraction of the coefficient $C_f$ for the variable $n$ , in the sum of all coefficients for all the variables selected in ISA
$z_1$	Fraction of raw material mass that is producing the desired product

**Subscripts or Superscripts**

ac	Aqueous phase
AP	Accumulation Path index
BP	By-Product index
c	Compound index
cp	Closed-path index
d	Demand flows in the process graph
DP	Desired Product index
ec	Index of the closed energy path flows
Ent	Entry
eq	Equipment index
EX	Exclusively
f	Final
fp	Final product
h	Compound pair index
i	Initial
I	Indicator index
i <sub>v</sub>	Vertices index
j	Batch operation index
k	Path index
n	Selected variable index
NL	Nested Loop
o	Organic phase
OF	Operational flowsheet
op	Open-path index
pd	Product index
r	Index of the reactive unit operations
R	Residual flowrate
Rc	Recovery Compound Index

React	Reacted
rk	Reaction index
rm	Raw material index
s	Stream index
S	Solvent Index
su	Supply index
SA	Variables sensitivity index
S <sub>E</sub>	Stream belonging exclusively to on given closed-path index
S <sub>NL</sub>	Stream common to nested loops index
T	Profit term index
TDE	Time dependent entry stream
TDL	Time dependent leave stream
u	Sub-operations index
uk	Index of all compound path flows in u
va	Variable index

### Greek Letters

$\Delta\rho$	Density difference
$\Delta H_c$	Compound heat of combustion
$\Delta H_f$	Enthalpy of formation
$\Delta H_R$	Enthalpy of Reaction
$\Delta H_{vap}$	Enthalpy of Vaporization
$\Delta H_{sub}$	Enthalpy of Sublimation
$\rho$	Density
$\xi$	Extent of reaction
$\mu$	Viscosity
$\mu_g$	Specific cell growth rate
$\nu$	Stoichiometric coefficient



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