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COMPUTER AIDED DESIGN

OF SUSTAINABLE INDUSTRIAL PROCESSES

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Letiția Toma

SUMMARY

Computer simulation has been used by the chemical industry, for several decades, as a decision support tool. The possibility of analyzing and optimizing a chemical process is one of the advantages offered by such a tool.

The present thesis deals with the description of a methodology to quantify the environmental impact of a chemical or a biochemical process. The methodology, integrated and implemented in the Process Sustainability Prediction (PSP) Framework, can be taken into account in the early stages of new plants design, or, it can be applied to the existing plants. Taking into account environmental, technological and economical aspects at design time, an answer to the question "which design is more environmentally friendly, and implicitly more sustainable, for a specific chemical process?" can be provided.

The thesis is structured as follows.

The importance of the research, its background and motivation are given in *Chapter 1*.

In *Chapter 2*, a general overview of sustainable development and sustainability concepts are presented. Sustainability elements (society, environment and economy) as well as their interactions are discussed. The connection between chemical industry and sustainable development as well as the chemical engineer' role in the sustianable development debate are also considered in the present chapter.

In this *Chapter 3*, different sustainability indicators are discussed. The most inportant indicators are the three dimensional indicators (3D indicators) and one dimensional indicators (1D indicators). 3D indicators, are used as a first evaluation of the global sustainability of a chemical process. Sometimes, this information is not sufficient for deciding the best solution, in terms of sustainability, from different alternative designs. In this case one may resort to the 2D indicators and 1D indicators evaluation. One relevant 1D indicator taken into consideration is the Waste Reduction (WAR) Algorithm. Details regarding 3D and 1D indicators, their definition and calculation are reported in the present chapter.

Chapter 4 presents the software developed for sustainability evaluation. The software, Process Sustainability Prediction (PSP) Framework, used during the design phase of a chemical process, allows choosing, from different alternative design of a chemical process, the most environmental friendly.

To be effective, the proposed software should be based on international standard, so that the connection to any commercial process simulator would be possible. For this reason, PSP Framework has been developed using the CAPE OPEN(CO) standard. Beside the CO Modules, PSP contains also a toxicological database and a set of software modules for post-processing the information from the process simulator software.

Chapter 5 is dedicated to the toxicological database used in PSP Framework. The logical and conceptual schema, as well as, the integration and implementation of the database are reported.

The environmental impact categories used in the WAR Algorithm are described in *Chapter 6*. Eight impact categories are taken into account: Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Inhalation or Dermal Exposure (HTPE), Terrestrial Toxicity Potential (TTP), Aquatic Toxicity Potential (ATP), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photochemical Oxidation or Smog Formation Potential (PCOP), Acidification Potential (AP). Different molecular modeling methods are proposed in order to estimate each impact category. Representative examples are reported in the present chapter.

Representative chemical processes examples are presented in *Chapter 7,* in order to validate PSP methodology. Two main classes of processes are discussed: processes described in scientific literature and processes correspondent to chemical plants situated in developing countries. For each process a brief introduction, a process description, process simulation and environmental impact results are reported. Different design alternatives, for each process, are proposed and through PSP Framework, the most environmentally friendly is selected.

Chapter 8 contains explanations regarding the PSP Framework distribution strategy and the organizations involved in this process.

Finally, conclusions and recommendations are given in *Chapter 9*.

PROGETTAZIONE ASSISTITA DAL COMPUTER DI PROCESSI INDUSTRIALI SOSTENIBILI

Letiția Toma

RIASSUNTO

La simulazione di processo è ormai utilizzata come strumento di supporto nell'ambito dell'ingegneria chimica.

L'argomento trattato nella presente tesi di dottorato riguarda lo sviluppo di una metodologia utilizzata per quantificare l'impatto ambientale di un processo chimico o biochimico. La metodologia, inserita e implementata nella Process Sustainability Prediction (PSP) Framework, va presa in considerazione nella fase di progettazione dei nuovi impianti chimici o può essere applicata ai processi industriali già esistenti. Tenendo conto degli aspetti ambientali, tecnologici ed economici fin dalla fase di progettazione può essere così fornita una risposta alla domanda: "Quale alternativa dello stesso processo chimico è la più ecocompatibile, cioè più sostenibile?"

La struttura della tesi è la seguente.

L'importanza dell'attuale ricerca, il suo background e la motivazione di un tale argomento vengono esposti nel primo capitolo, *Chapter 1*.

Nel secondo capitolo, *Chapter 2*, vengono approfonditi i concetti di "sviluppo sostenibile" e "sostenibilità". Sono stati analizzati gli elementi di sostenibilità (società, ambiente, economia) e le loro interazioni. Vengono infine trattati il collegamento tra l'industria chimica e lo sviluppo sostenibile e il ruolo dell'ingegnere chimico nel dibattito della sostenibilità.

Nel terzo capitolo, *Chapter 3*, vengono esaminati diversi indici per la valutazione della sostenibilità. Le classi degli indici più importanti sono: gli indici tridimensionali (3D) e gli indici monodimensionali (1D). Gli indici tridimensionali vengono utilizzati come una prima valutazione della sostenibilità globale di un processo chimico. Se ciò non fosse sufficiente per decidere qual'è l'alternativa più sostenibile devono essere valutati gli indici bidimensionali (2D) e monodimensionali (1D). Un indice monodimensionale molto rilevante, che viene spesso utilizzato, è l'algoritmo WAR (Waste Reduction Algorithm). Questo capitolo riporta anche dettagli riguardanti gli indici 3D e 1D, la loro definizione e il modo in cui vengono calcolati.

Il quarto capitolo, *Chapter 4*, presenta lo sviluppo ed il funzionamento del software, Process Sustainability Prediction (PSP) Framework, per la valutazione della sostenibilità. Il PSP Framework, usato nella fase di progettazione, permette la selezione della versione più ecocompatibile, tra diverse alternative dello stesso processo chimico.

Per essere efficace il software proposto deve essere basato su standard internazionali, in modo tale che sia possibile la connessione con qualsiasi simulatore di processo. Per questo motivo, PSP Framework è stato sviluppato usando lo standard CAPE OPEN (CO). Accanto ai moduli CO, PSP contiene anche una base di dati tossicologica ed altri programmi di supporto per ulteriori calcoli.

Il quinto capitolo, *Chapter 5*, è riservato alla base di dati tossicologica. Lo schema logico e concettuale e l'implementazione della base di dati vengono trattati in questa parte della tesi.

Le categorie d'impatto ambientale utilizzate nell'Algoritmo WAR sono descritte nel sesto capitolo, *Chapter 6*. Otto categorie d'impatto ambientale sono state prese in considerazione: l'indice di tossicità umana causata dall'ingestione (HTPI), l'indice di tossicità umana causata dall'inalazione e dall'esposizione dermica (HTPE), l'indice di tossicità terrestre (TTP), l'indice di tossicità acquatica (ATP), l'indice di riscaldamento globale (GWP), l'indice di distruzione dell'ozono (ODP), l'indice di formazione di smog fotochimico (PCOP) e l'indice della capacità di causare piogge acide (AP). Sono stati proposti diversi metodi di modellistica molecolare per valutare ogni categoria d'impatto ambientale. Degli esempi rappresentativi vengono inoltre riportati in questo capitolo.

Nel settimo capitolo, *Chapter 7,* per validare la metodologia PSP, sono presentati esempi di processi chimici. Sono stati presi in considerazione due classi importanti di processi: processi descritti nella letteratura scientifica e altri situati nei paesi in via di sviluppo. Per ogni processo vengono riportati; la descrizione, la simulazione e i risultati della valutazione d'impatto ambientale. Per lo stesso processo chimico sono state proposte diverse alternative e la più sostenibile viene scelta attraverso la metodologia PSP.

La strategia di distribuzione del PSP viene presentata nell'ottavo capitolo, *Chapter 8.*

Infine le conclusioni del lavoro svolto e gli sviluppi futuri vengono forniti nel nono capitolo, *Chapter 9*.

PROIECTAREA ASISTATĂ DE CALCULATOR A PROCESELOR INDUSTRIALE DURABILE

Letiția Toma

REZUMAT

Simularea proceselor chimice este folosită de mult timp în ingineria chimică ca instrument de suport şi decizie. Unul dintre avantajele utilizării acestui instrument este posibilitatea analizei şi optimizării unui proces chimic încă din fazele inițiale ale proiectării.

Tema de cercetare a actualei teze de doctorat este implementarea unei metodologii pentru evaluarea impactului, pe care îl poate avea asupra mediului înconjurător, un proces chimic sau biochimic. Metodologia, integrată şi implementată în Process Sustainability Prediction (PSP) Framework, poate fi folosită în fazele inițiale ale proiectării unei viitoare instalații chimice sau poate fi aplicată în cazul instalațiilor deja existente. Încă din faza de proiectare, luând în considerare aspectele referitoare la protecția mediului înconjurător, aspectele tehnologice, precum şi pe cele economice, poate fi dat un răspuns concret la întrebarea: "Care este cea mai bună variantă, din punctul de vedere al durabilității, pentru un anumit process chimic?".

Lucrarea este structurată după cum urmează:

Importanța acestei teme de cercetare, background-ul ei, precum şi motivul alegerii acestei teme, sunt prezentate în primul capitol, *Chapter 1*.

În cel de-al doilea capitol, *Chapter 2,* sunt prezentate conceptele generale privind "dezvoltarea durabilă" şi "durabilitatea". Sunt analizate elementele dezvoltării durabile (societatea, mediul înconjurător şi economia) şi interacțiunile dintre ele. Este prezentată, de asemenea, legătura dintre industria chimică şi dezvoltarea durabilă, precum şi rolul inginerului chimist în dezvoltarea durabilă.

Cel de-al treilea capitol, *Chapter 3*, conține o descriere a diferiților indici de dezvoltare durabilă. Indicii pot fi: indici tridimensionali (3D) şi indici monodimensionali (1D). Indicii tridimensionali sunt folosiți pentru o primă evaluare a durabilității unui proces chimic. Uneori, această informație nu este suficientă pentru a lua o hotarâre asupra celei mai durabile alternative. În acest caz, indicii bidimensionali (2D) şi cei monodimensionali (1D) sunt de un real folos. Unul dintre cei mai importanți indici monodimensionali este Algoritmul WAR (Waste Reduction (WAR) Algorithm). În acest capitol sunt prezentate detalii referitoare la indicii 3D şi 1D, semnificația acestora şi modul de calcul.

Soft-ul creat pentru evaluarea durabilități unui proces chimic este prezentat în cel de-al patrulea capitol, *Chapter 4*. Soft-ul, Process Sustainability Prediction (PSP) Framework, folosit în faza de proiectarea a unui proces chimic, permite alegerea celei mai durabile variante din mai multe posibile.

Pentru a fi eficient, soft-ul trebuie să fie construit conform unor standarde internaționale, astfel încât să poată fi folosit în orice simulator de proces. Din acest motiv, Process Sustainability Prediction (PSP) Framework, a fost construit folosind standardul

CAPE OPEN (CO). În afară de modulele CO, PSP mai conține o bază de date toxicologică şi alte programe de suport pentru calcule ulterioare.

Capitolul cinci, *Chapter 5*, tratează baza de date toxicologică. Sunt prezentate schema logică şi conceptuală precum şi implementarea bazei de date.

Categoriile de impact asupra mediului înconjurător, care sunt folosite în Algoritmul WAR, sunt descrise în capitolul şase, *Chapter 6*. Au fost luate în considerare opt categorii de impact asupra mediului: intoxicarea umană cauzată de ingerare (HTPI), inhalare sau expunere dermică (HTPE), terestră (TTP) şi acvatică (ATP), încălzirea globală (GWP), distrugerea stratului de ozon (ODP), oxidarea fotochimică (PCOP), formarea ploilor acide (AP). Au fost propuse diverse metode de modelare moleculară pentru estimarea categoriilor de impact asupra mediului înconjurător. Capitolul de față este ilustrat cu exemple reprezentative.

În capitolul şapte, *Chapter 7,* sunt analizate diferite procese chimice cărora li s-a aplicat metodologia PSP. Au fost luate în cosiderare două mari clase de procese: procese preluate din literatura de specialitate şi procese corespunzătoare unor instalații aflate în țările în curs de dezvoltare. Fiecare proces conține o scurtă introducere, o descriere, rezultatele simularii şi ale evaluarii durabilității procesului respectiv. Pentru fiecare proces sunt propuse diferite variante de design şi, cu ajutorul soft-ului creat – Process Sustainability Prediction (PSP) Framework – este aleasă cea mai bună soluție din punctul de vedere al durabilității.

Strategia de distribuție a metodologiei PSP este discutată în capitolul opt, *Chapter 8.*

Concluziile finale şi perspectivele de continuare sunt prezentate în capitolul nouă, *Chapter 9*.

Dedicated to all the people
who believed in me and to
all the ideas I believe in…

"Every experience in life, everything with which we have come in contact in life, is a chisel which has been cutting away at our life statue, molding, modifying, shaping it. We are part of all we have met. Everything we have seen, heard, felt or thought has had its hand in molding us, shaping us. "

Orison Swett Marden

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Chapter 1

Introduction and Motivation

Summary

In this chapter, the importance of the present research, its background and motivation are presented.

"Goals are dreams with deadlines."
Diana Scharf Hunt

1.1 Research Background and Motivation

Sustainability is an important social, political and scientific issue of this century. Sustainable development has been defined as the creation of goods and services using processes and systems that are non-polluting; conserving energy and natural resources; economically viable; safe and healthy for employees, communities and consumers; socially and creatively rewarding for all working people (Veleva and Ellenbecker, 2001).

Economy, society and environment are three basic elements of sustainability. Each of these elements is connected to, and dependent upon, the others (NJSSI, 2007). Industrial sustainability means employing technologies and know-how to use less material and energy, maximizing renewable resources as inputs, minimizing generation of pollutants or harmful waste during product manufacturing and use, and producing recyclable or biodegradable products (Jenk *et al.*, 2004). Sustainable industrial development certainly requires a balance between economical and environmental aspects. In the past, technological and economical, but not environmental factors used to be considered for the optimization of a chemical plant. In the last decade of the last century, scientific and public awareness on this issue increased considerably. Much progress has been registered in industrial activities and human behavior with regard to environmental issues. Consequently, the environmental factor is increasingly taken into account.

In the sustainable development context, an important role is played by chemical engineering, basically for two main reasons: 1) the production of chemical process plants contributes greatly to national income and is absolutely essential to modern society; thus, the society development depends on the development of the chemical process industry and vice versa; 2) many critical environmental problems can be associated directly with chemical processes or to the use of chemical products and by-products that result in waste streams to soil, water and air. In addition, the analysis of such waste streams and their avoidance belongs to the field of chemical engineering (Korevaar, 2004).

Chemical industry produces materials for multiple consumer markets, which need to be produced, used and recycled by manufacturing processes that are clean, safe and economical (Jenk *et al*., 2004). In order to eliminate or reduce negative environmental problems, the environmental performance of chemical processes should be identified and quantified at an early stage of process design. When designing new materials, products or processes, engineers should take into account the 12 basic principals that consider environmental, economical and social factors:

- mass and energy in and outputs should be as inherently non-hazardous as possible
- prevention of waste is better than clean up
- minimize energy in separation/purification processes
- maximize mass, energy, volume and time efficiency in product/process
- output-pulled is preferred to input-pushed
- energy is the main criteria of choice between recycle, reuse or disposal
- durability must be targeted (no eternal life)

- avoid one-size-fits-all, minimize excess
- minimize material diversity in multi-component products integration and interconnectivity are a way to industrial ecology
- design for performance in a commercial "after-life", favor mass and energy inputs from renewable sources (Anastas *et al.*, 2003).

Taking into account all these aspects at design time, an answer to "which design is more environmentally friendly, and implicitly more sustainable, for a specific chemical process?" can be provided.

1.2 Research Goal and Importance

The present PhD thesis is concerned with the research, development, implementation and application of sustainable development concept in solving industrial problems. This means:

- Sustainable development concept analysis
- Identification of different methods/indicators for industrial sustainable development evaluation
- Development and implementation of a specific tool, Process Sustainability Prediction (PSP) Framework, to be used in the design stage, for choosing the best solution, environmentally speaking, among different design alternatives
- Toxicological data estimation using molecular modelling techniques and implementation of a toxicological database
- PSP application in different case studies

There are several advantages deriving from such a research. The most important advantage is the possibility of including the potential environmental impact criteria in the optimization and not only the technical and economical criteria. A valid tool in developed, developing and emerging countries is absolutely necessary for a complete support to the global sustainability.

Modern tools such as molecular modelling and process simulation, which have been used in the present work, are of crucial importance because they can evaluate possible technological solutions with much lower costs, and are less time consuming then experimental activity. Benefits from the coupling of molecular modelling with process simulation and design include but are not limited to (i) shortened product-process development cycles, (ii) optimization of existing processes to improve energy efficiency and minimize production of waste, (iii) efficient design of new products and processes; and (iv) improvements in health, safety, and environment (Fermeglia *et al.,* 2003).

This project has been developed in collaboration with the **International Centre for Science and High Technology-United Nations Industrial Development Organization (ICS-UNIDO)**, Area of Earth, Environmental and Marine Sciences and Technologies, being part of the Program 2.1 *Cleaner Production and Sustainable Industrial Development*. The project is supposed to become an important decision support tool in developing and emerging countries.

Chapter 2

The Concepts of Sustainable Development and Sustainability

Summary

In this chapter, a general overview of sustainable development and sustainability concepts is presented.

Sustainability elements (society, environment and economy) and their interactions are also discussed.

The connection between chemical industry and sustainable development as well as the role of the chemical engineer in the sustainable development debate are briefly treated in the present chapter.

"Kindly leave this planet as
you would wish to find it."
Source not known

2.1 Overview of Sustainable Development and Sustainability Concepts

In the last decade, the terms "sustainable development" and "sustainability" have been used very often in different scientific papers, monographs, textbooks, annual reports of companies, governmental policy usage, and media.

The vagueness of these concepts, coupled with their increasing importance in national, international and corporate policies, has led to a large political battle for influence over our future by linking interpretation to the concepts. This has resulted in a wide variety of definitions and interpretations that are skewed towards institutional and group prerogatives rather than compounding the essence of the concept, which has been inherent in traditional beliefs and practices (Mebratu, 1998). There may be as many definitions of sustainable development and sustainability as there are groups trying to define it (Sustainable Measures, 2007).

The availability of various information sources increases the spread of sustainability terms and their definitions, as employed by different authors and organizations. Consequently, numerous new terms are emerging, or the existing ones are being extended in the sustainability field, but not enough critical attention has been given to the definitions and their semantic meanings. The multitude of definitions causes much confusion about their usage, since the meaning of some terms is carelessly defined or similar, or there is only a slight difference from one another (Glavič *et al.,* 2007).

Analyzing individually the terms "sustainable" and "development", one can find that:

- "Sustainable" means "capable of being sustained", being linked to the capacity of durability, stability, permanence or even eternalness. This adjective has a kind connotation of immobility or perpetuity.
- "Development" connotes the act of improving by expanding, enlarging or refining. This includes both qualitative and quantitative features. The word itself induces the thought of movement as the way of improving. Therefore, dynamics is clearly included in the definition (García-Serna *et al*., 2007).

The most widely known definition of "sustainable development", which has been used as the basis for innumerable number of definitions because its openness and wide range of possible interpretations, is that given in the Brundtland Report in 1987 (García-Serna *et al.,* 2007). After years of discussion within an intercultural and international workgroup, the so-called "Brundtland-Commission" agreed upon the following definition, which is the most well known part of their book "Our Common Future":

Sustainable development is not a fixed state of harmony, but a process of change in which the exploitation of resources, the direction of investments, the orientation of technological development and institutional change are made consistent with future as well as present needs. ***Sustainable development is development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs.*** *It contains within two key concepts: 1) The concept of "needs", in particular the essential needs of the world's poor, to which overriding priority should be*

given; and 2) The idea of limitations imposed by the state of technology and social organization on the environment's ability to meet present and future needs.
(World Commission on Environment and Development *1987*)

Explanations regarding the Brundtland definition have been given by Korevaar (Korevaar, 2004). The definition is focused on some important elements: human being, their needs, the extend time-scale (future generations), and the extended geographical scale (the whole world). In other words:

- Sustainable Development is anthropocentric. Sustainable development gives priority to the needs of the human beings. Although the whole planet's welfare is also considered, in terms of vitality of eco-systems and biodiversity, this is mainly to conserve the planet as a supplier of raw materials and as a place to live in for humans.
- "Needs" are the starting point. The most important aspect of sustainability is the meeting of needs. This includes of everybody's needs in the world, especially the poor'. It is clear that every person in the world has a number of basic needs that should at least be fulfilled in a sustainable world. Examples of such basic needs are shelter, food, access to clean water, medical care, education, etc. However, beyond these basic needs, it is difficult to define what people really need. This is one of the things that make sustainability a complex subject to work with, because it should be based on a societal debate.
- The time scale. Sustainability does not only take into account the way the world is now, but also the way the world would be for the future generations. It is important that, in every sustainability debate, the time scale is defined explicitly.
- The geographical scale. Although, in many parts of the world, people live in luxury, in other parts of the world there are still people who do not even have access to clean drinking water, proper schooling, or nutritious food. If the desired event could be reached that all people on earth could have access to similar luxuries as the developed world is enjoying now, the earth's natural resources would never be sufficient to supply the required resources (Korevaar, 2004).

It should be noted that sustainable development is a continuing process during which the definitions and activities it generates are in constant evolution. The evolutionary process, which consists of reflecting on how we can ensure that our descendants have a decent future and of assuming responsibility for our actions, is in itself positive, although there is also the risk that theory will be put into practice in a number of different ways, creating a highly complex situation. It is for this reason that there are many different interpretations of sustainability and sustainable development, terms which are often misused well-worn concepts to serve particular interests (García-Serna *et al.,* 2007).

Sustainability is a characteristic of a process or state that can be maintained at a certain level indefinitely. The term, in its environmental usage, refers to the potential longevity of vital human ecological support systems, such as the planet's climatic system, systems of agriculture, industry, forestry, and fisheries, and human communities in general and the various systems on which they depend (Wikipedia, 2007a).

Sustainability is achieved through the promotion of sustainable development, and sustainable development can be promoted from a very wide variety of disciplines, all of them necessary to achieve the final goal (García-Serna *et al*., 2007).

The Brundtland report (1987) is now 20 years old, and its definition of sustainability is now more urgently in need of addressing than it was back then (Gaughran *et al*., 2007). Nearly twenty years away from the first definition of "sustainable development" and "sustainability" sentences like 'much remain to be done in the areas of sustainability' or 'the underlying science is still far from exact and we all still need to make a big effort' are common introducing and/or concluding phrases in both literature and scientific forums. Hopefully, in the last years underlying science has been promoted and clarified and, as a result of this, a coloured variety of successful industrial and academic examples of sustainable products processes and production systems are now available (García-Serna *et al.,* 2007).

2.2 Sustainability Elements and Their Interactions

The three main sustainable development' elements are: economy, environment and society. Each of these elements is briefly defined below.

Economy is defined as the system of human activities related to the production, distribution, exchange, and consumption of values like goods and services in a particular geographic region. The composition of a given economy is inseparable from technological evolution, civilization's history and social organization, as well as from Earth's geography and ecology (Wikipedia, 2007b).

Eenvironment is defined as external conditions and surroundings in which people, animals or plants live (Paperback Dictionary and Thesaurus, 1994).

Society represents a grouping of individuals, which is characterized by common interests and may have distinctive culture and institutions (Wikipedia, 2007c).

There are two different approaches regarding the interactions of the above presented elements. The two concepts are illustrated in Figure 2.1.

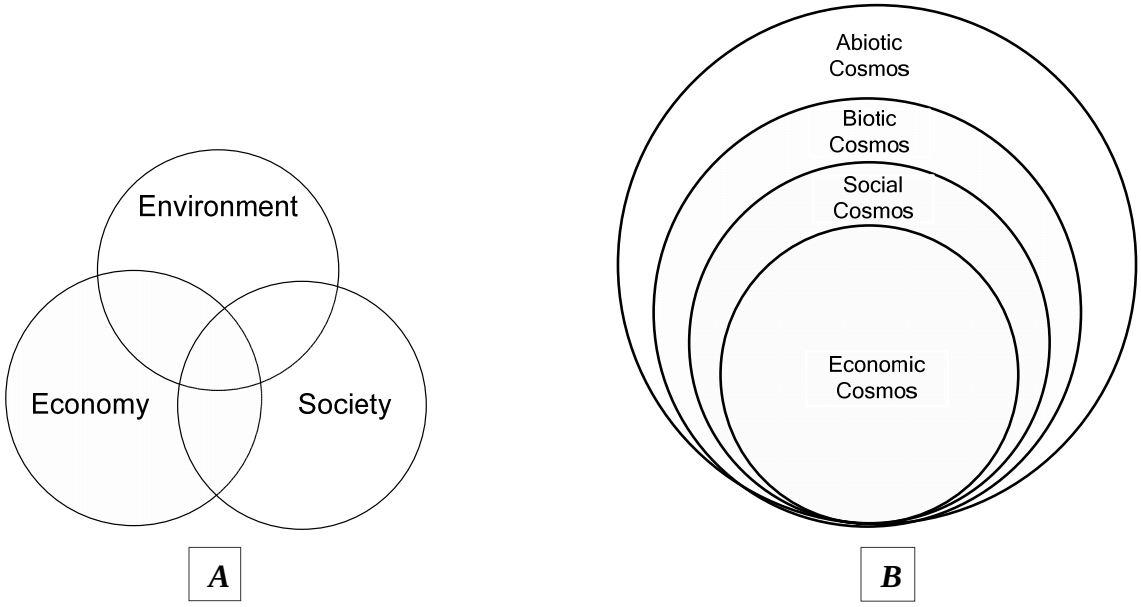

Figure 2.1 Sustainability models A) the Dominant Model; b) the Cosmic Model

The Dominant Model suggests that (Holmberg *et al*., 1994):

• The natural, economic, and social systems are independent systems and may be treated independently.

• The interactive zone where the three different systems interact is the solution area of integration where sustainability is achieved, whereas the area outside the interactive zone is assumed to be an area of contradiction.

• The ultimate objective of sustainability is the full integration of the natural, economic, and social systems, and this may be achieved through the integration of these objectives.

To the contrary, the Cosmic Model considers that (Mebratu, 1996):

• The human universe, in general, and the economic and social cosmos, in particular, never have been, and never will be, a separate system independent from the natural universe.

• The intersection area of the four cosmos is the area where we have millions of combinations of conflict and harmony relations serving as a seedbed for the process of co-evolution of the natural and human universe.

• The vehicles of interaction within the interactive zone are millions of systems that do not belong exclusively to one cosmos but have a four dimensional (or three-dimensional, if we put the biotic and abiotic under the ecological dimension) systemic parameter.

• The environmental crisis recorded throughout human history is an outcome of the cumulative effect of deliberate, or otherwise, human neglect of one or more of the systemic parameters, resulting in millions of feedback deficient systems.

• There is an abiotic region that is essentially free of interaction with the biotic, economic, and social cosmos; and, by the same token, there is a biotic region that is not yet in interaction with the human universe. However, neither of these regions can be claimed to be free from the second-degree effect of the interactive region (Mebratu, 1998).

In the present thesis the Dominant Model has been used.

2.3 Sustainable Development and Chemical Industry

2.3.1 Connection between Sustainable Development and Chemical Industry

One question arises from the above presented context: What has this to do with chemical engineering (Korevaar *et al.,* 2000)?

In today's economy, chemical and process engineering must respond to the changing needs of the chemical processes and related industries in order to satisfy both the increasing market requirements for specific end-use properties of the product required by the customer, the social, the raw material and energy savings, and environmental constraints of the industrial-scale process (Charpentier, 2007).

It is beyond discussion that chemical industry is of large importance in our modern society, which gets the benefits of this industry. Besides that, we have also to consider that important environmental problems come from chemical industry, but, on the other hand that branch also has a lot of knowledge present to solve these problems (Korevaar *et al.,* 2000).

Chemical engineering has a history of embracing new disciplines and has a special role to play in the change process. An understanding at the micro and molecular

levels and the integration of this knowledge into macro systems will be integral to the shift towards process engineering addressing the sustainability framework (Batterham, 2006).

In the frame of globalization and sustainability, the future of chemical engineering can be summarized in four main objectives:

(a) Increase productivity and selectivity through intensification of intelligent operations and a multiscale approach to processes control (e.g. nano- or micro tailoring of catalyst)

(b) Design novel equipment based on scientific principles and new production methods: process intensification in using multifunctional reactors, micro engineering and micro technology.

(c) Extend chemical engineering methodology to product design and engineering using the "triplet molecular Processes-Product-Process Engineering (3PE)" approach to manufacture end-use properties.

(d) Implement multiscale application of computational chemical engineering modelling and simulation to real-life (Charpentier, 2007).

2.3.2 The Role of the Chemical Engineer in Sustainable Development

In the above presented context another question comes out: How can a trained chemical engineer design a chemical process plant or a chemical product in such a way that the final result contributes to sustainable development (Korevaar, 2004)?

The chemical engineer, as the designer of chemical processes, also has a central role in designing chemical processes that have a minimal impact on the environment (Hesketh and Abraham, 2000). Chemical engineers are trained to be reductionist, deductive, deterministic and they are capable of integration, too. They consider outcomes and implications-core enabling skills in working towards sustainable development, itself a strategic framework which builds on the traditional frameworks of mass and energy balances. Chemical engineers can take relevant information, incorporate it with best practice to achieve a process and product that takes into account life-cycle analysis and satisfies the needs of the community and try to find a preferred pathway through uncertainty (Batterham, 2006). Now it is time for process and chemical engineers to look also at computational chemistry, aiming at applying theoretically consolidated concepts and tools to real products and to real processes for a better understanding of the existing processes and for the possibility of producing new materials (Fermeglia *et al.,* 2003).

Sustainable development needs to be taken on by chemical engineers as a managerial responsibility, so that they can show leadership within their professional institutions and at an industry level. Individual engineers, at all levels in enterprises, need to expand their comfort zone and increase their familiarity with sustainability concepts and, most importantly, how to implement the actions they require. They need to foster integrated approaches as well as continue to use the traditional tools and synthesis of unit operations. They have a contribution to make to step-changes beyond best practice by using new tools (Batterham, 2006). The tools are very useful elements but it is professional engineer's legal and professional responsibility to exercise good engineering judgment in making design decision (IchemE, 1999).

In conclusion, the engineering knowledge together with a correct use of different design tools can significantly contribute to sustainable development.

Chapter 3

Sustainability Evaluation

Summary

In this chapter, different indicators for sustainability evaluation are discussed.

The two main indicators classes, taken into account in this thesis, are the three dimensional indicators (3D indicators) and one dimensional indicators (1D indicators). 3D indicators are used as a first evaluation of the global sustainability of a chemical process. Sometimes, this information is not sufficient for deciding the best solution, in terms of sustainability, from different design alternatives. In this case one may resort to the 1D indicators evaluation. One relevant 1D indicator taken into consideration is the Waste Reduction (WAR) Algorithm.

Details regarding 3D and 1D indicators, their definition and calculation are reported in the present chapter.

"Today's problems cannot be solved if we still think the way we thought when we created them."
Albert Einstein

3.1 Sustainability Indicators

It is generally acknowledged that sustainability results from a balance among the three aspects of sustainable development: economical, environmental and social. Several attempts have been made to measure the progress of process technologies and manufacturing operations toward sustainability (Martins *et al.,* 2006). Sustainability can be evaluated using different indicators or metrics.

The selection of an adequate set of indicators (metrics) is very important, for comparative analysis between different versions of a process. The metrics must satisfy several main aspects, such as (i) a coherent set of quantifiable variables that are consistent with the principles of sustainability; (ii) they must be clear, simple and unambiguous; and (iii) they must be representative of the physical system under study (Sikdar, 2003).

Published works on metrics (or indicators) for sustainability show that: either (i) the chosen metrics are not truly reflective of all three aspects of sustainability; (ii) they are too many and, consequently, they are difficult to apply; or (iii) both. An aggregate indicator does allow easy comparison between processes, but the loss of information in the analysis is not conducive to the adoption of specific measures for improvement. The use of a small set of quantifiable indicators offers the advantage of assessing technological or policy changes needed to make a manufacturing system more sustainable. Ideally, the indicators chosen should be independent of each other, in addition to being small in number. The independence requirement makes it easy to change the definition of some indicators or the way they are calculated, when suitable, according to the characteristics and type of data available, without affecting the others. With the objective of providing an easy-to-implement method for applying indicators or metrics for the purpose of analyzing industrial systems for sustainability, Sikdar proposed a typology of indicators, considering the three dimensions of sustainability (Figure 3.1) in three distinct hierarchical groups:

(1) One dimensional (1D) indicators, which provide information about only one dimension of sustainability: economical, ecological, or social;

(2) Two dimensional (2D) indicators, which provide information simultaneously about two dimensions of sustainability: socio-ecological, socio-economical, or economic-ecological;

(3) Three dimensional (3D) indicators, which provide information about all three dimensions of sustainability (Martins *et al.,* 2006).

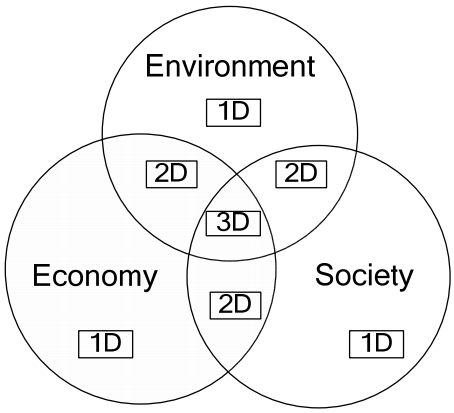

Figure 3.1 Schematic depiction of the sustainability dimensions

This idea calls for measuring the 3D indicators first and, if decision-making needs further elaborations, the 2D and 1D indicators shall be explored as well to address certain issues that might be important in specific situations. Because of the large variety of manufacturing cases that are possible to consider, the determination of 3D indicators would be necessary, but not sufficient.

A general framework of sustainability indicators usage is presented in Figure 3.2. The 3D indicators are calculated based on the inventory analysis of the process under study. If needed, 2D and 1D indicators are identified and calculated based on specific information about the system. Finally, decisions for improving the process are made after the results of the indicators calculations and cost estimation have been analyzed (Martins *et al.,* 2006).

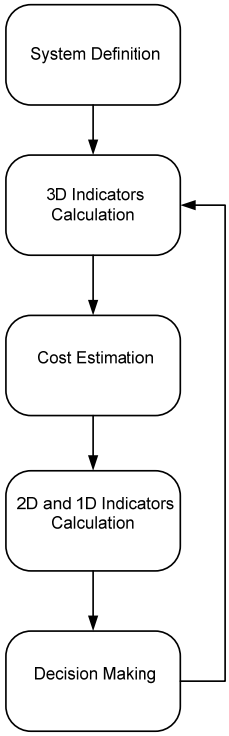

Figure 3.2 General structure of the sustainability indicators framework

Some indicators examples are given in the next section.

Energy is the prime driver for economic growth, and if non-renewable, always has an ecological impact through the emission of pollutants and greenhouse gases, and, since limited, it does affect future generations. It would appear that non-renewable energy use is inherently a 3D indicator. Likewise, material use can have direct ecological impact, is associated with value creation, and can have intergenerational impact. Process wastes that are well controlled and contained are economic value-losses and are 1D economic indicators. Some wastes, such as gypsum piles, could, however, be 2D eco-efficiency indicator, the effect being environmental nuisance and potential pollution. Pollutant dispersion is a 3D indicator, as it represents environmental impact; it has economic cost associated with it, and, frequently, it has an impact on the health of people and ecosystems that are in the neighborhood of the manufacturing units. The water use could be a 1D or 2D indicator depending on circumstances. In some cases the residuals from water works could be an environmental nuisance, in which case it would be an eco-efficiency indicator, otherwise just an economic one (Martins *et al*., 2006).

3.2 Three Dimensional (3D) Indicators

For chemical processes, in most cases, four 3D indicators can be identified or defined to assess their comparative merits from a sustainability viewpoint. In most cases, a unit product or a time period of operation are the natural and more effective choices, in particular, the first. Using the ideas on which the hierarchy of indicators is based, first, 3D indicators are calculated and then, if needed, 2D and 1D indicators are identified and calculated based on specific information about the system (Martins *et al.,* 2006).

Four 3D indicators have been identified. The description of the 3D indicators is given below.

1.*Material Intensity (MI) Indicator*

This indicator measures the amount of non-renewable resources required to obtain a unit mass of products. It includes raw materials, solvents, and other ingredients (Martins *et al.,* 2006). Material intensity is expressed as pounds of material wasted (not converted to desirable product) per unit output. This indicator is calculated by subtracting the mass of product and saleable co-products from the mass of raw materials input to the process. Water and air are not included in the calculation of the material metric unless hydrogen or oxygen from water or air becomes part of the molecular make-up of the product. In these cases, the stoichiometric requirement of hydrogen or oxygen is included, which ensures that the material indicator will be positive (Scwarz *et al.,* 2002).
The material intensity is reported to the unit output. One of the unit outputs is the mass of product. The mass of product is expressed in pounds, and is the mass of product plus the mass of saleable co-products per pound of product. When no co-products are produced, the mass denominator equals one (Scwarz *et al.,* 2002). The following formula depicts the MI calculation (Tanzil *et al*., 2004).

$$MI = \frac{mass\ of\ raw\ materials - mass\ of\ products}{output} \qquad (3.1)$$

$$output = \frac{mass\ of\ product + mass\ of\ salable\ coproducts}{mass\ of\ product} \qquad (3.2)$$

2. *Energy Intensity (EI) Indicator*

This indicator measures the energy demands of the process. It is calculated per unit mass of products and focuses primarily on the use of non-renewable energy (Martins *et al.,* 2006). The formula for the calculation of the energy intensity is depicted below (Tanzil *et al*., 2004):

$$EI = \frac{net\ energy\ consumed\ in\ primary\ fuel\ equivalents}{output} \qquad (3.3)$$

$$output = \frac{mass\ of\ product + mass\ of\ salable\ coproducts}{mass\ of\ products} \qquad (3.4)$$

3. Potential Chemical Risk Evaluation (PCRE) Indicator

The potential chemical risk evaluation method is schematically represented in Figure 3.3.

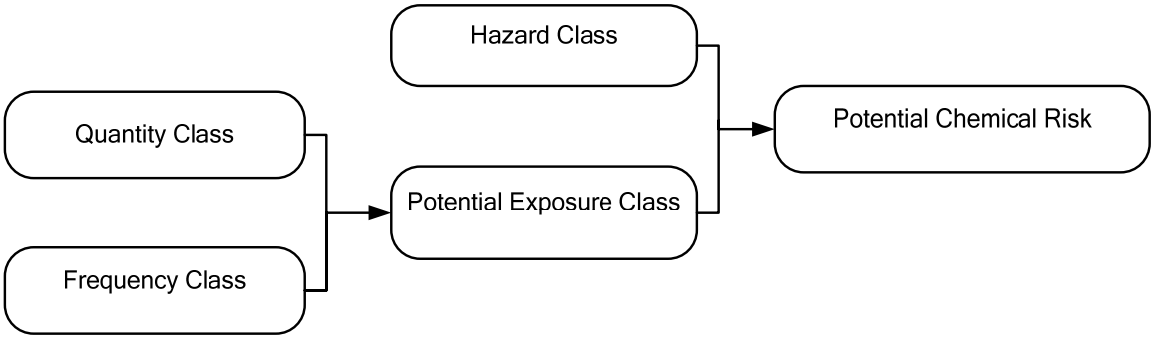

Figure 3.3 Potential Chemical Risk Evaluation

The chemicals used in the process system under study are classified depending on their relative quantity, frequency of use, danger characteristics and potential exposure. Thus, for each chemical, the designated "frequency class", "quantity class", "hazard class" and "potential exposure class" are determined.

The "quantity class" for a compound i is calculated for a time interval and is expressed as the ratio of the quantity of each chemical, q_i, to the quantity of the most used chemical in the process, q_{max}. Five levels of quantity class are defined: level 1 for $q_i/q_{max} \leq 1\%$; level 2 for $1\% < q_i/q_{max} \leq 5\%$; level 3 for $5\% < q_i/q_{max} \leq 12\%$; level 4 for $12\% < q_i/q_{max} \leq 33\%$ and level 5 for $q_i/q_{max} > 33\%$. The quantity class is a relative value that is less than or equal to one and it is useful for classifying different chemicals in a given process, regardless of their quantities (Martins *et al.,* 2006).

For the "frequency class", five levels are defined, in terms of the duration of use of each chemical (see Table 3.1, reproduced from (Vincent *et al.,* 2005)): level 0- when the use of the chemical compound has been interrupted for more than a year; level 1- for occasional use; level 2- for intermittent use; level 3- for frequent use and level 4- for permanent use. Although many chemical processes are operated in continuous mode (corresponding to level 4 of frequency class), the growing importance of the batch processes requires consideration of the remaining levels of frequency class.

Table 3.1 Frequency class determination

USE	**OCCASIONAL**	**INTERMITTENT**	**FREQUENT**	**PERMANENT**
Day	< 30 minutes	30 - 120 minutes	2 - 6 hours	> 6 Hours
Week	< 2 hours	2 - 8 hours	1 - 3 days	> 3 days
Month	< 1 day	1 - 6 days	6 - 15 days	> 15 days
Year	< 5 days	15 days - 2 months	2 - 5 months	> 5 months
Class	1	2	3	4
	Class is 0 when the use of chemical agent has been interrupted for more than one year			

The "hazard class" of each chemical is determined considering the risk phrases (R-phrases). R-phrases contain one or more numeric codes that denote special risks associated with the substance. R-phrases consist of the letter R followed by a number. The precise meaning of each of these appears in ANNEX 1. For example Styrene (CAS - Number 100-42-5) has the following risk phrase: R10, R20, R36/38. The special risks indicated by the number codes are: (a) Flammable, (b) Harmful by inhalation and (c) Irritating to eyes and skin (STNEasy, 2007)

R-phrases can be obtained from the Material Safety Data Sheet (MSDS) or from the security pictograms available in the packaging label. When the MSDS and packaging labels are not available, one can use the International Chemical Safety Cards (ICSC) that are available via the Internet (ILO, 2007) to obtain the R-phrases. This way, one guarantees that, in any situation, it is possible to identify the "hazard class" of the chemicals used. When a compound has more than one hazard class, according to the R-phrases associated with it, the largest value is selected to evaluate its potential chemical risk (Martins *et al.,* 2006).

In Table 3.2, which has been reproduced from Vincent's work (Vincent *et al.,* 2005), five levels (from 1 to 5) of hazard class are defined, depending on the R-phrases, or the pictogram available in the packaging labels. For example, for chlorine, the R-phrases indicated in the ICSC are R23 (which means toxic by inhalation), R36/37/38 (which means irritating to the eyes, respiratory system, and skin), and R50 (which means very toxic to aquatic organisms). According to Table 3.2, R23 corresponds to a hazard class of 4 and R36/37/38 corresponds to a hazard class of 2; R50 is not considered in Table 3.2, because it represents a risk to the environment and not a chemical risk to

human health. Thus, for chlorine, the hazard class is 4, which is the higher value obtained from Table 3.2 (Martins *et al.,* 2006).

Table 3.2 Hazard class determination

HAZARD CLASS	RISK PHRASES AND COMBINATIONS
1	None
2	R36, R37, R36/37, R33/38, R36/37/38, R37/38, R66
3	R20, R21, R22, R20/21, R20/22, R20/21/22, R21/22 R33, R34, R40, R42, R43, R42/43 R68/20, R68/21, R68/22, R68/20/21, R68/20/22 R68/21/21, R68/20/21/22 R48/20/22, R48/20/21/22 R62, R63, R64, R65, R67, R68
4	R15/29 R23, R24, R25, R29, R33, R23/24, R23/25 R23/24/25, R35, R39/23, R39/25 R29/23/24, R39/23/25, R39/24/25, R39/23/24/25 R41,R45,R46, R48, R49, R48/23, R48/23, R48/24, R48/25 R48/23/24, R48/23/25, R48/24/25, R48/23/24/25 R60, R61
5	R26, R27, R28, R32 R26/27, R26/28, R26/27/28, R27/28, R39, R39/26 R39/27, R39/28, R39/26/27, R39/26/28

For the "potential exposure class", five levels (from 1 to 5) are defined, depending on the quantity class and frequency class that have been determined previously. Thus, for each chemical, the level of the potential exposure class is determined using Table 3.3. For example, from Table 3.3, considering a chemical compound with a quantity class of 4 (first column) and a frequency class of 2 (first row), one obtains a potential exposure class of 4 (the value where the column and row intersect) (Martins *et al.,* 2006).

Table 3.3 Potential exposure class determination

QUANTITY CLASS	FREQUENCY CLASS 0	FREQUENCY CLASS 1	FREQUENCY CLASS 2	FREQUENCY CLASS 3	FREQUENCY CLASS 4
5	0	4	5	5	5
4	0	3	4	4	5
3	0	3	3	3	4
2	0	2	2	2	2
1	0	1	1	1	1

Now, the "potential chemical risk" of each chemical compound is determined combining the potential exposure class with the hazard class previously determined, using Table 3.4. For example, from Table 3.4, considering a chemical compound with a hazard class of 4 (first column) and potential exposure class of 4 (first row), one obtains a potential chemical risk of 30 000. The determination of the potential chemical risk to human health allows for prioritization and measures to minimize it (Martins *et al.,* 2006).

Table 3.4 Potential chemical risk determination

HAZARD CLASS	POTENTIAL EXPOSURE CLASS 1	POTENTIAL EXPOSURE CLASS 2	POTENTIAL EXPOSURE CLASS 3	POTENTIAL EXPOSURE CLASS 4	POTENTIAL EXPOSURE CLASS 5
5	100	1000	1000	100000	100000
4	30	300	3000	30000	300000
3	10	10	1000	10000	100000
2	3	30	300	3000	30000
1	1	10	100	1000	10000

4. Potential Environmental Impact

The method for the potential environmental impact evaluation is similar to the one for the potential chemical risk, as represented in Figure 3.4.

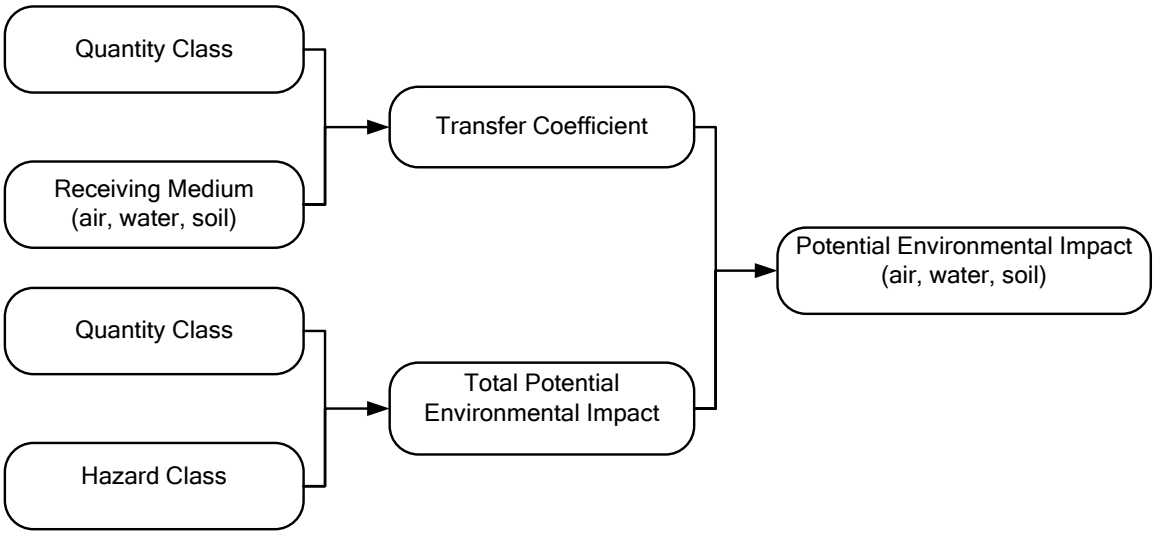

Figure 3.4 Potential Environmental Impact Evaluation

The chemicals are classified according to their relative quantity, hazard characteristics, physical state and total potential environmental impact. The potential environmental impact of interest is dependent on the transfer to a receiver medium, such as air, water or soil, which is governed by physicochemical characteristics and transfer coefficients. An estimate of total environmental impact by just considering the quantity class and hazard class can be obtained (Vincent *et al.*, 2005). However, a realistic impact evaluation is dependent on a transfer to appropriate environmental media. The latter is obtained by determining a transfer coefficient by knowing the physical state and the receiving medium, as shown in Figure 3.4. The determination of the "quantity class" here is similar to that for potential chemical risk. As previously described, five levels (from 1 to 5) are defined, expressed as the ratio of the quantity of each chemical, q_i, to the quantity of the most-used chemical in the process, q_{max} (Martins *et al.,* 2006).

For "hazard class", five levels (from 1 to 5) are defined, according to the R-phrases of each chemical, as shown in Table 3.5, which has been adapted from Vincent's work (Vincent *et al*., 2005)

Table 3.5 Determination of hazard class using R- phrases and their combinations

RISK PHRASES AND COMBINATION
Hazard Class 1
none the residue type is not mentioned on the residue classification list no hazardous industrial waste
Hazard Class 2
R66, R67 the type of residue is mentioned in the residue classification R29 and accidental probability of a contact with water R31 and accidental probability of a contact with acid
Hazard Class 3
R20, R21, R22, R33, R36, R37, R38 R40/20, R40/21, R40/22, R40/20/21/22, R48/20, R48/21, R48/22 R48/20/21, R48/20/22, R48/21/22, R48/20/21/22 R52, R53, R52/53, R65 R29 and R32 and accidental probability of a contact with water R31 and accidental probability of a contact with acid
Hazard Class 4
R23, R24, R25, R34, R35, R40, R41, R42, R43, R48 R48/23, R48/24, R48/25, R48/23/34, R48/23/25, R48/24/25 R48/23/24/25, R51, R51/53, R54, R55, R56, R57, R58, R59 R62, R63, R64 R29 and permanent probability of a contact with water R31 and permanent probability of a contact with acid R32 and occasional probability of a contact with acid
Hazard Class 5
R26, R27, R28 R39/23, R39/24, R39/25, R39/23/24, R39/23/25, R39/24/25 R39/23/24/25, R39/26, R39/27/28, R39/26/27/28 R4, R46, R49 R50, R46, R49 R50, R50/53 R60, R61 R32 and accidental probability of a contact with acid

Considering the example of chlorine again, the risk phrase R23 (toxic by inhalation) corresponds to a hazard class of 4, the risk phrase R36/37/38 (irritating to the eyes, respiratory system, and skin) is not represented in Table 3.5 and the R-phrase R50 (very toxic to aquatic organisms) corresponds to a hazard class of 5. Concerning the

evaluation of the potential chemical risk, the highest value of the hazard class is used in potential environmental impact evaluation.

The total "potential environmental impact" for each chemical is then determined according to Table 3.6, which has been adapted from Vincent's work (Vincent *et al.,*2005) knowing that the "quantity class" and the "hazard class" have been previously determined. For example, from Table 3.6, for a chemical compound with a hazard class of 5 (first row) and a quantity class of 4 (first column), the total potential environmental impact is 30 000. The total potential environmental impact thus obtained is an aggregated value valid for a particular chemical, because it does not yet consider the impact per receiving medium. Therefore, after the total potential environmental impact has been determined, one can determine the potential environmental impact on air, water, or soil, by knowing the transfer coefficients of each chemical in each receiving medium (Martins *et al.,* 2006).

Table 3.6 Determination of Total Potential Environmental Impact

HAZARD CLASS	**QUANTITY CLASS 1**	**QUANTITY CLASS 2**	**QUANTITY CLASS 3**	**QUANTITY CLASS 4**	**QUANTITY CLASS 5**
5	2000	5000	10000	30000	10000
4	100	1000	2000	5000	10000
3	10	30	100	1000	2000
2	2	5	10	30	100
1	1	1	2	5	10

As shown in Table 3.7, which has been adapted from Vincent's work (Vincent *et al.,* 2005) considering the physical state (gas, liquid, solid, or powdered solid) and the receiving medium (air, water, or soil), one can obtain the transfer coefficients of each chemical. For example, for a liquid, under process operation, the transfer coefficients for air, water, and soil are 0.5, 0.35, and 0.002, respectively.

The transfer coefficients from Table 3.7 are average values that could be refined if more information is available on the transfer and dispersion of the chemicals in the various media, in particular, concerning the distribution of the mass of chemicals in the different receiving media.

Table 3.7 Transfer coefficients relative to the chemical's physical state and the receiving medium

PHYSICAL STATE	**RECEIVING MEDIUM**		
	Air	Water	Soil
Gas	0.95	0.05	0.001
Liquid	0.5	0.35	0.002
Solid	0.001	0.005	0.005
Solid as a powder	0.1	0.85	0.005

Finally, multiplying the transfer coefficients by the previous total value of the potential environmental impact, one can determine the potential environmental impact per receiving medium, which is the quantity of interest for this indicator (Martins *et al.,* 2006).

3.3 One Dimensional (1D) Indicator - the Waste Reduction (WAR) Algorithm

The concept of WAR Algorithm was first introduced by Hilaly and Sikdar in 1994. They also introduced the concept of a pollution balance. Later, Cabezas proposed that an environmental impact balance, analogous to mass or energy balances, has to be incorporated into the traditional process design methodology for taking into account the environmental effects. The algorithm presented by Cabezas and Young is described in the next section (Cabezas *et al.*, 1997), (Young *et al.*, 1999), (Young *et al.*, 2000).

General Description

The overall balances for a general chemical process, including also the energy generation facility, are illustrated in Figure 3.5.

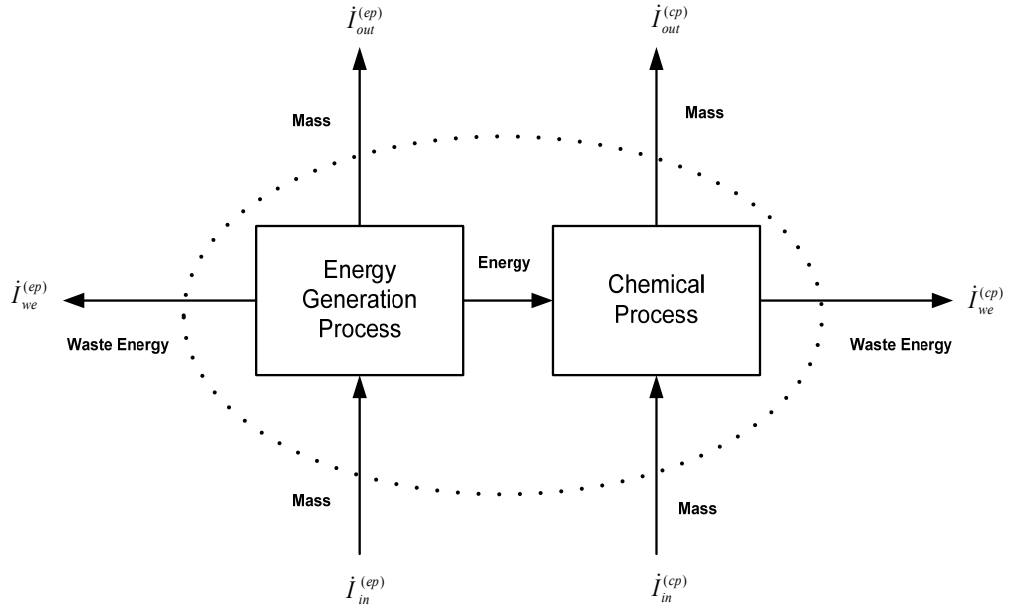

Figure 3.5 The overall environmental balances around a chemical process including the energy generation facility

The key element of the assessment involves a balance equation similar to the mass and energy balance equations. The equation has the following form:

$$\frac{\partial I_{syst}}{\partial t} = \dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} - \dot{I}_{we}^{(cp)} - \dot{I}_{we}^{(ep)} + \dot{I}_{gen}^{syst} \qquad (3.5)$$

where I_{syst} is the amount of potential environmental impact inside the system, $\dot{I}_{in}^{(cp)}$ and $\dot{I}_{out}^{(cp)}$ are the input and output rates of potential environmental impact to the chemical process, $\dot{I}_{in}^{(ep)}$ and $\dot{I}_{out}^{(ep)}$ are the input and output rate of potential environmental impact to the energy generation process, and $\dot{I}_{gen}^{syst}$ is the rate of generation of potential environmental impact inside

the system, $\dot{I}_{we}^{(cp)}$ is the rate of potential environmental impact output due to the emission from the chemical process (Young *et al.,* 1999).

The expressions for the chemical process are:

$$\dot{I}_{in}^{(cp)} = \sum_{j}^{cp} \dot{I}_{j}^{(in)} = \sum_{j}^{cp} \dot{M}_{j}^{(in)} \sum_{k} x_{kj} \psi_{k} + ... \qquad (3.6)$$

$$\dot{I}_{out}^{(cp)} = \sum_{j}^{cp} \dot{I}_{j}^{(out)} = \sum_{j}^{cp} \dot{M}_{j}^{(out)} \sum_{k} x_{kj} \psi_{k} + ... \qquad (3.7)$$

$$\dot{I}_{we}^{(cp)} = \sum_{i}^{cp} \dot{E}_{j}^{(cp)} \psi \; x_{we} \approx 0 \qquad (3.8)$$

where $\dot{I}_{i}^{(cp)}$ is the potential environmental impact input ($i = in$) or output ($i = out$) of the chemical process, $\dot{I}_{j}^{(i)}$ is the potential environmental impact flow rate with the stream j which may be an input or an output stream. $\dot{M}_{j}^{(i)}$ is the mass flow rate of stream j which may be an input or an output stream, x_{kj} is the mass fraction of chemical k in stream j, and ψ_{k} is the specific potential environmental impact of chemical k. $\dot{I}_{we}^{(cp)}$ is the rate of potential environmental impact output due to the emission from the chemical process. $\dot{E}_{j}^{(cp)}$ is the rate of waste energy emission from the chemical process and ψ_{we} is the potential environmental impact for energy emission which is assumed to be zero. This is consistent to the fact that: chemical process plants do not generally emit large amounts of waste energy into the environment and for the chemical process plants, the potential environmental impact associated with the emission of mass is usually much greater than that associated with the emission of energy (Young *et al*., 1999).

The expressions for the energy generation process are analogous to the expression for the chemical process.

$$\dot{I}_{in}^{(ep)} = \sum_{j}^{ep} \dot{I}_{j}^{(in)} = \sum_{j}^{ep} \dot{M}_{j}^{(in)} \sum_{k} x_{kj} \psi_{k} + ... \approx 0 \qquad (3.9)$$

$$\dot{I}_{out}^{(ep)} = \sum_{j}^{ep} I_{j}^{(out)} = \sum_{j}^{ep-g} \dot{M}_{j}^{(out)} \sum_{k} x_{kj} \psi_{k} +$$

$$\sum_{j}^{ep-s} \dot{M}_{j}^{(out)} \sum_{k}^{x_{kj} \psi_{k}} + \qquad (3.10)$$

$$.... \approx \sum_{j}^{ep-g} \dot{M}_{j}^{(out)} \sum_{k} x_{kj} \psi_{k} + ...$$

$$\dot{I}_{we}^{(ep)} = \sum_{j}^{ep} \dot{E}_{j}^{(ep)} \psi_{we} \approx 0 \qquad (3.11)$$

where $\dot{I}_i^{(ep)}$ is the rate of potential environmental impact in (i = *in*) or out (i = *out*) of the energy generation process, $\dot{I}_{we}^{(ep)}$ is the rate of potential environmental impact output due to the emission of waste energy from the energy generation process, $\dot{E}_j^{(ep)}$ is the rate of waste energy emission from the energy generation process, and ψ_{we} is the potential environmental impact for the waste energy emission. For the input, $\dot{I}_i^{(ep)}$ and the waste energy, $\dot{I}_{we}^{(ep)}$ the sums over j and k are respectively taken over all input or all output streams and all components k associated with the energy generation process. For the output, $\dot{I}_{out}^{(ep)}$, the sum over streams j is broken into a sum over gaseous output streams, *ep-g*, and another sum over solid output streams, *ep-s*. The potential environmental impact of the solid output streams can be assumed to be negligible compared to that of the gaseous output streams (Young *et al.,* 1999).

The potential environmental impact of the mass inputs, $\dot{I}_{in}^{(ep)}$, to the energy generation process is also assumed to be approximately zero. The energy generation process is assumed to be a coal-fired electrical power plant, but other energy sources will be added in the final Process Sustainability Prediction (PSP) Framework. For the coal-fired electrical power plant the mass inputs consist mainly of coal and air along with water. Of these input streams, the only one that has a significant potential environmental impact is the coal feed stream. The ψ_k for the components in coal is approximately set to zero. The air and the water have no potential environmental impact so ψ_{air} and ψ_{water} are set to zero and $\dot{I}_{air}^{(in)}$ and $\dot{I}_{water}^{(in)}$, are, consequently, zero. Summarizing, all of the terms under the summation can be approximately set to zero so that the entire term $\dot{I}_{in}^{(ep)}$ is zero or at least very small compared to the output term, $\dot{I}_{out}^{(ep)}$ (Young *et al.,* 1999).

The potential environmental impact of the mass outputs, $\dot{I}_{out}^{(ep)}$, from the energy generation process are divided into gaseous and solid streams, as already mentioned. The gaseous streams mainly consist of air pollutants, e.g. NO_x, CO_2, SO_2, etc., and they are included in the analysis.

The solid streams consist of coal slag, i.e. non-combustible ashes and residue, and coal impurities such as metals removed during coal pre-treatment process. All of these are in solid form which makes them relatively unavailable for causing environmental impacts as compared to gases. It is assumed here that the potential environmental impact of the components in the solid output streams is negligibly small (Young *et al.,* 1999).

Environmental Impact Categories

The overall potential environmental impact of chemical k, ψ_k, can be determined by summing the specific potential environmental impact of chemical k, ψ_{kl}^s, over all of the possible impact categories (Young *et al.*, 1999):

$$\psi_k = \sum_l \alpha_l \psi_{kl}^s \qquad (3.12)$$

where α_l represents the relative weighting factor of impact category l (Cabezas *et al.*, 1999).

Eight Impact Categories are used in evaluation of potential environmental impact using the WAR Algorithm. The categories are the following: Global Warming Potential (GWP), Acidification Potential (AP), Ozone Depletion Potential (ODP), Photochemical Oxidation or Smog Formation Potential (PCOP), Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Inhalation or Dermal Exposure (HTPE), Aquatic Toxicity Potential (ATP), Terrestrial Toxicity Potential (TTP) (Young *et al.,* 1999). The above enumerated impact categories are divided in two classes: Global Atmospheric and Local Toxicological as it can be noticed from Figure 3.6.

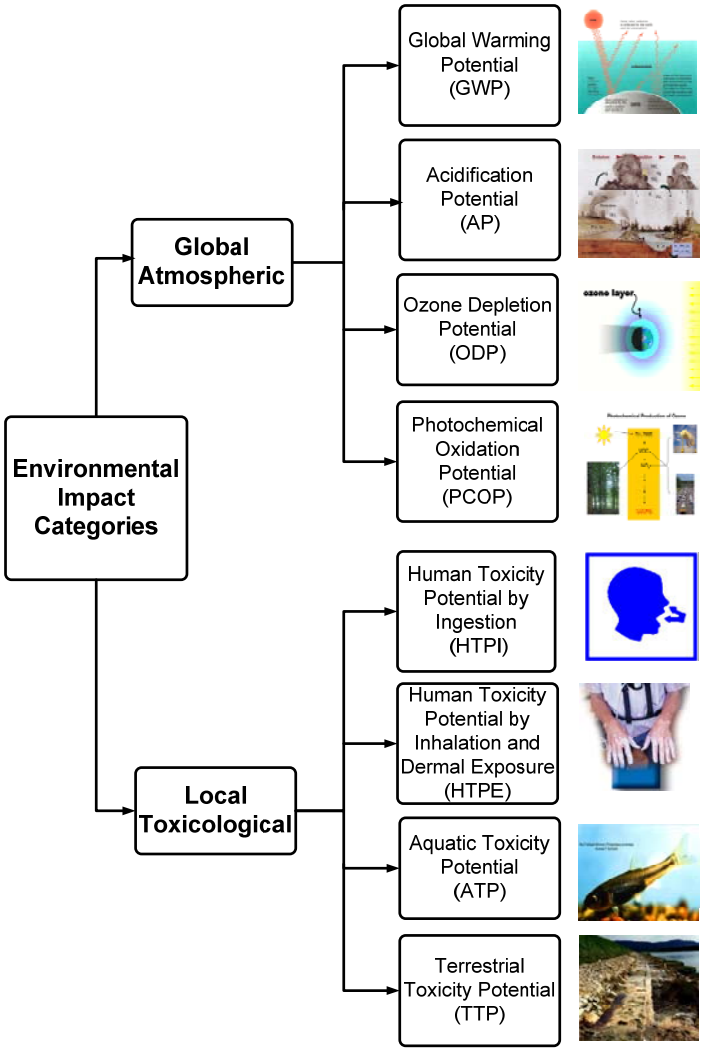

Figure 3.6 Environmental Impact Categories used in the WAR Algorithm

The impact categories have been defined by Young and Cabezas (Young *et al.,* 1999). A brief description of each category and of the way they are calculated is presented below.

GWP is determined by comparing the extent to which a unit mass of a chemical absorbs infrared radiation over its as atmospheric lifetime to the extent the CO_2 absorbs infrared radiation over its respective lifetimes. All measures of GWP are given relative to carbon dioxide, the most well-known gas whit global warming potential, which has a GWP of 1.

$$(Score_k)_{GWP} = \frac{\begin{array}{l}absorption\ of\ infrarared\ radiation\\ by\ a\ unit\ mass\ of\ chemical\ k\end{array}}{\begin{array}{l}absorption\ of\ infrarared\ radiation\\ by\ a\ unit\ mass\ of\ CO_2\end{array}} \tag{3.13}$$

AP or acid rain potential is determined by comparing the rate of release of H^+ in the atmosphere as promoted by a chemical to the rate of release of H^+ in the atmosphere as promoted by SO_2.

$$(Score_k)_{AP} = \frac{\begin{array}{l}release\ rate\ of\ H^+\ in\\ the\ atmosphere\ by\ a\ chemical\ k\end{array}}{\begin{array}{l}release\ rate\ of\ H^+\ in\\ the\ atmosphere\ by\ SO_2\end{array}} \tag{3.14}$$

ODP is determined by comparing the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen.

$$(Score_k)_{ODP} = \frac{\begin{array}{l}total\ amount\ of\ ozone\ eventually\\ destroyed\ by\ a\ unit\ mass\ of\ a\ chemical\ k\end{array}}{\begin{array}{l}total\ amount\ of\ ozone\ eventually\\ destroyed\ by\ a\ unit\ mass\ of\ CFC-11\end{array}} \tag{3.15}$$

PCOP or smog formation potential is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical OH to the rate at which a unit mass of ethylene reacts with OH.

$$(Score_k)_{PCOP} = \frac{\begin{array}{l}reaction\ rate\ of\ a\ unit\ mass\\ of\ chemical\ i\ with\ hydroxyl\ radical\end{array}}{\begin{array}{l}reaction\ rate\ of\ a\ unit\ mass\\ of\ ethylene\ with\ hydroxyl\ radical\end{array}} \tag{3.16}$$

HTPI is calculated for a chemical if it existed as a liquid or solid at a temperature of 0°C and atmospheric pressure.

As a first approximation, the lethal-dose that produced death in 50% of rats by oral ingestion (LD_{50}) has been used as an estimate for the HTPI. The value was chosen because of its prevalence in the literature and acceptance as a standard toxicity indicator. LD_{50} are typically reported in units of mg of chemical/kg rat. A chemical with a higher LD_{50} represents a chemical with lower toxicity. This scale is inverted from the manner in which the WAR Algorithm is presented where a higher score represents a greater potential environmental impact.

Thus, the score for chemical k in the HTPI category was calculated by:

$$\left(Score_k\right)_{HTPI} = \frac{1}{\left(LD_{50}\right)_k} \tag{3.17}$$

HTPE was determined for that chemical if it existed as a gas a temperature of 0° C and atmospheric pressure.

The ATP was estimated by using toxicological data for a single, representative species of fish, Pimephales Promelas (Fathead Minnows). This species has been chosen because of its acceptance as a universal aquatic indicator and it prevalence of data. The data for this assay comes in the form of a LC_{50}, a lethal concentration which causes death in 50% of the test specimens.

The scores for this category were calculated by the following:

$$\left(Score_k\right)_{ATP} = \frac{1}{\left(LC_{50}\right)_k} \tag{3.18}$$

Different molecular modelling methods to evaluate the thermo-physical properties which lead to environmental impact categories are described in *Chapter 6.*

Environmental Impact Categories Normalization

The ψ_{kl}^{s} values are normalized within each impact category. There are two reasons for this. First, normalization will ensure that values of different categories contain the same units to allow for their combination as in equation 3.12. Second, a proper normalization will ensure that values from different categories will have on average equivalent scores. Without the second condition, implicit weighting factors could be present in the chemical database causing unintentional bias in the calculation of the PEI indexes. The scores used in the WAR algorithm will be calculated using the following normalization scheme:

$$\psi_{kl}^{s} = \frac{(Score)_{kl}}{< (Score)_k >_l} \tag{3.19}$$

where $(Score)_{kl}$ represents the value of chemical k on some arbitrary scale category and $< (Score)_k >_l$ represents the average value of chemical in category l (Young and Cabezas, 1999).

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Environmental Impact Indexes

Indexes are used to characterize the relative environmental efficiency of the process. There are two different classes of indexes:

- those associated with potential environmental impact output
- those associated with potential environmental impact generation.

Of the output indexes, the two most important ones are the total rate of impact output, $\dot{I}_{out}^{(t)}$, and the total impact output per mass of products, $\hat{I}_{out}^{(t)}$.

These indexes are defined as below (Young *et al.,* 1999):

$$\dot{I}_{out}^{(t)} = \dot{I}_{out}^{(cp)} + \dot{I}_{out}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{(ep)} = \sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k \tag{3.20}$$

$$\hat{I}_{out}^{(t)} = \frac{\dot{I}_{out}^{(cp)} + \dot{I}_{out}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{(ep)}}{\sum_p \dot{P}_p} = \frac{\sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k}{\sum_p \dot{P}_p} \tag{3.21}$$

$\dot{P}_p$ is the mass flow rate of product p and the sum is taken over all the product streams p.
Of the generation indexes, the two most important indexes are, similarly, the total rate of impact generation, $\dot{I}_{gen}^{(t)}$ and the total impact generated per mass of product, $\hat{I}_{gen}^{(t)}$ defined by:

$$\begin{aligned}
&\dot{I}_{gen}^{(t)} = \dot{I}_{out}^{(cp)} - \dot{I}_{in}^{(cp)} + \dot{I}_{out}^{(ep)} - \dot{I}_{in}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{ep} = \\
&= \sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k - \sum_{j}^{cp} \dot{M}_j^{(in)} \sum_k x_{kj}\psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k \\
&I_{gen}^{(t)} = \frac{\dot{I}_{out}^{(cp)} - \dot{I}_{in}^{(cp)} + \dot{I}_{out}^{(ep)} - \dot{I}_{in}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{ep}}{\sum_p \dot{P}_p} = \\
&= \frac{\sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k - \sum_{j}^{cp} \dot{M}_j^{(in)} \sum_k x_{kj}\psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_k x_{kj}}{\sum_p \dot{P}_p}
\end{aligned} \tag{3.22}$$

The comparison of the above presented indexes permits to choose the most environmentally friendly design between different process alternatives.

Chapter 4

Process Sustainability Prediction (PSP) Framework

Summary

The software developed for sustainability evaluation is presented in this chapter.

The software, Process Sustainability Prediction (PSP) Framework, used during the design phase of a chemical process, consents to choose, the most environmentally friendly design for a chemical process from various design alternatives.

To be effective, the software proposed should be based on international standard, so that the connection to any commercial process simulator would be possible.

For this reason, PSP Framework has been developed using the CAPE OPEN (CO) standard. Beside the CO Modules, PSP also contains a toxicological database and a set of software modules for post-processing the information extracted from the process simulator software.

Framework structure, development, implementation and running are presented in this chapter.

"A good scientist is a person with original ideas.
A good engineer is a person who makes a design
that works with as few original ideas as possible."
Freeman Dyson

4.1 Elements Requested for PSP Development

The objective of chemical processes is to convert a specific feed stream into specified products (Korevaar, 2004). A large number of steps are taken into account between the original idea and the final product. One of these steps is the process design.

The general goal in plant design, is to construct or synthesize "optimum designs" in the neighborhood of the desired constraints, in other words it means finding a satisfying solution to the given design problem within given boundary conditions. Three kinds of boundary conditions or constraints can be distinguished- technological, physical, and societal constraints:

- Technological constraints
- Physical constraints. Every design is limited by physical and chemical laws, like thermodynamics or kinetics. Although, the profitability of the design or the available knowledge are the main limiting factors, every engineering activity is strongly dependent on the science knowledge level.
- Societal constraints. From sustainable development perspective, a design should be pointed at fulfilling the societal needs now and in the future. Innovation and development of societal structures can be maintained on a long term. This is true for physical resources, but also for societal trends (Korevaar, 2004).

Taking into account all these constrains in the design phase, the conceptual flow-sheet as well as several design alternatives can be generated and evaluated for a specific chemical process.

A general schema describing all the design synthesis steps is presented in Figure 4.1 (Biegler *et al.,* 1997). The first step is the concept generation, the step where different concepts, on which the design is based, are described. The generation of alternatives is considered with the next step. Examples of sources for alternative concepts are the library (patent literature, journal articles and encyclopedias of technologies), corporate files, consultants, etc. The next step is the analysis of each alternative to establish what it performs. For process design, this typically means carrying out mass and energy balances on the process to find what flows, temperatures, pressures, etc. will be. At the next step, the process's performance is evaluated. This means computing economical, flexibility and safety analysis. Finally, optimization requires the adjustment and refinement of decisions to improve the design. In this way, an abstract description is transformed in a proposed process flow-sheet which satisfies the desired goals (Biegler *et al.,* 1997).

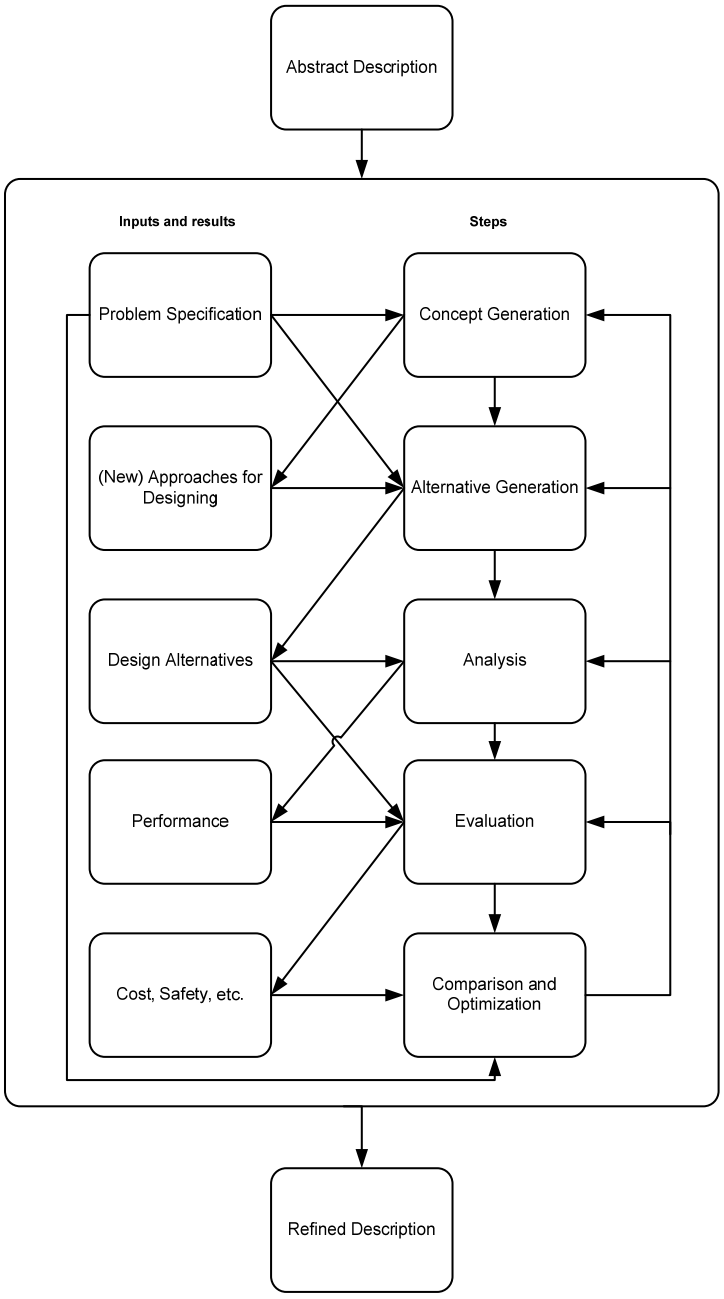


Figure 4.1 Steps in design synthesis

To enhance the understanding of the design step, the process is simulated using specific tools such as commercial process simulators.

4.1.1 Process Simulation

Process Simulation (PS) is the natural computing environment for sustainability assessment of a given process since it generates material and energy balance. Figure 4.2 gives a general description of a process simulator without pollution prevention or waste minimization incorporated (Bumble, 2000).

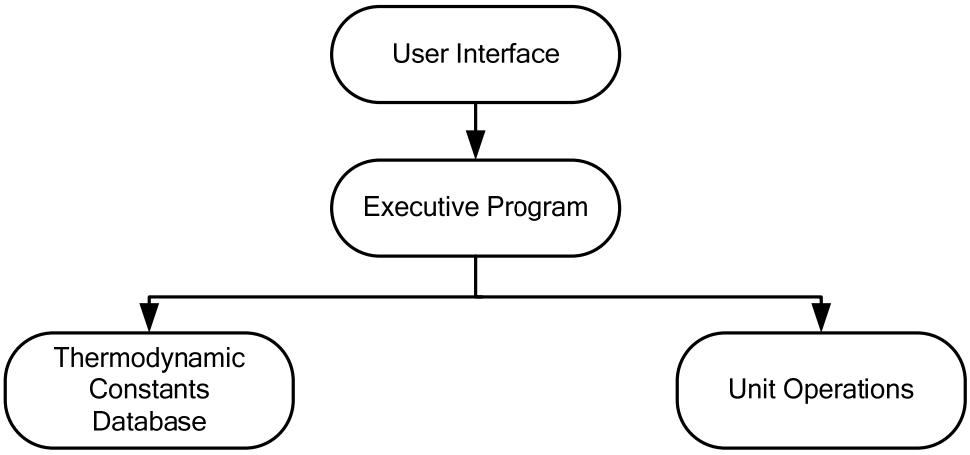


Figure 4.2 Process simulator structure

The structure consists of four parts:

1. User Interface
2. Executive Program
3. Thermodynamic, Constants, Databases
4. Unit Operations

The first part is the user interface. This is where the user enters data (e.g. stream temperature, pressure, composition and design parameters such as the distillation column number stages). The second part, the executive program, takes the user input and follows the instructions to control such things as the calculation sequence and convergence routines. It finds a solution in which all the recycle loops have converged and all the user specifications have been met. In the third part, the chemical, physical and thermodynamic properties are calculated. The thermodynamics constant database, the correlation constants and the limits of the correlations and of the equations are stored here. The fourth part deals with the unit operations modules. They perform the engineering calculations (Bumble, 2000).

The process simulators used in the present work are PROII (developed by Ivensys), Aspen Plus (developed by Aspen Tech), and COCO/COFE (developed by AmsterCHEM). The main steps to perform a simulation are, more or less, the same in all available simulators on the market (see Figure 4.3).

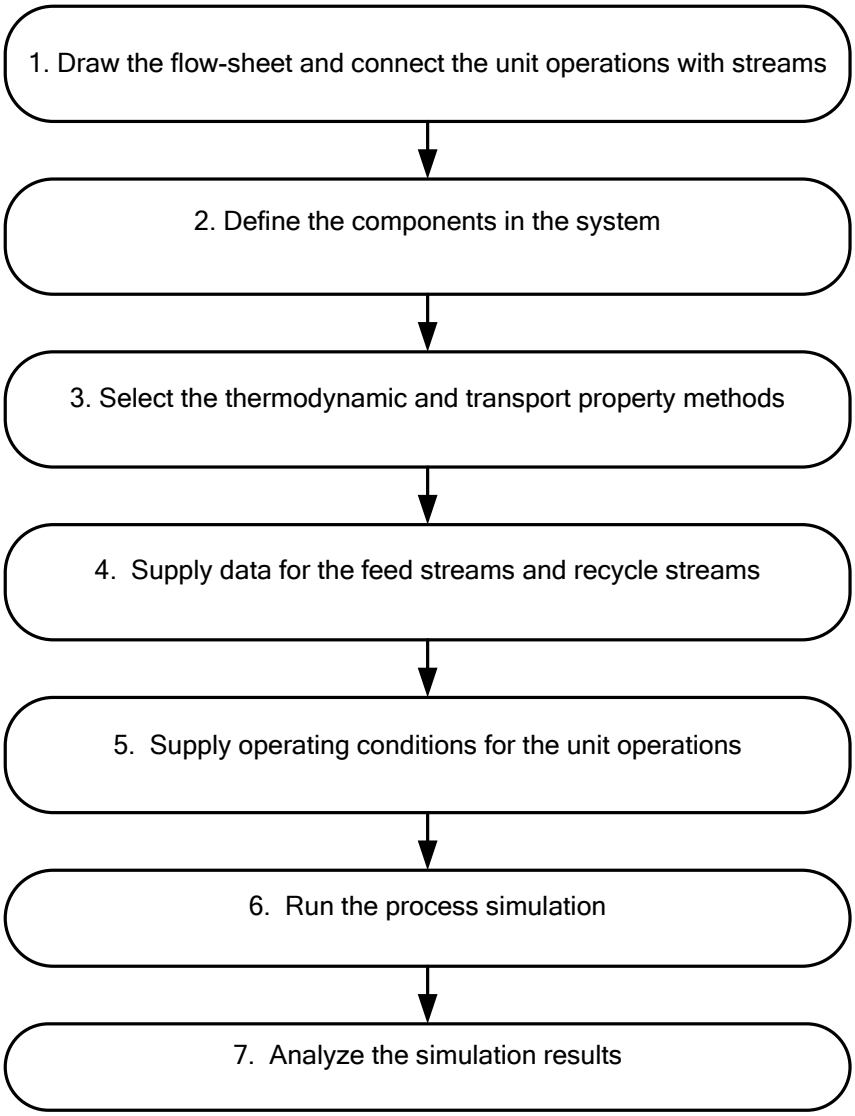


Figure 4.3 Process simulator steps

As it has been mentioned, the above presented paragraph describes a general process simulator where environmental aspects are not taken into account.

The goal of the present work is to incorporate the toxicology problem into PS. For this aim, toxicological effects of the substances, present in the process flow-sheet, and their quantities are processed in some special unit operations, implemented using the CAPE OPEN (CO) methodology (see Figure 4.4).

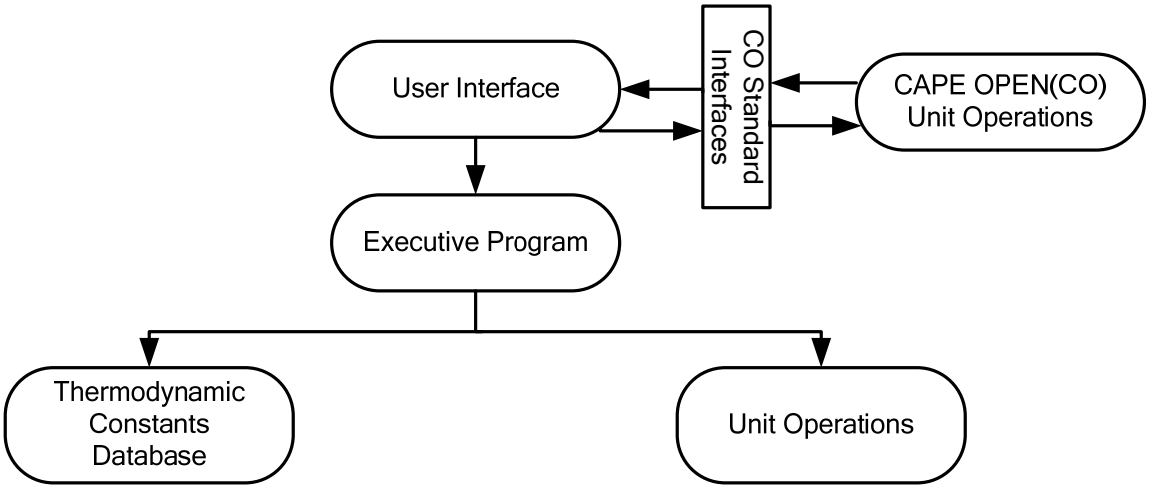


Figure 4.4 Process simulator structure and CO procedure

The manner in which environmental aspects are taken into consideration is presented in the next sections and is exemplified in *Chapter 7*.

4.1.2 CAPE OPEN (CO) Procedure

Process industries are facing increasing economical, environmental and safety constraints being forced to improve the performance of their plants by reducing the costs of and time required for plant and product development. Simulation software, specific to process industries, provides a vital tool for achieving these goals and being competitive on a market with increasingly short innovation cycles. CAPE (Computer Aided Process Engineering) is progressively required more by process industries. A standard to allow communication between CAPE software components from different sources (software and equipment vendors, universities, and in-house) constitutes one of the ways to provide process industries with faster, cheaper, more accurate process simulation, leading to enhanced competitive and environmental performance (Pons, 2003). With this goal in mind, the CAPE OPEN project has been created. CAPE OPEN is a cooperation project aimed at defining software interfaces for plug-and-play simulation components for the various process simulators on the market.

CAPE OPEN objectives are to enable native components of a simulator to be replaced by those from another independent source or from another simulator with minimum effort, in as seamless manner as possible (CAPE OPEN Project Team, 2000).

The CAPE OPEN standard distinguishes two kinds of software components: Process Modelling Components (PMCs) and Process Modelling Environments (PMEs) (Pons, 2003).

The range of technical capability needed for a given process simulation is often so great that no single provider is likely to deliver best-in-class in every area. This requires the use of PMCs from multiple sources in the chosen PME. This situation makes full interoperability a requirement for taking full advantage of the possibilities of CAPE. There are many examples of environments and components where interoperability is applicable. Complete interoperability is the ability of a PMC to run as if it were an integral

component within any PME. It provides full "plug-and-play" operation, so that there is no longer any need for a different version of a PMC for each PME, or for the interface to be revised each time a new version of the PME is issued (Banks *et al.,* 2005). A schema containing the connection between the PMC and PME is presented in Figure 4.5.

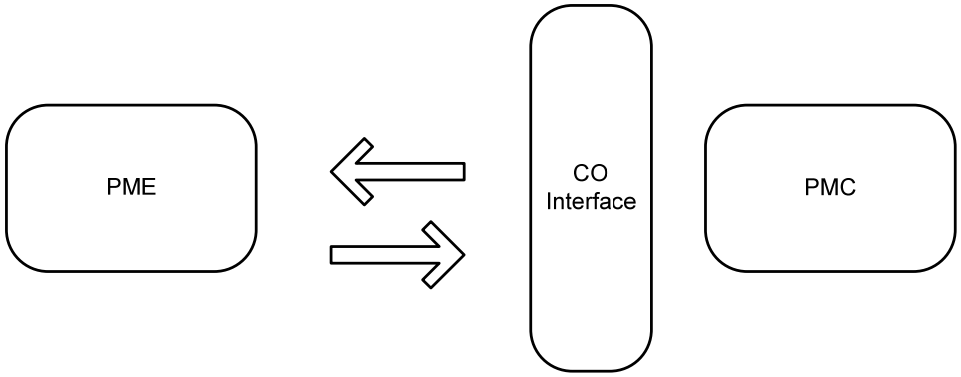


Figure 4.5 Connection between PMC and PME

From a process engineer point of view, a CAPE OPEN compliant PME is mainly responsible for managing interactions with users, accessing, and storing data and reporting simulation calculations. Using some external business codes requires their integration in the computational framework. This generally leads to activate components, develop thermodynamics package, put Unit Operations (UO) in a suitable state to perform calculations and of course ordering and then launch computations on each UO (Pigeon *et al.,* 2005).

The traditional process simulator is the obvious PME, but CAPE covers the entire process-engineering arena, not just process simulation. Furthermore, the end users of CAPE tools extend beyond the process engineers themselves into other technical domains (e.g. chemists). Possible PMEs include, for example, some custom applications, for example, a spreadsheet. Possible PMCs that would be required in this environment would be: physical property systems or single detailed unit operations. An example of this could be a reactor model used by the chemists in design of experiments and data analysis.

The following table lists a number of commercial or research PMCs and PMEs providing CAPE OPEN interfaces (GCO Consortium, 2000).

Table 4.1 Software programs providing CO interfaces

SUPPLIER	SOFTWARE	INTERFACES	TECHNOLOGY
AspenTech www.AspenTech.com	Aspen Plus 11.1	Thermodynamic and physical properties socket, Unit operations socket	COM
AspenTech	Aspen Properties 11.1	Thermodynamic and physical properties plug	COM
Hyprotech www.hyprotech.com	HYSYS.Plant 2.4	Thermodynamic and physical properties socket, Unit operations socket	COM
Hyprotech	Distil	Thermodynamic and physical properties socket	COM

Process Systems Enterprise (PSE) www.psenterprise.com	gPROMS	Thermodynamic and physical properties socket, Unit plug	COM CORBA
Process Systems Enterprise (PSE)		Numerical solvers sockets (linear algebraic, nonlinear algebraic, differential-algebraic)	CORBA
Process Systems Enterprise (PSE)	gO:CAPE-OPEN	gO:CAPE-OPEN Equation Set Object (unit) plug	COM
Belsim www.belsim.com	VALI III	Thermodynamic and physical properties socket	COM
Prosim S.A. www.prosim.net	ATOM	Thermodynamic and physical properties plug	COM
Prosim S.A.	Odysseo	Dynamic flash unit plug	COM
Infochem www.infochemuk.com	Multiflash 3.1	Thermodynamic and physical properties plug	COM
RSI www.rsi-France.com	INDISS	Thermodynamic and physical properties plug and socket Unit Operation plug and socket	COM COM
IFP www.ifp.fr	SPIP	Thermodynamic and physical properties plug	
IFP	FIBER	Unit Operation plug	
INP Toulouse-LGCCNRS www.inptoulouse.fr/lgc	Numerical Services Provider and Continuous Model Builder M&S	Numerical Solvers plug and socket Unit socket	CORBA COM
INP Toulouse-LGCCNRS	Flow sheet Server	Sequential Modular Specific Tools plug	CORBA
DECHEMA www.dechema.de	DETHERM	Physical Properties Data Bank Plug	COM
RWTH.LPT www.lfpt.rwthaachen.de		Numerical solvers plug	CORBA
RWTH.I5 www-i5.informatik.rwth-aachen.de	COM-CORBA Bridge Java Unit Skeleton Java Material Object Skeleton	Bridge Unit Operation plug Material Object and Material Template	COM CORBA CORBA CORBA
CO-LaN www.colan.org	Tester Suite (1)	Thermodynamic and physical properties plug and socket Unit Operation plug and socket	COM, CORBA through bridging
CO-LaN	Tester Suite (1)	MINLP socket PPDB socket SMST socket & plug	COM
NORSK HYDRO www.hydro.com		Heating Tank Unit Operation Fluent Wrap Unit Operation CASE test socket	CORBA
UPC www.upc.es/eq/	MOPEDR MOPP	PEDR Prototype Planning and Scheduling Package	CORBA CORBA

The CAPE-OPEN Interface System architecture is based on an object-oriented technology, which allows software systems to be constructed from binary software components. These components are able to "talk to each other" via defined interfaces. The software components can come from different vendors and may reside on the same machine or be on different machines across a network. The CAPE-OPEN Interface System is a standard means of connecting an external software component. The Interface can be thought of as a "socket" and "plug", which exchanges information between the two parts. The simulator and UO do not have to know anything about the internal coding and standards used by the other. The job of the interface is to translate requests for information or action, by either part, into something the other understands (CAPE OPEN Open Interface Specifications Unit Operations, 1999).

The connection between a process simulator and an external UO is depicted in Figure 4.6.

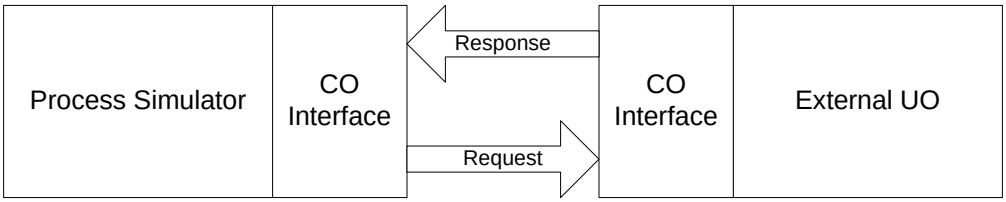


Figure 4.6 Stream data transfer between a process simulator and a UO

Basically, we can underline three concepts which well define a CAPE simulation: Physical Property Package (PPP), Material Object (MO) and Unit Operation (UO) components. The first one allows modelling the properties and the behaviour of the materials used or created by the process (thermodynamics calculations). The second one can be directly mapped to the concept of a Material Stream and provides access to all thermodynamics calculations. The last one represents physical processing unit operations and can perform specialized roles such as computing additional calculations to support process optimization (Pigeon *et al.,* 2005).

CO defines a comprehensive set of standard interfaces for unit operation modules being used within modular and steady-state PMEs. For a UO the concepts "stream" and "port" are defined in the specification. Stream is used to describe different internal representations that simulators use to record the different types of flows that exist in physical processes. Streams are divided into material streams, energy streams and information streams. Ports are used to represent a software interface that enables contents of the proprietary simulator streams to be accessed. Ports provide a standard way to fetch data from the simulator executive and to return data to the simulator executive (Karhela, 2002). A unit operation module may have several ports that allow it to be connected to other modules and to exchange material, energy or information with them. In the material case (which is also the most common), the port is associated with a MO. Ports are given directions (input, output, or input-output). Unit operation modules also have sets of parameters. These represent information that is not associated with the ports, but that the modules wish to expose to their clients. Typical examples include equipment design parameters (e.g. the geometry of a reactor, pressure drop for a valve, outlet hot

temperature for a heat exchanger) and important quantities computed by the module (e.g. the capital and operating cost of a reactor) (CO-LaN, 2007).

The main steps to develop a CO Unit Operation are presented in Figure 4.7.

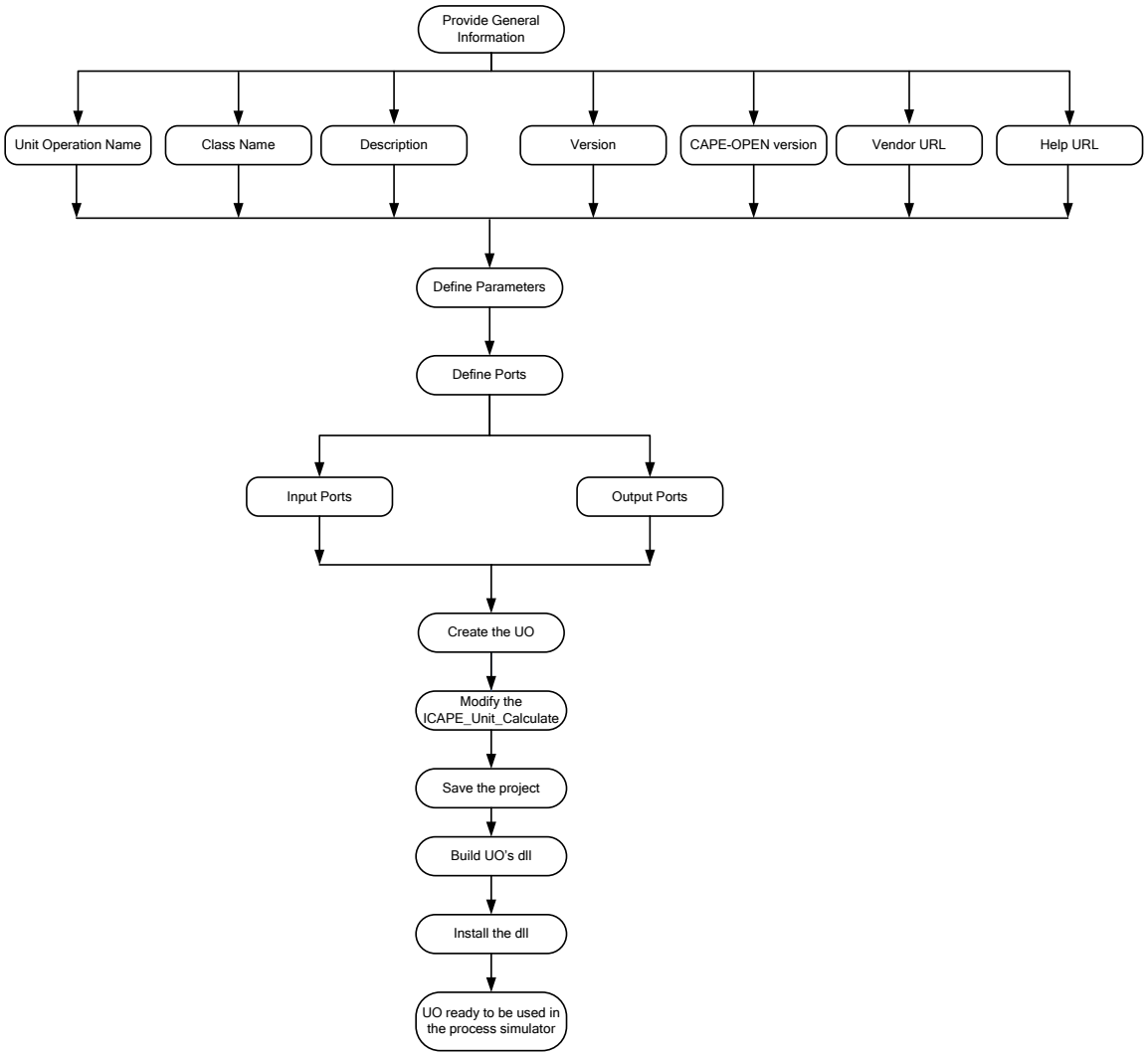


Figure 4.7 Main steps to develop a UO

A process simulator should be used to obtain environmental information during the process design phase. The goal is to evaluate the friendliness or unfriendliness of a chemical process, independently of the process simulator used, in other words, once the modules are developed, they are available for use anywhere. In this context, parts of the PSP Framework have been implemented as CAPE OPEN Unit Operations. The CAPE OPEN Unit Operations have been built using the CAPE OPEN Unit Wizard. The first CAPE OPEN Unit Wizard used has been the CAPE OPEN Unit Wizard (version 0.9.3). Later PSP Framework has been modified to be compatible with the new wizard version CAPE OPEN Unit Wizard (version 1.0). The CAPE OPEN Unit Wizard is available on CAPE OPEN Laboratories Network CO-LaN website (www.colan.org).

The characteristics (ports and parameters) of each CO Module developed for PSP Framework are presented in detail in the sections 4.2.2.1.1 and 4.2.2.2.2

4.1.3 Toxicological Database

Toxicity data are requested in order to calculate the environmental impact of chemical plants. These data are stored in databases. The starting point of the present work was the Impact Categories Database, kindly provided by Martin Todd, from U.S. Environmental Protection Agency (EPA). The initial database enclosed a number of 1707 substances. The database has been reconstructed as a relational database. Other chemical compounds have been added and their environmental impact has been estimated. The final database contains 4900 substances. Details regarding the database construction and implementation are given in *Chapter 5*.

4.2 Framework Structure

4.2.1 Framework Description

The implementation has been made according to Martins and Vincent (Martins *et al.,* (2006); Vincent *et al.,* (2005)). The two starting points for calculating the sustainability indicators are the process simulator and the database containing toxicity and risk phrases data. Four CAPE OPEN (CO) Modules have been developed beside the database. These modules are inserted in the process flow-sheet with the aim of extracting all the necessary data requested for further calculations.

The data obtained through the CO Modules are processed in the PSP software generating the sustainability indicators.

A general schema illustrating the above presented description is given in Figure 4.8.

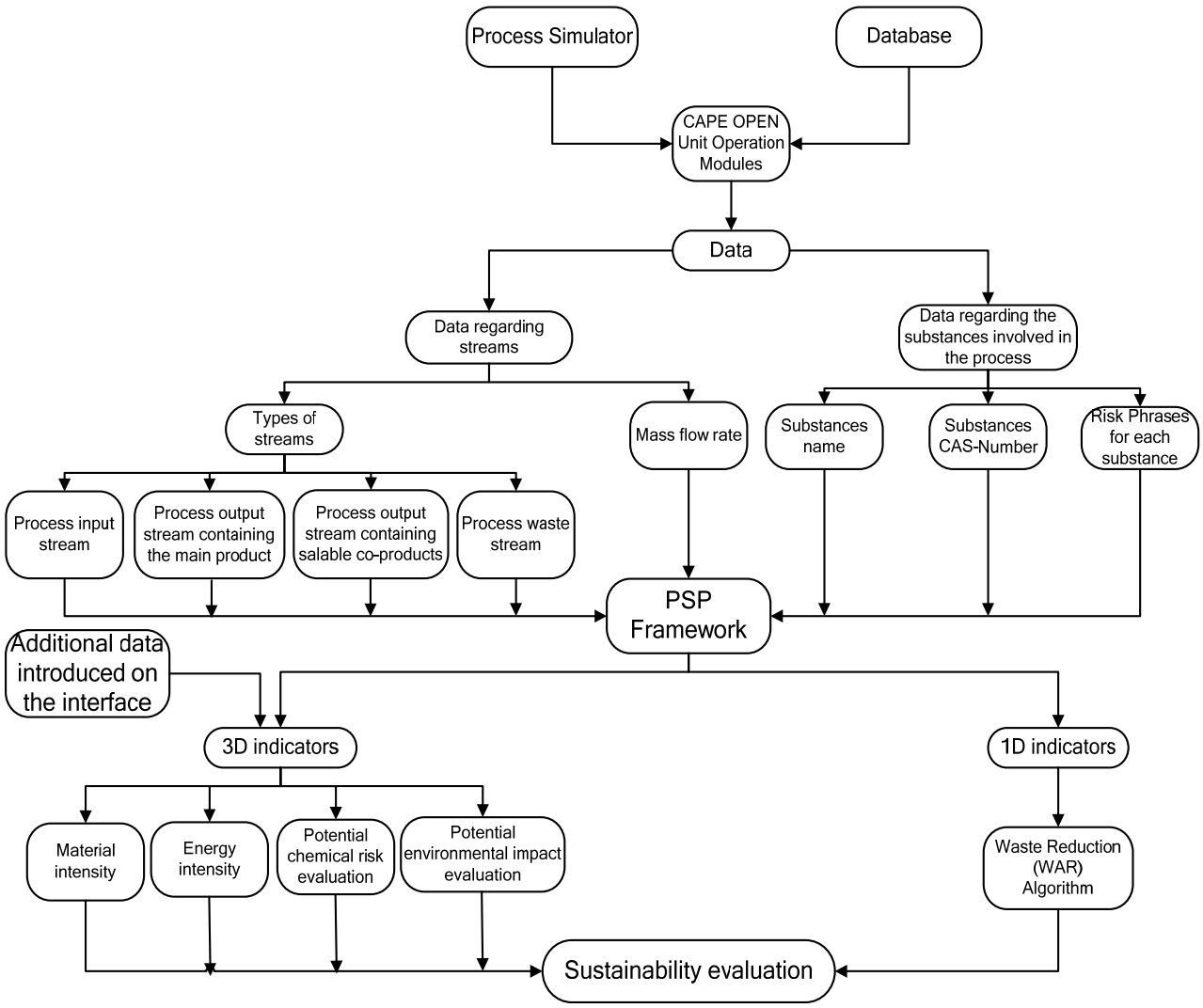


Figure 4.8 General schema of PSP Framework development

4.2.2 Framework Implementation

4.2.2.1 3D Programs

4.2.2.1.1 CO Modules Development

Two CO Modules have been developed in order to extract the requested data for the 3D indicators calculation from the process simulator.

The first module, called Promatrics, should be connected to the input and output process streams: its goal is to extract data for material intensity (MI), energy intensity (EI) and potential environmental impact (PEI) calculation. This module has four parameters, one input port and one output port. The parameter "name" is used to identify

the CO Module. The parameter "connection" is a good indicator of the CO Module position in the flow-sheet. The "water_usage" and "air_usage" parameters are essential for the MI indicator calculation.

The second CO Module, called Pro_Point_Risk, should be inserted in a plant strategic point, the most dangerous or risky, in order to extract data for the potential chemical risk (PCR) evaluation. This module has only one parameter, one input port and one output port. The parameter "name", the only parameter this module has, is used to identify the CO Module. The CO Modules' characteristics are summarized in Table 4.2.

Table 4.2 CO Modules properties used in the 3D indicators

CO MODULES NAME	**PORTS**	**PARAMETERS**	**PARAMETERS VALUES**
Promatrics	One input port One output port	name	From 1 to N, where N represents the number of the CO Modules (Promatrics.dll) inserted in the process flow-sheet
		connection	0 if Promatrics is connected with a process input stream
			1 if Promatrics is connected with a waste process stream
			2 if Promatrics is connected with an output process stream
			3 if Promatrics is connected with an output containing salable co-products
		water_usage	0 if Promatrics is connected with a stream in which the water is not present
			10 if Promatrics is connected with a stream in which the water is present but is not included in the MI calculation
			11 if Promatrics is connected with a stream in which the water is present and is included in the MI calculation
		air_usage	0 if Promatrics is connected with a stream in which the air (oxygen and nitrogen) is not present
			10 if Promatrics is connected with a stream in which the air (oxygen and nitrogen) is present but is not included in the MI calculation
			11 if Promatrics is connected with a stream in which the air (oxygen and nitrogen) is present and is included in the MI calculation
Pro_Point_Risk	One input port One output port	name	From 1 to N, where N represents the number of CO Modules (Pro_Point_Risk.dll) inserted in the process flow-sheet

After designing the CO Modules ports and parameters the next step is the CO development. The main steps of the CO Modules development are described in Table 4.3.

Table 4.3 Development of CO Modules for 3D indicators calculation

	STEPS	TOOLS	RESULTS
1. Development of CO Unit Operation (Promatrics and ProPoint_Risk)	1.1 Build the CO Unit Operation	CAPE-OPEN Unit Wizard	CO Unit Operation
	1.2 Modify the ICapeUnit_Calculate	VB, Toxicological Database	CO Unit Operation with WAR Algorithm
	1.3 Build the dll	VB	dll of CO
	1.4 Install the dll	VB	CO installed
	1.5 Test the CO Unit Operation	CAPE Tester	CO tested
2. Development of the process flow sheet	2.1 Design the flow sheet	Process Simulator	Chemical process flow-sheet
	2.2 Define the components	Process Simulator	Chemical process flow-sheet
	2.3 Define the thermodynamic method	Process Simulator	Chemical process flow-sheet
	2.4 Define the streams	Process Simulator	Chemical process flow-sheet
	2.5 Define the units operation	Process Simulator	Chemical process flow-sheet
	2.6 Design specifications	Process Simulator	Chemical process flow-sheet
3. Convergence of the process flow-sheet with the CO Modules included	3.1 Recognize the CO Unit Operation in process simulator	Process Simulator	CO Unit Operation recognized in the process simulator
	3.2 Insert the CO Unit Operation in the chemical process flow sheet (Promatrics on the input and output process streams and ProPoint_Risk in the most dangerous or risky point)	Process Simulator	Process flow- sheet for the chemical process with CO Modules
	3.3 Run the simulation	Process Simulator	Chemical process flow-sheet convergence
4. Get the results			CAS_data.txt Energy.txt material_intensity_data.txt quantity_class_data_risk.txt risk_phrases.txt

As it can be noticed from Table 4.3, after running the simulation, with the CO Modules inserted in the process flow-sheet, five text files are created: CAS_data.txt, Energy.txt, quantity_class_data_risk.txt, material_intensity_data.txt, risk_phrases.txt.

The information contained in these files is used in the calculation of the 3D indicators (MI, EI, PCR, and PEI). A logical schema containing all the steps for the 3D indicators calculation is presented in Figure 4.9.

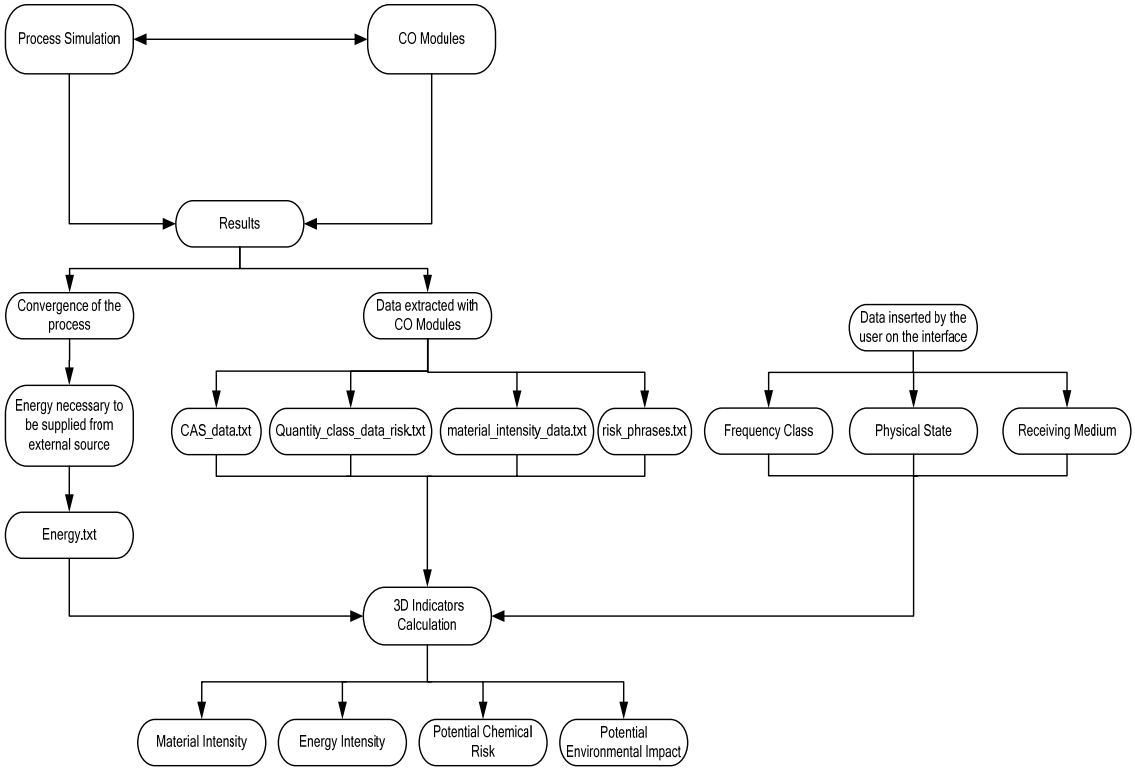


Figure 4.9 Logical schema for the 3D indicators calculation

One important issue of the CO Modules, used in the 3D indicators calculation, is the access to the database. The database contains risk phrases for 2726 substances.

The connection between the CO Modules and the database is done by using ADO (ActiveX Data Objects) technology. The R-phrases are searched in the database as a function of the CAS-Number. The access methodology is described in Figure 4.10.

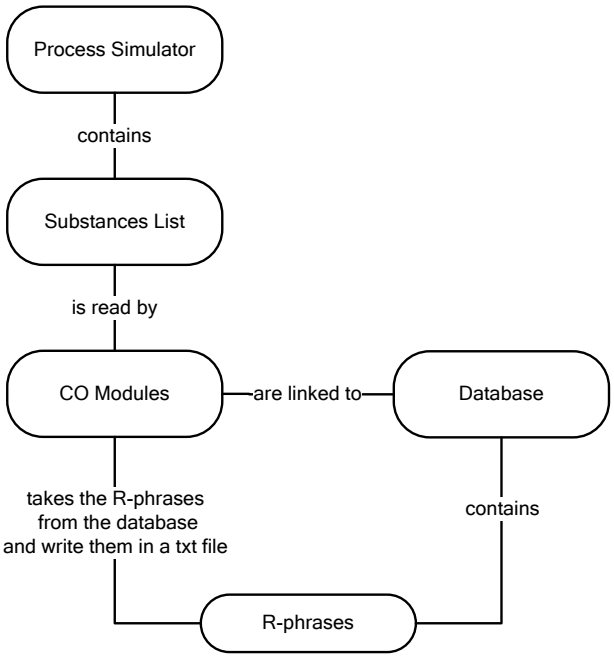


Figure 4.10 Logical schema to access the database using the CO Modules

4.2.2.1.2 Program Interface

The schemas illustrated in the previous section have been implemented in Visual Basic (version 6.0). The graphical user interfaces of the software are presented in the next part and the User Manual is attached (see ANNEX 2).

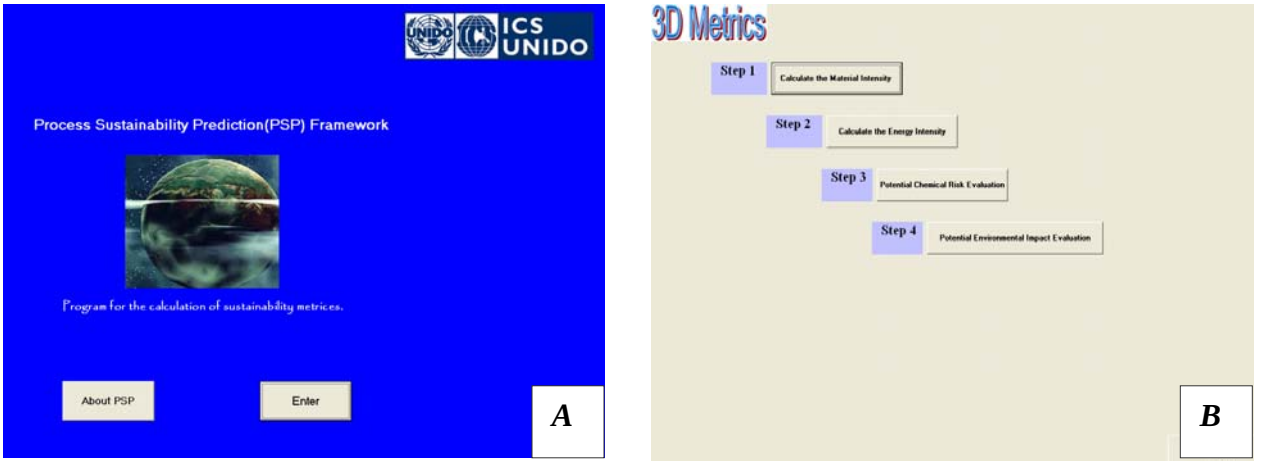
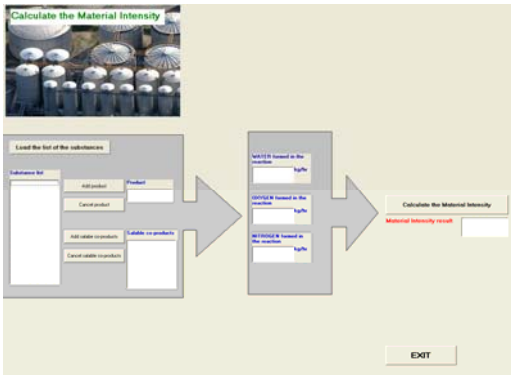
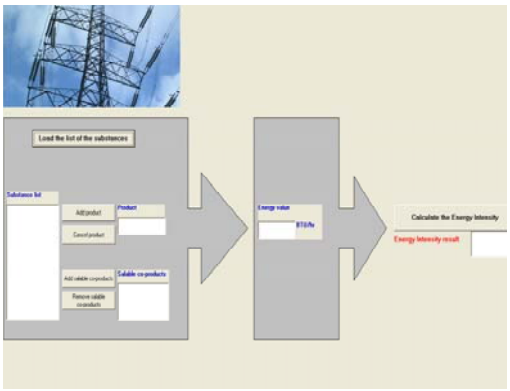


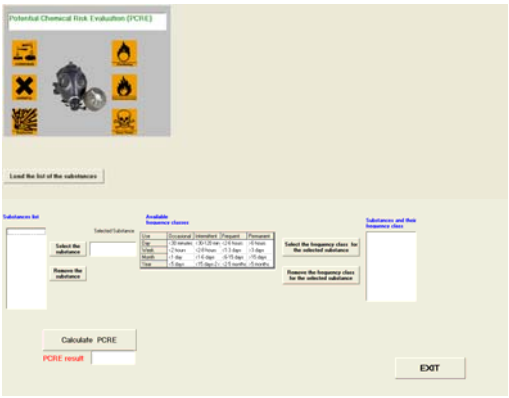
Figure 4.11 Graphical user interfaces for A) PSP software, B) 3D Indicators (Metrics)



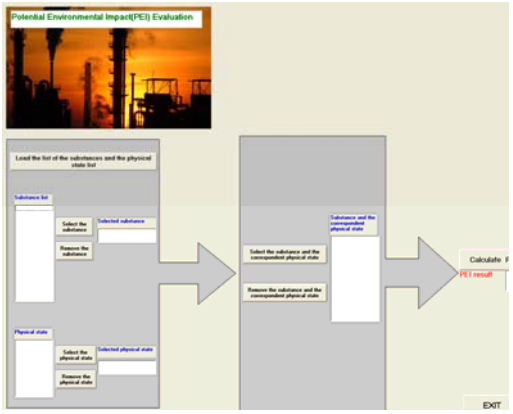
Step 1: Material Intensity Calculation



Step 2: Energy Intensity Calculation



Step 3: Potential Chemical Risk Evaluation



Step 4: Potential Environmental Impact Evaluation

4.2.2.2 1D Programs

A general schema regarding the WAR Algorithm implementation is presented in Figure 4.12. The schema contains three main steps:

Step 1- Weighting Factors Interface Development

Step 2- CAPE OPEN Modules Development

2.1 COWAR-WAR Algorithm implemented in a CAPE OPEN Module

2.2 Energy generation process implemented in a CAPE OPEN Module

Step 3- Final Interface, for the calculation of potential environmental indexes (PEI calculation), development

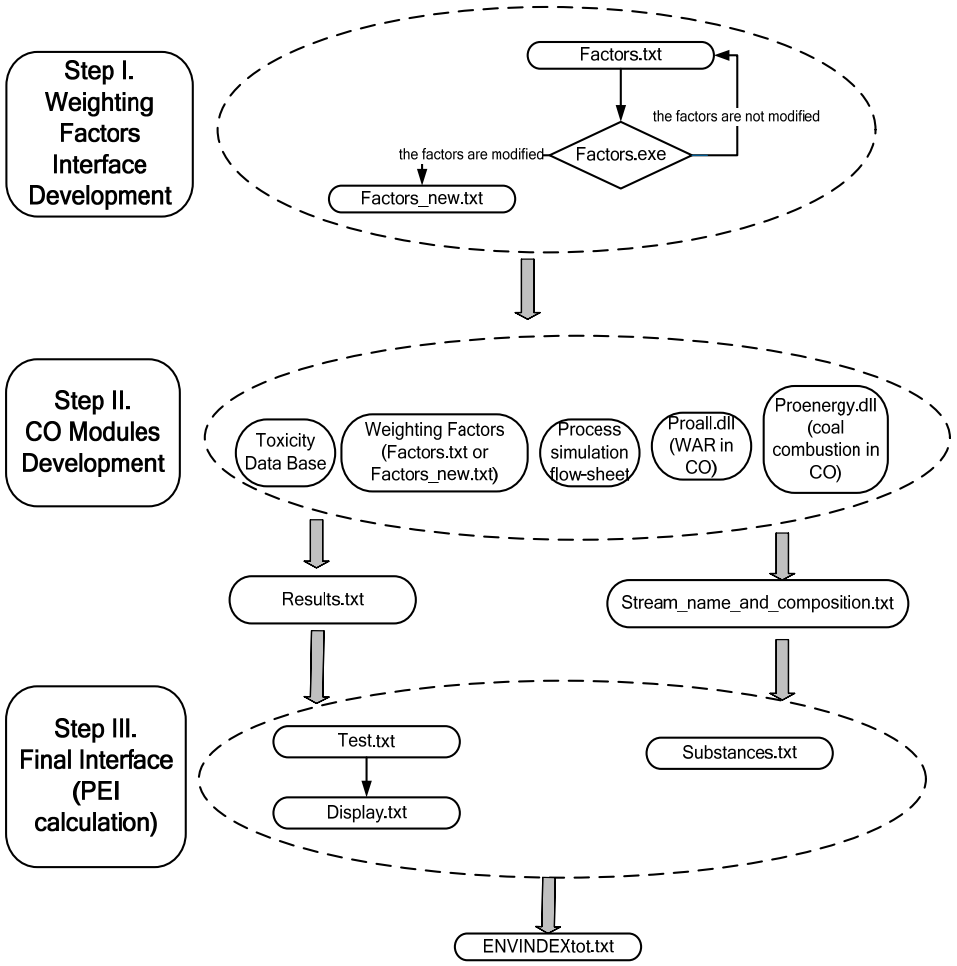


Figure 4.12 Main steps of WAR Algorithm implementation

4.2.2.2.1 Weighting Factors Interface

The weighting factors are essential for WAR Algorithm because they permit the combination of the impact categories according to local needs and policies. Aiming at offering the possibility of modifying the factors, the following graphical user interface has been created. The main development steps are presented in the next section.

For calculating the $\dot{I}_{in}^{(cp)}$ - the potential environmental impact input of the chemical process, $\dot{I}_{out}^{(cp)}$ - the potential environmental impact output of the chemical process, $\dot{I}_{in}^{(ep)}$ - the potential environmental impact input of the energy generation process, $\dot{I}_{in}^{(ep)}$ - the potential environmental impact output of the energy generation process, the overall potential environmental impact for all the substances are required. The overall potential environmental impact of chemical k, ψ_k, can be determined by summing up the specific potential environmental impact of chemical k, ψ_{kl}^{s}, on all of the possible impact categories (Young *et al.*, 1999):

$$\psi_k = \sum_l \alpha_l \psi_{kl}^{s} \tag{4.1}$$

where α_l represents the relative weighting factor of impact category l.

The relative weighting factors, α_l, are numbers used to express the relative importance of the impact categories. They should range between 0 and 1 (according to local needs and policies). Some examples of the weighting factors are presented below:

- PCOP would be weighted more heavily than other impacts in an area that suffers from smog.
- ATP would be weighted more heavily than other impacts if the process plant is discharging in a water body.
- HTPI, HTPE would be ranked higher then other effects for chemical that normally come in contact with humans
- AP would have small values if the chemical plant is situated in the dessert.

In the previous versions of WAR Algorithm implementation, the weighting factors were considered constants. This implied that all the impact categories were equally important. In that format, the user had no possibility to modify the factors according to his needs. The interface developed here permits the modifications of the impact categories. The interface is presented in Figure 4.13.

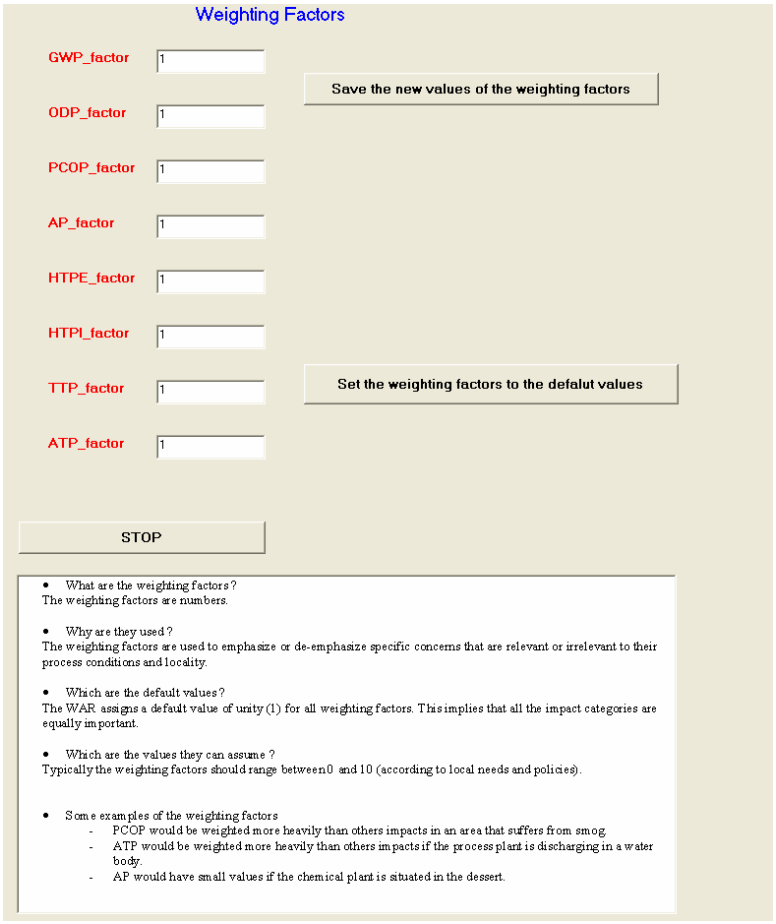


Figure 4.13 Weighting Factors Interface

The text file, containing the default weighting factors values, is read and displayed on the interface. The user has the possibility to modify the default values.

The program also permits to restore the impact categories values to default ones. If the default impact categories values are modified, the new values are used in further calculation, otherwise, the default values are read and processed. The procedure is explained in Figure 4.14.

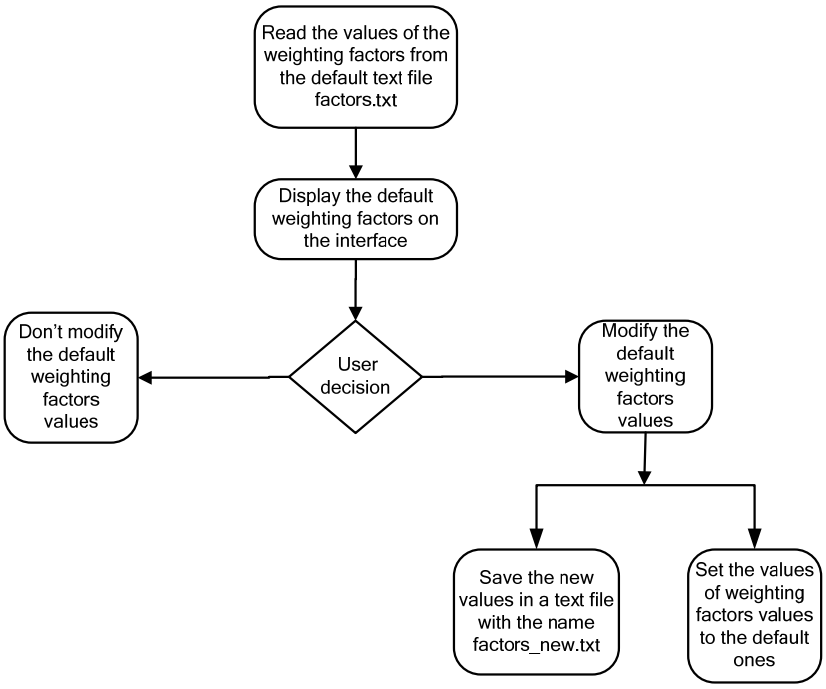


Figure 4.14 Logical schema of the Weighting Factors Interface

4.2.2.2.2 CO Modules Development

COWAR Module

Introduction

As is has been mentioned in section 4.1.2, a process simulator should be used in order to obtain the environmental information during the process design. The goal is to evaluate the friendliness or unfriendliness of a chemical process, independently of the process simulator used. The equations of the WAR Algorithm have been implemented in a CAPE OPEN module called COWAR.

Development

The COWAR module is a unit operation that has one input port, one output port and three parameters. The process type, position and name of the CO Unit Operation have been defined as real parameters. With regard to the necessity of using three parameters, it should be specified that: the process type parameter is used to identify the type of process (chemical or energy generation process); the position parameter is needed for the location detection of the CO in the flow sheet (the CO could be on an input, output, intermediary or waste stream of the process); and the name parameter is needed to find the CO units which were first classified using the position parameter. The values assumed by the parameters are presented in Table 4.4.

Table 4.4 Values assumed by the COWAR parameters

CHEMICAL PROCESS		ENERGY GENERATION PROCESS	
Parameter Name	**Parameter Value**	**Parameter Name**	**Parameter Value**
process_ type	0	Process type	1
cape_ position	0 (for input stream)	CO position	0 (for input stream)
	1 (for waste stream)		1 (for waste stream)
	2 (for output product stream)		
	3 (for internal stream of chemical process)		
cape_ID	0 1 . N-number of CO modules inserted in the process	CO name	0 1 . N-number of CO modules inserted in the process

As mentioned in section 4.1.2, the CO Unit Operation Module creation is facilitated by a wizard. The CAPE OPEN Unit Wizard does not generate all the code needed for a complete unit operation. In this regard, the ICapeUnit_Calculate subroutine of the Visual Basic code should be modified. The ICapeUnit_Calculate subroutine is also connected to a database (of the Environmental Protection Agency (EPA)), which contains the Environmental Impact Categories for many substances. The COWAR Module is able to assign the input stream properties to the output stream. In other words, the output stream is equal to the input stream (flow-rate, temperature, pressure, composition). The subroutine reads from the database the normalized values for the environmental impact categories of the substances involved in the chemical process. The Environmental Impact Indexes ($\dot{I}_{out}^{(t)}$ - the total rate of impact output, $\hat{I}_{out}^{(t)}$ the total impact output per mass of products, $\dot{I}_{gen}^{(t)}$ - the total rate of impact generation, and $\hat{I}_{gen}^{(t)}$ - the total impact generated per mass of product) are calculated using the potential environmental impact balance equations around the chemical process and the energy generation process. The schema containing the main steps, tools and expected results of the methodology described above is presented in Table 4.5.

Table 4.5 The WAR Algorithm implementation in a CO Unit Operation

	STEPS	**TOOLS**	**RESULTS**
1. CO Unit Operations Development (Proall.dll and Proenergy.dll)	1.1 Build the CO Unit Operation	CAPE-OPEN Unit Wizard	CO Unit Operation
	1.2 Modify the ICapeUnit_Calculate	VB, EPA Database	CO Unit Operation with WAR Algorithm
	1.3 Build the dll	VB	dll of CO
	1.4 Install the dll	VB	CO installed
	1.5 Test the CO Unit Operation	CAPE Tester	CO tested
	2.1 Design the flow- sheet	Process Simulator	Chemical process flow-sheet
	2.2 Define the components	Process Simulator	Chemical process flow-sheet

2. Process flow-sheet Development	2.3 Define the thermodynamic method	Process Simulator	Chemical process flow-sheet
	2.4 Define the streams	Process Simulator	Chemical process flow-sheet
	2.5 Define the Unit Operations	Process Simulator	Chemical process flow-sheet
	2.6 Design specifications	Process Simulator	Chemical process flow-sheet
3. Chemical process impact calculation	3.1 Recognize the CO Unit Operation in process simulator	Process Simulator	CO Unit Operation recognized in the process simulator
	3.2 Insert the CO Unit Operation in the chemical process flow-sheet	Process Simulator	Chemical process flow- sheet with CO Modules inserted
	3.3 Run the simulation	Process Simulator	The chemical process flow-sheet convergence
Energy generation process impact calculation	3.4 Insert the CO Unit Operation in the energy generation process flow-sheet	Process Simulator	The energy generation process flow-sheet
	3.5 Run the simulation	Process Simulator	The energy generation process convergence

Details regarding the development of COWAR using the CAPE OPEN Unit Wizard are presented in ANNEX 3.

CO Module containing the energy generation process

Introduction

For a complete estimation of the environmental impact of a chemical plant, not only the chemical process, but also the energy process connected to the chemical process should be considered. Following this logic, the energy generation process has been implemented too using the CO methodology.

Development

The starting point in the implementation of the energy process has been the coal combustion process developed in Aspen Plus (Aspen Plus, 2003).

The material and energy balance equations of coal combustion process have been implemented in a CO Module. This Module reads the quantity of energy necessary to be supplied from external sources. From the energy value, the module calculates the gaseous emissions.

The emissions stream is linked to COWAR for the calculation of the environmental impact of the energy process. The schema is summarized in Figure 4.15.

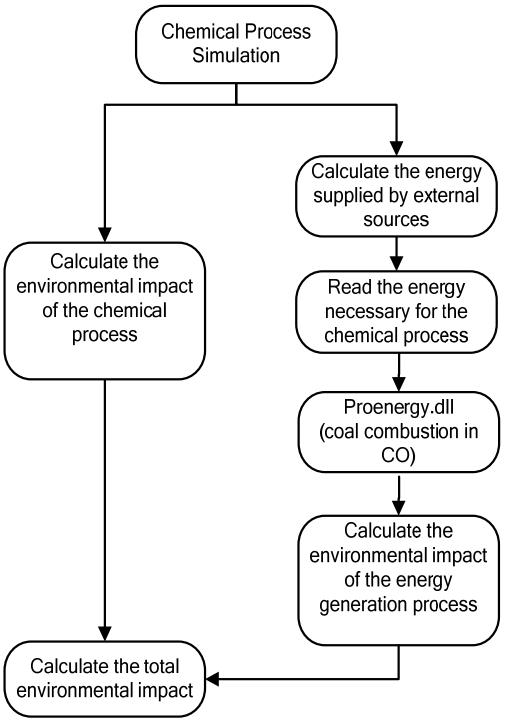


Figure 4.15 Energy generation process schema

The energy can be obtained from coal or another fuel. The application developed here uses coal as fuel and other energy sources will be considered in the future.

The remarks made in Section 3.3 have been taken into consideration when the CO Module for energy generation process has been implemented.

Details regarding the development of the energy generation process implemented in CO are presented in ANNEX 4.

It should also be specified that it would be ideal to use renewable energy, which has zero environmental impact.

4.2.2.2.3 Final Interface

The final interface has been developed in order to calculate the environmental indexes of a chemical process. This represents the post-processing phase. Using the environmental indexes, different processes can be compared and the best solution, from the environmental point of view, can be chosen.

The results of the process simulators are two text files (results.txt and stream_name_and_composition.txt). A brief description of these files is given below:

Results.txt file contains:

- CO Module *type* - if the module is situated on a chemical process or on the energy generation process
- CO *name*- CO Module's name
- CO Module *index* - if the CO module is situated on:

- an input stream of a chemical process

- an output stream of a chemical process
- a waste stream of a chemical process
- an input stream of energy generation process, or, on a waste stream of the energy generation process),

- *value* - value calculated using the mass composition and toxicological data. These values are used in the final environmental indexes calculation.
- *mass flow rate* of the stream where the CO Module is inserted

Stream_name_and_composition.txt file contains:

- CO Module *type* - if the module is situated on a chemical process or on the energy generation process
- CO Module *index* - if the CO module is situated on:

- an input stream of the chemical process
- an output stream of the chemical process
- a waste stream of the chemical process
- an input stream of energy generation process, or, on a waste stream of the energy generation process),

- the *name* of chemical substance(s)
- *mass flow rate* for each chemical substance

The contents of these files are processed in the final interface according to the schema presented in Figure 4.16.

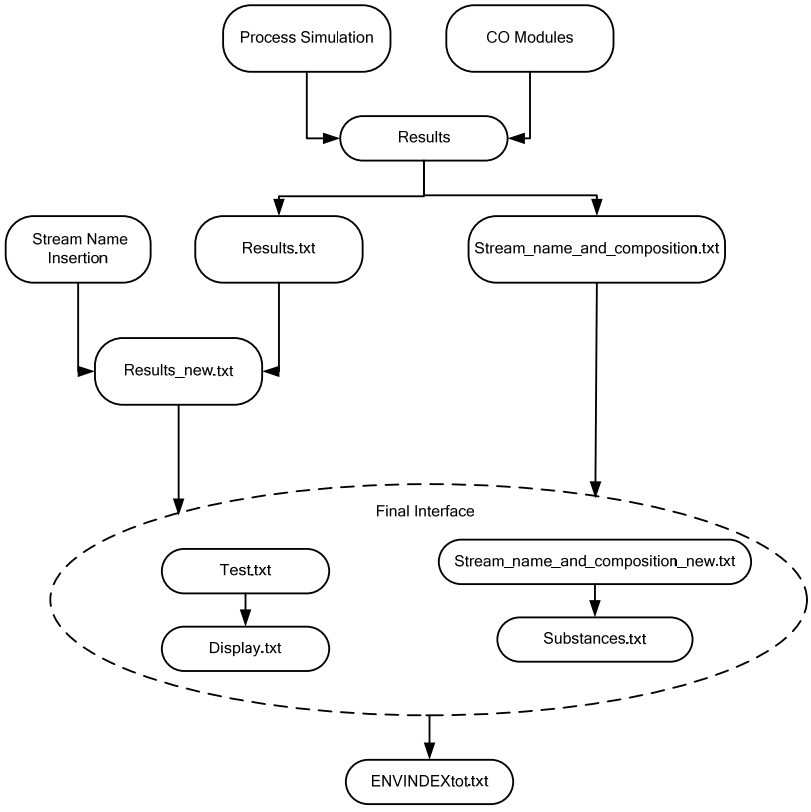


Figure 4.16 Final Interface schema

The VB6 code rearranges the results_new.txt file, containing the CO modules, in such a way that each CO module appears only once (the last value of each CO module is stored). This operation is requested when in the results.txt file the same CAPE OPEN module with the same parameters is repeated (this happens when the CO module is situated on a recycle loop). This ensures the user that only the last value of that specific CO module is taken into account. The new file created is called test.txt file. The test.txt file is used to create another file (display.txt) which is displayed on the interface.

Following the same logic, the stream_name_and_composition.txt is rearranged too, in such a way that only the last values for the chemical substances flow rates, correspondent to the triplet (type, name, index) are taken into account. The new text file created is stream_name_and_composition_new.txt. From this file some information, more exactly the chemical substance names, will be displayed on the interface (substances.txt file).

Environmental indexes are calculated in the Final Interface, using the last value of each unit operation and the quantity of selected products.

The interface has been implemented in Visual Basic version 6.0 (VB6). Figure 4.17 presents the graphical user interface for the environmental indexes calculation.

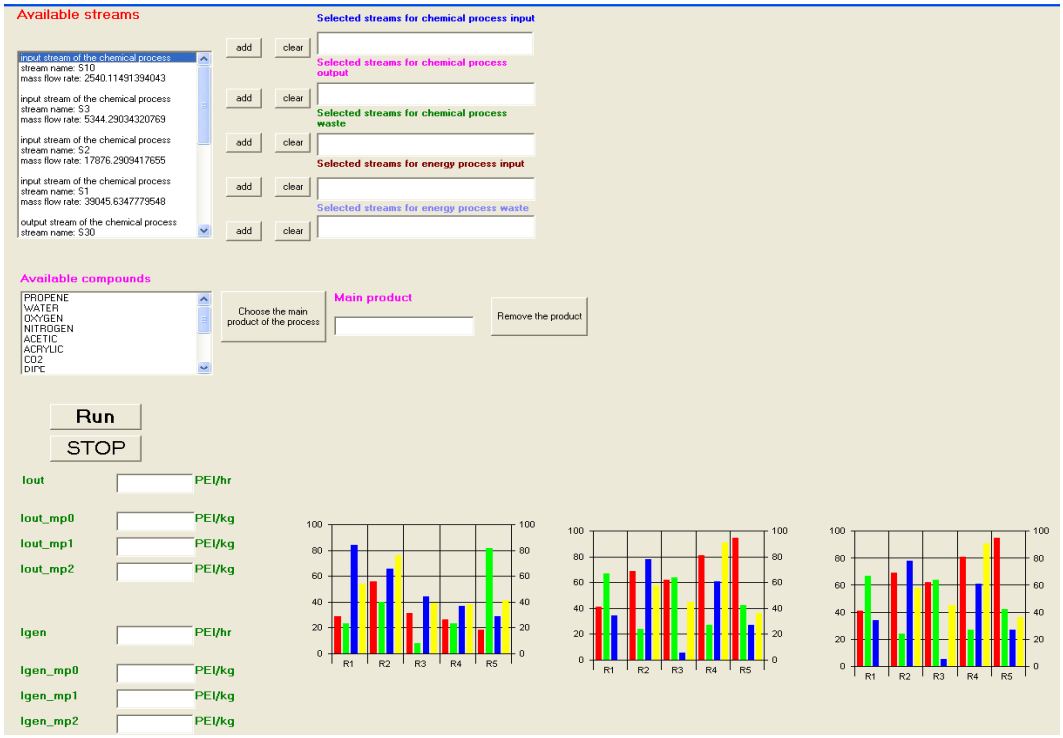


Figure 4.17 Final Interface (PEI calculation)

Four types of environmental indexes are calculated in the Final Interface. The meaning of the indexes is presented in Table 4.6 and the User Manual is attached (ANNEX 5).

Table 4.6 Potential Environmental Indexes

PSP NAME	WAR NAME*	MEANING	UNITS OF MEASURE
Iout	$\dot{I}_{out}^{(t)}$	The total rate of PEI leaving the system	Units of PEI/time
Iout_mp	$\hat{I}_{out}^{(t)}$	The total rate of PEI leaving the system per mass of product (main product of chemical process)	Units of PEI/mass of product
Igen	$\dot{I}_{gen}^{(t)}$	The total rate of PEI generated within a system	Units of PEI/time
Igen_mp	$\hat{I}_{gen}^{(t)}$	The total rate of PEI generated within a system per mass of product (main product of chemical process)	Units of PEI/mass of product

*names correspondent to the WAR Algorithm theory (see section 3.3 *Environmental Impact Indexes*)

Chapter 5

Toxicological Database

Summary

This chapter is dedicated to the toxicological database used in the PSP Framework.

The logical and conceptual schema, as well as the integration and implementation of the database are reported.

"*Data is a precious thing and will last longer than the systems themselves.*"
Tim Berners-Lee

5.1 Database Introduction

Databases are the primary form of storage in both today's online and offline worlds. Databases are used to store millions of different types/combinations of information (MySQL, 2007).

A database is a set of data that has a regular structure and that is organized in such a way that a computer can easily find the desired information.

The contents of a database can hold a variety of different elements, such as:

- Schema: represented by the structure (how many tables, how many records, etc.)
- Instance: represented by the content
- Data: organized in records
- Hardware
- Software
- Users

Databases are classified according to their organizational approach. Several basic types of database models have been developed, including flat, hierarchical, network and relational. The most prevalent approach is the relational database. Dr. E.F.Codd proposed a new theory of representing data structure in 1970. He also created 12 famous rules for a relational database. A relational database is a way of organizing data such that it appears to the user to be stored in a series of interrelated tables (BELUG, 2007). All data are represented in tabular form. The description of a particular entity is provided by the set of its attribute values, stored as one row or record of the table. Similar items from different records can appear in a table column. The relational approach supports queries that involve several tables by providing automatic links across tables (Answers, 2007a).

There are different types of relationship:

- one-to-one (1:1) relationship occurs where, for each instance of table A, only one instance of table B exists, and vice-versa.
- one-to-many (1:m) relationship is where, for each instance of table A, many instances of the table B exist, but for each instance of table B, only once instance of table A exists.
- many to many (m:n) relationship occurs where, for each instance of table A, there are many instances of table B, and for each instance of table B, there are many instances of the table A (Gilfillan, 2002)

Different design succession schemas are used to describe a database. Figure 5.1 summarizes the main steps of the database design.

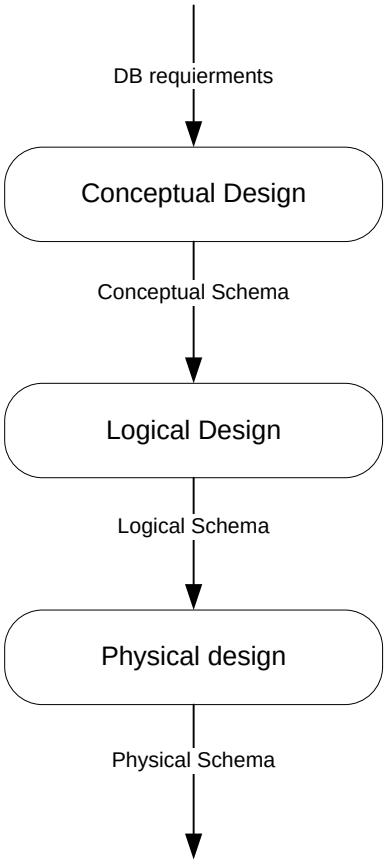


Figure 5.1 Steps of the database design

The toxicological database developed and implemented in the present work is a relational database.

As it has been mentioned in section 4.1.3, the starting point for the development of the toxicological database has been the database of the Environmental Impact Categories developed by the Environmental Protection Agency (EPA). EPA's database has been created in Microsoft Office Access and contains 1,707 records enclosing the name of the substance, the CAS-Number, the molecular weight, the class the substance belongs to, the formula, the toxicity data values and the toxicity data sources.

One of the goals of the present research was to recreate and improve the existing database. This goal has been achieved using two main approaches:

- inserting other substances and the correspondent environmental impact categories from scientific literature
- calculating different environmental impact categories using molecular modelling methods (see *Chapter 6*)

The database development and implementation is presented in a logical sequence (following the schema presented in Figure 5.1) in the next section.

5.2 Database Conceptual Schema

A conceptual schema or conceptual data model is a map of concepts and their relationships. It describes the things of significance to an organization (entity classes), about which it is inclined to collect information, and characteristics of (attributes) and associations between pairs of those things of significance (relationships) (Wikipedia, 2007d). The conceptual schema hides the details of the physical storage structures and concentrates, basically, on entities, relationships, and constraints (Management-Hub.com, 2007).

The conceptual schema of the toxicological database is presented below.

Requirements in natural language

A database containing toxicological data for different chemical substances should be created. For each substance, identified by a code, the CAS-Number (Chemical Abstract Service-Number), the name, the class, the formula should be stored.

Each substance/chemical compound may have different names/synonyms. There are different sources from where the synonyms can be achieved.

The toxicity data that should be inserted in the database are: logKow, Human Toxicity Potential by Ingestion-HTPI (lethal dose for rat-RatOralLD50), Human Toxicity Potential by Exposure-HTPE, Aquatic Toxicity Potential (lethal concentration, $LC_{50,}$ for Fathead Minnow), Global Worming Potential-GWP, Ozone Depletion-OD, Photochemical Oxidation Potential PCOP, Aquatic Potential-AP, Human-Health, Aquatic Oxygen Demand, Ecotoxicity to aquatic life and Eutripication. Additional information like the toxicity data sources can be also given for each impact categories.

The risk and safety phrases, associated to each compound, should be also stored in the database. R and S-Phrases may be obtained from different sources. The significance of each phrase should be explained too.

Glossary of terms

Table 5.1 Database glossary of terms

TERM	DESCRIPTION	SYNONYMS	LINKS
Chemical substance	Any material with a definite chemical composition	Chemical compound	Synonym Impact Categories' values R-Phrases S-Phrases
Synonym	A different name for the same chemical substance	Different name	Chemical Substance Synonym Reference
Impact Categories' value	A specific group of the potential environmental impact (e.g. GWP, ODP, PCOP, AP, HTPI, HTPE, TTP, ATP)		Chemical Substance Reference DB Kow LC50Notes LD50Notes HTPINotes LC50Source LD50Source

Risk Phrases	Phrases used in the classification, packaging, labelling and provision of information on dangerous substances	R-Phrases	Chemical Substance Risk Phrase Meaning Risk Phrase Source
Safety Phrases	A system of hazard codes and phrases for labelling dangerous chemicals and compounds	S-Phrases	Chemical Substance Safety Phrase Meaning Safety Phrase Source

Requirements specifications

- *General phrases*: A database with toxicological data should be created.
- *Requirements regarding the chemical substance*: For each substance, identified by a code, the CAS-Number (Chemical Abstract Service-Number), the name, the class and the formula should be stored.
- *Requirements regarding the synonyms*: For each synonym, the name and the source of the synonym should be introduced.
- *Requirements regarding the toxicity data*: Toxicity values for each chemical substance should be supplied. Additional information, such as the sources of toxicity or methods used to calculate the toxicity data, can be given for the impact categories under study.
- *Requirements regarding the risk phrases*: The risk phrases associated with each compound should be also reported. The R-Phrases may be obtained from different sources. The significance of each R-Phrases should be also given.
- *Requirements regarding the safety phrases*: The safety phrases associated with each compound should be also reported. The S-Phrases may be obtained from different sources. The significance of each S-Phrases should be supplied also.

Entity- Relationship (E-R) Diagram

Entity Relationship Modelling (E-R modelling) is by far the most common way of expressing the analytical result of an early stage in the construction of a new database (Development Cycles, 2007). The E-R data model views the real world as a set of basic objects (entities) and relationships among these objects (Zaïane, 1995). An entity is a piece of data, an object, or concept about which data is stored (Webopemedia, 2007). In a relational database, all entities have bonds between them, expressed as relationships. A relationship is a link between two entities and it tells us something about which relationships exists between our entities (Development Cycles, 2007).

The entity-relationship diagram for the toxicological database is presented in Figure 5.2.

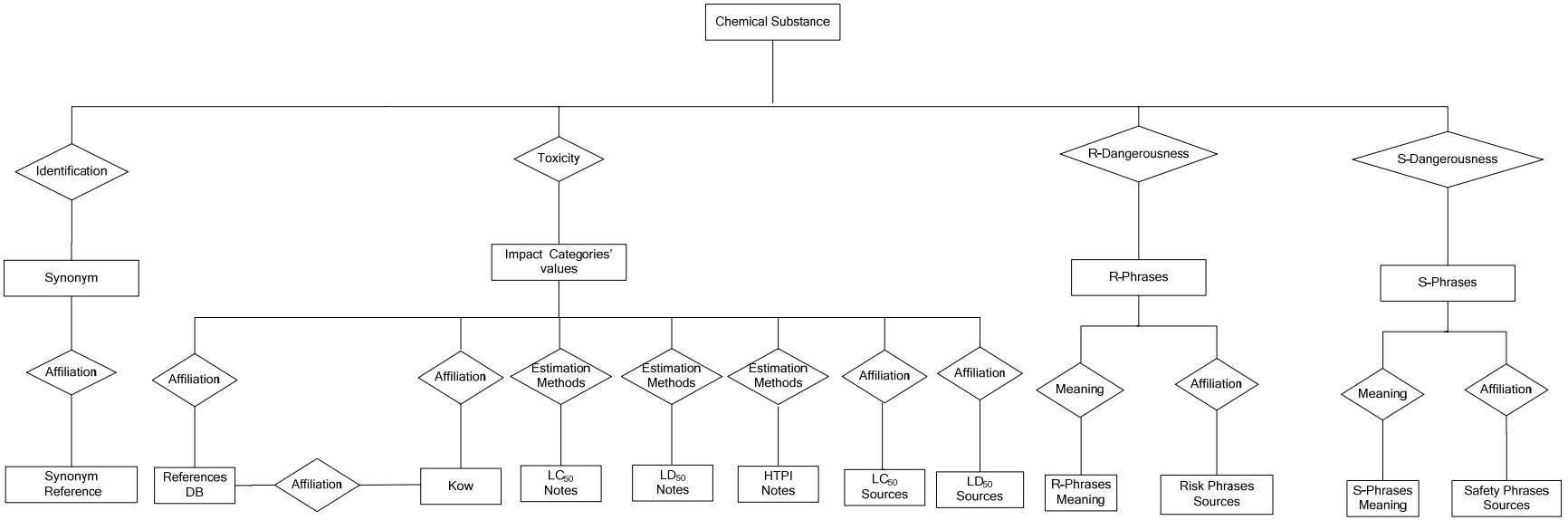


Figure 5.2 E-R Schema

The entity and relationship analyses are presented in the next section.

Entity Analysis

Tables 5.2-5.18 contain details regarding all the entities present in the toxicological database.

Table 5.2 "Chemical Substance" entity analysis

	CHEMICAL SUBSTANCE
ID_chemical	A unique code used to identify a chemical substance.
CAS	The Chemical Abstract Service Number correspondent to each chemical substance.
Chemical Name	The IUPAC name of the chemical substance.
MW	The molecular weight for the chemical substance.
Class	The class the substance belongs to.
Formula	The brut formula.

Table 5.3 "Synonym" entity analysis

	SYNONYM
ID_Synonym	A unique code used to identify a synonym.
Synonyms	Different names given to a chemical substance.

Table 5.4 "Synonym Reference" entity analysis

	SYNONYM REFERENCE
ID_Synonyms Reference	A unique code used to identify the references of the synonyms.
References_Synonyms	Sources (DB, web sites) from where the synoym(s) has/have been taken.

Table 5.5 "Impact Categories' values" entity analysis

	IMPACT CATEGORYS' VALUES
ID_value	A unique code used to identify a record for the Impact Categories' value.
LD50RatValue	Lethal dose (used in the Human Toxicity Potential by Ingestion and Terrestrial Toxicity Potential' calculation)
OSHA_TWA_Value	Human Toxicity Potential by Inhalation or Dermal Exposure.
FHM_LC50_Value	Lethal concentration for Fathead Minnow (used in the Aquatic Toxicity Potential' calculation)
GWP_Value	Global Warming Potential.
OD_Value	Ozone Depletion Potential.
PCO_Value	Photochemical Oxidation Potential.
AP_Value	Acidification Potential.
ETP_1,4dichlorobenzene_air	Air Toxicity Potential reported to 1,4 dichlorobenzene.
ETP_1,4dichlorobenzene_water	Aquatic Toxicity Potential reported to 1,4 dichlorobenzene.
human_health	The Occupational Exposure Limits set by the UK Health and Safety Executive.
HTP_1,4dichlorobenzene_air	Human Toxicity Potential reported to 1,4 dichlorobenzene (air).
HTP_1,4dichlorobenzene_water	Human Toxicity Potential reported to 1,4 dichlorobenzene (water).
Aquatic_oxygen_demand	The maximum potential of emissions into water able to remove dissolved oxygen, that would otherwise support fish and other aquatic life.

Ecotoxicity_to_aquatic_life	Ecotoxicity to aquatic life.
Eutrophication_water	An increase in chemical nutrients - typically compounds containing nitrogen or phosphorus - in an ecosystem.
Eutrophication_air	An increase in chemical nutrients - typically compounds containing nitrogen or phosphorus - in an ecosystem

Table 5.6 "Reference DB" entity analysis

	REFERENCE DB
ID_ref	A unique code used to identify a reference source for the Impact Categories' value.
referenceDB	The DB from where the Impact Categories' value has been taken.

Table 5.7 "Kow" entity analysis

	Kow NOTES
ID_Kow	A unique code used to identify the octanol-water partition coefficient.
Reference_Kow_DB	Octanol-water partition coefficient source.
LogKowValue	The logarithmic value of the octanol-water partition coefficient.

Table 5.8 "LC_{50} Notes" entity analysis

	LC_{50} NOTES
ID_FHM_LC50_Notes	A unique code used to identify the LC_{50} Notes.
FHM_LC50_Notes	LC_{50} Notes for Fathead Minnow.
FHM_LC50_NotesMeaning	LC_{50} Notes Meaning.

Table 5.9 "LD_{50} Notes" entity analysis

	LD_{50} NOTES
ID_LD50Rat_Notes	A unique code used to identify the LD_{50} Notes.
LD50RatNotes	LD_{50} Notes for Rat.
LD50RatNotesMeaning	LD_{50} Notes Meaning.

Table 5.10 "HTPI Notes" entity analysis

	HTPI NOTES
ID_OSHA_TWA	A unique code used to identify the HTPI Notes.
OSHA_TWA_Notes	HTPI Notes.
OSHA_TWA_NotesMeaning	HTPI Notes Meaning.

Table 5.11 "LC_{50} Sources" entity analysis

	LC_{50} SOURCES
ID_FHM_LC50	A unique code used to identify the LC_{50} Sources.
FHM_LC50_Sources	LC_{50} Sources for Fathead Minnow.
FHM_LC50_SourcesMeaning	LC_{50} Sources Meaning.

Table 5.12 "LD_{50} Sources" entity analysis

LD_{50} SOURCES	
ID_LD50Rat_Sources	A unique code used to identify the LD_{50} Sources
LD50RatSources	LD_{50}Sources for Rat.
LD50RatSourcesMeaning	LD_{50} Sources Meaning.

Table 5.13 "R-Phrases" entity analysis

R-PHRASES	
ID_Risk	A unique code used to identify the risk correspondent to each chemical substance.

Table 5.14 "R-Phrases Meaning" entity analysis

R-PHRASES MEANING	
ID_Risk_Meaning	A unique code used to identify each record, which contains a risk phrase.
R-Phrases	Risk Phrases e.g. R-10, R50/53.
Risk_Phrases_ Meaning	The meaning for each R-Phrase.

Table 5.15 "Risk Phrases Sources" entity analysis

RISK PHRASES SOURCES	
ID_Risk_Source	A unique code used to identify the source of the risk phrases.
Risk_Source	The source name/web link from where the R-Phrases have been taken.

Table 5.16 "S-Phrases" entity analysis

S-PHRASES	
ID_Safety	A unique code used to identify the safety correspondent to each chemical substance.

Table 5.17 "S-Phrases Meaning" entity analysis

S-PHRASES MEANING	
ID_Safety_Meaning	A unique code used to identify each record, which contains a safety phrase.
S-Phrases	Safety Phrases e.g. S-26, S36/39.
Safety_Phrases_ Meaning	The meaning for each S-Phrase.

Table 5.18 "Safety Phrases Sources" entity analysis

SAFETY PHRASES SOURCES	
ID_Safety_Source	A unique code used to identify the source of the safety phrases.
Safety_Source	The source from where the S-Phrases have been taken.

Relationship and Cardinality Analysis

Cardinality indicates the number of instances (zero or many) of an entity. Many describe the cardinality through relationships: one-to-one, one-to-many, many-to-many (Database Design Resource, 2007).

The main relationships of the toxicological database are presented in Figure 5.3 and are detailed in Tables 5.19-5.35.

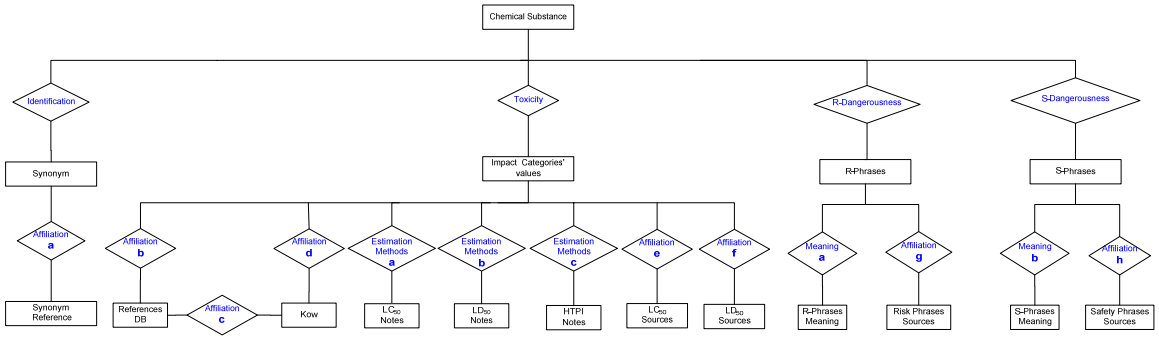


Figure 5.3 E-R Schema with detailed relationships

Table 5.19 "Identification" relationship analysis

IDENTIFICATION	
This relationship links up the entities "Chemical Substance" and "Synonym".	
Cardinality	one-to-many. Each chemical substance can have one, more then one or none synonyms; one synonym corresponds to a single chemical substance.

Table 5.20 "Affiliation-a" relationship analysis

AFFILIATION-a	
This relationship links up the entities "Synonym" and "Synonym-Reference".	
Cardinality	one-to-many. Each synonym belongs to one reference; each reference contains many synonyms.

Table 5.21 "Toxicity" relationship analysis

TOXICITY	
This relationship links up the entities "Chemical Substance" and "Impact categories' value".	
Cardinality	many-to-many. Each chemical substance is characterized by one, more then one or none impact category; each impact category corresponds to many chemical substances.

Table 5.22 "Affiliation-b" relationship analysis

AFFILIATION-b	
This relationship links up the entities "Impact Categories' value" and "Reference DB".	
Cardinality	one-to-many. Each value of the impact category belongs to one database; each database contains many impact categories.

Table 5.23 "Affiliation-c" relationship analysis

AFFILIATION-c	
This relationship links up the entities "Reference DB" and "Kow".	
Cardinality	one-to-many. Each referenceDB can have one or more then one Kow values ; each Kow value corresponds to one referenceDB.

Table 5.24 "Affiliation-d" relationship analysis

AFFILIATION-d	
This relationship links up the entities "Impact Categories' value" and "Kow".	
Cardinality	one-to-many. Each octanol-water partition coefficient can belong to one impact category; each impact category contains many octanol-water partition coefficients.

Table 5.25 "Estimation Methods-a" relationship analysis

ESTIMATION METHODS-a	
This relationship links up the entities "Impact Categories' value" and "LC_{50}Notes".	
Cardinality	one-to-many. Each value of the impact category can have one, more then one or none LC_{50} notes; one note corresponds to one impact category.

Table 5.26 "Estimation Methods-b" relationship analysis

ESTIMATION METHODS-b	
This relationship links up the entities "Impact Categories' value" and "LD_{50}Notes".	
Cardinality	one-to-many. Each value of the impact category can have one, more then one or none LD_{50} notes; one note corresponds to one impact category.

Table 5.27 "Estimation Methods-c" relationship analysis

ESTIMATION METHODS-c	
This relationship links up the entities "Impact Categories' value" and "HTPINotes".	
Cardinality	one-to-many. Each value of the impact category can have one, more then one or none HTPI notes; one note corresponds to one impact category.

Table 5.28 "Affiliation-e" relationship analysis

AFFILIATION-e	
This relationship links up the entities "Impact Categories' value" and "LC_{50}Sources".	
Cardinality	one-to-many. Each value of the impact category can have one or more LC_{50} sources; each source contains an impact category.

Table 5.29 "Affiliation-f" relationship analysis

AFFILIATION-f	
This relationship links up the entities "Impact Categories' value" and "LD_{50}Sources".	
Cardinality	one-to-many. Each value of the impact category can have one or more LD_{50} sources; each source contains an impact category.

Table 5.30 "R-Dangerousness" relationship analysis

RISK DANGEROUSNESS	
This relationship links up the entities "Chemical Substance" and "R-Phrases".	
Cardinality	many- to-many. Each chemical substance can have one, more then one or none R-Phrases; one R-Phrases corresponds to one or many chemical substances.

Table 5.31 "Meaning-a" relationship analysis

MEANING-a	
This relationship links up the entities "R-Phrases' value" and "R-Phrases Meaning".	
Cardinality	one-to-one. Each R-Phrase has a distinct significance; each single meaning corresponds to a unique risk phrase.

Table 5.32 "Affiliation-g" relationship analysis

AFFILIATION-g	
This relationship links up the entities "R-Phrases" and "Risk Sources".	
Cardinality	one-to-many. Each R-Phrase can be taken from one or more sources; each source contains one R-Phrase.

Table 5.33 "S-Dangerousness" relationship analysis

SAFETY DANGEROUSNESS	
This relationship links up the entities "Chemical Substance" and "S-Phrases".	
Cardinality	many-to-many. Each chemical substance can have one, more then one or none S-Phrases; one S-Phrases corresponds to one or more chemical substances.

Table 5.34 "Meaning-b" relationship analysis

MEANING-b	
This relationship links up the entities "S-Phrases' value" and "S-Phrases Meaning".	
Cardinality	one-to-one. Each S-Phrases has a distinct significance; each single meaning corresponds to a unique safety phrase.

Table 5.35 "Affiliation-h" relationship analysis

AFFILIATION-h	
This relationship links up the entities "S-Phrases" and "Safety Sources".	
Cardinality	one-to-many. Each S-Phrases can be taken from one or more sources; each source contains one R-Phrase.

The final E-R Schema containing the entities, relationships and attributes is presented in Figure 5.4.

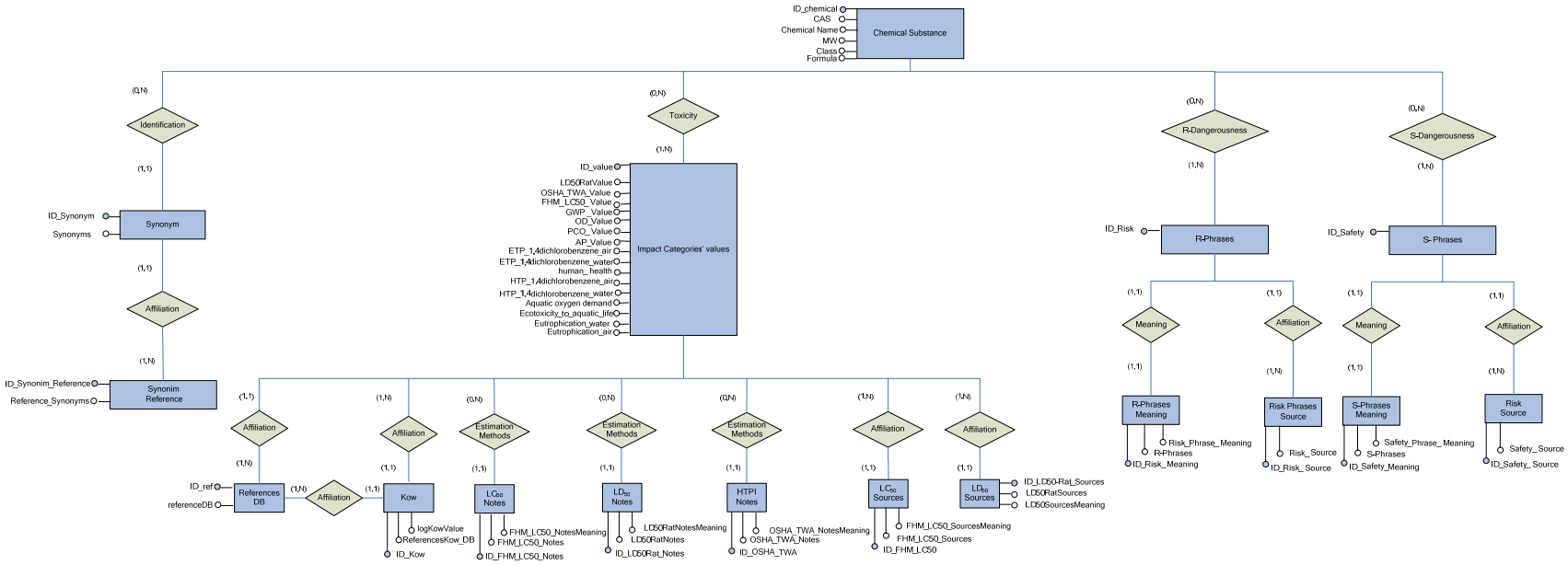


Figure 5.4 Final E-R Schema

5.3 Database Logical Schema

The objective of the logical design is to convert/transform a conceptual schema into a logical schema, which contains the same data but organized in a more correct and efficient way. The elements and the steps requested to design the logical schema are presented in Figure 5.5.

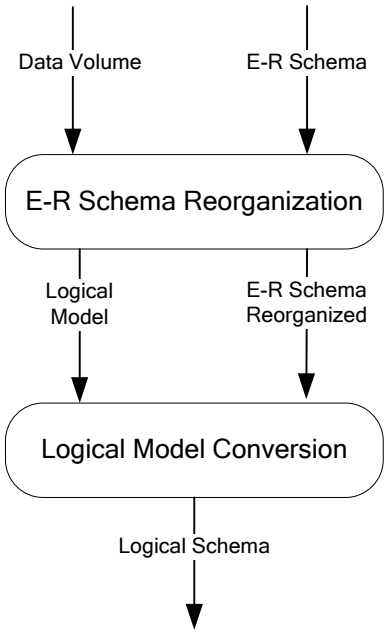


Figure 5.5 Elements and steps of the Logical Schema

Performance analysis on the E-R Schema

Table 5.36 Performance analysis

CONCEPT	TYPE	VOLUME
Chemical Substance	E	5000
Synonym	E	30000
Synonym Reference	E	10
Impact Categories' value	E	32000
Reference DB	E	5
Notes	E	65
LC_{50}Notes	E	25
LD_{50}Notes	E	25
HTPI Notes	E	15
Sources	E	15
LC_{50}Sources	E	10
LD_{50}Sources	E	5
R-Phrases	E	10000
R-Phrases Meaning	E	125
Risk Phrases Sources	E	5
S-Phrases	E	10000

S-Phrases Meaning	E	80
Safety Phrases Sources	E	5
Identification	R	5000
Affiliation-a	R	10
Toxicity	R	5000
Affiliation-b	R	5
Estimation Methods	R	10
Affiliation-c	R	15
R-Dangerousness	R	5000
Meaning-a	R	125
Affiliation-d	R	5
S-Dangerousness	R	5000
Meaning-b	R	80
Affiliation-d	R	5

E-entity; R-relationship

The main operations preformed on the DB and the correspondent frequency are presented in Table 5.37.

Table 5.37 Operation performance analysis

OPERATION	**TYPE**	**FREQUENCY**
Chemical Substance Insertion	iterative	15 times/week
Synonym Name Insertion	iterative	50 times/week
Impact Categories' value Insertion	iterative	10 times/month
Update Impact Categories' value for one chemical substance	iterative	5 times/year
R-Phrase Insertion	iterative	20 times/month
Update R-Phrases for one chemical substance	iterative	5 times/year
S-Phrase Insertion	iterative	20 times/month
Update R-Phrases for one chemical substance	iterative	5 times/year

Figure 5.6, representing a part of the E-R Diagram, has been chosen to discuss the way in which the data/information is accessed.

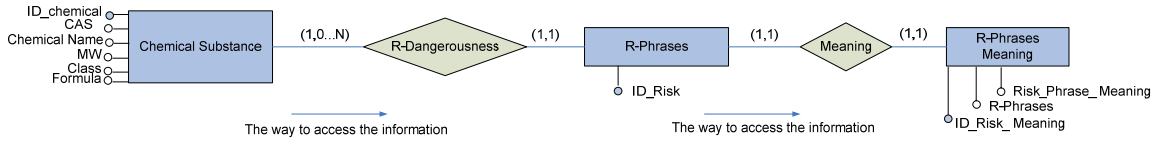


Figure 5.6 Information access schema (example)

Access table presented below has been built using the information from the Information access schema (Figure 5.6).

Table 5.38 Access table

CONCEPT	CONCEPT DETAIL	ACCESSED	TYPE
Chemical Substance	entity	3	R
R-Dangerousness	relationship	3	R
R-Phrases	entity	3	R
Meaning	relationship	1	R
R-Phrases Meaning	entity	1	R

R-reading

In general, the logical design has four steps:

1. generalization exclusion
2. entities and relationships partitioning/unification
3. redundancy analysis
4. main identifiers selection

The first three points are not considered here for the following reasons:

- the E-R Schema has no generalizations
- due to the low quantity of data, the entities and relationships partitioning/unification are not performed. The partitioning is not executed because the data volume is not big. The unification is not carried out because it is preferred to have a DB without any redundancies.

Regarding the selection of the identifiers, it should be specified that the identifiers should have the following characteristics:

- they don't have to contain null values; for each single entity, an identifier (ID) has been created
- they are internal identifiers

Each entity described in the entities analysis has its own identifiers.

The logical schema is presented in Figure 5.7.

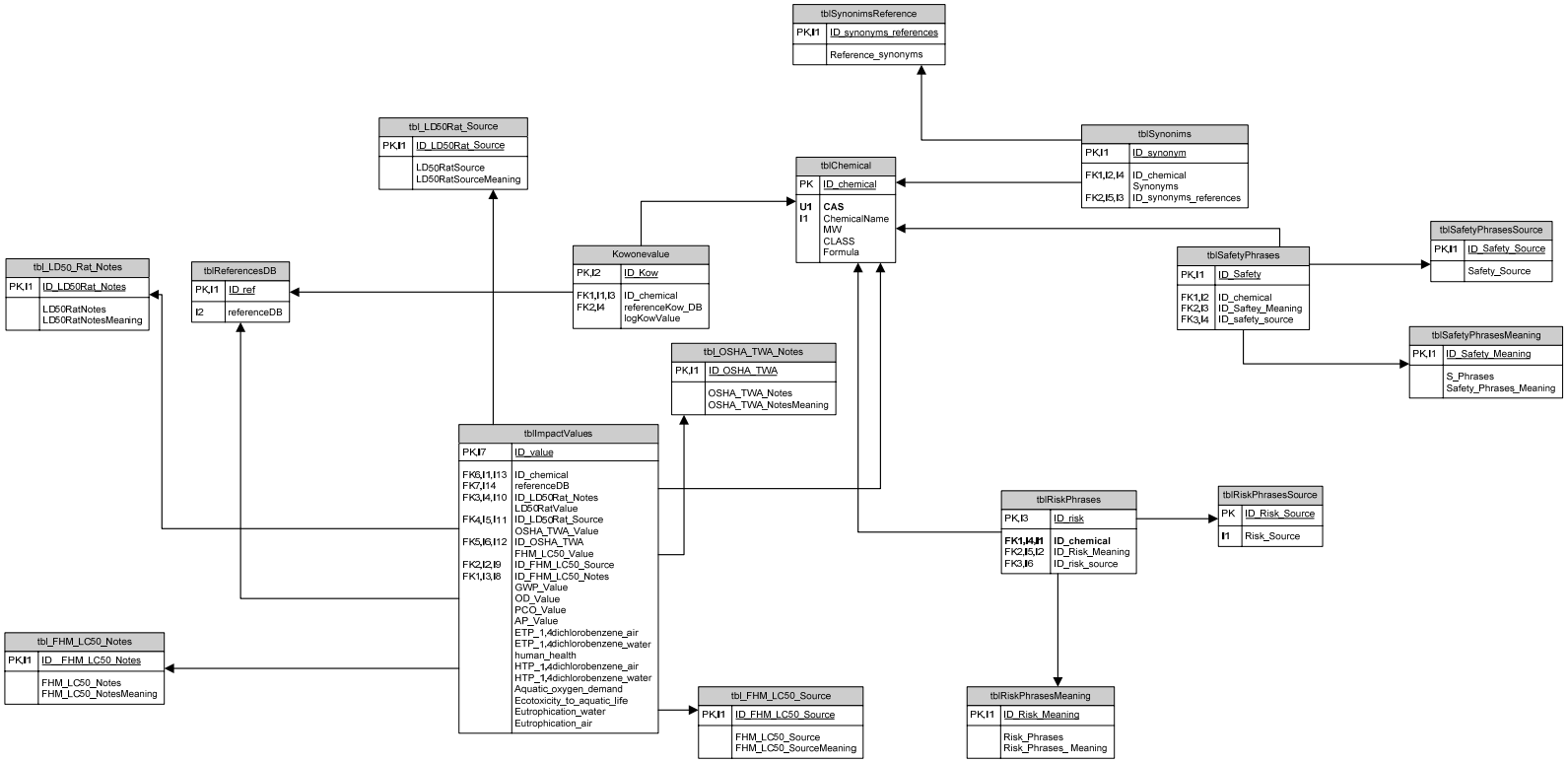


Figure 5.7 Logical DB Schema

5.4 Database Integration and Implementation

Finally the logical schema has been implemented in a physical schema using the relationship database management system. A database management system (DBMS) is a complex set of software programs that controls the organization, storage, management, and retrieval of data in a database (Wikipedia, 2007e). Some common relational database management systems are: Oracle, Sybase, Microsoft SQL Server, Access, Ingres, etc. In this work SQL (Structured Query Language) Server 2000 has been used. SQL statements are used to perform tasks such as update data on a database, or retrieve data from a database. SQL server provides high performance, scalability and availability, plus a vast array of easy-to-use features (SQLserver, 2007)

To use data and to add data to the DB the ADO technology has been used in all the software programs developed in this work.

Chapter 6

Molecular Modelling Techniques used for Toxicological Data Prediction

Summary

In this chapter, different molecular modelling methods used to estimate the thermo-physical properties which lead to the calculation of the Environmental Impact Categories, are proposed, described and applied.

The chapter contains also a sensitivity analysis on the effect one modification of the Environmental Impact Categories has on the final 1D indicator.

"*To do good work, one must first have good tools.*"
source not known

The rapid increase in the world's human population and the development of human society have been accompanied by an equally rapid increase in the utilization of chemical compounds and the subsequent deterioration of the environment by the release of these compounds (Hansen *et al.,* 1999).

In addition to chemicals that are placed on the market, either as intermediates within a production process, or as part of final products, there is the unintentional formation of chemical by-products in a number of processes, such as energy production and metal refining, which can also have an impact on the environment (EEA, 2007). Furthermore, compounds undergo transformations during their life generate new compounds, which means that new information must be obtained about the toxicity of the transformation products (Benfenati and Gini, 1997).

Toxicological data are usually necessary to assess the impact of such compounds on the environment and on human health.

Toxicity is defined as the degree to which something is poisonous (WordReference.com, 2007). Toxicology, from the Greek words *toxicon* and *logos*, is the study of the adverse effects of chemicals, more exactly, the study of symptoms, mechanisms, treatments and the detection of poisoning, especially the poisoning on living organisms (Answers, 2007b).

Toxicological data can be obtained by performing appropriate toxicity tests (Ren *et al*., 2003). The number of existing chemicals on the market is large, but the exact number is unknown (EEA, 2007). Currently, more than 100,000 chemical compounds are used worldwide. However, because of the time and financial resources required, it is impractical to perform toxicity tests for all the chemical compounds in use. As a result, toxicological data are not available for all chemical compounds (Ren *et al*., 2003). In this context, molecular simulation methods become an important tool for toxicological data prediction.

The connection between the potential environmental impact of a chemical plant and the toxicological data of the chemical compounds involved in the process is quite evident. The potential environmental impact/risk of a chemical plant can be evaluated using different algorithms such as: Process Environmental Performance Assessment (PEPA), Global Environmental Risk Assessment (GERA), and WAR Algorithm. In almost all these algorithms the same/or different Environmental Impact Categories are taken into consideration. One precious Environmental Impact Categories' source is the scientific literature. When the scientific literature does not cover the large amount of chemical compounds, the Environmental Impact Categories can be calculated using different molecular modelling techniques.

A general view of the above-mentioned elements is presented in Figure 6.1.

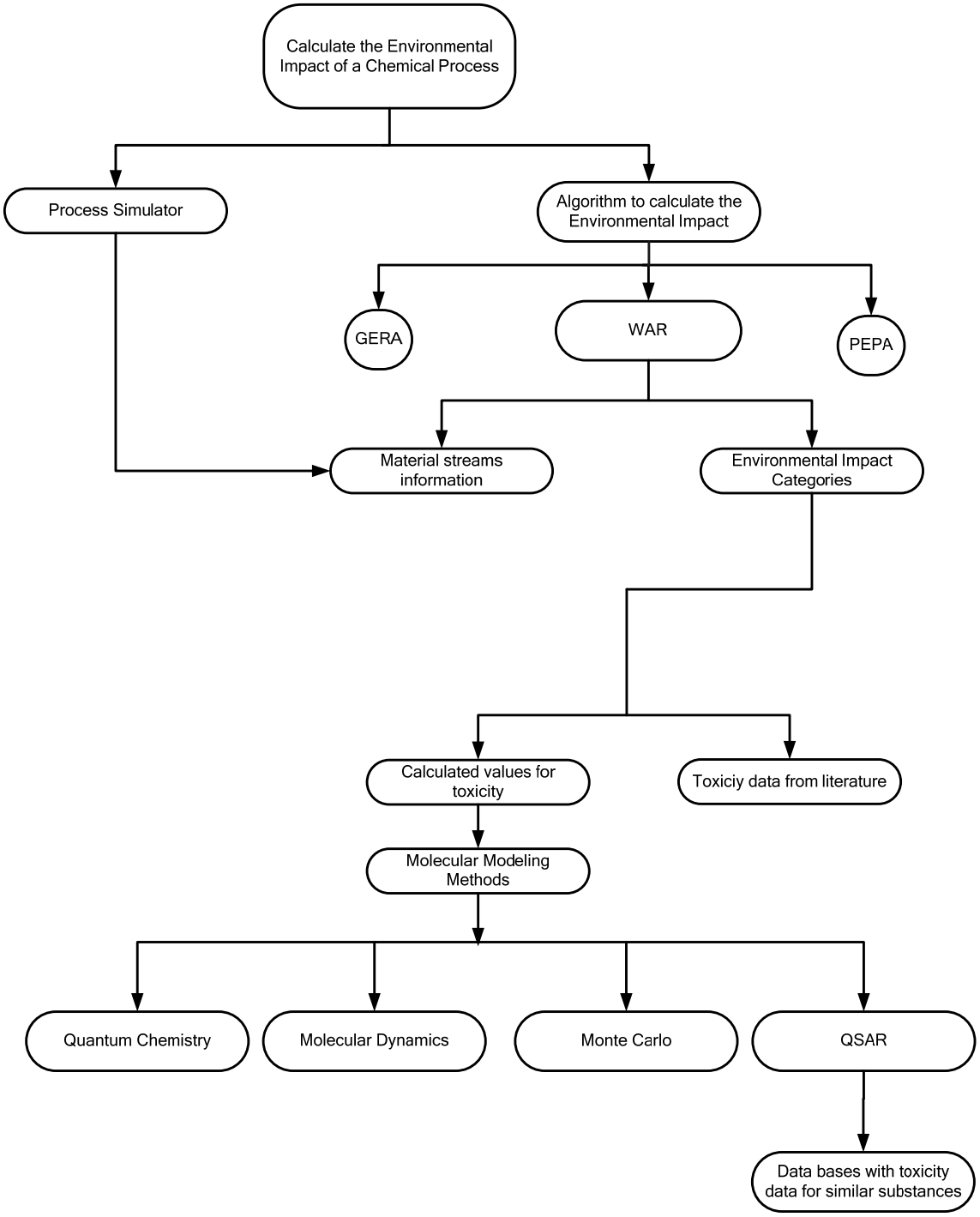


Figure 6.1 Environmental Impact Calculation schema starting from toxicity data

6.1 Methods Used to Evaluate the Environmental Impact Categories: General Overview

As it has been detailed in *Chapter 3*, eight Environmental Impact Categories have been used in the WAR Algorithm. The categories considered are:

- Global Warming Potential (GWP)
- Ozone Depletion Potential (ODP)
- Photochemical Oxidation or smog formation Potential (PCOP)
- Acidification Potential (AP)
- Human Toxicity Potential by either Inhalation or dermal Exposure (HTPE)
- Human Toxicity Potential by Ingestion (HTPI)
- Terrestrial Toxicity Potential (TTP)
- Aquatic Toxicity Potential (ATP)

The formulas used in the calculation of the Environmental Impact Categories are also given in *Chapter 3*. It can be inferred, from that chapter, that the calculation of the Environmental Impact Categories can be reduced to some thermo-physical properties, some of which can be estimated using different molecular modelling techniques. This concept is illustrated in Figure 6.2.

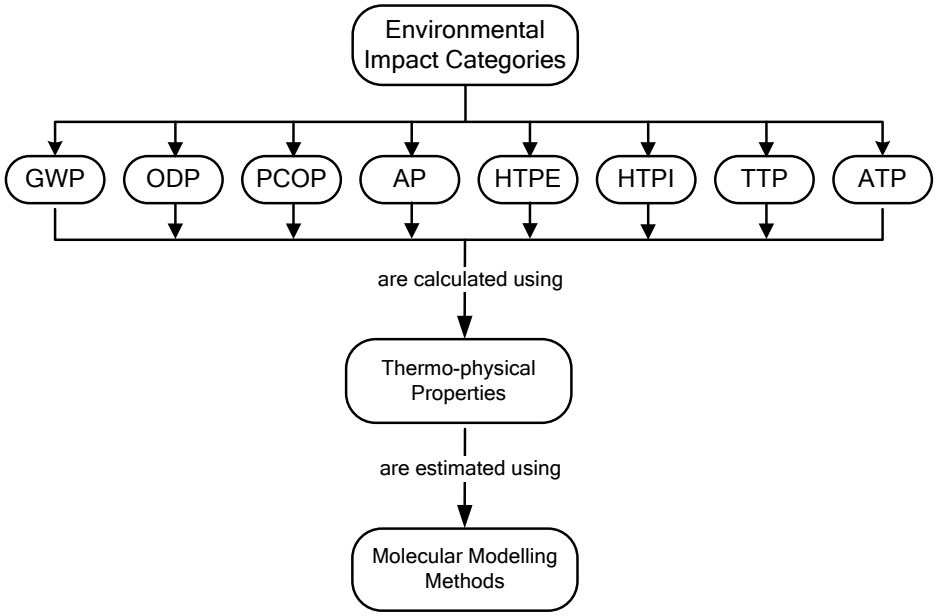


Figure 6.2 Environmental Impact Categories' calculation schema

Details regarding the last two statements of the schema depicted in Figure 6.2 are given below (see Figure 6.3).

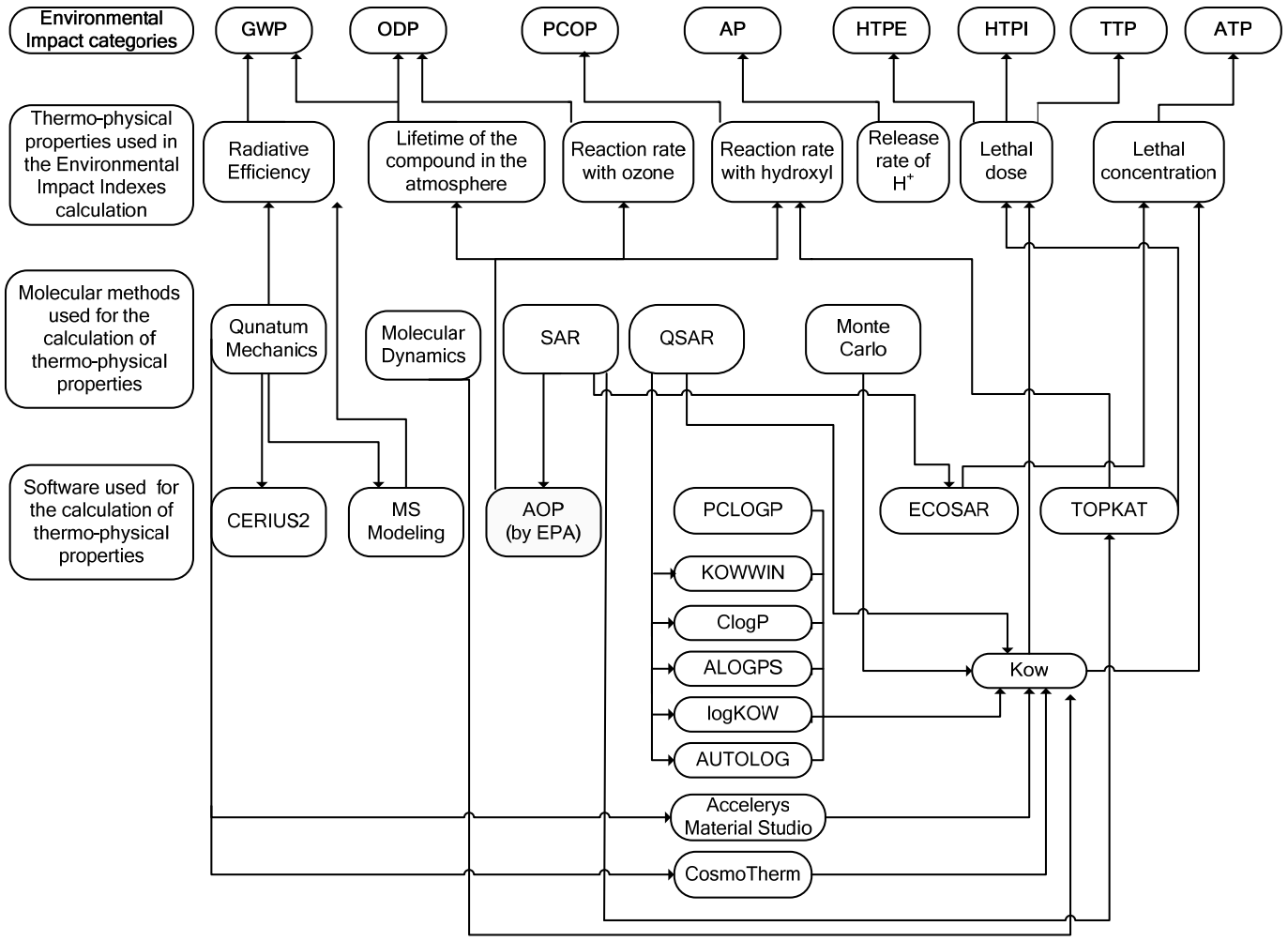


Figure 6.3 Thermo-physical properties and software programs used in the calculation of the Environmental Impact Categories

The nomenclature correspondent to the elements present in Figure 6.3 is briefly discussed below. SAR is the acronym for Structure Activity Relationship, while QSAR is the acronym for Quantity Structure Activity Relationship.

AOP is the Atmospheric Oxidation Program, based on SAR calculation, developed by U.S.EPA. The program has been used in the present thesis for the estimation of lifetime a compound in the atmosphere has, for the reaction rate with ozone and reaction rate with hydroxyl.

For the octanol-water partition coefficient calculation, Kow, different molecular modelling methods can be used. For example KOWWIN, the Log Octanol-Water Partition Coefficient Program, is a software developed by U.S.EPA which is based on SAR. ClogP is a program, based on group-contribution methods, which can be also used for the octanol-water partition coefficient. ALOGPS is a software based on neural networks developed by the Virtual Computational Chemistry Laboratory. COSMOTherm (Conductor like Screening Model Thermodynamics) is an advanced software tool based on quantum mechanics, which calculates different thermo-physical properties such as: vapour pressures, boiling points, activity coefficients, excess enthalpy and entropy, Henry's Law constants, solubility, octanol-water partition coefficient, vapour-liquid equilibrium, liquid-liquid equilibrium, solid-liquid equilibrium, density and viscosity for pure compounds (COSMOTherm, 2006). COSMOTherm is one of the software used, in the present thesis, for octanol-water partition coefficient estimation.

ECOSAR, developed by the Risk Assessment Division of the U.S.EPA, is a computer program based on SAR, used to predict the aquatic toxicity of chemicals based on their similarity of structure to chemicals for which the aquatic toxicity has been previously measured.

TOPKAT, a computer program developed by Accelrys, employs robust and cross-validated Quantitative Structure Toxicity Relationship (QSTR) models for estimating 16 toxicity endpoints (i.e. Mutagenicity, Rat Oral LD50, Carcinogencity, Developmental Toxicity, etc) (Acclerys, 2007).

It is evident, form Figure 6.3, that some properties are of fundamental importance for the calculation of the eight environmental impact categories. As it can be noticed HTPE, HTPI, ATP and TTP impact categories are related to a phase equilibrium property, more exactly to the octanol-water partition coefficient, Kow. The other four impact categories: GWP, ODP, PCOP and AP are related to some transport properties such as release rate of H^+ or to reactivity properties such as: reaction rate with hydroxyl, reaction rate with ozone, lifetime, and therefore can be calculated using quantum mechanics (QM) or (Q)SAR methods.

Based on these considerations, the octanol-water partition coefficient, the lifetime of a chemical compound in the atmosphere, the reaction rate with ozone and the reaction rate with hydroxyl are discussed in the next section.

6.2 Thermo-Physical Properties Estimation

6.2.1 Octanol-Water Partition Coefficient

Numerous properties, including bioavailability, skin permeability, toxicity and environmental fate, have all been successfully related to the differential solubility of solutes in aqueous and organic solvents (Best *et al.,* 1999). Partition coefficients have a history more than a century long as a measure of how chemical substances become dispersed in living systems and their ability to penetrate into biological boundaries (Buchwald and Bodor, 1998).

It is, therefore, very important to understand solute-solvent interactions in both aqueous (hydrophilic) and organic (lipophilic) solvents. Most theoretical studies of solvent effects have concentrated on water because water is the most important solvent in biological systems. Arguably, the most significant organic solvent for the study of biological systems is 1-octanol (henceforth referred to as octanol). Octanol has been widely used as a surrogate for much more complicated systems such as lipid molecules that comprise biological membranes. While octanol is primarily lipophilic (oily) in nature by virtue of its lengthy alkyl tail, it also possesses a polar head group that provides for local regions in the solvent that are capable of hydrogen bonding, and might be characterized as being relatively hydrophilic. This amphipathic character gives octanol characteristics that are similar to those of lipids in biological membranes (Best *et al.,* 1999). From the above presented context, the importance of the study of octanol-water partition coefficient is quite evident, as it is one of the most effective parameters used in the toxicity evaluation.

General Information

Octanol-water partition coefficient (Kow) is an important thermo-physical property used in the calculation of four Environmental Impact Categories: HTPI, HTPE, ATP, TTP (see Figure 6.3). The octanol-water partition coefficient is defined as the ratio of the concentration the component of interest has in octanol phase to its concentration in the aqueous phase in a two-phase octanol-water system (Lin *et al.,* 2002).

$$Kow = \frac{concentration\ in\ octanol\ \ phase}{concentration\ in\ aqueous\ \ phase} \qquad (6.1)$$

Values of Kow are unitless. Measured values of Kow, for organic chemicals, have been found as low as 10^{-3} and as high as 10^{7}, thus encompassing a range of ten orders of magnitude. In terms of log Kow, this range is from -3 to 7 (Pirika, 2004).

Some remarks on Kow should be made:

- The octanol-water partition coefficient is not the same as the ratio of a chemical's solubility in octanol to its solubility in water, because the organic and aqueous phases of the binary octanol-water system are not pure octanol and pure water (Pirika, 2004).
- In recent years, the octanol-water partition coefficient has become a key parameter in studies of the environmental fate of organic chemicals. It has been found to be related to

water solubility, soil/sediment adsorption coefficients, and bioconcentration factors for aquatic life. Because of its increasing use in the estimation of these properties, Kow is considered a required property in studies of new or problematic chemicals (Ren *et al.,* 2003; Lin *et al.,* 2002).

- The successfulness of Kow in predicting bioaccumulation and toxicity has been attributed to the fact that the octanol-water partitioning is a good representative of a compound going from more aqueous like-phases (extra cellular phase) to organic-like phases (cellular phase) inside the body, which is the rate controlling step during the interaction of a compound and a biological system. As it has been mentioned before, correlations between natural systems and Kow have been successful because octanol and lipids exhibit similar molecular structures and physical properties. Both octanol and lipids contain polar, hydrophilic oxygen at the end of a long hydrophobic alkyl chain. Comparison of 1-octanol's structure with a lipid's structure is made in Figure 6.4 (Ulas and Diwekar, 2006).

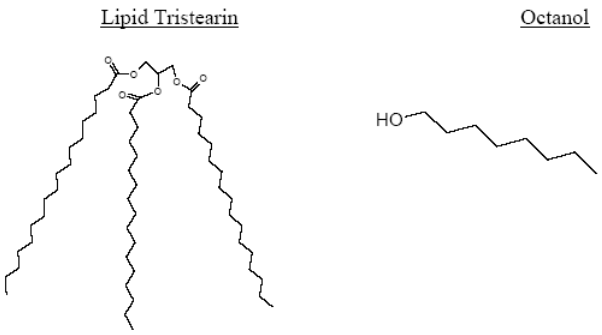


Figure 6.4 Comparison of 1-octanol's structure with lipid's structure

- Values of Kow can be considered to have some meaning in themselves, since they represent the tendency of the chemical to partition itself between an organic phase (e.g., a fish, a soil) and an aqueous phase. Chemicals with low Kow values (e.g., less than 10) may be considered relatively hydrophilic; they tend to have high water solubility, small soil/sediment adsorption coefficients, and small bioconcentration factors for aquatic life. Conversely, chemicals with high Kow values (e.g., greater than 10^4) are very hydrophobic (Ren *et al.,* 2003; Lin *et al.,* 2002).

Prediction Methods of Kow by Molecular Simulation

Octanol-water partition coefficient (Kow), in thermodynamics is a free energy function (like solubility and vapour pressure) and therefore, it is directly related to the energetics of transfer between two phases. The following figure (Figure 6.5) shows the interaction of a compound with a biological system (Ulas and Diwekar, 2006).

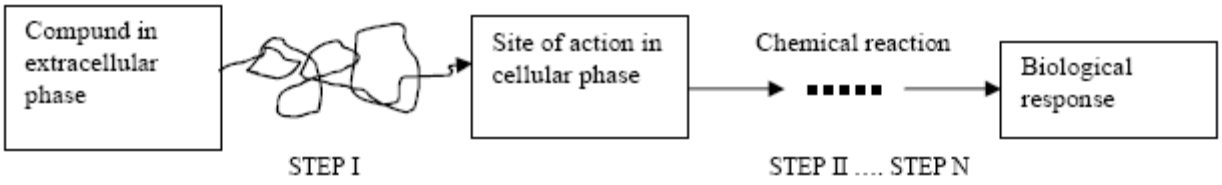


Figure 6.5 Interaction of a compound with a biological system

At first, the chemical compound arrives at a particular site in a cell from a dilute solution outside the cell following a random walk. Then the chemical compound goes through a relatively slow process of diffusion or permeation, which represents the partitioning of the compound between a polar aqueous phase and a non-polar organic phase. This partitioning is controlled by the molecular structure of the compound. Once the compound goes into the non-polar organic phase, it goes through a series of chemical reactions eliciting a biological response. However, the rate-controlling step in this scheme is the first step, which is the partitioning of the compound between a lipophilic and hydrophilic phase and octanol-water partition coefficient is a good indicator of this step. Octanol has a structure, which is composed of a hydrophilic head and a lipophilic tail, which has been found to mimic the complexities of biological and other environments very well. This is the reason for its importance in estimating various toxicological parameters such as the bioconcentration factor and LC_{50}, LD_{50} (Ulas and Diwekar, 2006).

There are different methods, available in literature, to calculate Kow using molecular simulations.

1. Free Energy Perturbation, Monte Carlo and Molecular Dynamics Method

The first method is the Free Energy Perturbation (FEP) method. Calculations of relative octanol-water partition coefficients have been reported using FEP method with the molecular dynamics and Monte Carlo simulation methods.

In order to compute octanol-water partition coefficient, the free energies of solvation must be calculated in both aqueous and organic phases. For example, consider solute A. Initially, the free energies of solvation are determined in the aqueous phase, $\Delta G_{aq}A$, and in the water-saturated octanol phase, $\Delta G_{oct}A$. The difference between the solvation free energies is the free energy of transfer ($\Delta G_{Tr}A$) for transferring solute A from water (A (aq)) to water-saturated octanol (A(oct)). This process is illustrated for two different solutes, A and B, by the vertical paths 1 and 3 in Figure 6.6.

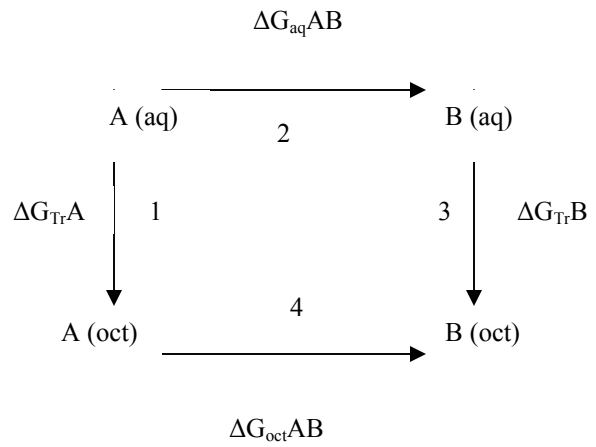


Figure 6.6 Thermodynamic cycle utilized in the calculation of octanol-water partition coefficient

The free energies of solvation can be calculated from the above-depicted thermodynamic cycle. The free energy of transfer for solutes A and B is related to octanol-water partition coefficients for A - $\log Kow(A)$ and for B - $\log Kow(B)$ through equations 6.2 and 6.3 where R is the gas constant and T is the temperature:

$$\Delta G_{Tr} A = -2.3RT \log Kow(A) \quad (6.2)$$

$$\Delta G_{Tr} B = -2.3RT \log Kow(B) \quad (6.3)$$

Unfortunately, it is difficult to compute absolute free energies of solvation. It is, however, computationally feasible to calculate a relative free energy of solvation in which solute A is slowly mutated into solute B. Thus, by taking advantage of the fact that free energy is a state function, the following relationship can be utilized based on the free energy cycle given:

$$\Delta G_{oct} AB - \Delta G_{aq} AB = \Delta G_{Tr} B - \Delta G_{Tr} A = \Delta\Delta G_{Tr} AB \quad (6.4)$$

The relative free energies of solvation of A and B can be used to calculate a relative free energy of transfer, $\Delta\Delta G_{Tr} AB$. This allows the relative partition coefficient ($\Delta \log Kow$) for solutes A and B to be calculated from the direct relationship between $\Delta\Delta G_{Tr} AB$ and $\Delta \log Kow$ as illustrated in equation 6.5 (Best *et al.,* 1999; Ulas and Diwekar, 2006):

$$\Delta\Delta G_{Tr} AB = -2.3RT\Delta \log Kow \quad (6.5)$$

2. Free Energy Calculation - Expanded Ensemble Method

The octanol-water partition coefficient can be directly related to the difference of solvation free energy in water and octanol phase, respectively:

$$\log Kow = \frac{1}{2.303RT}(G_{water} - G_{oct}) \qquad (6.6)$$

where G_{water} and G_{oct} are the solvation free energies of the solute substance in water and octanol, correspondingly (Lyubartsev *et al.*, 2001).

The second method to calculate Kow is the expanded ensemble method. The expanded ensemble (EE) method for solvation free energy calculations was originally developed within Monte Carlo methodology and later modified for molecular dynamics simulation techniques. Using this method, not only the relative partition coefficients but also absolute values for the partition coefficients can be obtained (Ulas and Diwekar, 2006). While most other methods need a series of repeated computer simulation runs to obtain the free energy value, using the EE method, only one single run is required after a proper choice of a set of the transition parameters (balancing factors) which can be easily determined in a few short trial runs (Lyubartsev *et al.*, 2001). This method involves the gradual insertion/deletion of studied solute particle into/from the solvent. One drawback of this method is that it requires optimization of two parameters, the insertion parameters and the balancing factors for the simulation, so some trial runs are needed (Ulas and Diwekar, 2006).

3. Monte Carlo Method

The third method used to calculate octanol-water partition coefficients is the configurational-bias Monte Carlo (CBMC) simulations in the Gibbs ensemble. The Gibbs ensemble is very suitable for this simulation because it creates a setup analogous to the experimental situation. Gibbs ensemble Monte Carlo simulation (GEMC) utilizes two separate simulation boxes, which are in thermodynamic contact, but do not have an explicit interface (Ulas and Diwekar, 2006). As a result, for a given state point, the properties of the coexisting phases, such as the mutual solubilities of the two solvents and the partitioning of solute molecules, can be determined directly from a single simulation.

The main advantages of CBMC/GEMC simulations over Free Energy perturbation (FEP) are:

- In both the experiment and CBMC/GEMC simulations, Gibbs free energy of transfer is directly determined from the ratio of solute number densities in the two phases (partition constant), while the difference in excess of the chemical potentials is used in FEP calculations.
- Number density ratio is a mechanical property that can be determined very precisely leading to small statistical errors in ΔG.
- The composition of the two solvent phases do not need to be specified in advance, whereas FEP simulations are performed at a fixed composition that might not correspond to a proper thermodynamic state for the force field used in the calculations (Acikgoz and Diwekar, 2005; Ulas and Diwekar, 2006).

4. Continuum Solvation Model (CSM)

Continuum Solvation Models are nowadays widely used in the modelling of solvent effects and the range of applications goes from the calculation of partition coefficients to chemical reactions in solution. One of the CSM methods is the Conductor like Screening Model (COSMO), a calculation method for determining the electrostatic interaction of a molecule with a solvent. The method has been developed by Klamt.

Conceptually, COSMO places the molecule inside a cavity formed within a homogeneous medium, taken to be the solvent. In COSMO, the solvent is treated as a continuum with a permittivity. It is also assumed that the medium reaches up to the "surface" of the solvated molecule. This interface is assumed to consist of spheres that surround the individual atoms. The COSMO method is more accurate for solvents with a higher permittivity because a solvent with infinite permittivity behaves like an ideal conductor. A very good accuracy is achieved with water. For solvents with low permittivities a complete solution of the electrostatic equations would be more accurate, though this would require greater effort. The COSMO model, as is the case with all continuum models, has the advantage of a substantial lower computational effort (Wikipedia, 2007f).

Several papers, based on variation and refinements of the same basic theory, appeared in the scientific literature in the last years. In all cases it is shown that models based on continuum salvation methods are capable to predict mixture properties with reasonable accuracy starting from quantum chemistry calculations and introducing a parameterization at element level. The basic theory of such models is a unimolecular quantum chemical calculations that provides the necessary information for the evaluation of molecular interactions in liquids. Combined with a very fast and accurate statistical thermodynamics, the new method is an alternative to structure-interpolating group contribution methods (Fermeglia *et al.*, 2003).

5. Quantitative Structure Activity Relationship (QSAR) Method

The individual properties of a chemical are all derived from, and related to, the unique molecular structure of that chemical. These properties include physical properties, chemical properties and toxicological properties (Barratt and Rodford, 2001). Therefore, the key to toxic effects of chemicals resides in their molecular structure (Kaiser, 2003). Hansch introduced in 1963 the relationship idea that biological activities of molecules are a function of their chemical and physical properties (Hansch *et al*., 1963). QSAR is another method used for the octanol-water partition coefficient. A structure activity relationship is a qualitative association between a chemical substructure and the potential of a chemical to exhibit a certain biological effect. A quantitative structure activity relationship is a mathematical model that relates a quantitative measure of chemical structure to a biological effect. Thus, the structure activity relationship of the molecules could be explained quantitatively (Di Marzio and Saenz, 2004).

There are two basic aims of toxicologically-based QSAR analyses. The first aim is to determine, as accurately as possible, the limits of variation in molecular structure that are consistent to the production of a specific toxic effect. The second aim is to define the ways in which alterations in structure, and thereby, the overall properties of a

compound, influence potency. In evaluating a structure–activity relationship, it is critical to define boundaries of application, by considering which types of molecules (the molecular domain), and range of descriptor values (descriptor domain), have toxicity that can be predicted confidently. Equally important is the requirement to have a statistical measure of fit, significance, and robustness. Models meeting such criteria can also lead to mechanistic hypotheses that guide future testing and validation (Schultz *et al*., 2003).

QSAR studies consist of two main stages. In the first step, the chemical compounds are translated into a computer readable form and afterwards the quantitative correlation between chemical structure and its property can be obtained using different statistical and learning procedures, like multiple linear regression model (MLR), several types of artificial neural networks, partial least square (PLS) method, etc. (Pompe and Veber, 2001). The accuracy of this method is good and it can be applied for a large number of chemical compounds.

The above presented section is a summary of the molecular modelling methods used to calculate Kow present in the scientific literature. The last two approaches have been applied in the present work.

The Kow results obtained using CSM (COSMO) and QSAR methods are presented in the *Results and Discussion Section* (section 6.3.1).

6.2.2 Lifetime

To evaluate the environmental impact of a given gas molecule, one needs to know, first, how long it remains in the atmosphere (Velders *et al*., 2007).

The environmental damage caused by atmospheric pollutants is proportional to the duration of their effects. The global impacts of greenhouse gases (as measured by global warming potential) and ozone depleting substances (as measured by ozone depletion potential) have traditionally been calculated using the atmospheric lifetime of the source gas as a quantitative measure of the impact's duration, assuming that the gas quickly reaches a steady state pattern which decays exponentially according to the lifetime (Prather, 2002). Consequently, lifetime is another important parameter used in the calculation of two environmental impact categories: GWP and ODP (see Figure 6.3).

General information

The atmospheric lifetime is a measure of how long a chemical remains in the atmosphere after release. Atmospheric lifetimes are generally modelled as "e-folding" lifetime. The concentration decays exponentially following the equation:

$$C_t = C_0 e^{-t/L} \qquad (6.7)$$

where C_0 is the initial concentration, C_t is the concentration at any time t and L is the atmospheric lifetime. After one lifetime, the gas concentration drops to *1/e* (approximately 0.369) of its value. According to this equation, the concentration never

reaches zero, although it can approach zero very closely. For example, after 5 lifetimes, the concentration drops to 0.0067 of its initial value (FAA, 2007; Tapscott *et al*., 1991).

Some green house gases are removed from the atmosphere in a few years, while others remain for hundreds of years. The lifetime of greenhouse gas is largely dependent on atmospheric photochemistry, which controls photolysis. The general definition of the atmospheric lifetime of a species A is:

$$\alpha_{lifetime}(A) = [A] / \nu_A \qquad (6.8)$$

where $\nu_A = -\frac{d[A]}{dt}$ is the rate of consumption of species A.

The gas-phase lifetime of species A can be written as follows:

$$\tau_{lifegas}(A) = \frac{1}{k_{OH_g}(A) * [OH_g] + J_g(A)} \qquad (6.9)$$

where $k_{OH_g}(A)$ and $J_g(A)$ are the rate constant of OH oxidation and the photolysis frequency of species A in the gas phase, and $[OH_g]$ is the concentration of OH radicals in the gas phase (Monod *et al.,* 2005).

Prediction Methods of lifetime by Molecular Simulation

Lifetime of chemical compounds in the atmosphere can be estimated using Structure Activity Relationship (SAR) methods. The basic assumption for all molecule-based hypotheses is that similar molecules have similar activities (Wikipedia, 2007g). The difference between SAR and QSAR, detailed in the previous section, is the following: SAR is a qualitative not a quantitative relationship, which is based on the notion of "similarity": *"*Similar compounds have similar activity*"* while QSAR aims to derive a quantitative model of the activity (Ambit, 2007).

The lifetime results obtained using the SAR method are presented in the *Results and Discussion Section* (section 6.3.2).

6.2.3 Reaction Rate with Ozone

Chemical persistence in the environment is one of the most important factors to be considered when assessing environmental risk due to chemicals, evaluating chemical fate and determining possible adverse effects (Gramatica *et al.*, 2004).

The atmosphere is a complex medium where numerous chemicals are released, dispersed by physical processes and oxidized by photochemical reactions initiated by solar radiations (Monod *et al*., 2005). In recent decades, global increase in troposphere ozone concentrations has been attributed mainly to anthropogenic emissions (from industry and traffic) (Sousa *et al.*, 2007). The reaction with ozone represents one of the

most common reactions, which take place in the atmosphere. The reaction rate with ozone is used to calculate the ODP environmental impact category.

General information

Ozone is a minor component of the earth's atmosphere (0.02 – 0.1 parts per million based on volume (ppmv)), yet it has a significant role in sustaining life on earth.

Ozone plays a central role in tropospheric chemistry. Not only is it a highly reactive and toxic species, but it absorbs both infrared and ultraviolet light, contributing to the "greenhouse effect" and providing protection from exposure to damaging UV (Finlayson-Pitts and Pitts, 2000). It absorbs ultraviolet (UV) radiation from the sun and hence reduces the levels of UV radiation reaching the earth's surface. UV radiation, being of short wavelength and hence highly energetic, can cause damage to plant and animal life on earth (Flynn, 2007). In the process of absorbing the UV, it generates electronically excited oxygen atoms that react to form OH, an ubiquitous atmospheric oxidant (Finlayson-Pitts and Pitts, 2000). The substances with C=C double bonds, can react with ozone at significant rates, and these reactions often have a net positive effect on ozone because of the subsequent reactions of the radicals formed. Although Atkinson and Carter discuss possible approaches for estimating O_3 rate constants, no comprehensive approach has been developed which performs very reliably for estimation purposes (Atkinson and Carter, 1984).

It should be also specified that ozone concentrations are very difficult to model because of the different interactions between pollutants and meteorological variables (Borrego *et al.*, 2003).

Prediction Methods of Reaction Rate with Ozone by Molecular Simulation

Reaction rate of chemical compounds with ozone in the atmosphere can be estimated using the QSAR method.

Different quantum-chemical descriptors are used in the QSAR method. One relevant example has been developed by Pompe and Veber (Pompe and Veber, 2001). According to the frontier molecular orbital theory of chemical reactivity, the formation of a transition state is due to an interaction between the frontier orbitals of reacting compounds. These interactions are encoded by HOMO energy (Highest Occupied Molecular Orbital) and average electrophilic reaction index for a C atom, which are representatives quantum-chemical descriptors. HOMO energy is related to the ionization potential as well as to affinity of the organic molecule towards the attack by electrophiles. Therefore, the selection of these two descriptors for the prediction of the reaction rate constants for the reaction of O_3 with different organic compounds is not surprising since it is known that ozone is an electrophilic agent. Charge distribution-related descriptors, which represent or depend on charge distribution in the molecule, have been considered. The strength of intramolecular bonding interactions and therefore, the stability of the molecule or its conformational flexibility, represent another descriptor (Sannigrahi, 1992). The quantum mechanical energy-related descriptors such as: max exchange energy for a C–C bond and max e–e repulsion for a C–C bond belong to another subgroup of descriptors. They characterize intramolecular energy distribution and may be

related to the conformational changes or atomic reactivity in the molecule. We can see that selected structural indices encode together chemical features which are important in the photochemical reaction of organic compounds with ozone, that is, information about the formation of transition state, the cleavage of the chemical bonds and about the different conformational changes (Pompe and Veber, 2001).

The results obtained, using the QSAR method for the calculation of the reaction rate with ozone, are presented in the *Results and Discussion Section* (section 6.3.3).

6.2.4 Reaction Rate with Hydroxyl

The reaction rate with hydroxyl is used to calculate the PCOP environmental impact category.

General information

Organic chemicals emitted into the troposphere are degraded by several important transformation processes that include reaction with hydroxyl OH radicals or other photo chemically-produced radicals, reaction with ozone or direct photolysis. The dominant transformation process for most compounds that occur in the troposphere is the daylight reaction with OH radicals. The rates at which organic compounds react with OH radicals are a direct measure of their atmospheric persistence. Rate constants have been measured experimentally for a small fraction of organic chemicals of environmental concern. The rate constant for the gas-phase reaction with OH radicals has been measured for less then 500 organic compounds (Kwok and Atkinson, 1995).

Since experimental measurements can be difficult, time-consuming and expensive, the ability to estimate rate constants has become very important. The estimation methods have become an important tool to reduce the number of compounds for which measurements are necessary (Klamt, 1993).

The scientific literature presents different methods of estimating the reaction rate with hydroxyl. A complete overview of the methods, found in the scientific literature, that calculate the reaction rate with hydroxyl was published by Sablijic and Peijnenburg in the IUPAC Technical Report for 2001 (Sablijic and Peijnenburg, 2001) and by Güsten (Güsten,1999).

The methods used to calculate the reaction rate with hydroxyl are described below.

Prediction Methods of Reaction Rate with Hydroxyl by Molecular Simulation

The prediction models can be grouped into the following classes:

1. Empirical Models
2. QSAR models
   - 2.1 QSAR models with measured physicochemical descriptors
   - 2.2 QSAR models with structural descriptors (topological, electrostatic, quantum chemical, etc.)
3. ab initio molecular orbital calculations

Each method is described below.

1. Empirical Model - Group Contribution Method

The group contribution methods are based on the principle that a property of an abstract structure can be expressed as the summation of the contribution of parts (groups) of that structure (D'Anterroches *et al.*, 2004). The advantage of group contribution methods is that the number of functional groups is much smaller than the number of possible molecules (Gmehling, 2003).

The group contribution methods have two underlying premises. Firstly, the additivity assumption implies that a particular property of a compound is a sum of the contributions associated with atoms or fragments. Secondly, the transferability assumption states that the contributions of identical atoms or fragments are identical to those in the original compounds (the training set) used to estimate these contributions (Jeliazkova and Jaworska, 2005).

As the contribution of each group to the property of the structure is not always known or the structure cannot be fully described as a group is missing, recent developments in the field of group contribution method for molecular property prediction have been to develop methods to predict the contribution of a missing group contribution through a connectivity indices method (Marrero and Gani, 2003). Having the model and the groups with their contributions means that for any structure that can be fully described with a subset of the model groups the property can directly be evaluated (D'Anterroches *et al.*, 2004).

It should be also added that group contribution methods are widely used because, in all the cases where interaction parameters between the groups are available, they are also capable of providing phase behaviour for systems for which no experimental data exist. However, the results provided by these methods should be accepted with caution because, other than the above-mentioned basic inconsistency concerning the additivity of the interactions, they cannot deal with mixtures of isomers (the method is not capable of distinguish them), they cannot manage molecules with more than one functional group (proximity effects are not considered), they do not manage mixtures containing conformers (the method does not consider them) and they have great difficulties with systems containing molecules with pronounced differences in dimension and shape (Fermeglia and Pricl, 2007).

Atkinson developed a group contribution method to estimate the reaction rate constants with OH radical. The method is based on:

(a) four possible reaction pathways and

(b) an additive fragment contribution scheme

The four possible reactions by which the OH radicals can react with organic compounds are:

(i) hydrogen atom abstraction,

(ii) addition to double and triple bonds

(iii) addition to aromatic rings

(iv) reaction with nitrogen-, sulphur-, and phosphorus- containing groups

It is assumed that the reaction rate constants can be estimated separately and that the estimation of the overall reaction rate constant of a chemical can be approached through an additive group contribution. The overall reaction rate is the sum of all possible individual reaction rates.

The most recent version of this method has 89 empirical parameters, i.e., 26 group rate constants and 63 substitute factors, to estimate the rate constants for three of four possible reaction pathways (Kwok and Atkinson, 1995).

The validation of the most recent version of Atkinson's group contribution method has shown that for about 90% of 485 organic compounds, the reaction rate constants, that are calculated, are within a factor of two of the experimental reaction rate constants. Disagreements most commonly occur between experimental and calculated rate constants for halogen-containing compounds, and, in particular, for haloalkanes, haloalkenes, and halogenated ethers (Zhang *et al.,* 1992). Disagreements also arise for ethers, especially for polyethers and cycloethers (Wallington *et al.,* 1988), certain haloalkenes, and haloalkanes containing $-CX_3$ (X = F, Cl, Br) groups. In addition, the group rate constants and the substitute group factors of nitrogen-containing organic compounds are only valid for alkyl-substituted amines (Kwok and Atkinson, 1995). Finally, this method is not working for perhalogenated compounds. It seems that the present estimation technique is reasonably reliable when applied to chemical classes used in its derivation. However, its use for compounds that belong to classes other than those used in its development is discouraged.

It is fair to conclude that Atkinson's method is accurate and can be applied to a large and diverse range of chemical classes (Sablijic and Peijnenburg, 2001) but it should be used carefully for other classes of substances (e.g. haloalkanes, haloalkenes, alkyl-substituted amines, perhalogenated compounds).

2. QSAR models

QSAR models have been defined in section 6.2.1. For the reaction rate with hydroxyl, the QSAR models are classified, according to the descriptors used, as follows:

- QSAR models with measured physicochemical descriptors
- QSAR models with structural descriptors

In this context, a general overview of the QSAR descriptors should be provided. In general, a descriptor is a number or set of numbers generated for a compound either by experimental determination or through a functional transformation which operates on a symbolic representation of the compound. The purpose of the descriptor is to create a numerical scale to capture the variation in some structural feature. The descriptors can be obtained experimentally or numerically. Since experimental descriptors can be time-consuming to determine and require that a compound be available for experimentation, much more emphasis has been placed on theoretical descriptors, which can be directly calculated using only the molecular representation of a compound's structure. Even if there is a certain amount of freedom in choosing descriptors, there are also some limitations, in the form of certain desirable characteristics that descriptors should have. If experimental descriptors are used, they should preferably be quick and inexpensive to measure. For theoretical descriptors, they should be easy to calculate and not require a lot of time for calculation. Therefore, the number of descriptors that are available for

calculation is extremely large. This allows a higher degree of freedom in creating structure-property relationships, but it also introduces the added need to select preferentially the most important descriptors (Eike, 2006). The QSAR models used for reaction rate with OH estimation are presented in the next pages.

2.1 QSAR models with measured physicochemical descriptors

Many QSAR models have been published that correlate spectroscopic (absorption maxima, torsional frequencies, ionisation energies, etc.) or thermodynamic (bond dissociation energies) with the reaction rate constant of organic chemicals in reaction with OH and/or NO_3. The most successful and not class-specific model is based on measured ionisation energies. Statistically significant linear correlations between the reaction rate constant for the OH and NO_3 free radical reactions with organic compounds in the gas phase at 298 K and the corresponding vertical ionisation energies (Ei) have been obtained (Güsten, 1999).

2.2 QSAR models with structural descriptors

Quantum-chemical descriptors are a new and rapidly developing class of molecular descriptors, which allow computer estimation of the gas-phase reactions of organic compounds with free radicals. As semiempirical quantum-chemical calculations can be performed routinely, they can provide a vast amount of molecular information about the internal electronic properties of molecules, which are not available from experimental techniques. The most frequently used quantum-chemical descriptors include the energy of the highest occupied molecular orbital (HOMO), reflecting electrophilicity, and that of the lowest unoccupied molecular orbitals (LUMO), reflecting nucleophilicity, frontier orbital electron densities, electron charge distribution, dipole moments, and bond energies (Güsten, 1999).

A QSAR method, called Molecular Orbital OH (MOOH method), has been developed by Klamt. The method contains a system of nonlinear quantitative structure-activity relationship (QSAR) models for the estimation of OH radical reactivity from molecular orbital (MO) calculations. MOOH is based on calculated descriptors such as charge-limited effective high occupied molecular orbital (HOMO)-energy or energy-limited effective HOMO charge.

To make predictions, the ground state of an organic molecule has to be optimized using the Austin Model 1 (AM1) parameterization in MOPAC, a semiempirical quantum-mechanics program (Stewart, 1990). This system of models covers the three most important reactions of OH radicals with organic chemicals, i.e., hydrogen abstraction from aliphatic carbons, addition to carbon double bonds, and addition to aromatic rings (Klamt, 1993). Reactions with oxygen-containing compounds have been modelled in a later version of the system (Klamt, 1996), but reactions with nitrogen-, sulphur-, and phosphorus-containing groups are not taken into account.

The six newly calculated MO descriptors have been devised and all are combinations of MO energies and atomic charges on appropriate reaction centres. A nonlinear optimization procedure was performed to obtain regression coefficients. The

calculated MO energies, as well as the atomic and MO coefficients used to derive those descriptors, have a clear physical meaning (Sablijic and Peijnenburg, 2001).

The MOOH method has also been evaluated and validated by the original author, as well as by an independent study. The system of models for hydrogen abstraction, addition to aromatic ring, and addition to double bonds has been developed using a training set of about 170 organic compounds. The average error of the estimated rate constants for the training set was 0.19 log units (factor of 1.54), once a small number of outliers were excluded. A test set of 38 chemicals was used to validate the predictive potential of the models. The average residual within the test set was 0.28 log units (factor of 1.9), and all estimated reaction rate constants were within a range of 0.48 log units of measured values. The result of this external validation test is very satisfactory, but it is not clear why only a part of available data has been used as the test set. It must also be pointed out that this method cannot be applied to nitro aromatic compounds and halo methanes. An extension of this method for oxygenated compounds (alcohols, aldehydes, ketones, organic acids and their esters) was achieved, using about 100 organic compounds. The average error of the estimated rate constants for the training set of 93 chemicals was 0.21 log units (factor of 1.6). Again, a small number of outliers were excluded from the training set.

The MOOH method and its extension were also evaluated within the EU project on modelling the fate of environmental pollutants. For the large dataset of 460 organic chemicals, it was found that the estimated reaction rate constants have much larger mean squared error than reported in the original studies, i.e., 0.609 log units (factor of 4.06). It was also revealed that the MOOH method systematically underestimates the reaction rate constants with hydroxyl radical.

The evaluation results show that the MOOH method is less accurate than the Atkinson's method. However, there are still two areas where the MOOH method can be useful: (i) for chemicals, for which Atkinson's method gives unreliable estimates and (ii) for compounds from chemical classes not used in the development of Atkinson's method (Sablijic and Peijnenburg, 2001).

3. *ab initio* Molecular Orbital

With the advent of large and inexpensive computer memories, accurate *ab initio* molecular orbital calculations of the abstraction of hydrogen atoms by hydroxyl radicals in the gas phase from organic molecules are now performed at workstations.

The *ab initio* calculations can provide a realistic description of the transition states for the hydrogen abstraction reaction. Barrier heights, bond dissociation energies, and reactions enthalpies as well as the geometry and vibrational frequencies of the transition states can be calculated. Good quality *ab initio* calculations are today restricted to molecules with a maximum of about 30 atoms. The near future will allow direct and accurate calculations of the OH radical reactivity of larger molecules. Furthermore, *ab initio* calculations will enable the prediction of the structure of the reaction products, too (Güsten, 1999).

In the present thesis, the reaction rate with hydroxyl radical has been evaluated using GCM and QSAR methods. The results obtained are reported in the *Results and Discussion Section* (section 6.3.4).

6.3 Results and Discussions on the Estimation of Thermo-Physical Properties

6.3.1 Results and Discussions on the Calculation of Octanol-Water Partition Coefficient

As it has been mentioned in section 6.2.1, different molecular modeling methods have been reported and described in the scientific literature for octanol-water partition coefficient.

Our attention was focused on two methods: QSAR and COSMO. The choice of these methods as well as the advantages and disadvantages correspondent to each of them is briefly summarized below.

The advantages of QSAR methods are: these methods are very fast, allowing them to be applied to large databases of structures, in many cases they require only 2-D molecular connectivity, and can be very accurate for molecules with well-defined group equivalents. The disadvantages of QSAR methods are that they require large numbers of empirically derived parameters; they cannot be used to examine conformational effects in the solute and, many times, no parameters exist for calculating the logKow for the new chemical classes (Best *et al.,* 1999). Another problem with such models is their extremely limited scope. In other words, they perform well, but only for very narrow classes of compounds (Kaiser, 2003).

Direct calculation of octanol-water partition coefficients, using the CSM (COSMO) method, offers the promise of calculating accurate partition coefficients for a wide variety of molecules with a degree of generality not available from the fragment-based methods (Best *et al.,* 1999).

It should be specified that COSMO method, based on computational quantum mechanics (QM), allows us to predict different thermo-physical properties without any experimental data. The COSMO method contains two models: conductor like screening model-realistic solvation (COSMO-RS) and conductor like screening models-segment activity coefficient (COSMO-SAC), which predict intermolecular interactions based on only molecular structure and a few adjustable parameters. COSMO-RS is the first extension of dielectric continuum solvation model to liquid-phase thermodynamics, and COSMO-SAC is a variation of COSMO-RS (Mullins *et al.,* 2006).

As it has been mentioned before, Kow can be also calculated using quantum mechanics (QM), more exactly, the COSMO-RS theory. Few details regarding the COSMO-RS theory are given in the next section. The COSMO-RS theory takes the ideally screened molecules as starting points for the description of molecules in solution. The deviations from ideal screening, which occur in any real solvent, are described as pair wise misfit interactions of the ideal screening charges on parts of the molecules in contact in the fluid. Since COSMO-RS does not depend on experimental data or any parametrization for the solvent, it efficiently enables the calculation of the chemical potential of almost any solute in almost any solvent. Basically, COSMO-RS method assumes that the molecule is made up of small surface elements. The charge density of each of these elements is evaluated by means of quantum mechanics calculations. An ensemble of interacting molecules is replaced by the corresponding ensemble of interacting surface pieces characterized by a screening charge density, namely, the

contribution of all of the differences in polarity obtained when the molecules are not isolated. The characteristic distribution of charges obtained by considering all of these surface elements is the sigma profile (σ-profile) of the molecule. The sigma profile describes the amount of surface in the ensemble having a screening charge density between σ and σ + Δσ (Fermeglia *et al.*, 2006). Sigma profiles depict the surface charge density distribution over the entire molecule. It has to be specified that each molecule's profile is unique and the profiles are sensitive to conformation. The sigma profiles provide a rich and detailed quantitative information about the polarity of molecules (COSMOlogic, 2007; Klamt and Eckcert, 2000; Klamt, 2007)

The difference in the σ-potentials between the two phases can be considered as the local contribution to the partition coefficient, and the partition coefficient can be visualized as a surface property (Klamt, 2005).

Many are the advantages of the method. First, because each molecule is characterized by a sigma profile, the method can treat proximity effects, can distinguish among isomers, and can also take into account the result of a conformational analysis (Fermeglia *et al.*, 2006).

Methodology for Kow Estimation

The above-presented methods for Kow calculation have been implemented in different software programs: COSMO-RS method has been implemented in COSMO*Therm* software and QSAR has been implemented in Estimation Programs Interface (EPI) Suite software developed by EPA.

Correspondent to the COSMO-RS and QSAR methods, two categories of software can be distinguished:

1. Software programs which use as input file .cosmo files (e.g.Cosmo*Therm*)
2. Software programs which use as input file the chemical structure - SMILES files (e.g. EPI Suite software containing the standalone programs KOWWIN and ECOSAR).

A general schema containing the input files format and sources used in Kow calculation is presented in Figure 6.7.

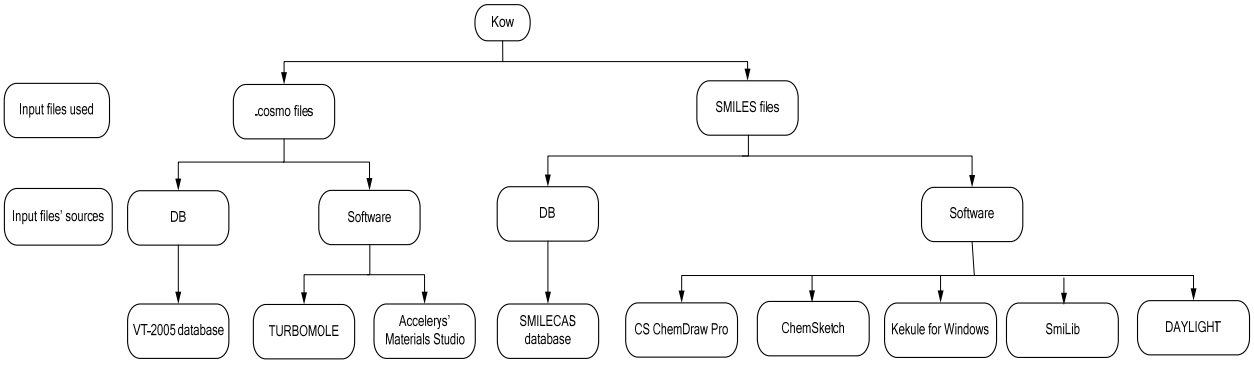


Figure 6.7 Kow input files and software programs schema

The input files correspondent to the COSMO-RS and QSAR methods are described below.

1. COSMO-RS Calculation Methodology

The COSMO-RS method, containing the sigma-profiles of the molecules under study, represents the background of the .cosmo input files. Two software programs have been used in the present thesis to generate the sigma-profiles: TURBOMOLE and Accelerys' Materials Studio. The methodologies for the calculation of Kow are presented below (see Figure 6.8 and Figure 6.9)

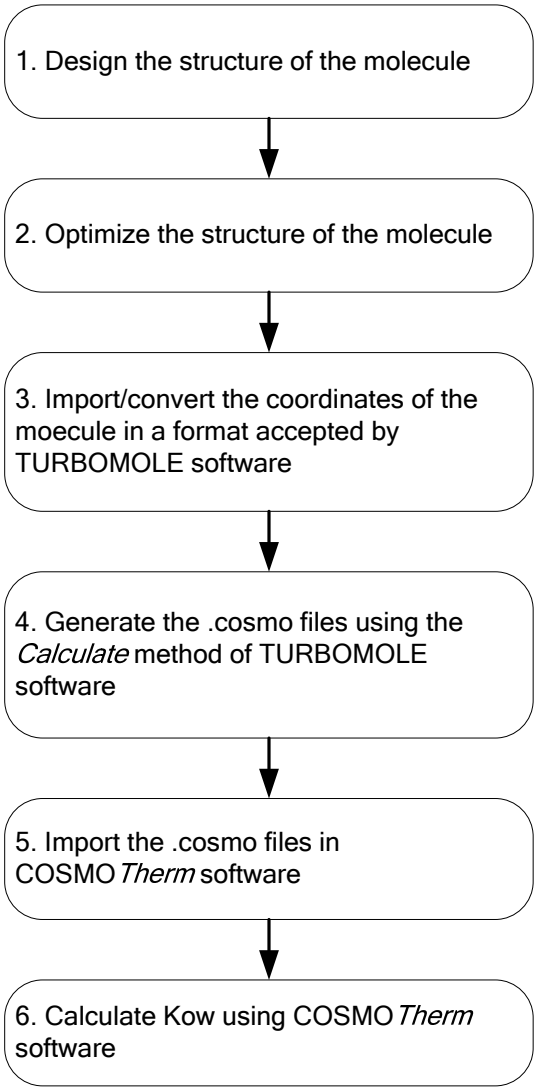


Figure 6.8 Kow calculation using TURBOMOLE software

The first step can be performed using different software programs: Material Studio, InsightII, Discover, Biosym, TRIPOS, Sybyl, MOE, MOPAC, HyperChem.

The second step is the optimization of the molecule structure. This process involves finding the geometry that is most stable and has a minimum energy. Usually, all the software programs used to design structure of the molecule have different optimizing methods. There are different computational modes for geometry optimization.

The third step is the conversion of the structure of the molecule in a format accepted by TURBOMOLE (.car, .ML2, .arc, .xyz).

The fourth step is the .cosmo files generation using the *Calculate* method. *Calculate* is a script that performs quantum chemical calculations. The script supports the user to process COSMO and gas phase calculations for a list of molecules. The general syntax to run *Calculate* script is: **Calculate –l <list of molecules> -m <method> -f < filetype> [-din < dir>] [-dcos <dir>] [-dcomp <dir>] > <logfile>**

Details regarding the elements of *Calculate* script the script are given in Table 6.1 (TURBOMOLE User Manual).

Table 6.1 Details regarding the elements of the Calculate script

SYNTAX	DETAILS	
–l <list of molecules>	The list contains one or more molecules and its/their charge. The names of the molecule have to be equal to the input file names, without the extension (.<filetype>)	
-m <method>	Implemented methods	
	BP-TZVP-GAS	RI-DFT gas phase geometry optimization utilizing the b-p functional and def-TZVP basis set with standard settings
	BP-TZVP-COSMO	RI-DFT COSMO geometry optimization similar to **BP-TZVP-GAS**
	BP-SVP-GAS	RI-DFT gas phase geometry optimization utilizing the b-p functional and def-svp basis set with standard settings
	BP-SVP-COSMO	RI-DFT COSMO geometry optimization similar to **BP-SVP-GAS**
	BP-SVP-GAS-SP	Single point calculation with the same settings as **BP-SVP-GAS**
	BP-SVP-COSMO-SP	Single point calculation with the same settings as **BP-SVP-COSMO**
	AM1-GAS	MOPAC AM1 gas phase geometry optimization
	AM1-COSMO	MOPAC AM1 COSMO geometry optimization
-f < filetype>	Implemented input files types	
	car	Biosym car files
	ML2	TRIPOS mol2 files
	arc	MOPAC archive files
	cosmo	Cosmo files(for recalculation)
	xyz	XYZ format: 1) number of atoms 2) comment line 3) symbol XYZ(for each atom)
- din <dir>	Input file(3D coordinate files) directory	
-dcos <dir>	cosmo/energy/arc file directory (to collect cosmo, energy or mopac archive files)	
-dcomp <dir>	Parent directory for TURBOMOLE calculation	

Details regarding the fifth and the sixth steps are reported in ANNEX 6.

Kow procedure calculation using Accelerys Materials Studio is given below.

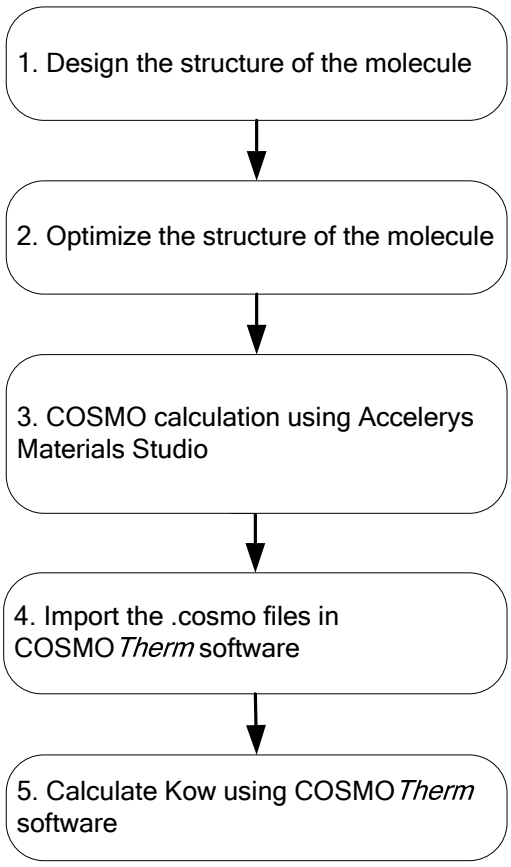


Figure 6.9 Kow calculation using Accelerys Materials Studio software

The first step can be performed using different software programs or can be downloaded from different databases such as:

- NIST database (NIST Chemistry WebBook, 2005)
- SciFinder (SciFinder, 2007)
- National Library of Medicine (NLM, 2007)

The second step is the geometry optimization. It predicts the energy level of the molecule in the ideal gas phase. This calculation is the longest step of the procedure and it will require ~ 75% of the time to produce a sigma profile. Geometry optimization, in Materials Studio software, has been performed using DMol3 Module.

The optimized geometry has been used in the third step to generate the .cosmo files. The .cosmo file contains information regarding: the volume of the cavity around the molecule in the theoretical conducting medium, the condensed phase energy, the number of surface segments, and their charge.

Details regarding the forth and fifth steps are also reported in ANNEX 6.

The procedure described here has been applied to 215 substances. The logKow values obtained have been inserted in the toxicological database.

2. QSAR Methodology

KOWWIN, developed by EPA, is one program based on QSAR, which estimates the octanol-water partition coefficient starting from SMILES files. The SMILES format represents another input file format used to calculate the Kow. SMILES is the acronym for Simplified Molecular Input Line Entry System. It is a chemical notation system used to represent a molecular structure by a linear string of symbols. SMILES notations are comprised of atoms (designated by atomic symbols), bonds, parentheses (used to show branching), and numbers (used to designate ring opening and closing positions) (Syrres, 1999). There are well-defined rules, which are not discussed in the present thesis, regarding the conversion of a chemical formula into a SMILES notation.

The software requires only the chemical structure, entered as a SMILES notation, to estimate the octanol-water partition coefficient (KOWWIN Software User's Guide, 2000). If the substance is present in the software database, logKow is calculated automatically, otherwise, the SMILES notation should be inserted or imported from other databases.

This procedure has been applied to 2625 substances. The logKow values obtained have been inserted in the toxicological database.

Results obtained

The logKow has been estimated, using QM (COSMO) and QSAR methods, for some representative substances, involved in the processes analyzed in *Chapter 7*. The results are presented in Table 6.2.

Analyzing the results shown in Table 6.2, it can be noticed that the logKow relative absolute deviation (RAD) calculated using the formula 6.10 has lower values for nine substances when the QM method has been used for the logKow estimation. The nine substances considered are: methanol, phenol, chloroform, toluene, methyl ethyl chloride, benzene, methane, ethane and propane.

$$\frac{\log Kow_{experimental} - \log Kow_{calculated}}{\log Kow_{experimental}} \qquad (6.10)$$

The mean relative absolute deviation (MRAD) has lower value (0.00765 vs. 0.10715) when the QM-COSMO method has been used for logKow calculations. The results confirm once more the affirmations made in section 6.2.1 regarding the good accuracy of the QM-COSMO method.

Table 6.2 Kow results using different methods

Substance name	**Substance formula**	**Substance CAS**	**logKow (exp.)**	**logKow CALCULATED**		**Kow RAD**	
				(1) **usingQSAR method** KOWWIN-software	(2) **using QM** COSMOTherm software	**RAD for (1)**	**RAD for (2)**
Methanol	CH_4O	67-56-1	-0.77	-0.63	-0.7292	0.1818	0.0529
Naphthalene	$C_{10}H_8$	91-20-3	3.30	3.17	3.0939	0.0393	0.0625
Phenol	C_6H_6O	108-95-2	1.46	1.51	1.4319	-0.0342	0.0192
Chloroform	$CHCl_3$	67-66-3	1.97	1.52	2.1001	0.2284	-0.0660
Toluene	C_7H_8	108-88-3	2.73	2.54	2.6549	0.0696	0.0275
Anisole	C_7H_8O	100-66-3	2.11	2.07	2.2271	0.0189	-0.0555
Methyl Ethyl Chloride	CH_2Cl_2	75-09-2	1.25	1.34	1.2591	-0.0720	-0.0073
Benzene	C_6H_6	71-43-2	2.13	1.99	2.1043	0.0657	0.0121
Methane	CH_4	74-82-8	1.09	0.78	1.0162	0.2844	0.0677
Ethane	C_2H_6	74-84-0	1.81	1.32	1.6319	0.2707	0.0984
Propane	C_3H_8	74-98-6	2.36	1.81	2.1782	0.2330	0.0770
Benzoic Acid	$C_7H_6O_2$	65-85-0	1.87	1.87	2.2379	0	-0.1967
						MRAD	
						0.10715	0.00765

6.3.2 Results and Discussions on Lifetime Calculation

As it has been described in section 6.2.2, SAR method has been used for the lifetime estimation.

Software for Lifetime Estimation

The Atmospheric Oxidation Program (AOP) is a computer program, based on SAR, developed by EPA, used to calculate atmospheric half-lives for organic compounds. The program belongs to the EPI suite software.

The only data required for AOPWIN to estimate the half-life of a chemical substance is the chemical structure of the compound. The chemical structure is entered into the program as a SMILES notation (AOP User's Guide, 2000).

Results obtained

The procedure has been applied to calculate the lifetime for several substances. Table 6.3 contains the experimental lifetime values for some representative chemical compounds as well as the results obtained using SAR. The experimental values have been taken from the World Meteorological Organization Global Atmosphere Watch Report (GAW Report, 2006)

Table 6.3 Lifetime of different chemical substances

Substance name	**Substance formula**	**Substance CAS**	**Lifetime**			**Lifetime RAD**
			Experimental Value (days)	**Methods used to measure experimental values**	**SAR AOP Value** (days)	
Methanol	CH_4O	67-56-1	12	GC/FID PTR-MS	17.364	-0.4470
Toluene	C_7H_8	108-88-3	2	GC/FID GC/MS	2.047	-0.0235
Benzene	C_6H_6	71-43-2	10	GC/FID GC/MS	5.486	0.4514
Ethane	C_2H_6	74-84-0	45	GC/FID	39.323	0.1262
Propane	C_3H_8	74-98-6	11	GC/FID	8.432	0.2335
n-Butane	C_4H_{10}	106-97-8	5	GC/FID GC/MS	4.064	0.1872
Formaldehyde	H_2CO	50-00-0	1	DOAS	1.316	-0.3160
Acetone	C_3H_6CO	67-64-1	51	GC/FID PTR-MS	52.431	-0.0280
Ethanol	C_2H_5OH	64-17-5	4	GC/FID PTR-MS	2.991	0.2523
						MRAD
						0.04843

GC-FID Gas Chromatography-Flame Ionization detection; GC-MS Gas Chromatography-Mass Spectrometry; DOAS Differential Optical Absorption Spectroscopy; PTR-MS Proton Transfer Reaction Mass Spectrometry

By analyzing the results shown in Table 6.3, it can be noticed that the lifetime relative absolute deviation (RAD) has a variation range of -0.0235-0.4514. The RAD is calculated using the following formula:

$$\frac{lifetime_{experimental} - lifetime_{calculated}}{lifetime_{experimental}} \qquad (6.11)$$

The mean relative absolute deviation (MRAD) is 0.04843. Taking into account the complexity of the problem and the limited number of methods, software programs and experimental data available in the literature, the results obtained using the SAR method are satisfactory.

6.3.3 Results and Discussions on Reaction Rate with Ozone Calculation

As it has been described in section 6.2.3, SAR method has been used for the reaction rate with ozone estimation.

Software for reaction rate with ozone estimation

The Atmospheric Oxidation Program (AOP) is a computer program, developed by EPA, used to calculate the reaction rate with ozone. The only data required for AOPWIN to estimate the reaction rate with ozone of a chemical substance is the chemical structure of the compound. The chemical structure is entered into the program as a SMILES notation. It should be specified that the program is able to estimate the reaction rate with ozone only for two classes of substances: acetylene and olefins.

Results obtained

The procedure has been applied to calculate the reaction rate with ozone for several substances. Table 6.4 contains the experimental reaction rate with ozone values for some representative chemical compounds as well as the results obtained using SAR.

The results shown in Table 6.4, presents also the relative absolute deviation (RAD) of the reaction rate with ozone. The RAD is calculated using the following formula:

$$\frac{reaction\ rate\ with\ O_{3\,experimental} - reaction\ rate\ with\ O_{3\,calculated}}{reaction\ ratewith\ with\ O_{3\,experimental}} \qquad (6.12)$$

As it can be noticed the method is able to calculate the reaction rate also for isomers (for example 2-butene cis and trans, 1-3 dichlorpropene cis and trans). The mean relative absolute deviation (MRAD) is 0.271. The results obtained using the SAR method are reasonable taking into account the complexity of the problem and the limited number of methods, software programs and experimental data available in the literature.

Table 6.4 Reaction rate with ozone for different chemical substances

Substance name	Substance formula	Substance CAS	Reaction rate with ozone		Reaction rate with ozone RAD
			Experimental Values (cm^3/molecule-sec)	AOP Values (cm^3/molecule-sec)	
Acetylene	C_2H_2	74-86-2	4.8e-20	3e-20	0.375
Hexene	C_6H_{12}	592-41-6	1.17e-17	1.2e-17	-0.0256
1-pentene	C_5H_{10}	109-67-1	1e-17	1.2e-17	-0.2
1,3 dichlorpropene	$C_3H_4Cl_2$	10061-01-5	1.5e-19	1.126e-19 (cis) 2.25e-19 (trans)	0.249 (cis) -0.5 (trans)
2-butene	C_4H_8	107-01-7	2e-16	1.3e-16 (cis) 2e-16 (trans)	0.35 (cis) 0 (trans)
1-propene	C_3H_6	115-07-1	1.13e-17	1.2e-17	-0.062
Ethene	C_2H_4	74-85-1	1.75e-18	1.75e-18	0
2-methyl 1-pentene	C_6H_{12}	763-29-1	1.31e-17	1.2e-17	0.084
					MRAD
					0.271

6.3.4 Results and Discussions on Reaction Rate with Hydroxyl Calculation

As it has been mentioned in section 6.2.4 in the present thesis the reaction rate with hydroxyl radical has been evaluated using GCM and QSAR methods.

Software for Reaction Rate with Hydroxyl Estimation

The QSAR method has been implemented in the Atmospheric Oxidation Program (AOP). AOP is a computer program, developed by EPA, used to calculate the reaction rate with hydroxyl. The only data required by AOP to estimate the reaction rate of a chemical substance with hydroxyl is the chemical structure of the compound. The chemical structure is entered into the program as a SMILES notation.

The MOOH-GCM method has been implemented in AM1-MOOH code developed by Klamt. The code runs under MOPAC software.

Results Obtained

Both procedures (QSAR and GCM) have been applied to calculate the reaction rate with hydroxyl. These estimation methods may yield different results for the same chemical, depending on the starting point of the estimations.

The results obtained are presented in Table 6.5. Analyzing the results shown in Table 6.5, it can be noticed that the relative absolute deviation (RAD) between the experimental and the estimated values (see formula) is lower for eight substances using the QSAR method.

$$\frac{reaction\ rate\ with\ OH_{experimental} - reaction\ rate\ with\ OH_{calculated}}{reaction\ rate\ with\ OH_{experimental}} \quad (6.13)$$

Investigating the results, we can conclude that the QSAR method is more accurate for the estimation of reaction rate with hydroxyl than the GCM.

Table 6.5 Reaction rate with hydroxyl for different chemical substances

Substance name	**Substance formula**	**Substance CAS**	**Reaction rate with hydroxyl**			**Reaction rate with hydroxyl RAD**	
			Experimental Value (cm^3/molecule-sec)	**GCM AOP Value** (cm^3/molecule-sec)	**QSAR AM1-MOOH Value**	**GCM-AOP RAD**	**QSAR AM1-MOOH RAD**
Methanol	CH_4O	67-56-1	9.44 e-13	6.16e-13	9.3e-13	0.3470	0.0148
Toluene	C_7H_8	108-88-3	5.96e-12	5.226e-12	4.79e-12	0.1231	0.1963
Benzene	C_6H_6	71-43-2	1.23e-12	1.9498e-12	1.51e-12	-0.5852	-0.2280
Ethane	C_2H_6	74-84-0	2.68e-13	2.7e-13	3.51e-13	-0.0075	-0.3097
Propane	C_3H_8	74-98-6	1.15e-12	1.2686e-12	1.276e-12	-0.1031	0.1095
n-Butane	C_4H_{10}	106-97-8	2.54e-12	2.6322e-12	2.519e-12	-0.0363	0.0083
Formaldehyde	H_2CO	50-00-0	9.37e-12	8.13e-12	9.77e-12	0.1323	-0.0427
Acetaldehyde	CH_3CHO	75-07-0	15.8e-12	16.98e-12	15.5e-12	-0.0747	0.0189
Acetone	C_3H_6CO	67-64-1	2.19e-13	2.04e-13	2.3e-13	0.0685	-0.0502
Ethanol	C_2H_5OH	64-17-5	3.27e-12	3.5763e-12	3.27e-12	-0.0937	0
Dimethyl Ether	CH_3OCH_3	115-10-6	2.98e-12	1.6592e-12	4.177e-12	0.4430	-0.4017

6.4 Sensitivity Analysis on the Environmental Impact Categories

The analysis performed in the previous section (6.3) has demonstrated that various molecular modelling methods provide different values for the thermo-physical properties used in the calculation of the Environmental Impact Categories. Consequently, different molecular modelling methods offer different values for the Environmental Impact Categories (GWP, ODP, AP, PCOP, ATP, TTP, HTPE, and HTPI). In order to understand what is the effect one modification of the Environmental Impact Categories has on the final environmental impact of a chemical plant, evaluated through the WAR Algorithm (1D indicator), a sensitivity analysis has been carried out. The procedure is schematic represented in Figure 6.10.

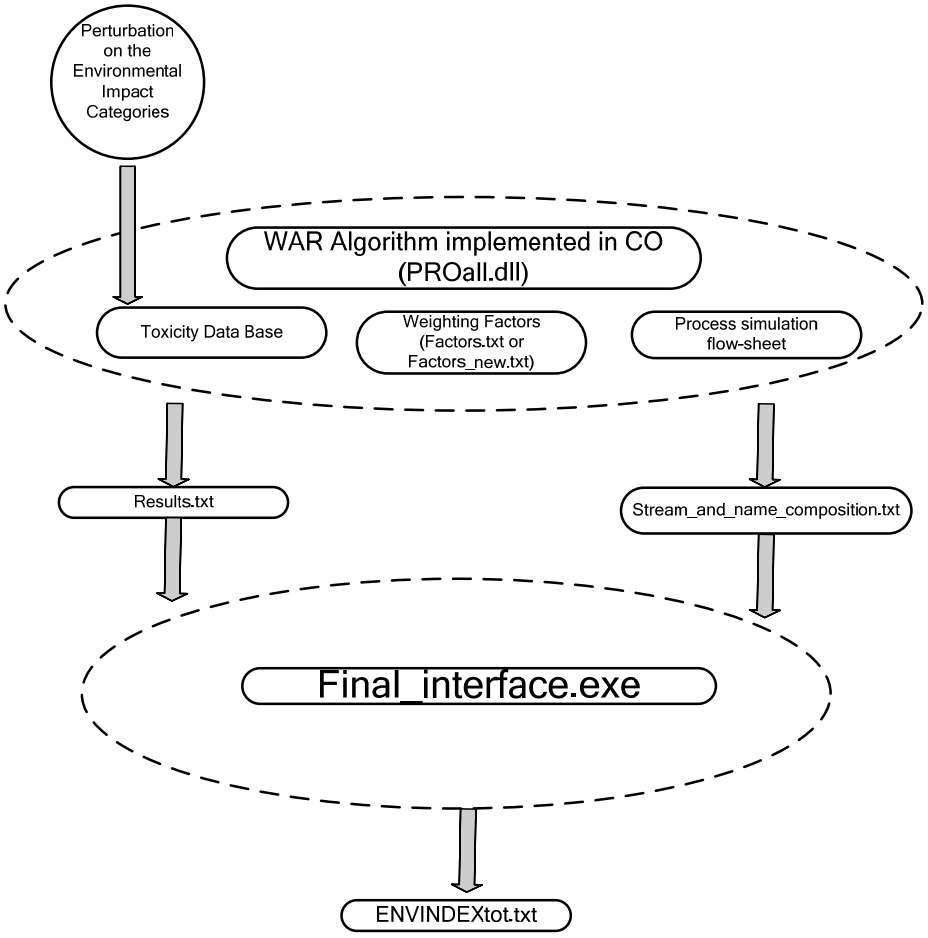


Figure 6.10 Calculation of Environmental Impact Categories and sensitivity analysis

The steps of the sensitivity analysis are schematically represented in Figure 6.11.

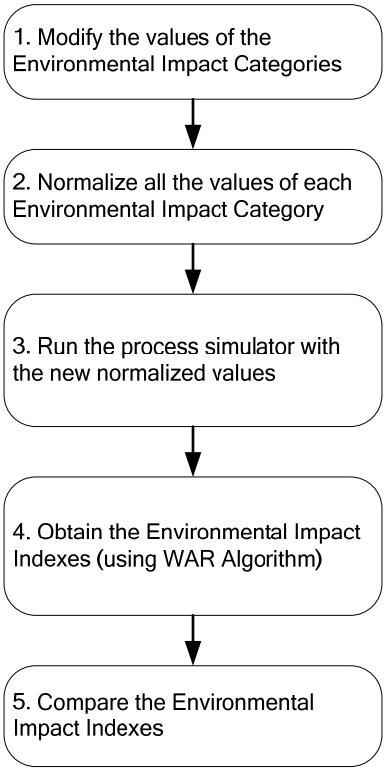


Figure 6.11 Steps of the sensitivity analysis

The sensitivity analysis has been performed on the acrylic acid production process, presented into details in section 7.1.1. The process has been selected from the long list of the processes studied in the present thesis (see *Chapter 7*), because it is a relevant process which was also examined by Young and Cabezas, the authors of the WAR Algorithm (Young and Cabezas, 1999).

The environmental impact categories of the substances presented in the acrylic acid production process are summarized in Table 6.6.

Table 6.6 Environmental impact of the substances used in the acrylic acid production process

SUBSTANCE NAME	**NORMALIZED ENVIRONMENTAL IMPACT CATEGORIES** (impact/kg)
Propylene	2.129
Nitrogen	0
Oxygen	0
Carbon dioxide	0.037959
Water	0
Acetic acid	0.128834
Acrylic acid	10.56628

The substance with the highest environmental impact is acrylic acid, which is the main product of the process. In the present work, the non-product analysis has been considered in the WAR Algorithm, consequently, the environmental impact of acrylic acid is not taken into account. The subsequent two substances with high environmental impact are propylene and acetic acid, so the sensitivity analyses have been performed for these two substances.

1. CASE 1: Sensitivity Analysis on Propylene Data

The propylene flow-rate obtained in the process is 12.785 kg-mol/hr. The total Environmental Impact Categories of propylene is 2.129, as it can be noticed from Table 6.6.

Looking in EPA's database, in the propylene's case, PCOP has the major impact from all the Environmental Impact Categories (see Table 6.7).

Table 6.7 Environmental Impact Categories for propylene

SUBSTANCE NAME	**NORMALIZED ENVIRONMENTAL IMPACT CATEGORIES**							
	GWP	**ODP**	**PCOP**	**AP**	**HTPE**	**HTPI**	**TTP**	**ATP**
Propylene	-	-	2.1165	-	-	-	-	0.0127

The normalized PCOP value is 2.116. This represents 99.4% of the total propylene environmental impact (2.129- see Table 6.6). The default PCOP value, without performing the normalization, has been modified with ±25%. The calculated values have been introduced in the DB. The normalization has been performed and the new normalized PCOP values are 2.51524, respectively 1.5321. The process simulator has been run with the new normalized values. The simulation results are sent to the final interface (PEIfinal.exe) and the final results are presented in Table 6.8.

Table 6.8 Environmental Impact Indexes (1D indicator) obtained in the sensitivity analysis of acrylic acid production process (CASE 1)

CASE STUDY	**ENIVORONMENTAL IMPACT INDEXES NAME**			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
Initial DB value	17047.553	2.673	5668.061	0.888
+25% of Initial DB value	17047.553	2.673	5668.061	0.888
-25% of Initial DB value	17047.553	2.673	5668.061	0.888

It can be noticed that the environmental impact indexes obtained for the cases under study are invariable. In conclusion, an error on the impact category calculation will not affect the final results.

2. CASE 2: Sensitivity Analysis on Acetic Acid Data

The acetic acid flow-rate obtained in the process is 6.05 kg-mol/hr. The total Environmental Impact Categories of acetic acid is 0.128834, as it can be noticed from Table 6.6.

Looking in EPA's database, in the acetic acid's case, HTPI and TTP have the major impact from all the Environmental Impact Categories (see Table 6.9).

Table 6.9 Environmental Impact Categories for acetic acid

SUBSTANCE NAME	**NORMALIZED ENVIRONMENTAL IMPACT CATEGORIES**							
	GWP	**ODP**	**PCOP**	**AP**	**HTPE**	**HTPI**	**TTP**	**ATP**
Acetic Acid	-	-	-	-	0.0118	0.1063	0.1063	0.0107

The normalized HTPI and TTP values are 0.1063. This represents 82.51% of the total acetic acid environmental impact (0.128834 see Table 6.6). The default HTPI and TTP values, without performing the normalization, have been modified with ±25%. The values calculated have been introduced in the DB. The normalization has been performed and the new normalized HTPI and TTP values are 0.085 and 0.1417, respectively. The process simulator has been run with the new normalized values. The simulation results are sent to the final interface (PEIfinal.exe) and the final results are presented in Table 6.10.

Table 6.10 Environmental Impact Indexes (1D indicator) obtained in the sensitivity analysis of acrylic acid production process (CASE 2)

CASE STUDY	**ENIVORONMENTAL IMPACT INDEXES NAME**			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
Initial DB value	17047.553	2.673	5668.061	0.888
+25% of Initial DB value	17047.553	2.673	5668.061	0.888
-25% of Initial DB value	17047.553	2.673	5668.061	0.888

Like in the previous sensitivity analysis, it can be noticed that the environmental impact indexes obtained for the cases under study are the same. In conclusion, an error on the impact category calculation will not affect the final results.

Conclusions

The main conclusions of the present study can be summarized as follows. Different molecular modelling methods used to estimate the thermo-physical properties, which lead to the calculation of the Environmental Impact Categories are proposed described and applied. The thermo-physical properties analyzed in the present chapter are: the octanol-water partition coefficient, the lifetime, the reaction rate with ozone, and the reaction rate with hydroxyl. These properties have been estimated/calculated for several substances. Taking into account the relative absolute deviation and the mean relative absolute deviation the most efficient methods for calculating the thermo-physical properties are: COSMO for octanol-water partition coefficient, SAR for lifetime and for reaction rate with ozone, and QSAR for reaction rate with hydroxyl

The results obtained in this study underline the importance of molecular modelling tools for evaluating the properties of the chemical substances which are not present in the DB.

The chapter contains also a sensitivity analysis on the effect of one modification of the Environmental Impact Categories on the final 1D indicator.

Chapter 7

Case Studies Developed

Summary

In this chapter, representative chemical process examples are analyzed using the PSP methodology.

Two main classes of processes are discussed: processes described in scientific literature and processes correspondent to chemical plants situated in developing countries.

A brief introduction, process description, process simulation and environmental impact results are reported for each process. Different process design alternatives are proposed and through PSP Framework, the most environmentally friendly is selected.

"The possible solutions to a given problem emerge
as the leaves of a tree, each node representing
a point of deliberation and decision."
Niklaus Wirth

The present chapter represents a collection of chemical processes studied during the PhD period. Its purpose is not to present all the technical, mechanical or economical details of the processes (detailed schema, sensitivity analysis, optimization, plant control, risk and safety analysis, materials used in the plant construction, etc.), but to show in which way the PSP Framework can be a valid tool in process design. Certainly, the above presented information is necessary to understand better the process. For this reason, for each process, a brief introduction, a process description, process simulation schema and results are reported.

Two main classes of processes are discussed in this part of the thesis: processes described in the scientific literature and processes correspondent to chemical plants situated in developing countries. This choice has been made according to the mandate of the **International Centre for Science and High Technology-United Nations Industrial Development Organization (ICS-UNIDO)**: ***"Promotion of and assistance in the development, selection, transfer and use of technology in favor of developing countries"*** (General Conference Vienna 3/7 December 2001-GC.9/12/Add.1).

Four process categories can be identified according to PSP Framework. These are:

1) processes where one or more parameters have been modified (e.g. Acrylic Acid Production Process, Sweetening Natural Gas by DGA Absorption, Formaldehyde Production Process, Ethanol Production Process from Sugar Cane Molasses)
2) processes where the same product is obtained starting from two different raw materials (e.g. Phthalic Anhydride Production Process, Maleic Anhydride Production Process)
3) processes with heat integration (e.g. Dimethylether Production Process, R-134a Production Process, Multiple Effect of Sugar Cane Juice Process)
4) processes with different streams recovery (e.g. Electroplating Wastewater Discharge Process)

Ten processes have been analyzed. Each process is detailed in the next section.

7.1 Processes Described in Scientific Literature

7.1.1 Acrylic Acid Production Process

Introduction

Acrylic acid is used as a precursor for a wide variety of chemicals in the polymers and textile industries. There are several ways to produce acrylic acid but the most common is via partial oxidation of propylene (Turton *et al.*, 2003).

The following reactions occur in the acrylic acid production:

$$C_3H_6 + \frac{3}{2}O_2 \rightarrow C_3H_4O_2 + H_2O$$

propylene *acrylic acid*

$$C_3H_6 + \frac{5}{2}O_2 \rightarrow C_2H_4O_2 + H_2O + CO_2$$

propylene *acetic acid*

$$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3\,H_2O + 3\,CO_2$$

The reaction kinetics (Turton *et al.*, 2003) is presented in Table 7.1.

Table 7.1 Kinetic data for acrylic acid production process

REACTION	**ACTIVATION ENERGY Ei (kcal/kmol)**	**KINETIC CONSTANT $k_{0,i}$ (kmol/m^{3}reactor h/ (kPa)^2)**
R 1	15000	$1.59*10^5$
R 2	20000	$8.83*10^5$
R 3	25000	$1.81*10^5$

The process flow diagram for acrylic acid production process is illustrated in Figure 7.1.

Simulation Goal

The goal of the present simulation is to analyze the process, to understand how a parameter modification (the reactor temperature) affects the final result streams and to identify the most environmentally friendly design from different process alternatives.

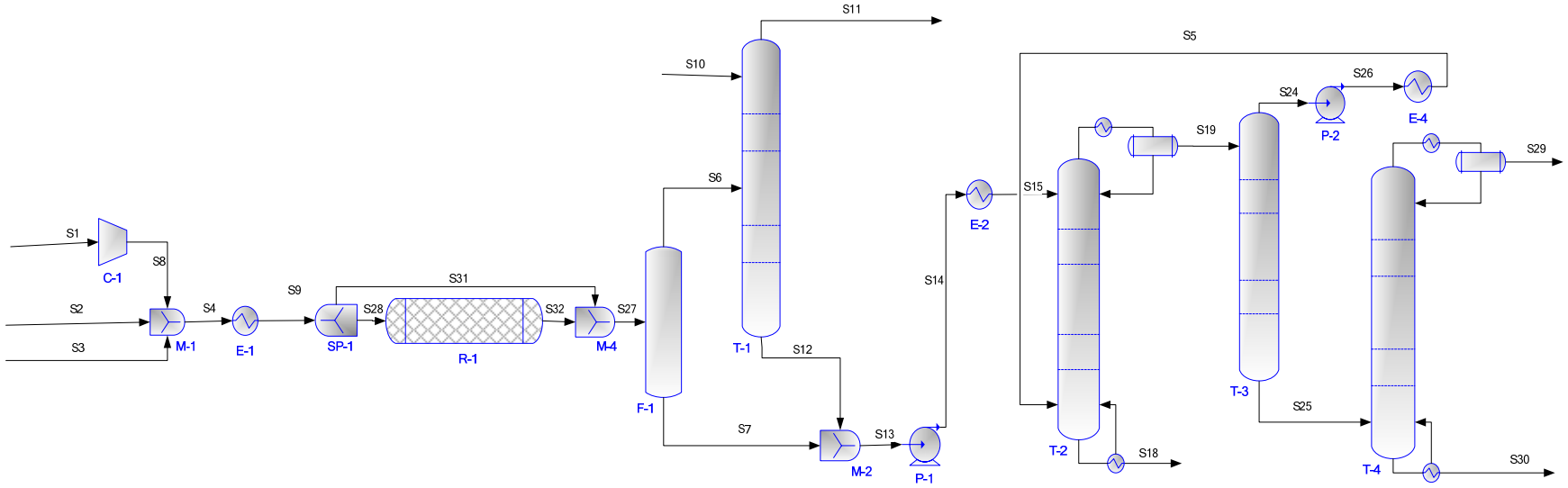


Figure 7.1 Acrylic acid production process

Process Description

Propylene, S3, is fed from a storage tank. Air, S1, is compressed in C-1 as a source of oxygen. Steam, S2, issued to provide thermal ballast for the exothermic heat of reaction. After being mixed in M-1, the feeds enter the reactor R-1. The reactor is assumed to operate isothermally at 310ºC (Young *et al.*, 1999). The reactor used for the present process is a fluidized bed. It is assumed that the bed of catalyst behaves as a well-mixed tank. The gas flow is assumed to be a plug flow through the bed, with 10% of the gas bypassing the catalyst (Turton *et al.*, 2003). This is the reason why the initial stream entering the reactor, S9, was split into two streams: S28 and S31 (10% of the gas bypassing the catalyst). The effluent from the reactor, S27, is quenched in an adiabatic flash drum, F-1. The vapour effluent is stripped with de-ionized water stream in T-1 to recover the small fraction of acrylic acid that escaped in the vapour stream. The vapour effluent of the stripper, S11, is delivered to an incinerator and is considered a waste stream. The liquid effluent of the flash drum is mixed in M-2, with the liquid effluent of the stripper to form S13. The non-recycled liquid effluent is sent to a liquid-liquid extractor, T-2, to remove the acid fraction from the water (Young *et al.*, 1999). Many possible solvents can be used (Turton *et al.*, 2003). In this case, diisopropyl ether (DIPE) is utilized. The organic phase is sent to a recovery column where the DIPE is recovered overhead in T-3 and recycled to the extractor, T-2, (Turton *et al.*, 2003). The bottom stream of this column, S25, containing acrylic acid and acetic acid is sent to another column, T-4. The products of this column are the acrylic acid 99.9%, S30, at the bottom of the column and the acetic acid obtained at the top, S29. The aqueous phase is sent to a wastewater column where a small amount of DIPE is recovered and returned in the extractor. The bottom product of T-2, S18, containing water and trace of solvent and acid is sent to a wastewater treatment plant (Turton *et al.*, 2003).

From the environmental point of view it is desired to reduce the waste flow-rates and concentration for S11, S18, S29 streams and, in the meantime, to obtain a high rate of acrylic acid with 99.9% purity.

Process Simulation

The process has been simulated using PROII and Aspen Plus process simulators.

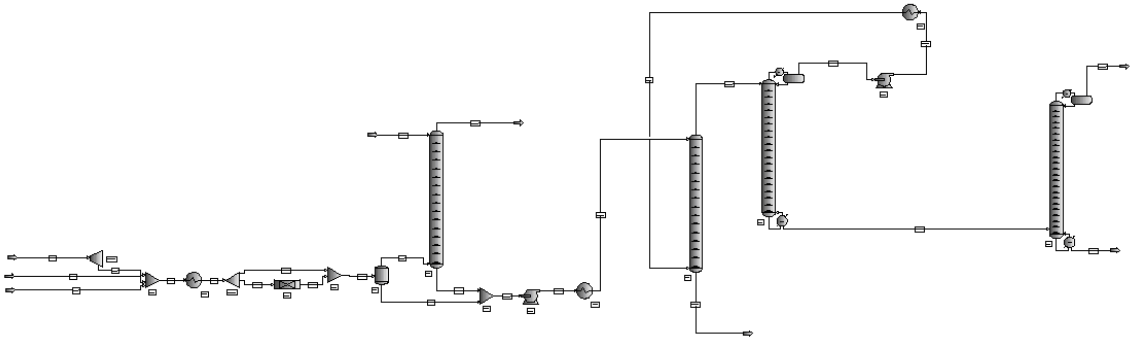


Figure 7.2 PROII schema of acrylic acid production process

UNIFAC is the thermodynamic method used in the present simulation. Input data for, air - S1, steam - S2, propylene - S3 and deionized water - S10, streams are summarized in Table 7.2.

Table 7.2 Input streams specifications for acrylic acid production process (base case)

STREAM NAME		**S1**	**S2**	**S3**	**S10**
STREAM DESCRIPTION					
TEMPERATURE	C	25	159	25	25
PRESSURE	BAR	1	6	11.5	5
ENTHALPY	M*KCAL/HR	0.710119665	11.75915051	0.507270336	0.063499026
MOLECULAR WEIGHT		28.64893723	18.01499939	42.08100128	18.01499939
MOLE FRACTION VAPOUR		1	1	1	0
MOLE FRACTION LIQUID		0	0	0	1
RATE	KG-MOL/HR	1362.899902	992.300415	127.0000763	141
FLUID RATES	KG-MOL/HR				
PROPENE		0	0	127.0000763	0
WATER		25.29999924	992.300415	0	141
OXYGEN		280.8999939	0	0	0
NITROGEN		1056.700073	0	0	0
ACETIC		0	0	0	0
ACRYLIC		0	0	0	0
CO2		0	0	0	0
DIPE		0	0	0	0

Data reported in Table 7.3 represent the simulation results for acrylic acid stream - S30, acetic acid stream - S29, wastewater stream - S18, and off-gases stream - S11.

Table 7.3 Output streams results for acrylic acid production process (base case)

STREAM NAME		**S30**	**S29**	**S18**	**S11**
STREAM DESCRIPTION					
TEMPERATURE	C	89.8706665	48.82608032	40	48.9803772
PRESSURE	BAR	0.159999996	0.07	2.400000095	1
ENTHALPY	M*KCAL/HR	0.274819464	0.041124947	0.832017601	2.602355957
MOLECULRA WEIGHT		72.05199432	60.20545959	18.05443001	27.89934921
MOLE FRACTION VAPOUR		0	1	0	1
MOLE FRACTION LIQUID		1	0	1	0
RATE	KG-MOL/HR	88.59455109	6.112485409	1154.734741	1334.856934
FLUID RATES	KG-MOL/HR				
PROPENE		0	0	0.00011257	12.78840446
WATER		4.36E-08	3.08E-05	1153.560791	155.5376282
OXYGEN		0	0	0.031451847	48.60069275
NITROGEN		0	0	0.429912388	1055.89563
ACETIC		0.088590592	6.051359653	0.089903452	0.488675058
ACRYLIC		88.50596619	0.054474119	0.081058107	1.052302241

CO2	0	0	0.222497851	60.49351501
DIPE	1.00E-06	0.006620856	0.31898275	0

The base case and other four design alternatives for this process have been simulated and analyzed in order to choose the best one. As mentioned before, it is desired to reduce the waste stream flow-rate and concentration for S11, S18, S29 streams and, in the meantime, to obtain a high acrylic acid flow-rate with high purity (99.9%).

The parameter modified in the process was the reactor temperature (the reactions are sensitive to the temperature modifications as can be noticed from the kinetics – Table 7.1). The temperature of the reactor has been decreased from 310ºC to 210ºC. The simulations results, in terms of acrylic acid rates and purities are presented in Table 7.4.

Table 7.4 Simulation results for acrylic acid production process (base case)

CASE STUDY	**REACTOR TEMPERATURE** (º C)	**ACRYLIC ACID RATE** (kg-mol/hr)	**ACRYLIC ACID PURITY** (%)
CASE 1(base case)	310	88.594	99.9004
CASE 2	280	95.43325	99.8987
CASE 3	260	98.3325	99.8998
CASE 4	230	97.485	99.8999
CASE 5	210	89.603	99.9003

Environmental Impact Results

The environmental impact of the process has to be estimated. The goal is to limit the environmental impact and, in the meantime, to maximize the acrylic acid production. 3D and 1D indicators have been calculated using the mass flow-rates, the input and output streams composition (mass fraction) and toxicological data.

The CO Modules for 3D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.5.

Table 7.5 CO Modules specifications for 3D indicators for acrylic acid production process

CO MODULE NAME	**CO MODULE PARAMETERS**				**CONNECTED STREAM**
	NAME	**CONNECTION**	**WATER_USAGE**	**AIR_USAGE**	
CO1	1	0	10	11	S1
CO2	2	0	10	0	S2
CO3	3	0	0	0	S3
CO4	4	0	10	0	S10
CO5	5	1	10	10	S11
CO6	6	1	10	10	S18
CO7	7	3	10	0	S29
CO8	8	2	10	0	S30
CO9	9	-	-	-	S27

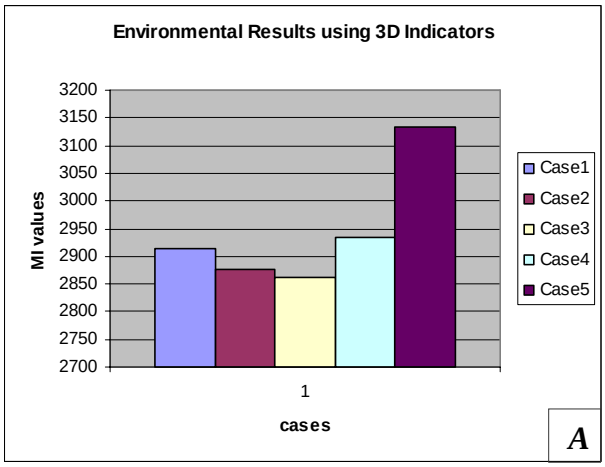
The 3D indicators calculated using data from the process simulator and from the database are presented in Table 7.6.

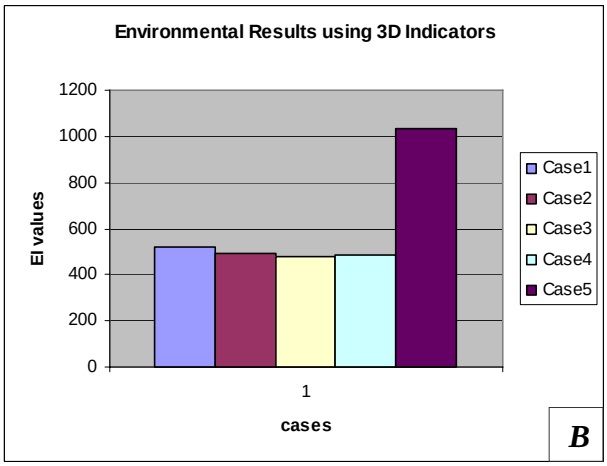
Table 7.6 3D indicators obtained in the acrylic acid production process

CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	2915.066	520.461	301020	8530.52
CASE 2	2877.105	494.714	301020	8530.52
CASE 3	2861.003	480.635	301020	8530.52
CASE 4	2934.939	485.545	310020	8530.52
CASE 5	3134.124	1034.755	310020	8530.52

The case with the lowest 3D indicators is the third case, CASE 3. This represents the most environmentally friendly design. PCR has lower values for CASE3, CASE2 and CASE1. PEI has the same values for all five cases because the physical states of the substances involved in the process are the same and the receiving medium (air, water, soil) is also the same.

In conclusion, CASE 3 represents the most environmentally friendly design, taking into account the 3D indicators. The same results are reported in Figures 7.3.





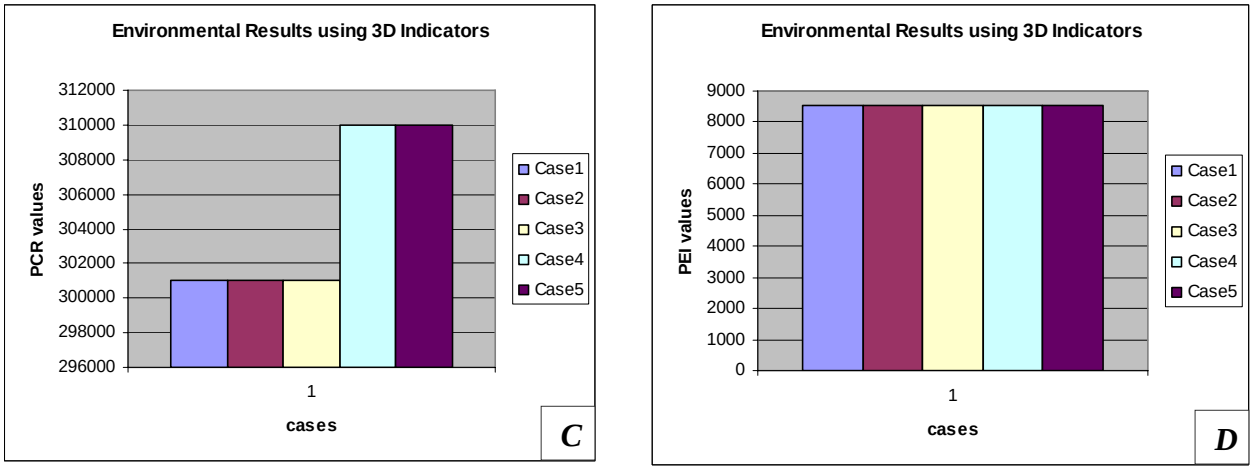


Figure 7.3 3D Indicators for acrylic acid production process A) MI; B) EI; C) PCR; D) PEI

For the same cases the WAR Algorithm has been applied.

The CO Modules for 1 D indicator (Proall and Proenergia) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.7.

Table 7.7 CO Modules specifications for 1D indicator for acrylic acid production process

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	0	2	S2
CO3	0	0	3	S3
CO4	0	0	4	S10
CO5	0	1	5	S11
CO6	0	1	6	S29
CO7	0	2	7	S30
CO8	0	1	8	S18
CO9	1	1	9	S37

The Environmental Impact Indexes, obtained using the 1D indicator- WAR Algorithm, are presented in Table 7.8.

Table 7.8 Environmental Impact Indexes obtained in the acrylic acid production process using WAR Algorithm

CASE STUDY	ENIVORONMENTAL INDEXES NAME			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	17047.553	2.673	5668.061	0.888
CASE 2	5424.005	0.791089	-5955.487	-0.868
CASE 3	5074.482	0.71691	-6305.001	-0.891
CASE 4	5203.7025	0.74146	-6175.789	-0.880
CASE 5	11665.58	1.8084	286.090	0.043

The Environmental Impact Indexes have lowest values in the third design alternative, CASE 3.

The same results are presented in Figures 7.4.

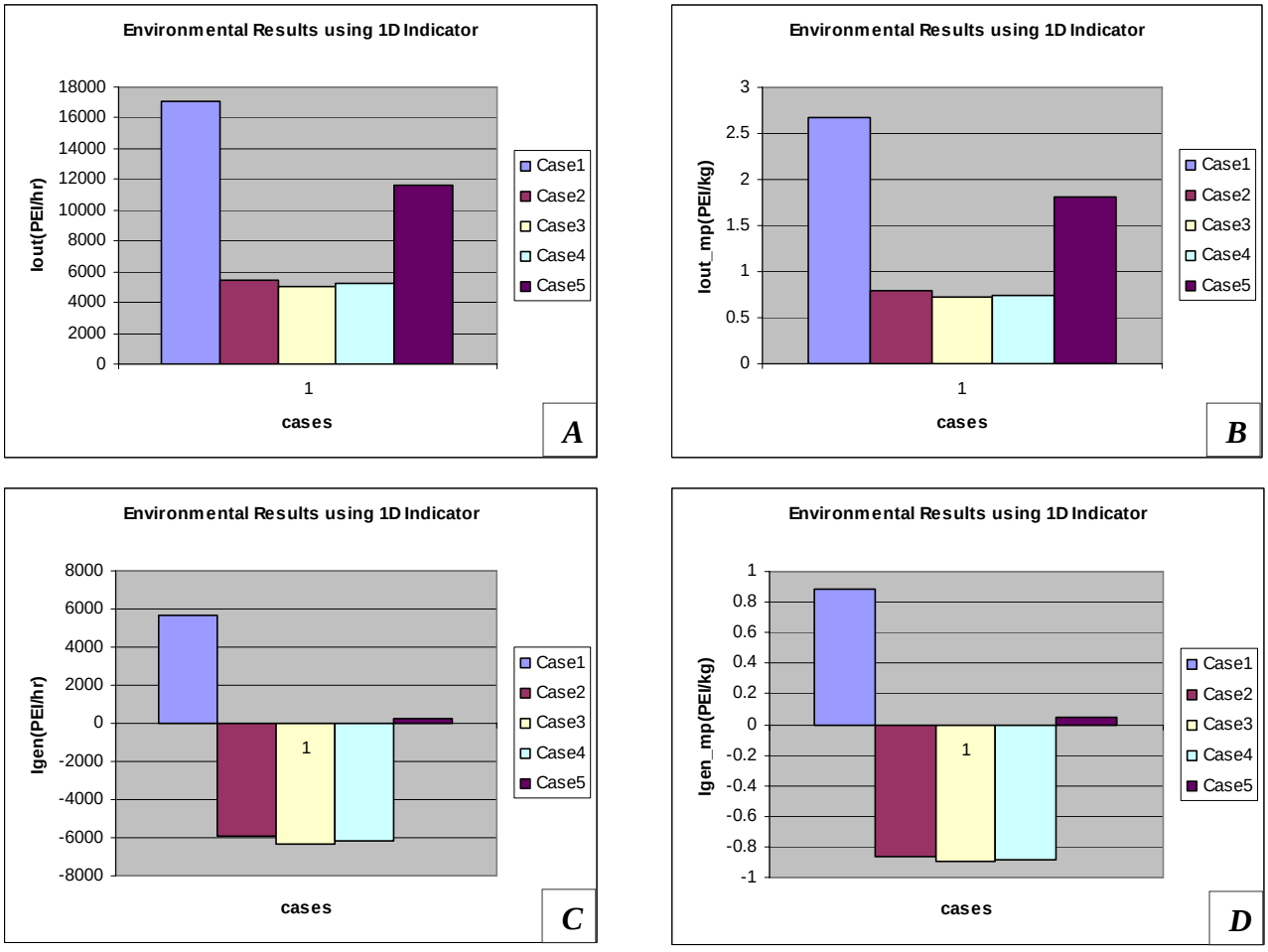


Figure 7.4 1D Indicators for acrylic acid production process A) Iout; B) Iout_mp; C) Igen; D) Igen_mp

Conclusions

The acrylic acid production process has been simulated using PROII and Aspen Plus process simulators. Sensitivity analysis for one process parameter (the reactor temperature) has been performed. Five process alternatives are proposed and analyzed in order to choose the most environmentally friendly one. The results obtained, using the 3D and 1D indicators of the PSP Framework, provide the third alternative design as best solution. This result is also stressed by economical motivations. As it can be noticed from Table 7.4 the highest acrylic acid rate is also obtained in the third case. The purity of acrylic acid obtained in the third case is also very high (see Table 7.4). After all these considerations we can emphasize that the decision to choose CASE 3 for acrylic acid production process is the best solution.

7.1.2 Sweetening Natural Gas by DGA Absorption

Introduction

Natural gas, as it is used by consumers, is much different from the natural gas that is brought from underground up to the wellhead. Although the processing of natural gas is in many respects less complicated than the processing and refining of crude oil, it is equally necessary before its use by end users (NaturalGas.org, 2004).

Hydrogen sulfide, carbon dioxide, mercaptanes and other contaminants are often found in natural gas streams. Gases containing H_2S or both H_2S and CO_2 are commonly referred to as sour gases or acid gases in the hydrocarbon processing industries. The process for removing hydrogen sulfide from sour gas is commonly referred to as 'sweetening' the gas. H_2S is a highly toxic gas that is corrosive to carbon steels. CO_2 is also corrosive to equipment and reduces the energetic value of the gas. Gas sweetening processes remove these contaminants so that that the gas is suitable for transportation and use. The sweetening is performed using different amine or amine mixtures solutions.

A typical amine gas treating process includes an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the down flowing amine solution absorbs H_2S and CO_2 from the up- flowing sour gas to produce a sweetened gas stream (i.e. H_2S-free gas) as a product and an amine solution rich in the absorbed acid gases. The resultant "rich" amine is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H_2S and CO_2 (Answers, 2007c). In the present process diglycolamine (DGA) is used.

The simplified schema of the process is presented in Figure 7.5.

Simulation Goal

The goal of the present simulation is to analyze the process, to reduce the energy consumption and to identify the most environmentally friendly design from different alternatives.

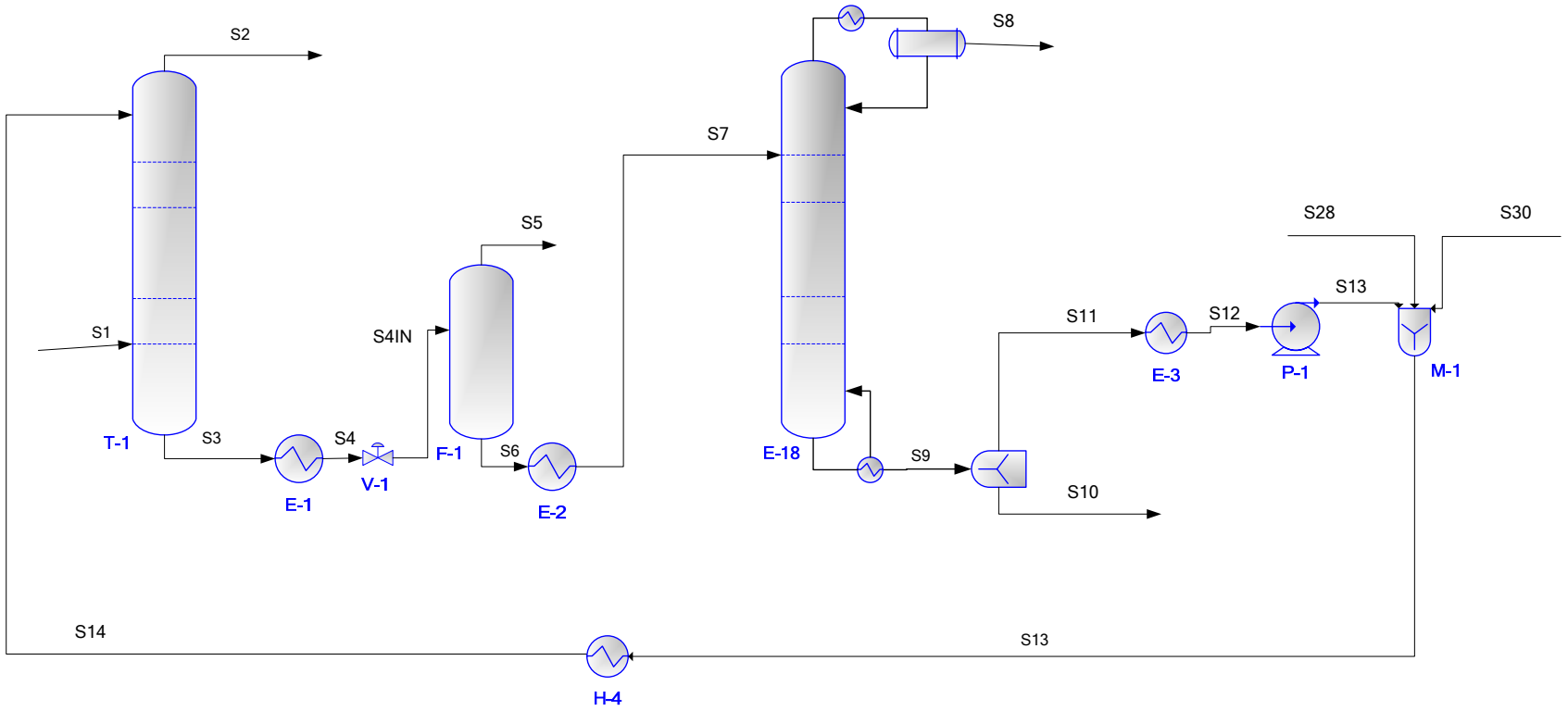


Figure 7.5 Sweetening natural gas by DGA absorption

Process Description

Natural gas, S1, containing CH_4, CO_2 and H_2S and the stream S14, containing absorption liquid (DGA solution), enter in the first distillation column, T-1. The goal of this absorption column is to separate the methane. The products of the column are: stream S2, containing the removed CH_4, obtained in the top of T-1, and stream S3 containing water, DGA, CO_2, H_2S and small amounts of CH_4, obtained in the bottom of the column. S3 is heated in E-1 and sent to the second separation device, F-1. The top stream of F-1, S5 contains the remained CH_4 traces. The bottom stream, S6, is sent to the second distillation column, T-2. This is the desulphurization column having the objective of separating the hydrogen sulfide. The top stream of the second column, S8, contains removed gases. The bottom stream, S9, is made of DGA and water. The losses of DGA and water are supplied with S28 and S30 streams. These are mixed with S13 in M-1 and recycled back to the absorber, T-1.

From an environmental point of view, it is desired to reduce the gaseous streams, S2, S5 and S8, released in the atmosphere.

Process Simulation

The process has been simulated using PROII and Aspen Plus process simulators.

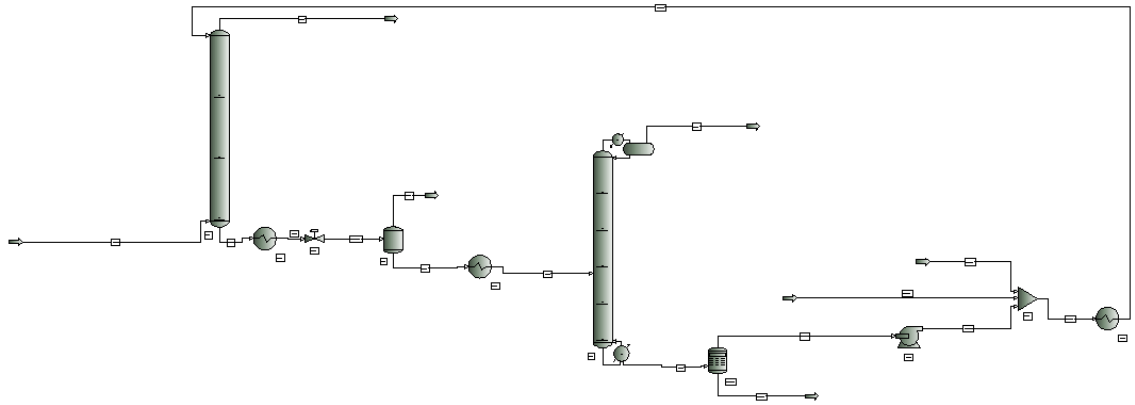


Figure 7.6 PROII schema for sweetening natural gas by DGA absorption

DGA electrolyte model is the thermodynamic method used in the present simulation. Input data for natural gas - S1, DGA makeup - S28, and water makeup - S30 streams are presented in Table 7.9.

Table 7.9 Input streams specifications for sweetening natural gas by DGA absorption (base case)

STREAM NAME		**S1**	**S28**	**S30**
STREAM DESCRIPTION				
TEMPERATURE	C	32.22223	15.55557	15.55557
PRESSURE	ATM	62.24167	61.96949	61.96949
ENTHALPY	MM BTU/HR	-418.701	0.120813	-799.127

MOLECULAR WEIGHT		18.34297	105.1369	18.01528
MOLE FRACTION VAPOUR		1	0	0
MOLE FRACTION LIQUID		0	1	1
RATE	KG-MOL/HR	4980.553	33.11222	2943.892
FLUID RATES	KG-MOL/HR			
H2O		0	0	2943.892
CO2		249.0232	0	0
H2S		249.008	0	0
CH4		4482.521	0	0
DDGA		0	33.11222	0
C3H8		0	0	0
C4H10		0	0	0
C2H6		0	0	0
N2		0	0	0
H2CO3		0	0	0
O2		0	0	0
NO2		0	0	0
NO		0	0	0
SO2		0	0	0
H2		0	0	0
CL2		0	0	0
HCL		0	0	0
CO		0	0	0

Data reported in Table 7.10 represent the simulation results for the output streams.

Table 7.10 Output streams results for sweetening natural gas by DGA absorption (base case)

STREAM NAME		**S2**	**S5**	**S8**
STREAM DESCRIPTION				
TEMPERATURE	C	44.24792	101.2003	94.04993
PRESSURE	ATM	61.96949	5.763496	1.068322
ENTHALPY	MM BTU/HR	-318.749	-0.65742	-367.938
MOLECULAR WEIGHT		16.04591	18.55001	22.98156
MOLE FRACTION VAPOUR		1	1	1
MOLE FRACTION LIQUID		0	0	0
RATE	KG-MOL/HR	4483.676	6.958488	1736.892
FLUID RATES	KG-MOL/HR			
H2O		6.729117	1.056329	1309.898
CO2		0.00393	0.15232	178.6378
H2S		1.64E-05	0.600735	247.9154
CH4		4476.935	5.146115	0.441006
DDGA		0.008375	0.00299	2.69E-05
C3H8		0	0	0
C4H10		0	0	0
C2H6		0	0	0
N2		0	0	0
H2CO3		0	0	0

O2	0	0	0
NO2	0	0	0
NO	0	0	0
SO2	0	0	0
H2	0	0	0
CL2	0	0	0
HCL	0	0	0
CO	0	0	0

Environmental Impact Results

Two process design alternatives have been simulated. The base case is identical with the schema presented in Figure 7.5. One modification has been made, starting from the base case. The stream, S9, coming from the bottom of the second column, T-2, was used to heat S7. In this way the heat for E-2 is supplied using some internal stream of the process. The schema for the second design alternative is presented in Figure 7.7.

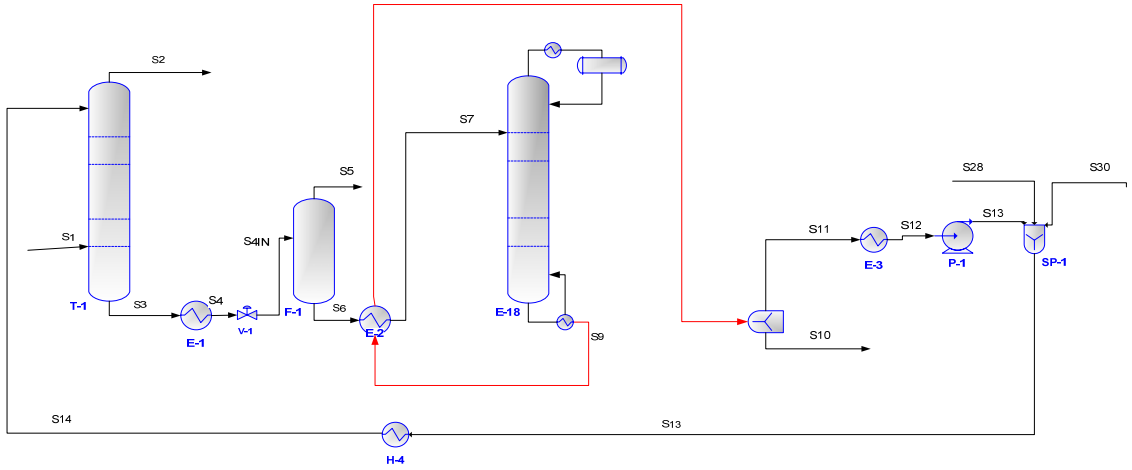


Figure 7.7 Sweetening natural gas by DGA absorption (CASE 2)

The CO Modules for 3D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.11.

Table 7.11 CO Modules specifications for 3D indicators for sweetening natural gas by DGA absorption

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	0	0	S1
CO2	2	2	10	0	S2
CO3	3	1	10	0	S5
CO4	4	1	10	0	S8
CO5	5	1	10	0	S10
CO6	6	0	0	0	S28
CO7	7	0	10	0	S30
CO8	8	-	-	-	S1

The 3D indicators calculated using data from the process simulator and from the database are presented in Table 7.12.

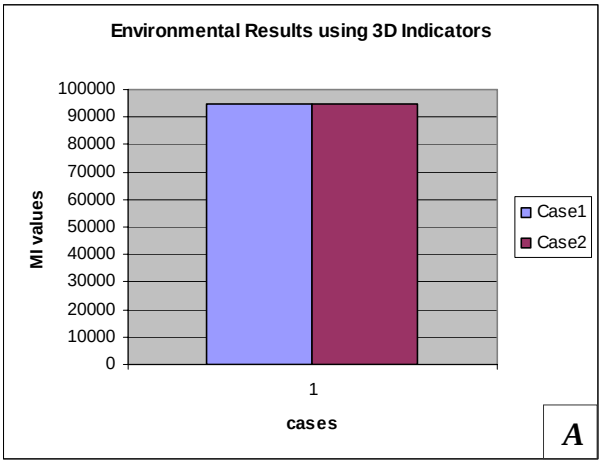
Table 7.12 3D Indicators obtained in the sweetening natural gas by DGA absorption

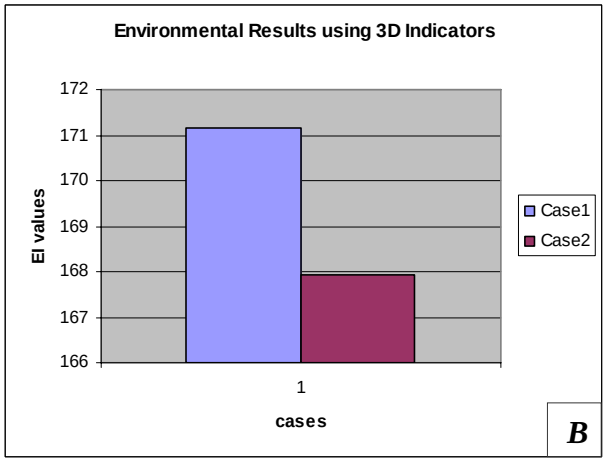
CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	94718.37	171.17	10023	5813.4
CASE 2	94718.37	167.94	10023	5813.4

MI indicator has the same values in both cases. EI is lower in the second design alternative, CASE 2. The reasons why PCR and PEI have equal values for both cases are explained below. Both processes are continuous processes, so the frequency class for the substances present in the process is the same (permanent use; > 6h/day- see Table 3.1) as are the risk phrases. PEI has the same values in both cases because the physical states of the substances involved in the process are the same and the receiving medium (air, water, soil) is also the same.

CASE 2 represents the most environmentally friendly design, taking into account the 3D indicators.

The same results are reported in Figures 7.8.





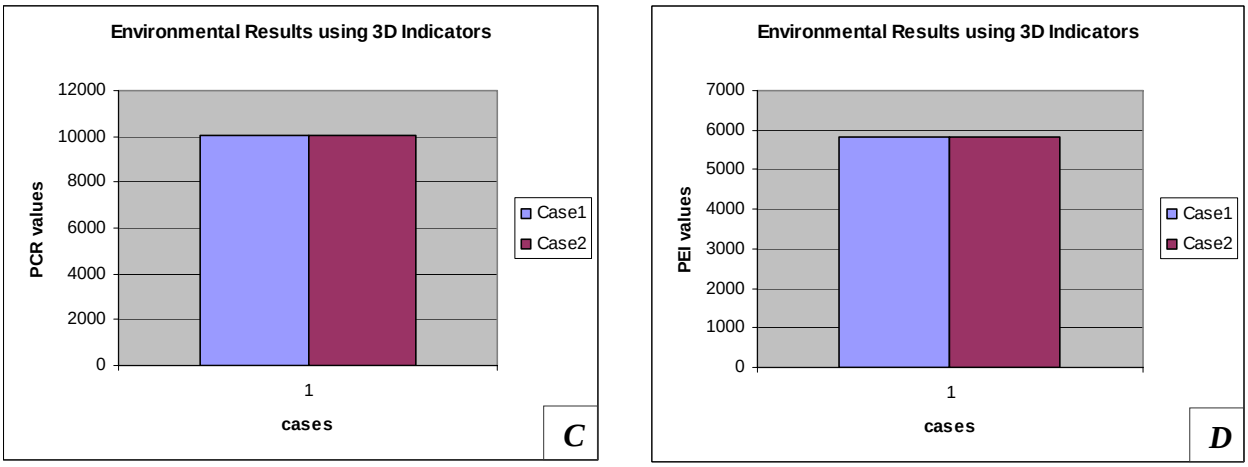


Figure 7.8 3D Indicators for sweetening natural gas absorption by DGA A) MI; B) EI; C) PCR; D) PEI

For the same cases, the WAR has been applied. The CO Modules for 1D indicator (Proall and Proenergia) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.13.

Table 7.13 CO Modules parameters for 1D indicator for sweetening natural gas by DGA absorption production process

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	2	2	S2
CO3	0	1	3	S5
CO4	0	1	4	S8
CO5	0	1	5	S10
CO6	0	0	6	S28
CO7	0	0	7	S30
CO8	1	1	8	S32

The results obtained using the 1D indicator, WAR Algorithm, are reported in Table 7.14 and these stress once more the choice of the second design alternative, CASE 2.

Table 7.14 Environmental Impact Indexes obtained in the sweetening natural gas by DGA absorption using WAR Algorithm

CASE STUDY	ENIVORONMENTAL INDEXES NAME			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	136005.24	1123.15	-45478.99	-375.57
CASE 2	135989.53	1123.02	-45494.70	-375.70

The same results are presented in Figures 7.9.

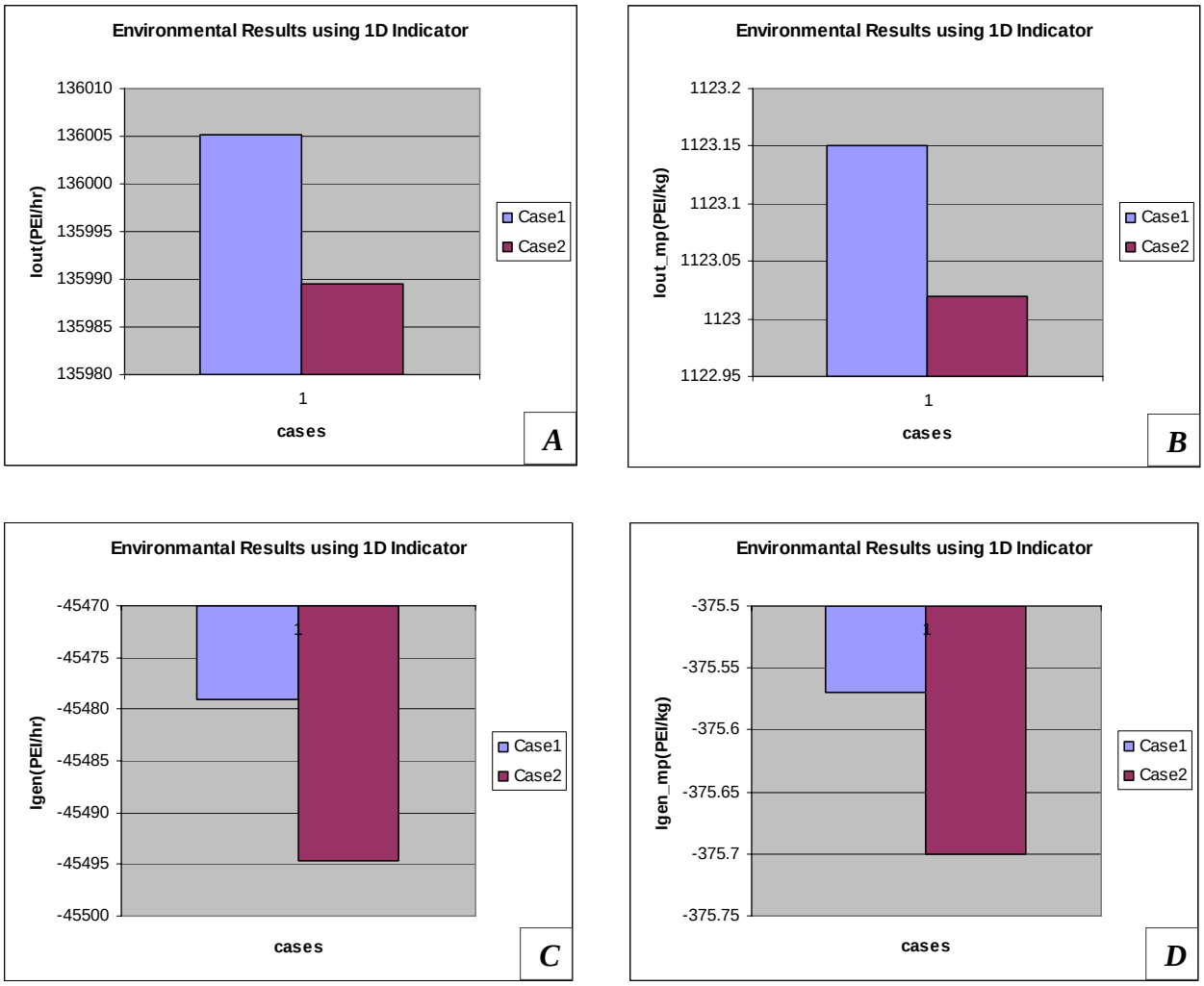


Figure 7.9 1D Indicators for sweetening natural gas by DGA absorption A) Iout; B)Iout_mp; C) Igen; D) Igen_mp

Conclusions

The sweetening natural gas by DGA absorption has been simulated using PROII and Aspen Plus process simulators. Two process alternatives are proposed and analyzed in order to choose the most environmentally friendly one. The most environmentally friendly design is the second one, as it can be noticed from the results obtained using the 3D and 1D indicators of the PSP Framework. Making the heat integration less amount of gasses is released into the atmosphere and a smaller quantity of energy has to be supplied from external sources. The second case is also preferred from economical point of view. This alternative requires less energy, consequently, less amount of money is spent to buy/produce that energy.

7.1.3 Formaldehyde Production Process

Introduction

Formaldehyde is a chemical compound used in a wide range of applications. It is primarily produced for the use in the manufacturing of chemical resins and as a chemical intermediate. The polymer industry is an example of how formaldehyde is used as an intermediate. The use of formaldehyde is extremely widespread and dependent on the additives (e.g. urea, melanin, phenol, ammonia). It is thus used in differing concentrations in adhesives (e.g. for the production of chipboard), foams, tanning agents, explosives, dyes, preserving agents, solvents, pharmaceuticals, resins and fungicides. Formaldehyde is produced by oxidizing methanol using silver or metal oxide catalyst methods (iron and molybdenum). As the gases pass through the catalyst the methanol is converted into formaldehyde. The reactions that characterize the process are (ChE, 2007):

$$CH_3OH + 0.5O_2 \rightarrow CH_2O + H_2O$$
$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$
$$CH_2O \rightarrow H_2 + CO$$
$$CH_2O + 0.5O_2 \rightarrow CH_2O_2$$

The entire quantity of oxygen is consumed; 98.6% of the methanol is converted. The selectivity is summarized in Table 7.15.

Table 7.15 Selectivity for formaldehyde production process

REACTION NAME	**REFERENCE COMPOUND**	**SELECTIVITY** (%)
R 1	Methanol	89.9
R 2	Formaldehyde	2
R 3	Formaldehyde	8
R 4	Formaldehyde	0.1

The simplified schema of the process is presented in Figure 7.10.

Simulation Goal

The goal of the present simulation is to analyze the process, to maximize the quantity of formaldehyde obtained and to identify the most environmentally friendly design from different alternatives.

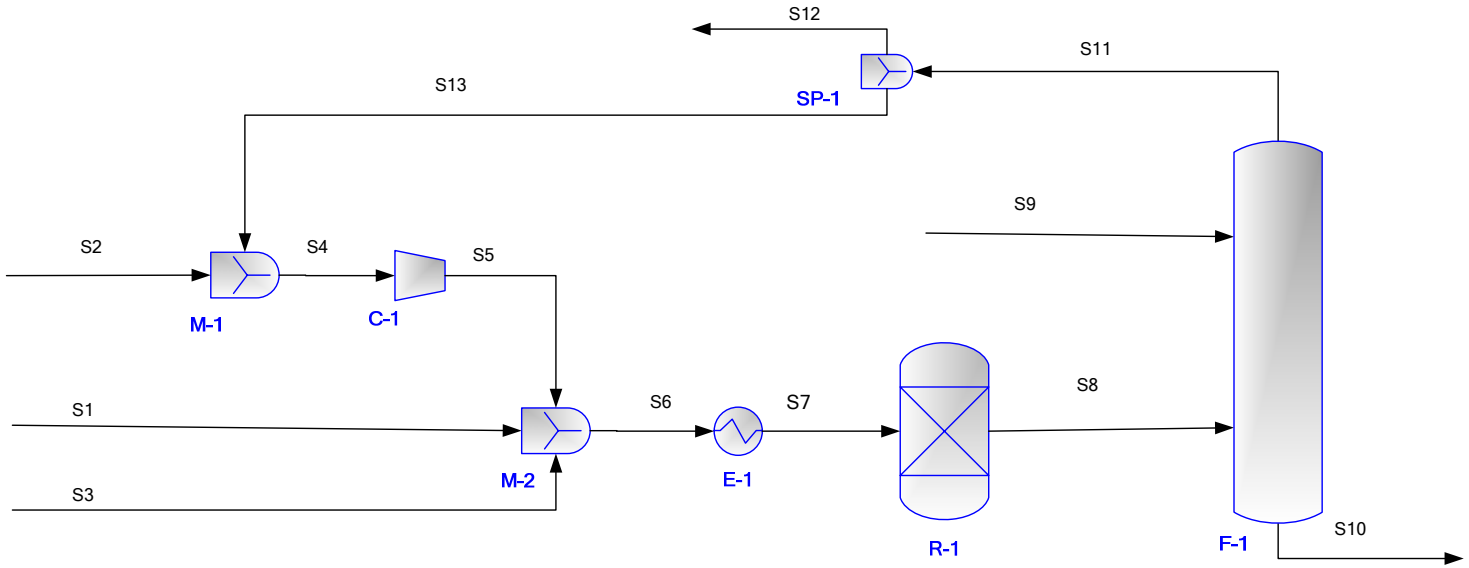


Figure 7.10 Formaldehyde production process

Process Description

The methanol stream, S1, is fed in the process. The air, S2, is mixed with the recycle stream coming from the distillation column, S13, and compressed in C-1. This stream encounters the methanol stream and the steam feed, S3. The above presented reactions take place in R-1. The reactor product gas, S8, is rapidly cooled and sent to the absorber, F-1, where the formaldehyde is absorbed in water, S9. The formaldehyde is obtained in the bottom of the column, S10. The top of the column, S11, is sent to a separator, SP-1. The purge S12 is released into the atmosphere. The other separator stream, S13, containing nitrogen, oxygen, water and un-reacted methanol is recirculated (ChE, 2007).

From environmental point of view, it is desired to reduce the quantity of waste gases, S12, released into the atmosphere.

Process Simulation

The process has been simulated using PROII and Aspen Plus process simulators.

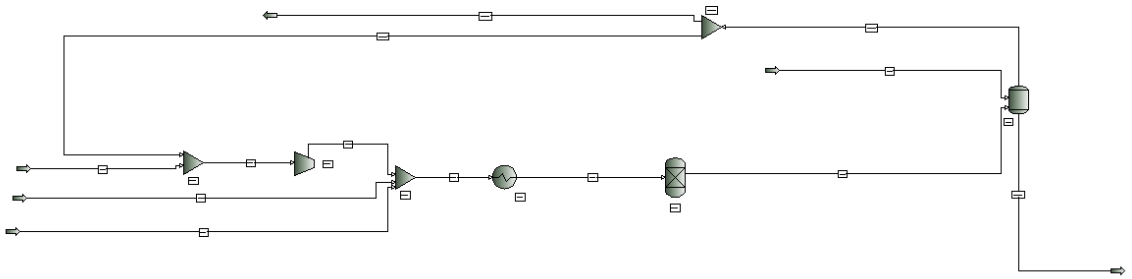


Figure 7.11 PROII schema for formaldehyde production process

NRTL and RK are the thermodynamic methods used in the present simulation.

Input data containing methanol - S1, air - S2, steam - S3, and demineralized water - S9, are presented in Table 7.16.

Table 7.16 Input streams specifications for formaldehyde production process (base case)

STREAM NAME		S1	S2	S3	S9
STREAM DESCRIPTION					
TEMPERATURE	C	26.6667	26.6667	107.5318	26.6667
PRESSURE	ATM	1.299403	1	1.2994	1.0207
ENTHALPY	MM BTU/HR	0.2377	0.5413	1.4218	1.8742
MOLECULAR WEIGHT		32.0214	28.7533	18.015	18.015
MOLE FRACTION VAPOUR		0	1	1	0
MOLE FRACTION LIQUID		1	0	0	1
RATE	KG-MOL/HR	120.178	309.874	30.970	983.273
FLUID RATES	KG-MOL/HR				
H2		0	0	0	0
N2		0	242.6077	0	0
O2		0	64.4971	0	0
CO		0	0	0	0

CO2	0	0	0	0
H2O	0.1763	2.7696	30.9696	983.2737
METHANOL	120.0019	0	0	0
FORMALD	0	0	0	0
FORMIC	0	0	0	0

Data reported in Table 7.17 represent the simulation results for the output streams.

Table 7.17 Output streams results for formaldehyde production process (base case)

STREAM NAME		**S10**	**S12**
STREAM DESCRIPTION			
TEMPERATURE	C	80	80
PRESSURE	ATM	1.0207	1.0207
ENATHALPY	MM BTU/HR	6.0783	9.3521
MOLECULAR WEIGHT		19.2584	23.9682
MOLE FRACTIONM VAPOUR		0	1
MOLE FRACTION LIQUID		1	0
RATE	KG-MOL/HR	1067.351	329.936
FLUID RATES	KG-MOL/HR		
H2		0.0052	0.6360
N2		0.4491	242.1462
O2		0.0122	4.9061
CO		0.0012	0.6403
CO2		0.0022	0.1580
H2O		956.8461	179.4879
METHANOL		0.4507	0.7050
FORMALD		109.5838	8.6190
FORMIC		0.0006	0.0001

Environmental Impact Results

Two design alternatives have been simulated for the process under study. The base case is presented in Figure 7.10. One modification has been made to the base case. The flash was replaced by a distillation column with 10 trays. By replacing the flash, the separation is more effective and more formaldehyde (118, 71 kg-mol/hr vs. 109.58 kg-mol/hr) is obtained in the bottom of the column.

The CO Modules for 3D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.18.

Table 7.18 CO Modules specifications for 3D indicators for formaldehyde production process

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	10	0	S1
CO2	2	0	10	11	S2
CO3	3	0	10	0	S3
CO4	4	0	10	0	S9
CO5	5	2	10	0	S10
CO6	6	1	10	0	S12
CO7	7	-	-	-	S8

The 3D indicators calculated for both cases are presented in Table 7.19.

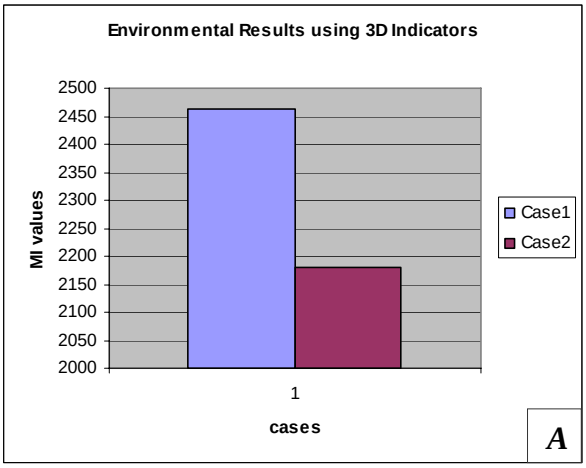
Table 7.19 3D indicators obtained in the formaldehyde production process

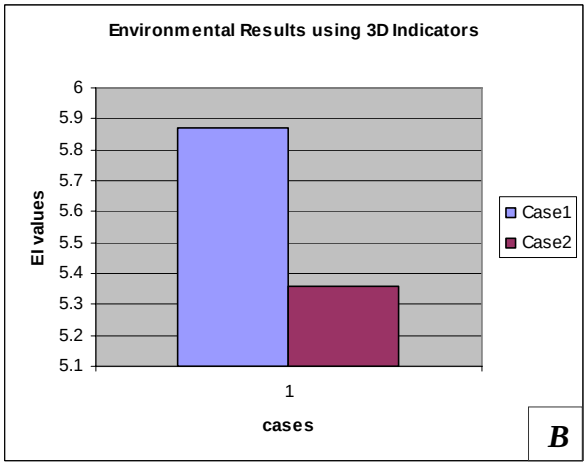
CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	2461.54	5.87	1000041	25647.2
CASE 2	2181.02	5.36	1000041	25647.2

The case with lowest MI and EI 3D indicators is CASE 2. The reasons why PCR and PEI have equal values for both cases are explained below. Both processes are continuous processes, so the frequency class for the substances present in the process is the same (permanent use; > 6h/day- see Table 3.1) as are the risk phrases. PEI has the same values for both cases because the physical states of the substances involved in the process are the same and the receiving medium (air, water, soil) is also the same.

In conclusion, CASE 2 represents the most environmentally friendly design, taking into account the 3D indicators.

The same results are reported in Figures 7.12.





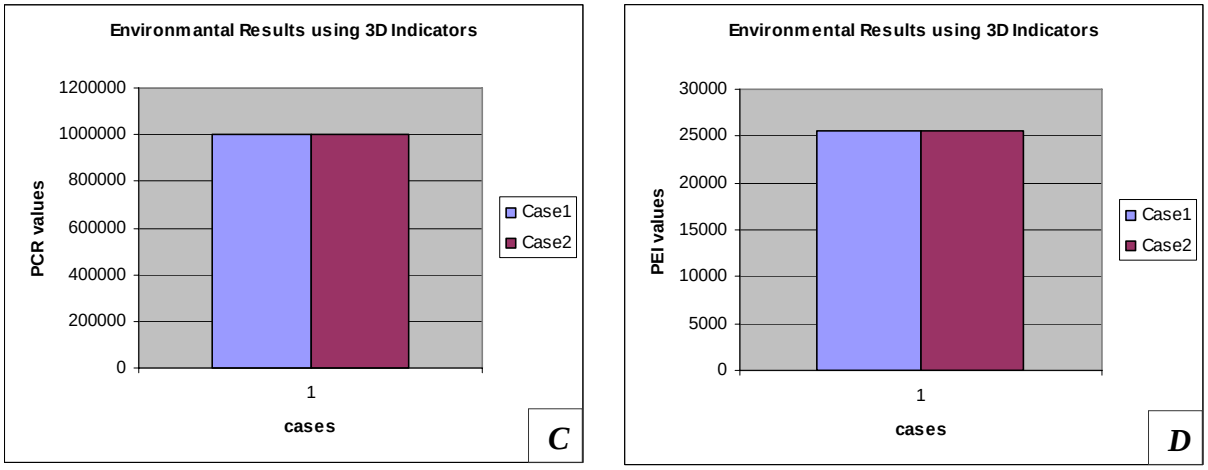


Figure 7.12 3D Indicators for formaldehyde production process A) MI; B) EI; C) PCR;D) PEI

For the same cases, the WAR Algorithm has been applied. CO Modules for 1D indicator (Proall and Proenergia) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.20.

Table 7.20 CO Modules specifications for 1D indicator for formaldehyde production process

CO MODULE NAME	**CO MODULES PARAMETERS**			**CONNECTED STREAM**
	PROCESS_TYPE	**CAPE_POSITION**	**CAPE_ID**	
CO1	0	0	1	S1
CO2	0	0	2	S2
CO3	0	0	3	S3
CO4	0	0	4	S9
CO5	0	2	5	S10
CO6	0	1	6	S21
CO7	1	1	7	S32

The results obtained are reported in Table 7.21.

Table 7.21 Environmental Impact Indexes obtained in the formaldehyde production process using WAR Algorithm

CASE STUDY	**ENIVORONMENTAL INDEXES NAME**			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	388.98	0.12	-827.71	-0.25
CASE 2	31.59	8.86	-1185.11	-0.33

Iout, Igen and Igen_mp are lower in the second case, CASE 2. These results stress once more the choice of the second alternative design, CASE 2.

The results obtained using the WAR Algorithm (1 D indicator) stress once more the choice of the second alternative design even if Iout_mp has a lower value for the first case. All the other indicators (3D and 1D indicators) are lower for the second case.

The same results are presented in Figures 7.13.

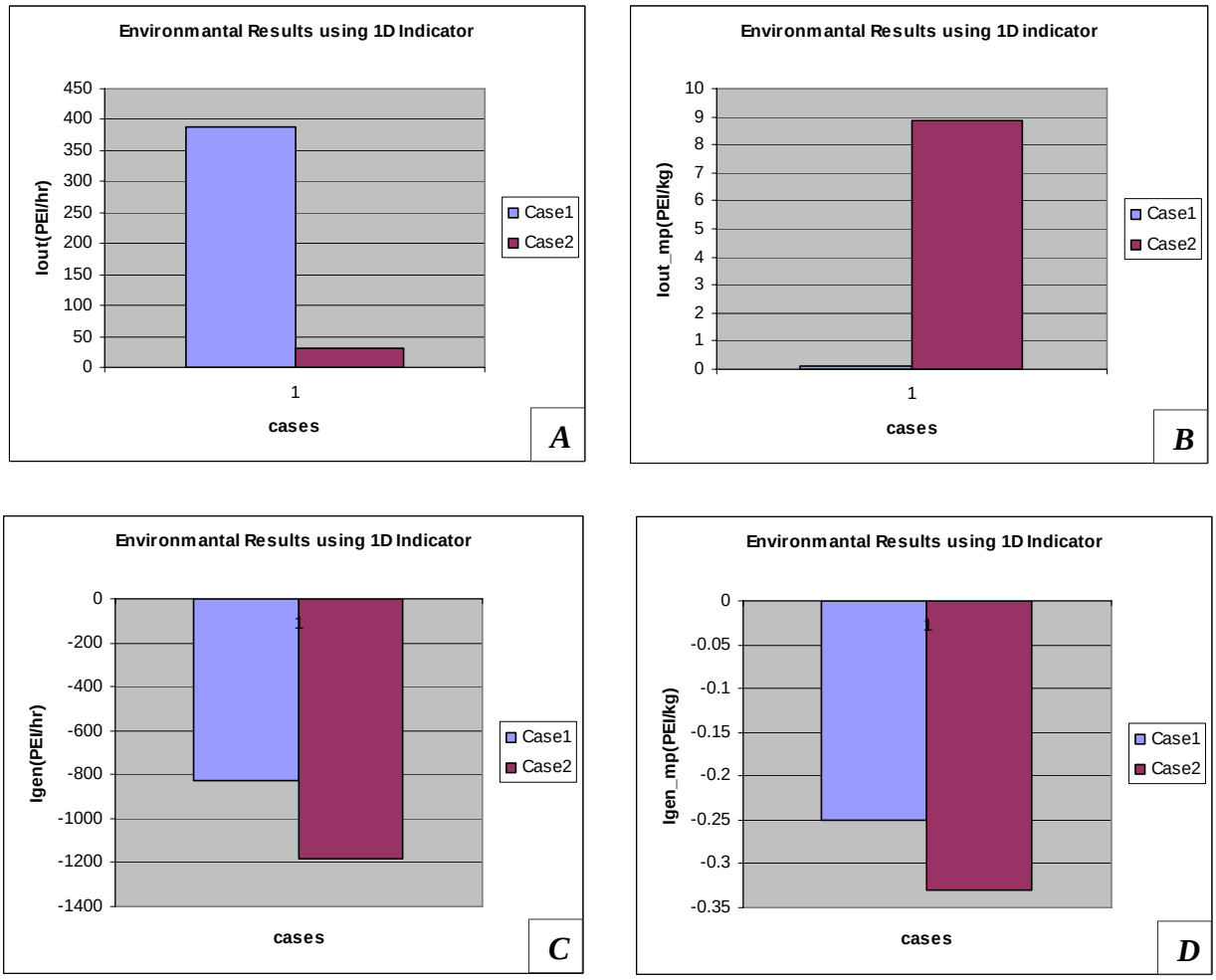


Figure 7.13 1D Indicators for formaldehyde production process A) Iout; B)Iout_mp; C) Igen;D) Igen_mp

Conclusions

The formaldehyde production process has been simulated using PROII and Aspen Plus process simulators. Two process alternatives are proposed and analyzed in order to choose the most environmentally friendly. One modification has been made to the separation system. The most environmentally friendly design is the second one, as it can be noticed from the results obtained using the 3D and 1D indicators of the PSP Framework. The choice is stress once more by technological and economical reasons: 118.71 kg-mol/hr formaldehyde is obtained in the second case vs. 109.58 kg-mol/hr obtained in the first case (more product is obtained and sold more efficient the process is).

7.1.4 Phthalic Anhydride Production Process

Phthalic anhydride is used in the manufacture of plasticizers (additives to polymers to give them more flexibility) and polyesters, among other applications.

There are different ways to obtain phthalic anhydride. The most common ways are:

A) Production of phthalic anhydride by the oxidation of o-xylene
B) Production of phthalic anhydride by the oxidation of naphthalene

Both process have been considered and simulated in the following section.

A)Production of phthalic anhydride by oxidation of o-xylene

Introduction

The following reactions take place in the phthalic anhydride production process:

$$\underset{o-xylene}{C_8H_{10}} + 3O_2 \rightarrow \underset{\substack{phtalic\\anhydride}}{C_8H_4O_3} + 3H_2O$$

$$\underset{o-xylene}{C_8H_{10}} + 7.5O_2 \rightarrow \underset{\substack{maleic\\anhydride}}{C_4H_2O_3} + 4H_2O + 4CO_2$$

$$\underset{o-xylene}{C_8H_{10}} + 11.5O_2 \rightarrow 8CO_2 + 5H_2O$$

$$\underset{o-xylene}{C_8H_{10}} + 6.5O_2 \rightarrow 8CO + 5H_2O$$

It has to be specified that the selectivity for the phthalic anhydride reaction is 70%, for the complete combustion of o-xylene it is 15%, for the incomplete combustion of o-xylene it is 5%, for maleic anhydride it is 9%, and for the heavy impurity it is 1% (Turton *et al.*, 2003).

Process schema for phthalic anhydride production by the oxidation of o-xylene is illustrated in Figure 7.14.

Simulation Goal

The goal of the present simulation is to analyze the process, to understand it and to identify the most environmentally friendly design from two different process alternatives.

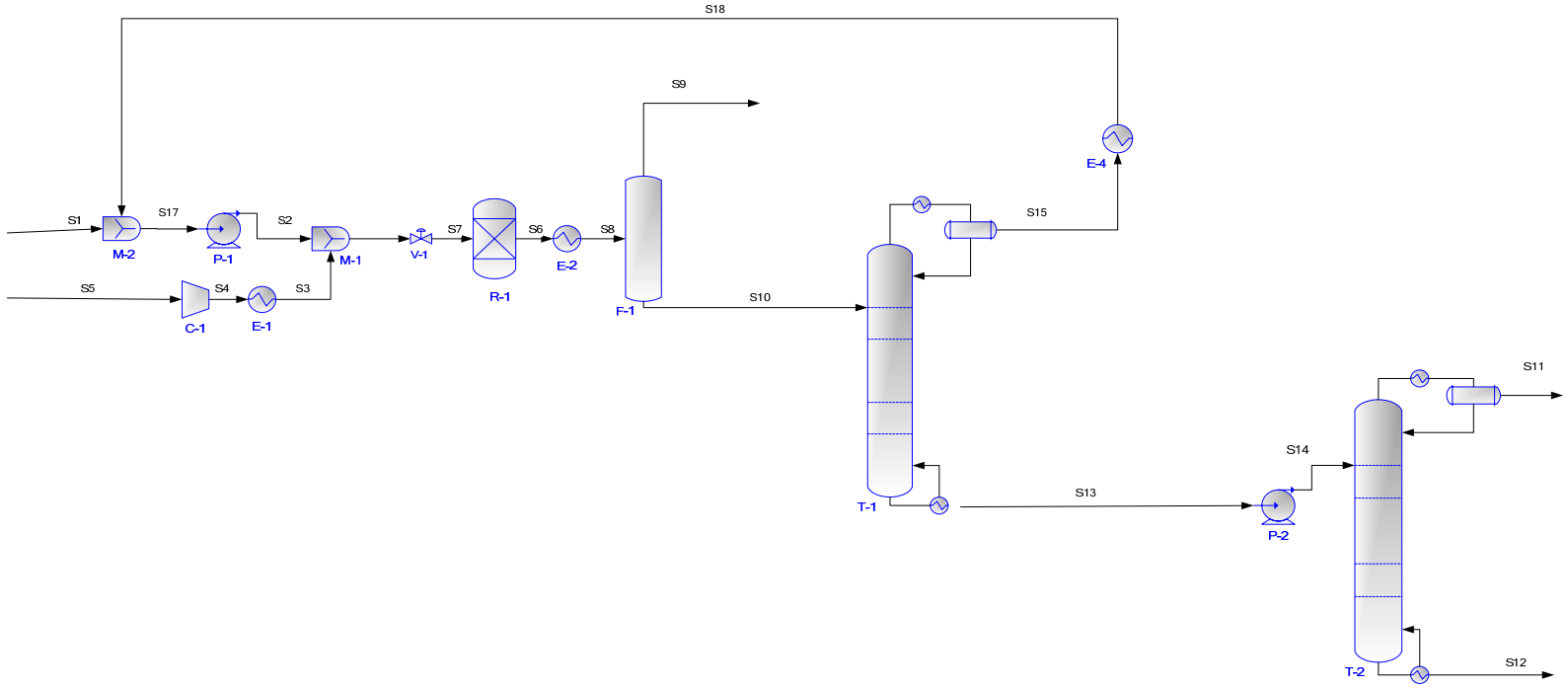


Figure 7.14 Phthalic anhydride production process from o-xylene

Process Description

The raw materials are air, S5, and o-xylene, S1. The o-xylene feed, S1, is mixed with the recycle, S18, coming from the first distillation column. The recycle stream, S18, contains also o-xylene. This feed meets the air stream. Air, which may be assumed to contain only O_2 and N_2, is compressed and heated. These operations take place in C-1 and E-1 units operation. The hot air and vapourized o-xylene are mixed, in M-1, and the resulting stream, S7, is sent to a packed bed reactor. In the reactor, R-1, the above described reactions occur.

The heavy impurity consumes a negligible amount of oxygen and produces a negligible amount of light gases. After the reactions, the products and by-products are heated and sent to a flash, F-1, where the gaseous phase, S9, is separated from the liquid phase, S10. The gaseous phase, S9, contains: carbon dioxide, carbon monoxide, un-reacted oxygen, nitrogen and water.

The next step is the separation of the liquid phase. This takes place in two distillation columns. The first distillation column, T-1, separates the o-xylene from the phthalic anhydride and maleic anhydride. The recovered o-xylene, S18, is recycled. The goal of the second column, T-2, is to separate the phthalic anhydride (process product) present in S12, from the maleic anhydride (process by-product) present in S11. The product must have a purity of 99.9% in phthalic anhydride (Turton *et al.*, 2003).

Process Simulation

The process has been simulated using PROII and Aspen Plus process simulators.

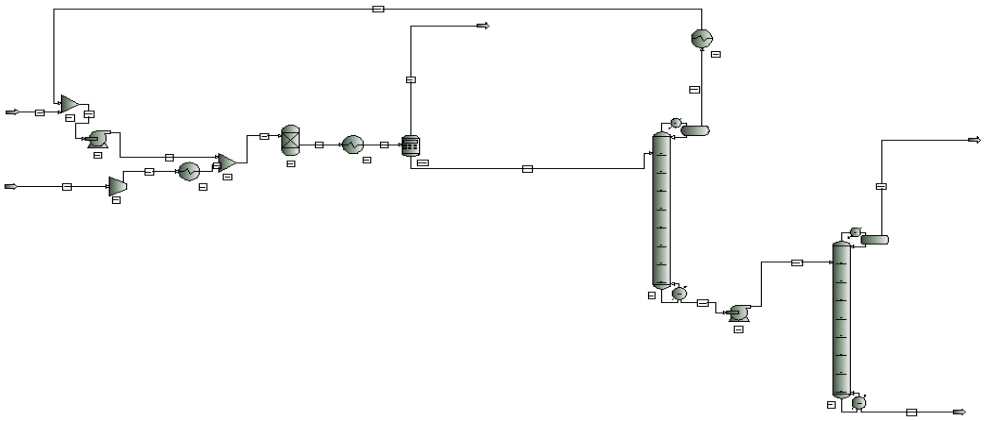


Figure 7.15 PROII schema of phthalic anhydride production process from o-xylene

UNIFAC and SRK are the thermodynamic packages used in the present simulation. Input streams for o-xylene stream - S1, and air stream - S3, are presented in Table 7.22.

Table 7.22 Input streams specifications for phthalic anhydride production process from o-xylene (base case)

STREAM NAME		**S1**	**S3**
STREAM DESCRIPTION			
TEMPERATURE	C	150	300
PRESSURE	ATM	0.75	3
ENTHALPY	MM CAL/HR	1564.727	8611.463
MOLECULAR WEIGHT		106.169	28.85035
MOLE FRACTION VAPOUR		1	1
MOLE FRACTION LIQUID		0	0
RATE	KG-MOL/HR	98.60694	2217.2
FLUID RATES	KG-MOL/HR		
OXYLENE		98.60694	0
O2		0	465.7739
N2		0	1751.426
CO2		0	0
H2O		0	0
MANH		0	0
PTAN		0	0
CO		0	0

The simulation results are reported in Table 7.23.

Table 7.23 Output streams results for phthalic anhydride production process from o-xylene (base case)

STREAM NAME		**S12**	**S11**	**S9**
STREAM DESCRIPTION				
TEMPERATURE	C	284.9854	204.4566	180
PRESSURE	ATM	1	1	1
ENTHALPY	MM CAL/HR	1210.684	166.8123	8958.7
MOLECULAR WEIGHT		148.114	98.46691	27.59451
MOLE FRACTION VAPOUR		0	1	1
MOLE FRACTION LIQUID		1	0	0
RATE	KG-MOL/HR	69.64433	9.045927	2291.389
FLUID RATES	KG-MOL/HR			
OXYLENE		6.92E-10	0.019991	0
O2		0	0	0.22516
N2		0	0	1751.426
CO2		0	0	155.3489
H2O		0	0	344.5559
MANH		0.006972	8.955463	0
PTAN		69.63736	0.070472	0
CO		0	0	39.83305

B)Production of phthalic anhydride by oxidation of naphthalene

Introduction

The following reactions characterize the most important phenomena that take place in the present process (ChE, 2007):

$$C_{10}H_8 + \frac{9}{2}O_2 \rightarrow C_8H_4O_3 + 2H_2O + 2CO_2$$
naphtalene *phthalic anhydride*

$$C_{10}H_8 + 6O_2 \rightarrow C_8H_4O_3 + 2H_2O + 2CO_2$$
naphtalene *maleic anhydride*

$$C_{10}H_8 + \frac{3}{2}O_2 \rightarrow C_8H_4O_3 + H_2O$$
naphtalene *naphthoquinone*

$$C_{10}H_8 + 12O_2 \rightarrow 4H_2O + 10CO_2$$
naphtalene

$$C_{10}H_8 + 7O_2 \rightarrow 4H_2O + 10CO$$
naphtalene

Table 7.24 summarizes the naphthalene conversion values for the above presented reactions.

Table 7.24 Conversion values for phthalic anhydride production process from naphthalene

REACTION NAME	**CONVERSION VALUE** (%)
R1	70
R2	8
R3	2
R4	15
R5	5

The process flow diagram is illustrated in Figure 7.16.

Simulation Goal

The goal of the present simulation is to analyze the process, to understand it and to identify the most environmentally friendly design from two different process alternatives.

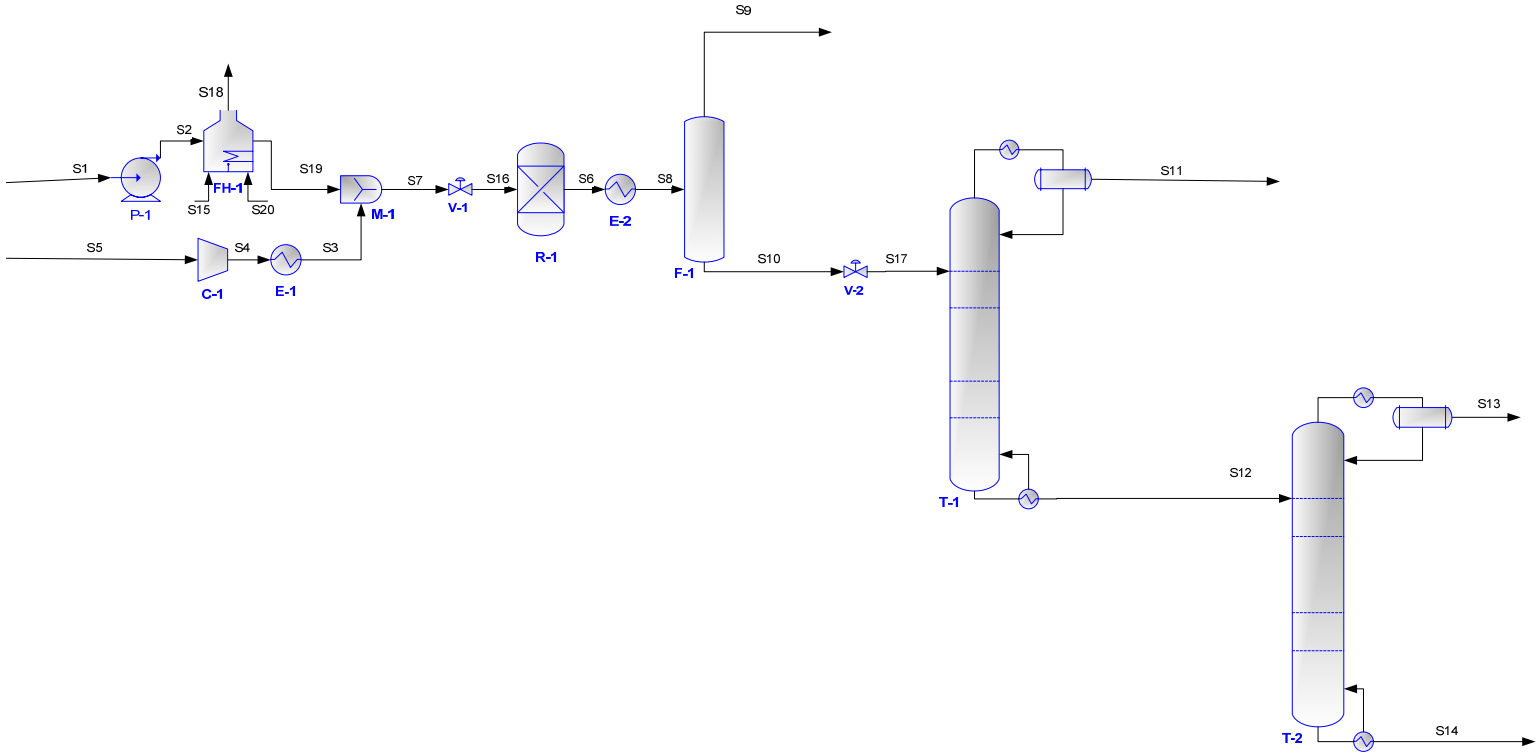


Figure 7.16 Phthalic anhydride production process from naphthalene

Process Description

The input streams are naphthalene, S1, and air feed, S5. The naphthalene feed is heated to 400º C in a furnace FH-1. The air is compressed in C-1, heated to 240º C and then mixed in M-1 with the hot naphthalene feed. The resulting stream, S7, is sent to the reactor, R-1, where the above described reactions take place.

The liquid phase is separated from the gas phase in a separator F-1. After the separation the liquid, S10, containing phthalic anhydride, maleic anhydride and heavy fuel is sent to the separation part of the plant which contains two distillation columns. In the first distillation column, T-1, maleic anhydride (which is a by-product) present in S11, is separated in the top of the column. The goal of the second column is to separate the phthalic anhydride (main process product), S13, from the heavy fuel (by-product), S14 (ChE, 2007).

Process Simulation

The process has been simulated using PROII and Aspen Plus process simulators.

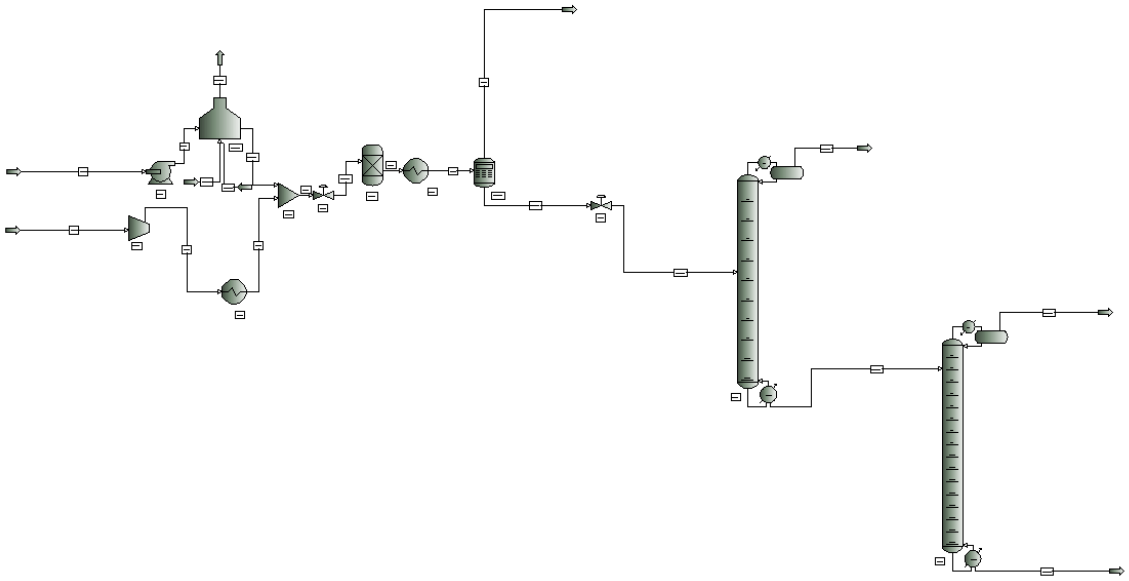


Figure 7.17 PROII schema of phthalic anhydride production process from naphthalene

UNIFAC and SRK are the thermodynamic packages used in the present simulation. Input data used for naphthalene - S1, and air - S5, as well as the input data for the fired heater - S15 and S20, streams are presented in Table 7.25.

Table 7.25 Input streams specifications for phthalic anhydride production process from naphthalene (base case)

STREAM NAME		**S1**	**S5**	**S15**	**S20**
STREAM DESCRIPTION					
TEMPERATURE	C	200	25	50	100
PRESSURE	BAR	0.8	1.01	1	1
ENETHALPY	MM CAL/HR	1071.5	-642.096	11.33428	197.4177
MOLECULAR WEIGHT		128.175	28.85006	16.043	28.85006
MOLE FRACTION VAPOUR		0	1	1	1
MOLE FRACTION LIQUID		1	0	0	0
RATE	KG-MOL/HR	100	5000.004	300	500.0004
FLUID RATES	KG-MOL/HR				
NAPHTHLN		100	0	0	0
PTAN		0	0	0	0
MANH		0	0	0	0
naphthoquinone		0	0	0	0
O2		0	1050.001	0	105.0001
H2O		0	0	0	0
CO2		0	0	0	0
CO		0	0	0	0
N2		0	3950.003	0	395.0003
CH4		0	0	300	0

Data reported in Table 7.26 represent the simulation results for phthalic anhydride production process from naphthalene. S9 represents the off-gases stream, S11 is the maleic anhydride stream, S13 represents the phthalic anhydride stream, S14 contains the heaviest fuel, and S18 is the output stream from the fired heater, FH-1.

Table 7.26 Output streams results for phthalic anhydride production process from naphthalene (base case)

STREAM NAME		**S9**	**S11**	**S13**	**S14**	**S18**
STREAM DESCRIPTION						
TEMPERATURE	C	160	130.6204	195.6501	245.8738	1802.976
PRESSURE	BAR	2.05	0.11	0.11	0.11	1
ENTHALPY	MM CAL/HR	13243.72	259.3133	1783.743	38.67545	56724.16
MOLECULAR WEIGHT		28.8877	98.07463	148.1159	157.6631	27.63363
MOLE FRACTION VAPOUR		1	1	1	0	1
MOLE FRACTION LIQUID		0	0	0	1	0
RATE	KG-MOL/HR	5013.004	15.99998	69.89996	2.100051	3162.318
FLUID RATES	KG-MOL/HR					
NAPHTHLN		0	7.42E-07	2.96E-09	4.63E-24	0
PTAN		0	0.004995	69.89166	0.103338	0
MANH		0	15.99499	0.005014	2.41E-20	0
naphthoquinone		0	7.08E-12	0.003287	1.996714	0
O2		469.0008	0	0	0	0
H2O		238	0	0	0	600
CO2		306	0	0	0	300

CO	50	0	0	0	0
N2	3950.003	0	0	0	2262.318
CH4	0	0	0	0	0

Environmental Impact Results

The environmental impact of this process has to be estimated. The goal is to choose, from these two process cases (phthalic anhydride production process from o-xylene and phthalic anhydride production process from naphthalene), the best environmental solution.

3D and 1D indicators have been calculated using the mass flow-rates, the input and output streams composition (mass fraction) and toxicological and risk information data.

The CO Modules for 3 D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.27 for phthalic anhydride production process from o-xylene and in Table 7.28 for phthalic anhydride production process from naphthalene.

Table 7.27 CO Modules specifications for 3D indicators for phthalic anhydride production process from o-xylene

CO MODULE NAME	**CO MODULES PARAMETERS**				**CONNECTED STREAM**
	NAME	**CONNECTION**	**WATER_USAGE**	**AIR_USAGE**	
CO1	1	0	0	0	S1
CO2	2	0	0	11	S5
CO3	3	1	10	10	S9
CO4	4	3	0	0	S11
CO5	5	2	0	0	S12
CO6	6	-	-	-	S6

Table 7.28 CO Modules parameters for 3D indicators for phthalic anhydride production process from naphthalene

CO MODULE NAME	**CO MODULES PARAMETERS**				**CONNECTED STREAM**
	NAME	**CONNECTION**	**WATER_USAGE**	**AIR_USAGE**	
CO1	1	0	0	0	S1
CO2	2	0	0	11	S5
CO3	3	1	10	10	S9
CO4	4	3	0	0	S11
CO5	5	2	0	0	S13
CO6	6	1	0	0	S14
CO7	7	-	-	-	S6

The 3D indicators results are presented in Table 7.29.

Table 7.29 3D Indicators obtained in the phthalic anhydride production process

CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	13061.31	56.69	100021	8616.21
CASE 2	16924.05	28.78	20040	10310.2

From Table 7.29 it can be noticed that MI and PEI are lower in the first case while EI and PCR are lower in the second design alternative. In order to decide which design is more environmentally friendly 1D indicator has been also calculated.

The same results are reported in Figures 7.18.

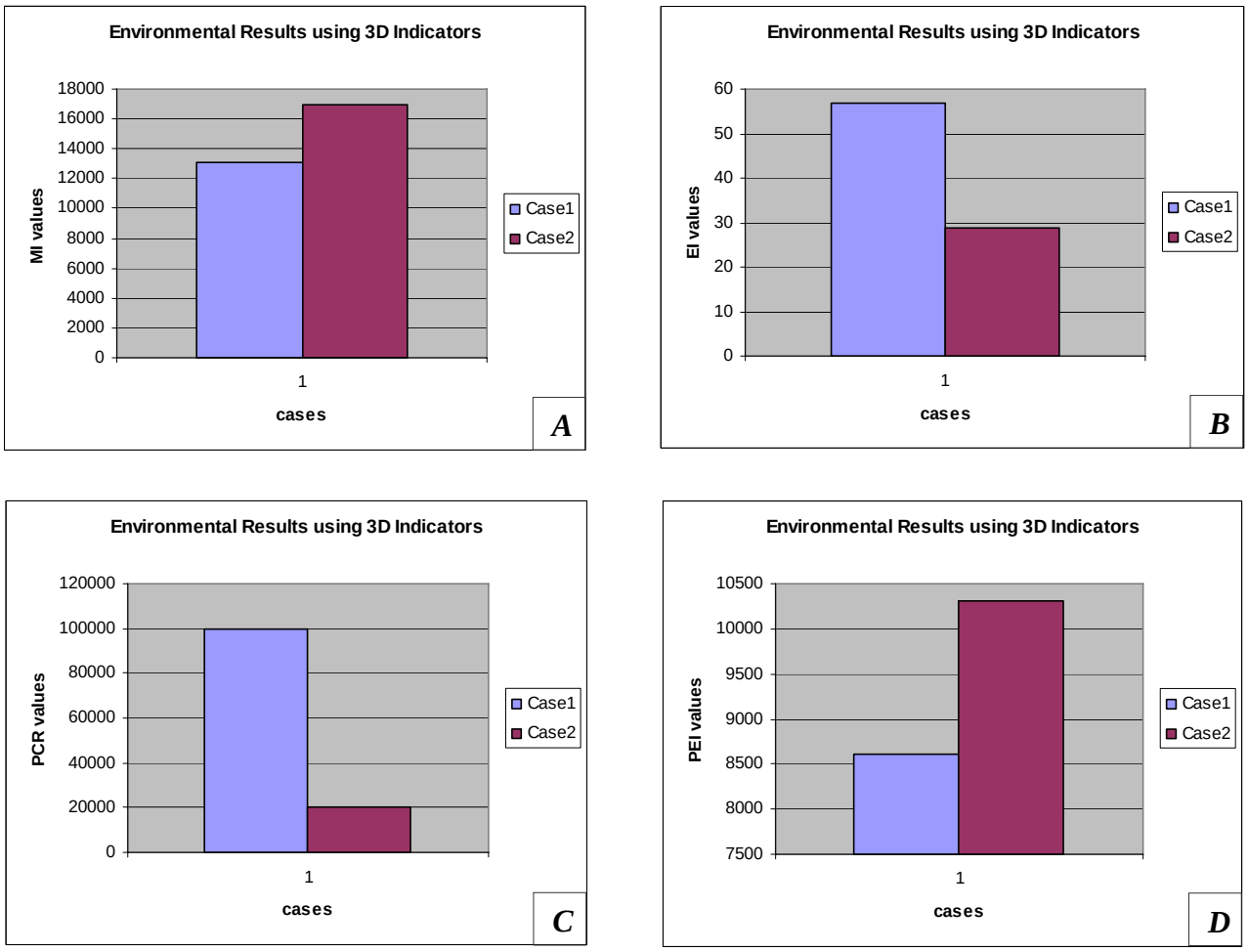


Figure 7.18 3D Indicators for phthalic anhydride production process A) MI; B) EI; C) PCR; D) PEI

For the same cases, WAR Algorithm has been applied. The CO Modules for 1D indicator (Proall and Proenergia) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table

7.30 for Phthalic Anhydride production process from o-xylene and in Table 7.31 for Phthalic Anhydride production process from naphthalene.

Table 7.30 CO Modules specifications for 1D indicator for phthalic anhydride production process from o-xylene

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	0	2	S5
CO3	0	1	3	S9
CO4	0	1	4	S11
CO5	0	2	5	S12
CO6	1	1	6	S32

Table 7.31 CO Modules specifications for 1D indicator for phthalic anhydride production process from naphthalene

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	0	2	S5
CO3	0	1	3	S9
CO4	0	1	4	S11
CO5	0	2	5	S13
CO6	0	1	6	S14
CO7	1	1	7	S32

The Environmental Impact Indexes obtained using the 1D indicator, WAR Algorithm, are reported in Table 7.32.

Table 7.32 Environmental Impact Indexes obtained in the phthalic anhydride production using WAR Algorithm

CASE STUDY NAME	ENIVORONMENTAL INDEXES NAME			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	1672.81	0.1622	-14881.41	-1.4427
CASE 2	2617.01	0.2528	-8545.47	-0.8254

Taking into account the 1D Indicator, more exactly the environmental impact evaluated using the WAR Algorithm, it can be noticed that the best alternative design, environmentally speaking, is the first one, because it has the lowest Environmental Impact Indexes.

The same results are illustrated in Figures 7.19

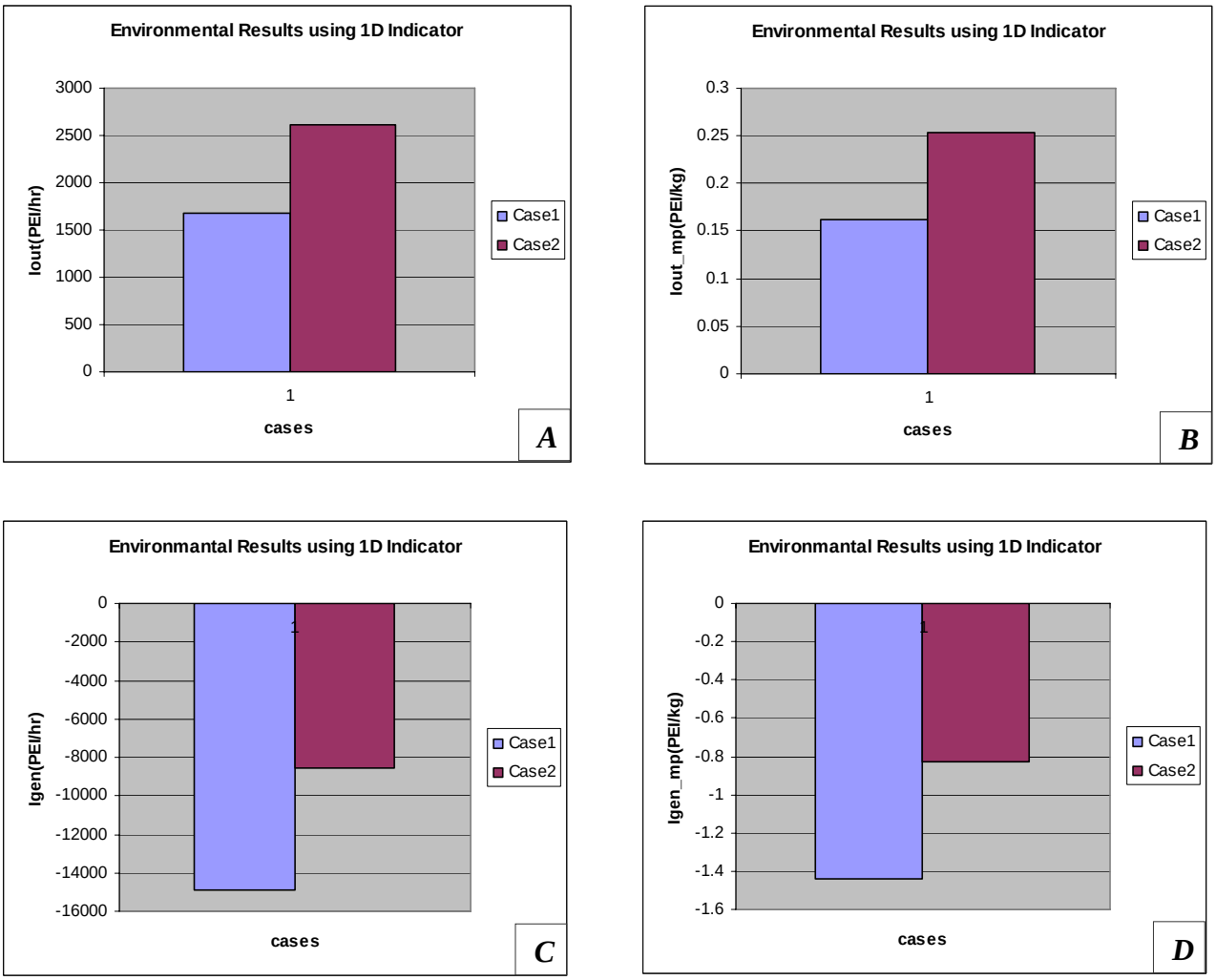


Figure 7.19 1D Indicators for phthalic anhydride production process A) Iout; B) Iout_mp; C) Igen; D) Igen_mp

Conclusions

The phthalic anhydride production process has been simulated using PROII and Aspen Plus process simulators. Two process alternatives (starting from o-xylene and from naphthalene as raw materials) are proposed and analyzed in order to choose the most environmentally friendly. The results obtained, using the 3D and 1D indicators of the PSP Framework, provide the first alternative design as best solution.

Economical concerns should be also considered. The productivity values for the phthalic anhydride in the two cases are close (69.64 kmol/h for the o-xylene process and 69.89 kmol/h for the naphthalene process). The difference in productivity terms is very low (69.64 kmol/h vs. 69.89 kmol/h). After all these considerations it can be emphasized the decision to choose CASE 1 for the phthalic anhydride production process.

7.1.5 Maleic Anhydride Production Process

Maleic anhydride is a versatile chemical intermediate used to make unsaturated polyester resins, lube oil additives, alkyd resins, and a variety of other products.

There are different ways to obtain maleic anhydride. The most common ways are:

A) Production of maleic anhydride from butane
B) Production of maleic anhydride from benzene

Both process have been considered and simulated in the following section.

A)Production of maleic anhydride from butane

Introduction

The goal of the present simulation is to design a facility that is capable to produce 40 million pounds of maleic anhydride per year from n-butane.

The following reactions occur when butane is mixed with oxygen:

$$C_4H_{10} + 3.5O_2 \rightarrow C_4H_2O_3 + 4H_2O$$
butane *maleic anhydride*

$$C_4H_{10} + 5.5O_2 \rightarrow 2CO + 2CO_2 + 5H_2O$$
butane

$$C_4H_{10} + 3.5O_2 \rightarrow C_3H_4O_2 + CO_2 + 3H_2O$$
butane *acrylic acid*

$$C_4H_{10} + 6O_2 \rightarrow CH_2O_2 + 3CO_2 + 4H_2O$$
butane *formic acid*

The butane conversion is summarized in Table 7.33.

Table 7.33 Selectivity data for maleic anhydride production process

REACTION NAME	**REFERENCE COMPOUND**	**SELECTIVITY** (%)
R 1	Maleic anhydride	78.825
R 2	Carbon dioxide	11.273
R 3	Acrylic acid	11.273
R 4	Formic acid	11.273

Process schema is presented in Figure 7.20.

Simulation Goal

The goal of the present simulation is to analyze the process, to understand it and to identify the most environmentally friendly design from two different process alternatives.

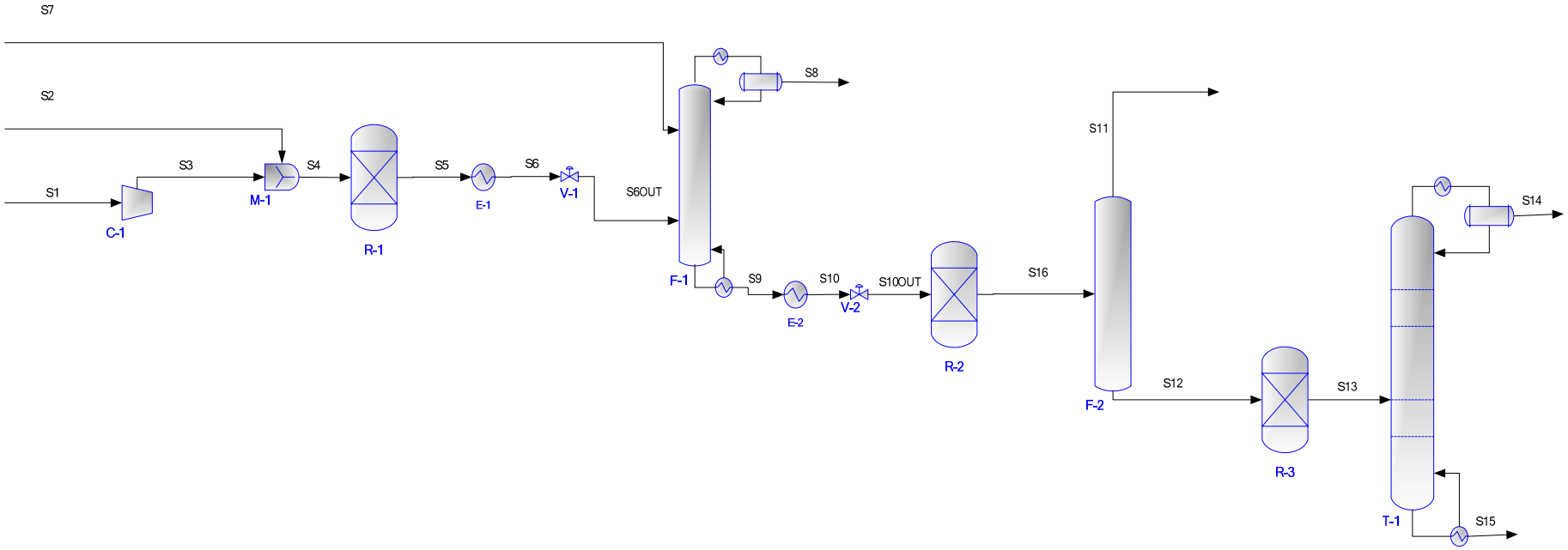


Figure 7.20 Maleic anhydride production process from butane

Process Description

Pure butane, S2, and air, S1, are mixed and fed to the first rector R-1. The reaction is exothermic, therefore, one could consider either a fluidized bed or a packed bed reactor with heat removal. The reactor effluent, S5, is cooled and sent to the absorber F-1, where it is in contact with water, S7, to remove the light gases, S8. All maleic anhydride reacts with water, in R-2, to form maleic acid. The output reactor stream, S16, is flashed. The bottom flash stream, S12, is sent to R-3 where maleic acid is broken down to maleic anhydride and water. The reactor effluent, S13, is sent to the distillation column T-1 where maleic anhydride and water are separated. The distillate, S14, is sent to waste treatment. The bottom stream, S15, consists of 99-wt% maleic anhydride.

Process Simulation

The process has been simulated using PROII process simulator.

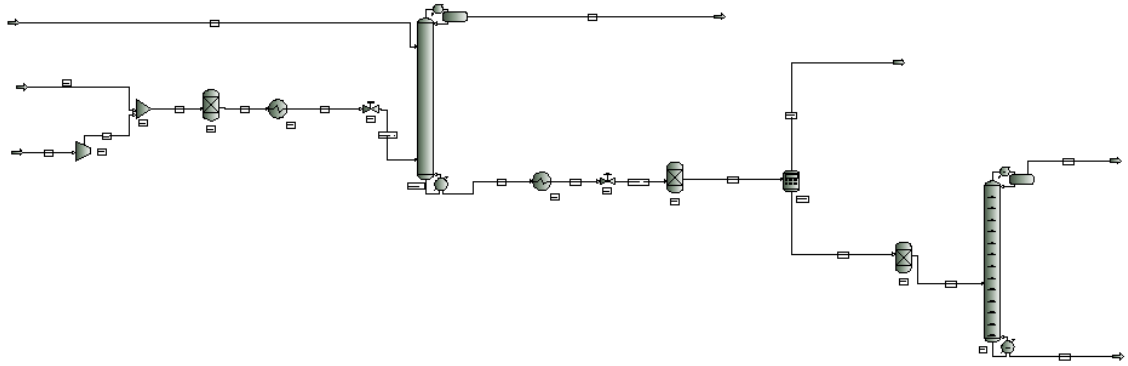


Figure 7.21 PROII schema for maleic anhydride production process from butane

UNIFAC and Peng-Robinson are the thermodynamic methods used in the present simulation.

Input data for air - S1, butane- S2, and water - S7, streams are presented in Table 7.34.

Table 7.34 Input streams specifications for maleic anhydride production process from butane (base case)

STREAM NAME		S1	S2	S7
STREAM DESCRIPTION				
TEMPERATURE	C	20	20	45
PRESSURE	KPA	101	275	170
ENTHALPY	MM BTU/HR	0.178623	0.0922	2.001445
MOLECULAR WEIGHT		28.66273	58.124	18.015
MOLE FRACTION VAPOUR		1	0	0
MOLE FRACTION LIQUID		0	1	1
RATE	KG-MOL/HR	1436.499	34.409	622.5923
FLUID RATES	KG-MOL/HR			
N2		1114.126	0	0
CO		0	0	0
O2		297.2281	0	0

CO2	0	0	0
BUTANE	0	34.409	0
H2O	25.14571	0	622.5923
FORMIC	0	0	0
ACRYLIC	0	0	0
MANH	0	0	0
MALEIC	0	0	0

Data reported in Table 7.35 represent the simulation results for the output streams.

Table 7.35 Output streams results for maleic anhydride production process from butane (base case)

STREAM NAME		**S8**	**S11**	**S14**	**S15**
STREAM DESCRIPTION					
TEMPERATURE	C	-148.695	120	98.80093	148.7919
PRESSURE	KPA	170	101	97.1	97.1
ENTHALPY	MM BTU/HR	-7.21041	34.27408	1.194142	0.626794
MOLECULAR WEIGHT		28.63743	18.4266	18.15824	93.92275
MOLE FRACTION VAPOUR		1	1	1	0
MOLE FRACTION LIQUID		0	0	0	1
RATE	KG-MOL/HR	1313.709	740.2234	26.12904	28.26253
FLUID RATES	KG-MOL/HR				
N2		1114.132	7.36E-11	0	0
CO		0.775794	1.37E-13	0	0
O2		196.48	2.34E-10	0	0
CO2		2.321996	0.005386	0	0
BUTANE		1.55E-05	6.120671	0.00172	1.51E-25
H2O		1.54E-19	733.0559	26.07345	1.459295
FORMIC		4.17E-22	0.383546	0.004317	2.84E-05
ACRYLIC		7.86E-23	0.368464	0.015909	0.003519
MANH		5.50E-21	0	0.033645	26.79968
MALEIC		0	0.289473	0	0

B)Production of maleic anhydride from benzene

Introduction

The goal of the present simulation is to design a facility that is capable of producing 20 million tones of maleic anhydride per year from benzene.

The following reactions occur during the reaction of benzene with oxygen:

$C_6H_6 + 4.5O_2 \rightarrow C_4H_2O_3 + 2CO_2 + 4H_2O$
benzene *maleic anhydride*

$C_6H_{16} + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$
benzene

$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O$
maleic anhydride

$C_6H_6 + 1.5O_2 \rightarrow C_4H_4O_2 + 4H_2O$
benzene *quinone*

Reaction kinetics is presented in Table 7.36.

Table 7.36 Kinetic data for maleic anhydride production process from benzene

REACTION	**ACTIVATION ENERGY** Ei (kcal/kmol)	**KINETIC CONSTANT** $k_{0,i}$ [m^3gas/(m^3reactor*s)]
R 1	25.143	$7.70*10^6$
R 2	29.850	$6.31*10^7$
R 3	21.429	$2.33*10^4$
R 4	27.149	$7.20*10^5$

Process schema is presented in Figure 7.22.

Simulation Goal

The goal of the present simulation is to analyze the process, to understand it and to identify the most environmentally friendly design from two different process alternatives.

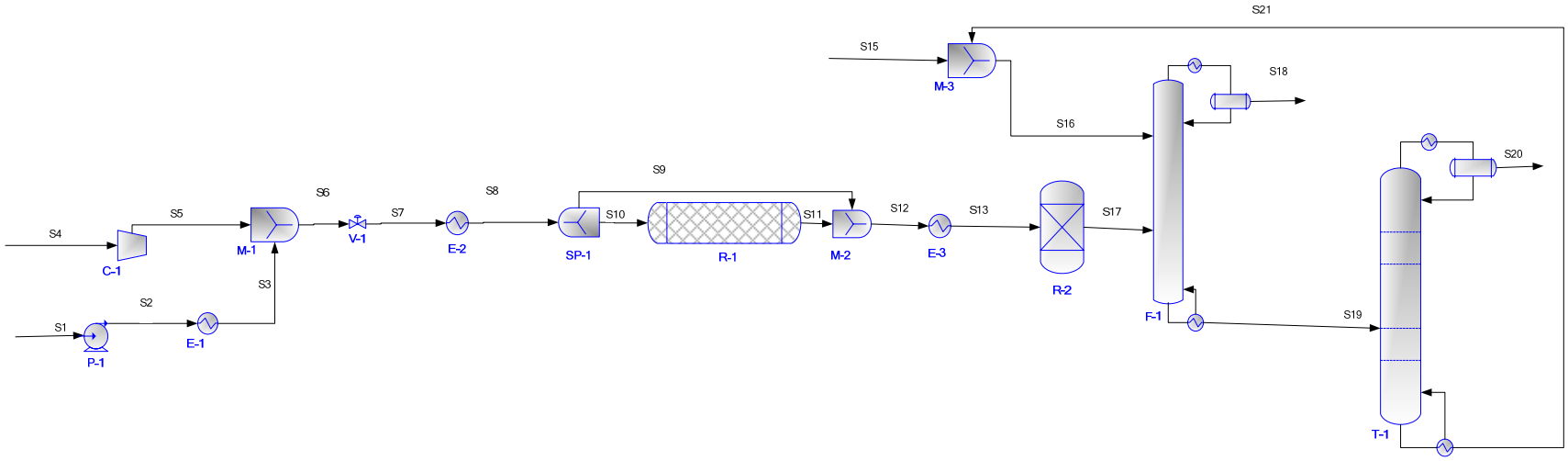


Figure 7.22 Maleic anhydride production process from benzene

Process Description

Benzene, S1, is vapourized in E-1 and mixed with compressed air, S4. The mixed stream, S6, is heated in E-2, priori to being sent to a packed catalytic reactor, R-1. The reactions described above take place in R-1. The reactor has been simulated as a plug flow reactor with 10% of input stream by-passing the reactor. The reactor effluent, S12, containing small amounts of un-reacted benzene, maleic anhydride, quinone and combustion products are cooled in E-3. Water can react with some maleic anhydride to form maleic acid. This phenomenon takes place in R-2. The R-2 output stream, S17, is sent to an absorber where it is contacted with heavy organic solvent (dibutyl phtalate), S16. This solvent absorbs the maleic anhydride, quinone, and small amounts of water. The F-1 top output stream, S18, contains off gasses, which are released into the atmosphere. The bottom stream, S19, is sent to T-1 where dibutyl phtahlate is recovered as the bottom product and recycled back to the absorber, S21. The product process - maleic anhydride, S20, is obtained in the top of T-1 column (ChE, 2007).

Process Simulation

The process has been simulated using PROII process simulator.

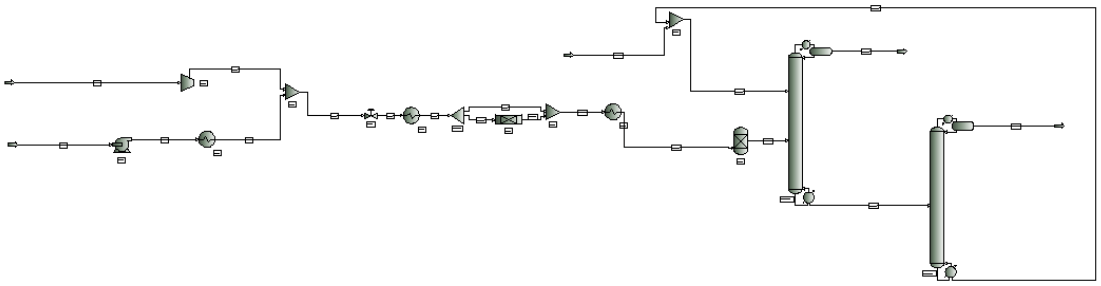


Figure 7.23 PROII schema for maleic anhydride production process from benzene

NRTL is the thermodynamic methods used in the present simulation.

Input data for benzene - S1, air - S4, and dibutyl phthalate - S14, streams are presented in Table 7.37.

Table 7.37 Input streams specifications for maleic anhydride production process from benzene (base case)

STREAM NAME		S1	S4	S14
STREAM DESCRIPTION				
TEMPERATURE	C	30	30	320
PRESSURE	KPA	101	101	100
ENTHALPY	MM KCAL/HR	0.04126	-0.26201	0.004584
MOLECULAR WEIGHT		78.115	28.84877	278.351
MOLE FRACTION VAPOUR		0	1	0
MOLE FRACTION LIQUID		1	0	1
RATE	KG-MOL/HR	42.3	2790	0.1
FLUID RATES	KG-MOL/HR			
MALEANHD		0	0	0

DBPHTHAT	0	0	0.1
NITROGEN	0	2205	0
H2O	0	0	0
OXYGEN	0	585	0
BENZENE	42.3	0	0
QUINONE	0	0	0
CO2	0	0	0
MALEIC	0	0	0

Data reported in Table 7.38 represent the simulation results for the output streams.

Table 7.38 Output streams results for maleic anhydride production process from benzene (base case)

STREAM NAME		**S18**	**S20**
STREAM DESCRIPTION			
TEMPERATURE	C	23.48596	197.4439
PRESSURE	KPA	75	70
ENTHALPY	MM KCAL/HR	2.047918	0.466628
MOLECULAR WEIGHT		29.05234	98.81654
MOLE FRACTION VAPOUR		1	1
MOLE FRACTION LIQUID		0	0
RATE	KG-MOL/HR	2798.37	25.50869
FLUID RATES	KG-MOL/HR		
MALEANHD		0.073932	25.26658
DBPHTHAT		8.72E-20	0.099221
NITROGEN		2205	0
H2O		86.4128	1.26E-07
OXYGEN		379.8419	0
BENZENE		4.244531	1.29E-10
QUINONE		0.06281	0.142765
CO2		121.7334	3.31E-25
MALEIC		1.00085	0.000127

Environmental Impact Results

The environmental impact of this process has to be estimated. The goal is to choose, from these two cases (maleic anhydride production from butane and maleic anhydride production from benzene), the best environmental solution.

3D and 1D indicators have been calculated using the mass flow-rates, the input and output streams composition (mass fraction) and toxicological and risk information data.

The CO Modules for 3 D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.39 for maleic anhydride production process from butane and in Table 7.40 for maleic anhydride production process from benzene.

Table 7.39 CO Modules specifications for 3D indicators for maleic anhydride production process from butane

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	10	11	S1
CO2	2	0	0	0	S2
CO3	3	0	11	0	S7
CO4	4	1	0	10	S8
CO5	5	1	10	0	S11
CO6	6	1	10	0	S14
CO7	7	2	10	0	S15
5CO8	8	-	-	-	S5

Table 7.40 CO Modules specifications for 3D indicators for maleic anhydride production process from benzene

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	0	0	S1
CO2	2	0	0	11	S4
CO3	3	0	0	0	S14
CO4	4	1	10	10	S18
CO5	5	2	0	0	S20
CO6	6	-	-	-	S12

The 3D indicators calculated using data from the process simulators and from the database are presented in Table 7.41.

Table 7.41 3D indicators obtained in the maleic anhydride production process

CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	29734.45	677.55	20070	8776.601
CASE 2	7416.67	62.9629	10110	16289.101

From Table 7.41, it can be noticed, MI, EI and PCR are lower in the second case while PEI is lower in the first alternative design. In order to decide which design is more environmentally friendly, 1D indicator has been also calculated.

The same results are reported in Figures 7.24.

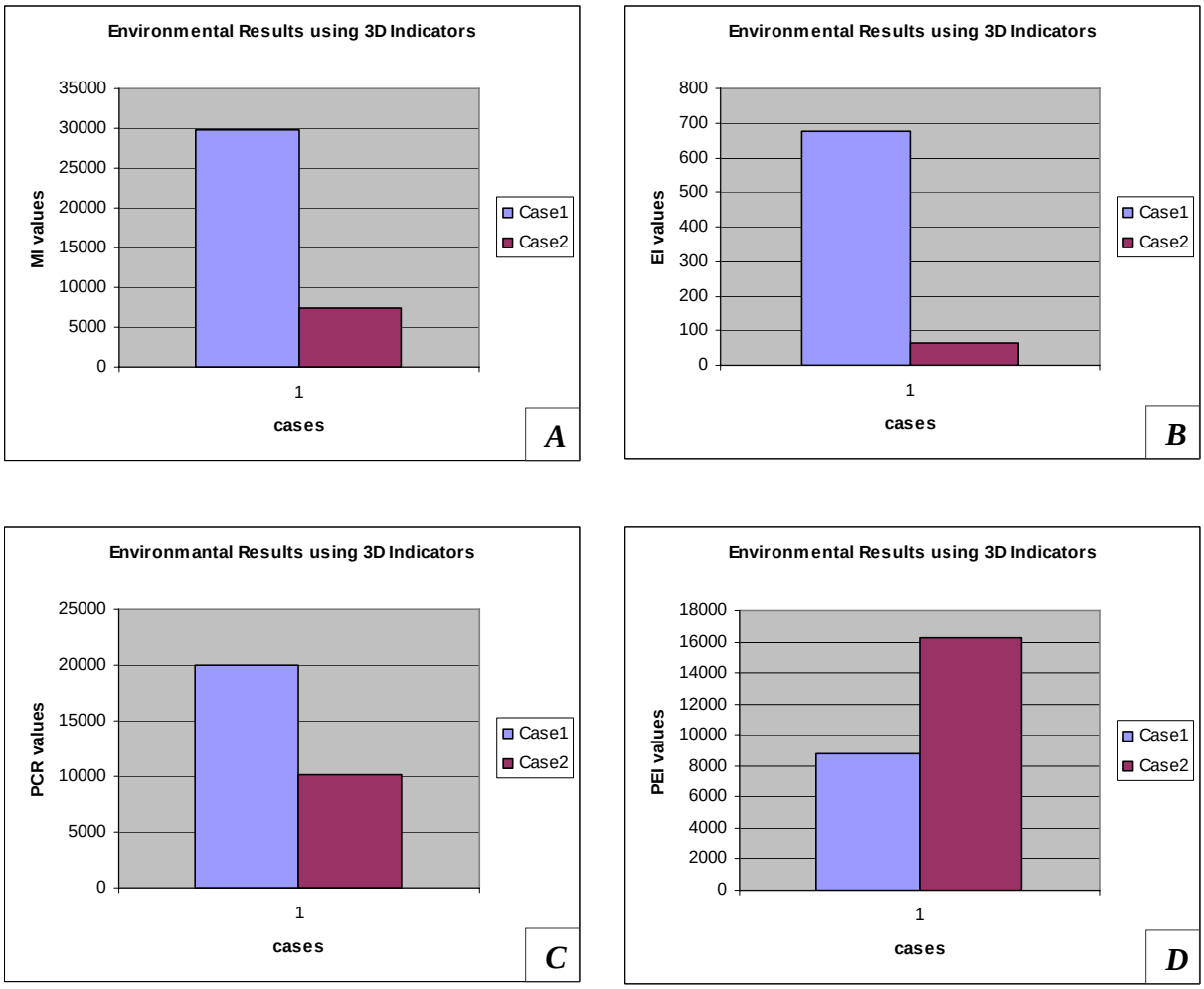


Figure 7.24 3D Indicators for maleic anhydride production process A) MI; B) EI; C) PCR; D) PEI

For the same cases, WAR Algorithm has been applied. The CO Modules for 1D indicator (Proall and Proenergia) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.42 for maleic anhydride production process from butane and in Table 7.43 for maleic anhydride production process from benzene.

Table 7.42 CO Modules specifications for 1D indicator for maleic anhydride production process from butane

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	0	2	S2
CO3	0	0	3	S7
CO4	0	1	4	S8
CO5	0	1	5	S11
CO6	0	1	6	S14
CO7	0	2	7	S15
CO8	1	1	8	S32

Table 7.43 CO Modules specifications for 1D indicator for maleic anhydride production process from benzene

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	0	2	S4
CO3	0	0	3	S14
CO4	0	1	4	S18
CO5	0	2	5	S20
CO6	1	1	6	S12

The results reported in Table 7.44 represent the Environmental Impact Indexes obtained using WAR Algorithm.

Table 7.44 Environmental Impact Indexes obtained in the maleic anhydride production using WAR Algorithm

CASE STUDY NAME	ENIVORONMENTAL INDEXES NAME			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	4056.57	1.54	1643.38	0.625
CASE 2	1095.02	0.44	-988.00	-0.398

Taking into account the 1D Indicator, more exactly the environmental impact evaluated using WAR Algorithm, it can be noticed that the best alternative design, environmentally speaking, is the second one, CASE 2.

The same results are illustrated in Figures 7.25.

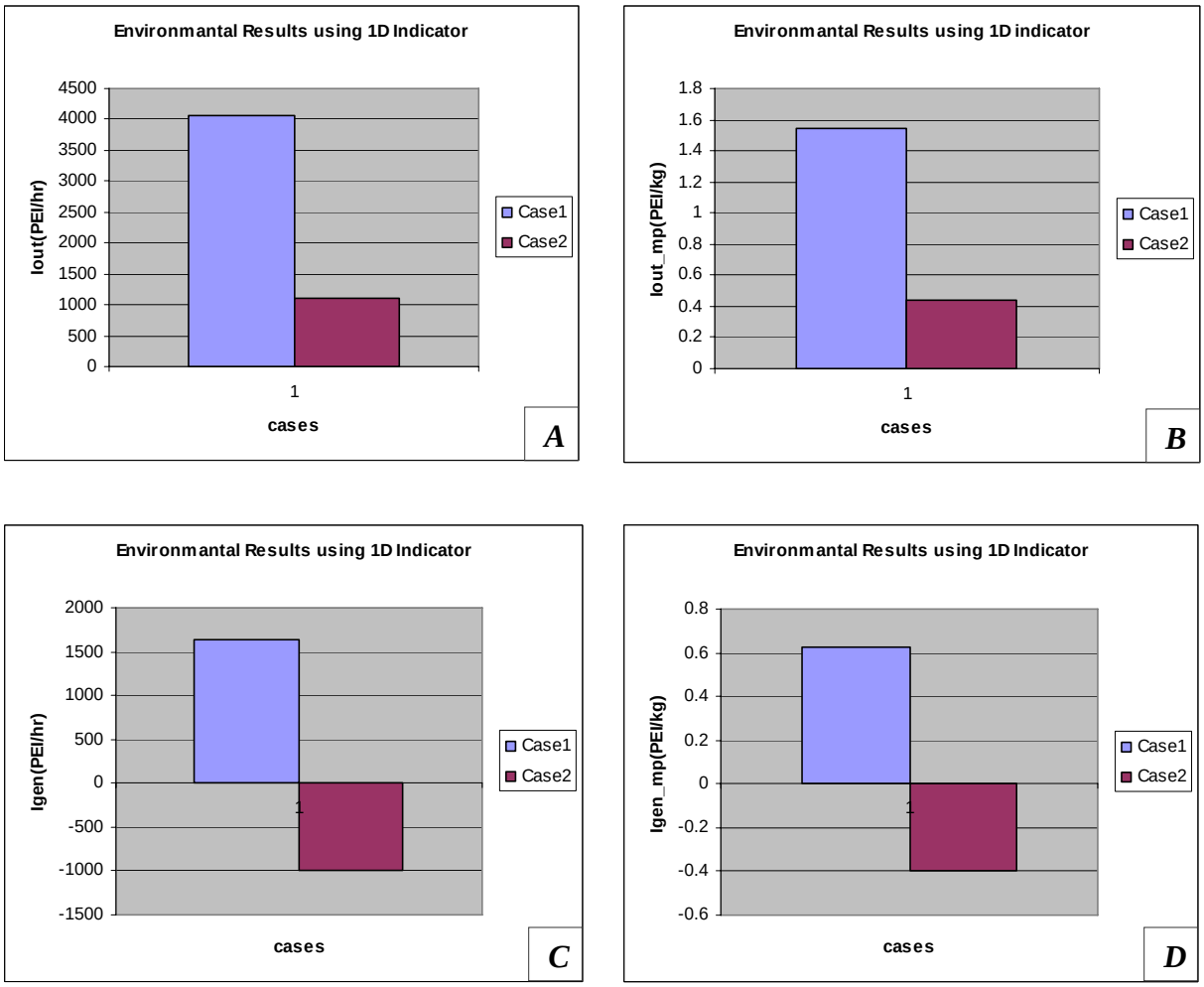


Figure 7.25 1D Indicators for maleic anhydride production process A) Iout; B) Iout_mp; C) Igen; D) Igen_mp

Conclusions

The maleic anhydride production process has been simulated using PROII process simulator. Two process alternatives, starting from butane and from benzene as raw materials, are proposed and analyzed in order to choose the most environmentally friendly. The results obtained, using the 3D and 1D indicators of the PSP Framework, provide the second alternative design as best solution.

7.1.6 Dimethylether Production Process

Introduction

Dimethylether (DME) is a substance used primarily as a propellant. Recently, the use of DME as a fuel additive for diesel engines has been investigated. DME is a clean and economical alternative fuel, which can be produced from various resources (Turton *et al.,* 2003).

The following reaction characterizes the process:

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O$$
$$methanol \quad DME$$

The reaction that takes place is exothermic with a standard heat of reaction:

$$\Delta H_{react}(25^{\circ}C) = -11770\ \frac{kj}{kmol}$$

The rate equation for this reaction is:

$$-r_{methanol} = k_0 \cdot \exp\left[-\frac{E_a}{R \cdot T}\right] \cdot p_{methanol}$$

$k_0 = 1.21 * 10^6\ \frac{kmol}{m^3}$ filled reactor

$E_a = 80.46\ \frac{kj}{kmol}$

Pmethanol = partial pressure of methanol

Significant catalyst deactivation occurs at temperatures above 400°C, and the reactor should be designed so that the temperature is not exceeded anywhere in the reactor.

The process flow diagram is illustrated in Figure 7.26.

Simulation Goal

The goal of the present simulation is to analyze the process, to optimize the energy consumption and to identify the most environmentally friendly design from different process alternatives.

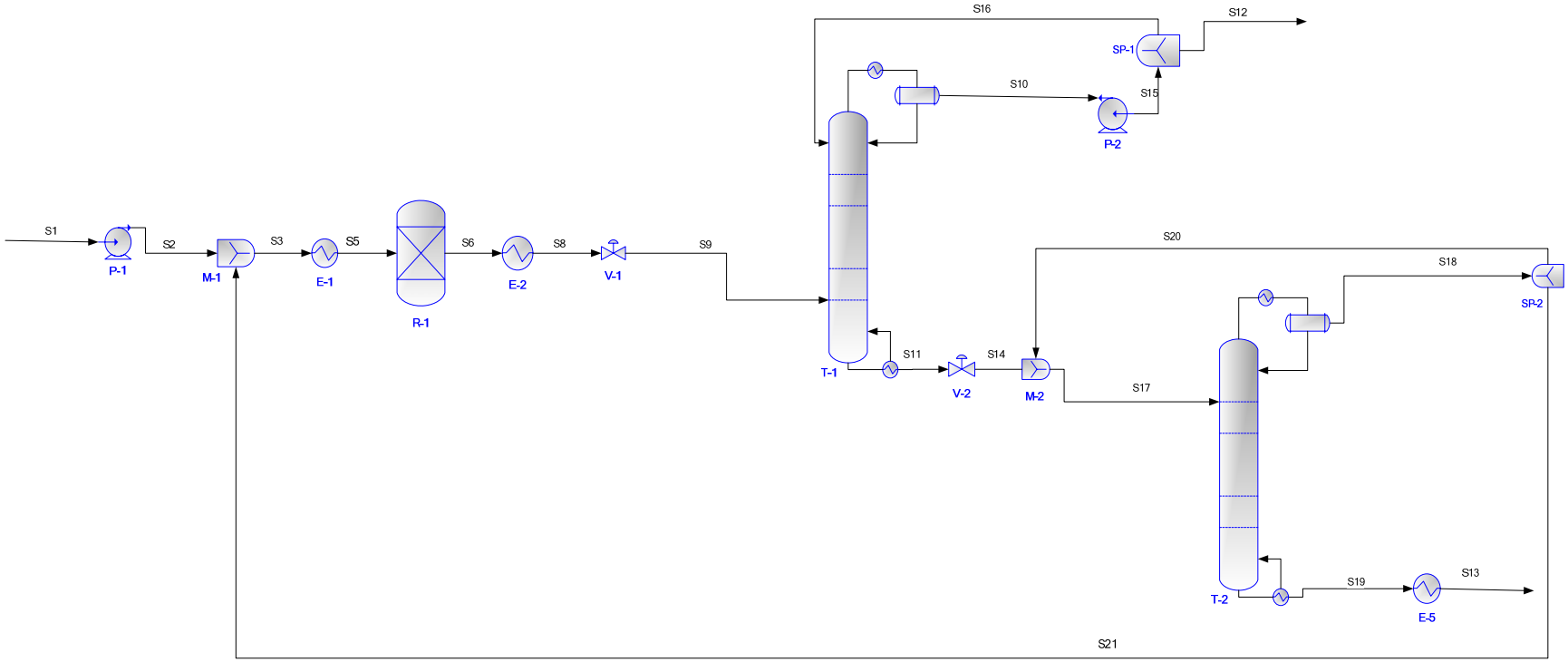


Figure 7.26 DME production process

Process description

The essential operations in the process are: preheating the raw material, the reaction of methanol to form DME, product separation, contaminant separation and methanol separation and recycle.

Fresh methanol, S1, is combined with recycled reactant, S21, and vapourized prior to being sent to a fixed bed reactor, R-1, operating between 250° C and 368°C. The reaction presented in the previous section takes place in R-1.

The single pass conversion of methanol in the reactor is 80%. The reactor effluent is cooled in E-2, prior to being sent to the first distillation column T-1. DME product, S12, is obtained in the top of the first column. The second column, T-2, separates the water from the unused methanol. The methanol, S21, is recycled back to the front end of the process, while the water, S13, is sent to wastewater treatment to remove trace amounts of organic compounds (Turton *et al.,* 2003).

From the environmental point of view, it is desired to reduce the waste flow-rate and the concentration of S13 and to reduce the energy supplied from external sources.

Process Simulation

The process has been simulated using PROII process simulator.

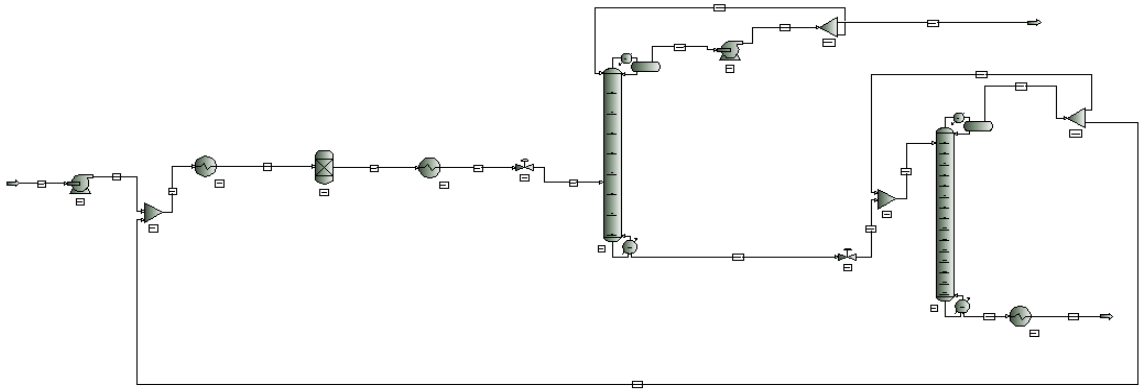


Figure 7.27 PROII schema of DME production process

UNIQUAC and Wilson are the thermodynamic methods used in the present simulation. Input data for methanol stream, S1, is summarized in Table 7.45.

Table 7.45 Input stream specifications for DME production process (base case)

STREAM NAME		**S1**
STREAM DESCRIPTION		
TEMPERATURE	C	25
PRESSURE	BAR	1
ENTHALPY	MM KJ/HR	0.511689
MOLECULAR WEIGHT		31.90826
MOLE FRACTION VAPOUR		0
MOLE FRACTION LIQUID		1
RATE	KG-MOL/HR	262.2
FLUID RATES	KG-MOL/HR	
DME		0
METHANOL		259.7
H2O		2.5

Data reported in Table 7.46 represent the simulation results for dimethylether - S12, and the wastewater - S13, streams.

Table 7.46 Output streams results for DME production process

STREAM NAME		**S12**	**S13**
STREAM DESCRIPTION			
TEMPERATURE	C	46.31458	50
PRESSURE	BAR	11.4	2.1
ENTHALPY	MM KJ/HR	0.682238	0.500403
MOLECULAR WEIGHT		46.0686	18.08513
MOLE FRACTION VAPOUR		0	0
MOLE FRACTION LIQUID		1	1
RATE	KG-MOL/HR	129.518	132.7814
FLUID RATES	KG-MOL/HR		
DME		129.505	3.69E-11
METHANOL		0.012953	0.663899
H2O		9.59E-08	132.1175

Environmental Impact Results

Two case studies have been considered and analyzed. The base case is identical with the schema presented in Figure 7.26. The second case represents the same process, but with heat integration. The stream coming out from the reactor, S6, is sent to the first heat exchanger, E-1. By integrating the heat, the second heat exchanger, E-2, is not necessary any more.

3D and 1D indicators have been calculated using the mass flow-rates, the input and output streams composition (mass fraction) and the toxicological and risk information data.

The CO Modules for 3 D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.47.

Table 7.47 CO Modules specifications for 3D indicators for DME production process

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	10	0	S1
CO2	2	2	0	0	S12
CO3	3	1	10	0	S13
CO4	4	-	-	-	S6

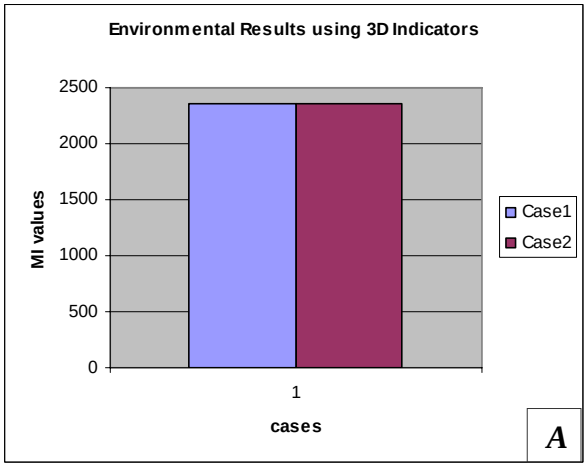
The 3D indicators calculated using data from the process simulator and from the database results are presented in Table 7.48.

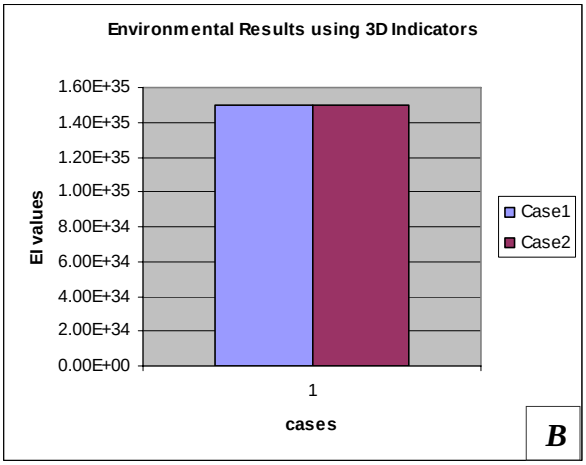
Table 7.48 3D indicators obtained in the DME production process

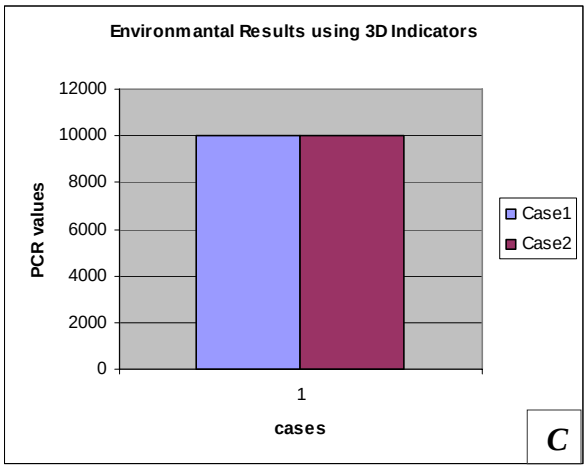
CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	2357.41	1.5e+35	10000	8.52
CASE 2	2357.41	1.5e+35	10000	8.52

The 3D indicators do not provide relevant information for choosing the most environmentally friendly design, being all equal.

The same results are reported in Figures 7.28.







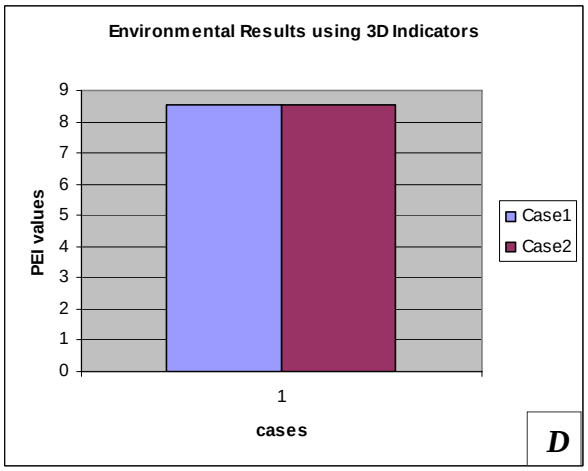


Figure 7.28 3D Indicators for DME production process A) MI; B) EI; C) PCR; D) PEI

Because the results obtained using 3D indicators are not relevant, 1D indicator, WAR Algorithm, has been applied. The CO Modules for 1D indicator (Proall and Proenergia) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.49.

Table 7.49 CO Modules specifications for 1D indicator for DME production process

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	2	2	S12
CO3	0	1	3	S19
CO4	1	1	7	S32

The results reported in Table 7.50 represent the Environmental Impact Indexes obtained using WAR Algorithm. They allow choosing the second alternative design, CASE 2, as the most environmentally friendly.

Table 7.50 Environmental Impact Indexes obtained for DME production process using WAR Algorithm

CASE STUDY	ENIVORONMENTAL INDEXES NAME			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	160.75	2.75e-2	-2472.35	-0.4145
CASE 2	153.18	2.57e-2	-2479.93	-0.4158

The same results are presented in Figures 7.29.

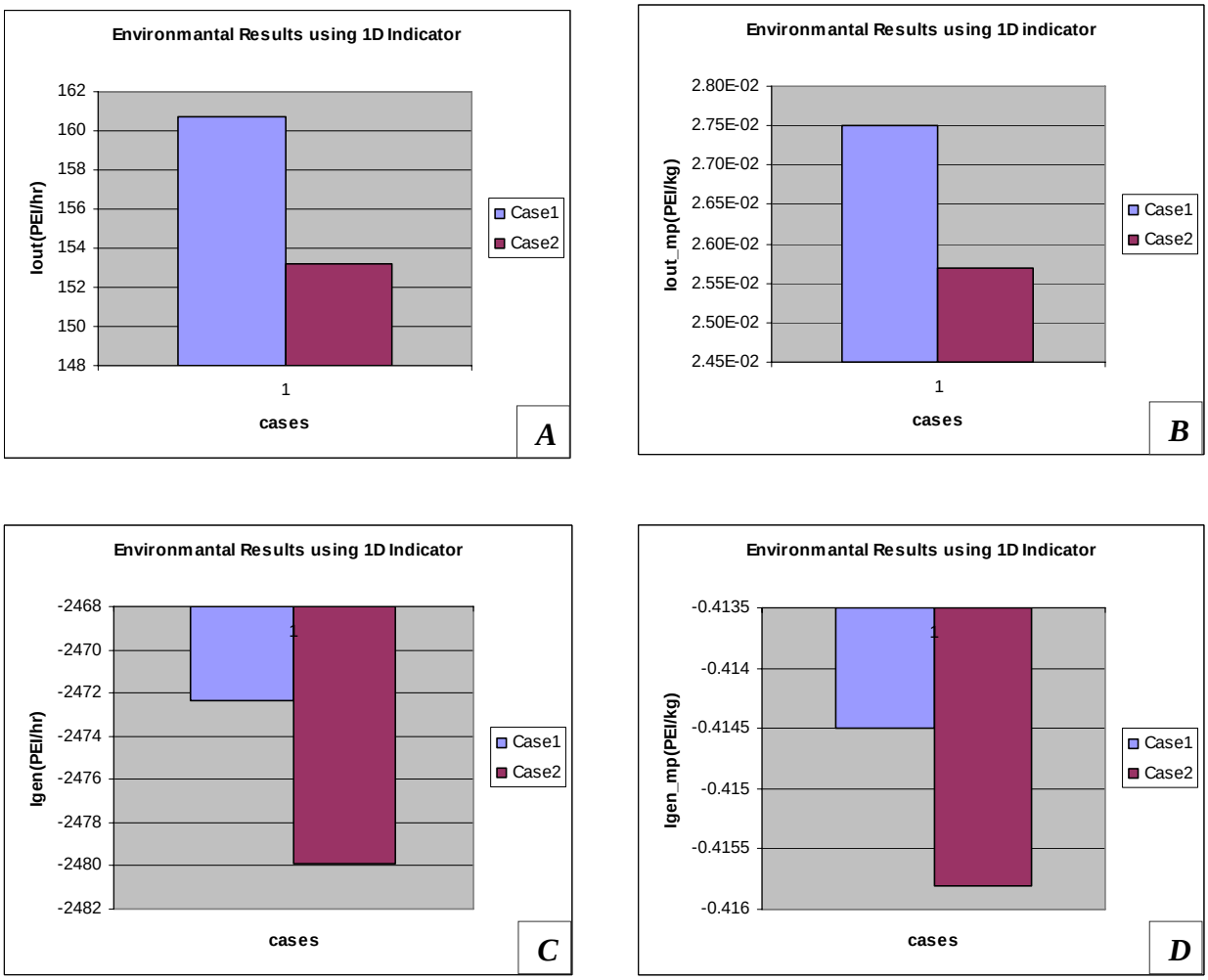


Figure 7.29 1D Indicators for DME production process A) Iout; B) Iout_mp; C) Igen; D) Igen_mp

Conclusions

The DME production process has been simulated using PROII process simulator. Two process alternatives are proposed and analyzed in order to choose the most environmentally friendly one. The results obtained using 3D indicators are not relevant being equal in both cases. The 1D indicators of the PSP Framework provide the second alternative design as best solution. Performing heat integration, the energy supplied from external source is less so the impact of the energy generation (gaseous emissions) process will be lower. The choice of the second alternative design is stressed, one more time, also by economical factor. Less energy is supplied from external source so less amount of money is spent for this design alternative.

7.1.7 R-134a Production Process

Introduction

In the 1930's, chlorofluorocarbons (CFC's) were developed as a supposedly safe alternative to ammonia and sulfur dioxide refrigerants. While sulfur dioxide is toxic and ammonia is both toxic and highly flammable, CFC's were found to be non-flammable, non-explosive, and non-corrosive. CFC's quickly become the compounds of choice for refrigeration as well as for cleaning and foam blowing agents.

However, the discovery of a hole in the ozone layer over Antarctica in 1985 led to a movement to reduce the use of CFC's. Due to their high ozone depleting potential, CFC's were scheduled to be phased out completely by 1996. This led to the need to find alternative refrigerants that are not ozone depleting substances. Some experts have suggested the use of hydrochlorofluorocarbons (HCFC's) for this use. Unfortunately, HCFC's also have some ozone depleting potential, and are scheduled to be banned by 2030. With this in mind, one replacement for CFC's in refrigeration is CF_3CH_2F (R-134a). R-134a is very attractive as a refrigerant because it has zero ozone depleting potential as well as a low direct Global Warming Potential (GWP).

One factor limiting the use of R-134a had been the fact that conventional lubricants are not miscible with R-134a. However, new lubricants have been developed which allow R-134a systems to run efficiently and reliably on a long-term period. This, along with the need to find refrigerants with a low ozone depleting potential, will greatly increase the market for R-134a in the future (ChE, 2007).

The process presented here is the R-134a production process starting from propylene. R-134a is produced by the following series of reactions:

$$3HF + TCE(HC_2Cl_3) \rightarrow R-133a(H_2C_2ClF_3) + 2HCl$$

$$R-133a(H_2C_2ClF_3) + HF \rightarrow R-134a(H_2C_2F_4) + HCl$$

These reactions are based on limited data found in US Patent 5,243,105. It was determined that the activation energies for the two main reactions have the following values: 167 kJ/mol for TCE to R-133a and 237 kJ/mol for R-133a to R-134a.

Using data from the patent, the rate constants were determined from the following equations:

$$-r_A = kC_AC_B$$

$$\tau = C_{A0}\int \frac{dX}{-r_A}$$

$k = 10.94 \dfrac{l}{mol \times s}$ for R-133a to R-134a

$k = 11.82 \dfrac{l}{mol \times s}$ for TCE to R-133a

and the preexponential factors were found to be:

$$A = 6.5 \times 10^{18} \frac{l}{mol \times s}$$ for TCE to R-133a

$$A = 5.5 \times 10^{20} \frac{l}{mol \times s}$$ for R-133a to R-134a

The simplified schema of the process is presented in Figure 7.30.

Simulation Goal

The goal of the present simulation is to analyze the process, to reduce the energy consumption and to identify the most environmentally friendly design from different process alternatives.

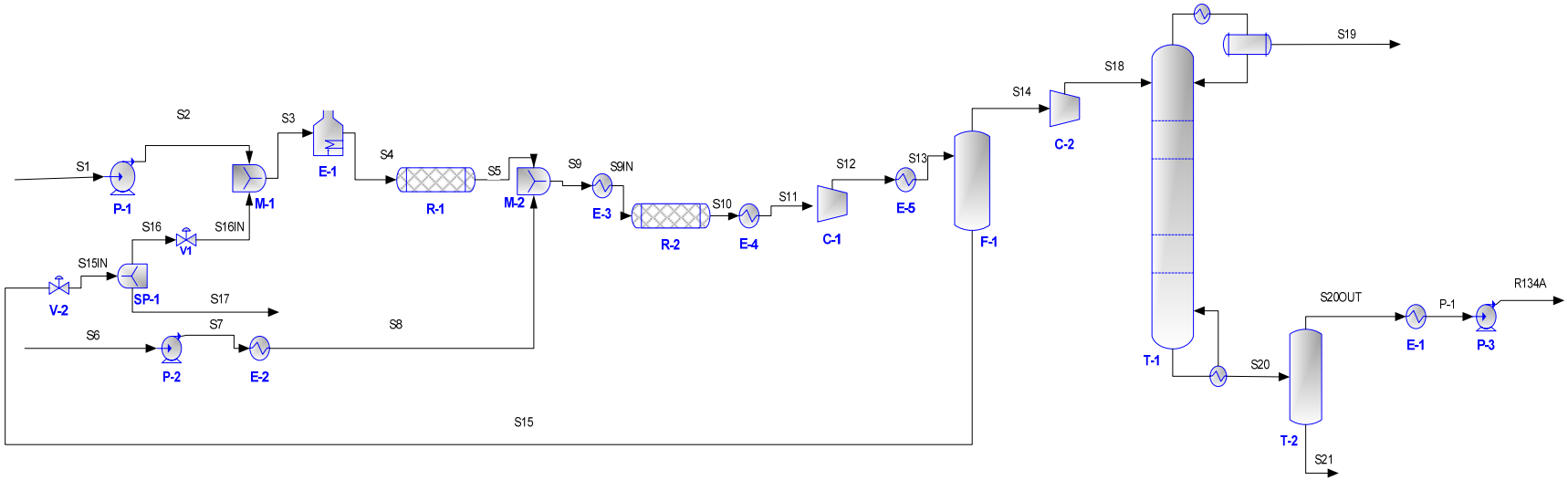


Figure 7.30 R-134a production process

Process Description

Liquid hydrogen fluoride, S1, enters the system at 25°C and 2 atm. It is pumped up in P-1 before being mixed in M-1 with a recycle stream consisting of HF, R-133a (CF_3CH_2Cl), R-134a (CF_3CH_2F), and trichloroethylene (TCE), S16IN. The mixed stream, S3, enters in a heat exchanger, E-1, where is heated to 400°C before being fed to the first reactor R-1. The first reactor, R-1, is an isothermal plug-flow reactor which converts 99.3% of the R-133a to R-134a. The product stream of the first reactor, S5, is then mixed with a feed of TCE, S8. The mixed stream, S9, is then fed through a heat exchanger, E-3, where it is cooled to 290°C. The second reactor, R-2, converts HF and TCE to R-133a and hydrochloric acid (HCl). The stream leaving the second reactor, S10 is cooled in the heat exchanger, E-4. After cooling, the stream, S11, is sent to a compressor, C-1. The stream, S12, is then cooled to 30°C in E-5. The cooled stream is then fed to the first flash, F-1. The bottom stream of F-1, S15, is recycled to be mixed with the HF stream, S1. The distillate from this flash, S14, consists mainly of R-134a and HCl. This stream is next compressed to 20 atm, in C-2, before being fed into the distillation column, T-1. The top stream of this column contains HCl. The bottom stream, S20 is sent to the second distillation column, T-2. Here, R-134a is removed from the rest of the refrigerants and from the HCl. The 99.99% pure R-134a stream, S20OUT, is cooled up to 40°C before being stored (ChE, 2007).

From the environmental point of view it is desired to reduce the waste streams S17 and S21 and from the economic-environmental point of view it is desired to reduce the heat consumption of the process.

Process Simulation

The process has been simulated using PROII process simulator.

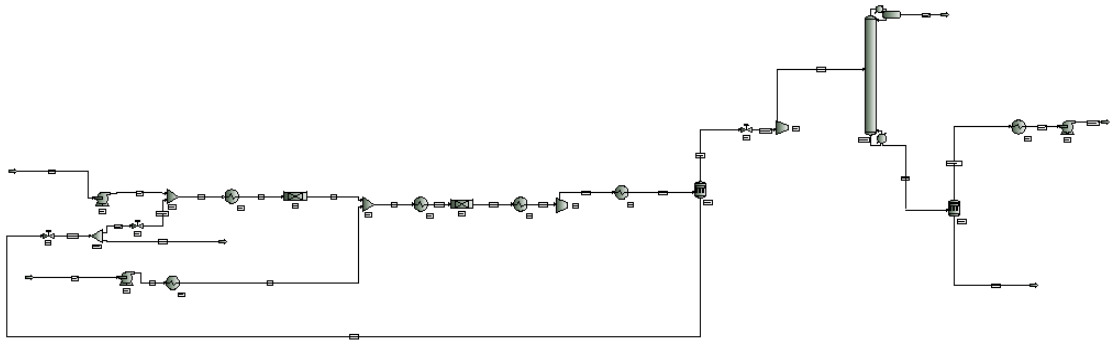


Figure 7.31 PROII schema of R-134a production process

UNIFAC group contribution method is the thermodynamic method used in the present simulation. Input data for HF - S1, and TCE - S6 streams are presented in Table 7.51.

Table 7.51 Input streams specifications of R-134a production process (base case)

STREAM NAME		**S1**	**S6**
STREAM DESCRIPTION			
TEMPERATURE	C	25	25
PRESSURE	KPA	202.6	202.6
ENTHALPY	MM KJ/HR	0.115246	0.065523
MOLECULAR WEIGHT		20	131.389
MOLE FRACTION VAPOUR		0	0
MOLE FRACTION LIQUID		1	1
RATE	KG-MOL/HR	91.6	22.3
FLUID RATES	KG-MOL/HR		
R134A		0	0
TCLETHLN		0	22.3
HYFLUORD		91.6	0
HYCHLORD		0	0
WATER		0	0
CLTRFETH		0	0

Data reported in Table 7.52 represent the simulation results for waste streams, S17 and S21, HCl stream, S19 and R-134a stream, R134A.

Table 7.52 Output streams results for R-134a production process (base case)

STREAM NAME		**S17**	**S19**	**S21**	**R134A**
STREAM DESCRIPTION					
TEMPERATURE	C	91.79324341	-8.767089844	67.99334717	40.4679
PRESSURE	KPA	952.5	2026.5	2026.5	2837
ENTHALPY	MM KJ/HR	0.036062051	0.767935574	6.86E-05	0.118219
MOLECULAR WEIGHT		40.02774811	36.47261429	36.46099854	102.0315
MOLE FRACTION VAPOUR		0.008689015	1	1	0
MOLE FRACTION LIQUID		0.991311014	0	0	1
RATE	KG-MOL/HR	5.30000782	66.00003815	0.011796094	20.28816
FLUID RATES	KG-MOL/HR				
R134A		0.327544868	0.011690835	0	20.28816
TCLETHLN		1.94E-06	0	0	0
HYFLUORD		4.134516239	0	0	0
HYCHLORD		0.03973176	65.98834229	0.011796094	0
WATER		0	0	0	0
CLTRFETH		0.798213005	0	0	0

Environmental Impact Results

Three design alternatives have been proposed and simulated for the process under study. The first case corresponds to the base case (Figure 7.30). In the second design the reaction heat of the first reactor is removed from the process by means of a cooling loop. This design is depicted in Figure 7.32. In the third design the heat integration between two heat exchangers (E-2 is a heater; E-4 is a cooler) is considered. This design is illustrated in Figure 7.33.

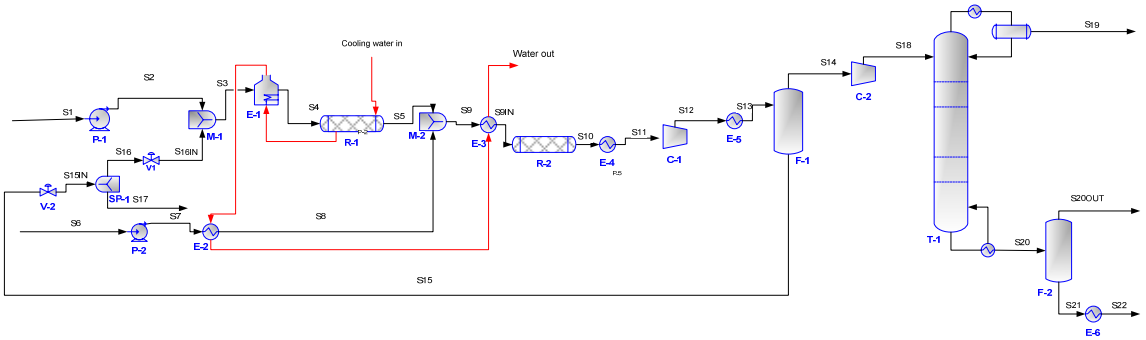


Figure 7.32 R-134a production process (CASE 2)

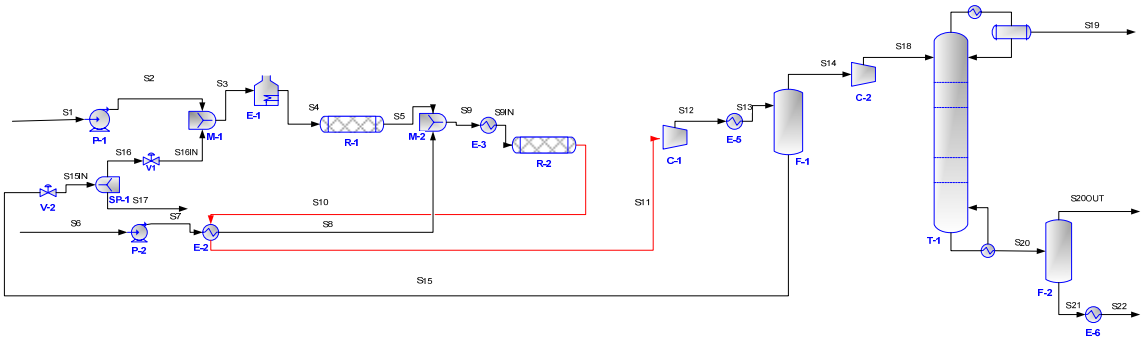


Figure 7.33 R-134a production process (CASE 3)

The CO Modules for 3D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.53.

Table 7.53 CO Modules specifications for 3D indicators for R-134a production process

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	0	0	S1
CO2	2	0	0	0	S6
CO3	3	1	0	0	S17
CO4	4	3	0	0	S19
CO5	5	2	0	0	R134A
CO6	6	1	0	0	S21
CO7	7	-	-	-	S10

The 3D indicators calculated using data from the process simulator and from the database are presented in Table 7.54.

Table 7.54 3D Indicators obtained in the R-134a production process

CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	132.24	4.327	1300010	1889.3
CASE 2	132.41	0.558	1300010	1889.3
CASE 3	672.73	5.31	1300010	1889.3

The case with the lowest MI and EI 3D indicators is the second one, CASE 2. The reasons why PCR and PEI have equal values for all the three cases are explained below. All three processes are continuous processes, so the frequency class for the substances present in the process is the same (permanent use; > 6h/day- see Table 3.1) as are the risk phrases. PEI has the same values for all three cases because the physical states of the substances involved in the process are the same and the receiving medium (air, water, soil) is also the same. In conclusion, CASE 2 represents the most environmentally friendly design, taking into account the 3D indicators.

The same results are reported in Figures 7.34.

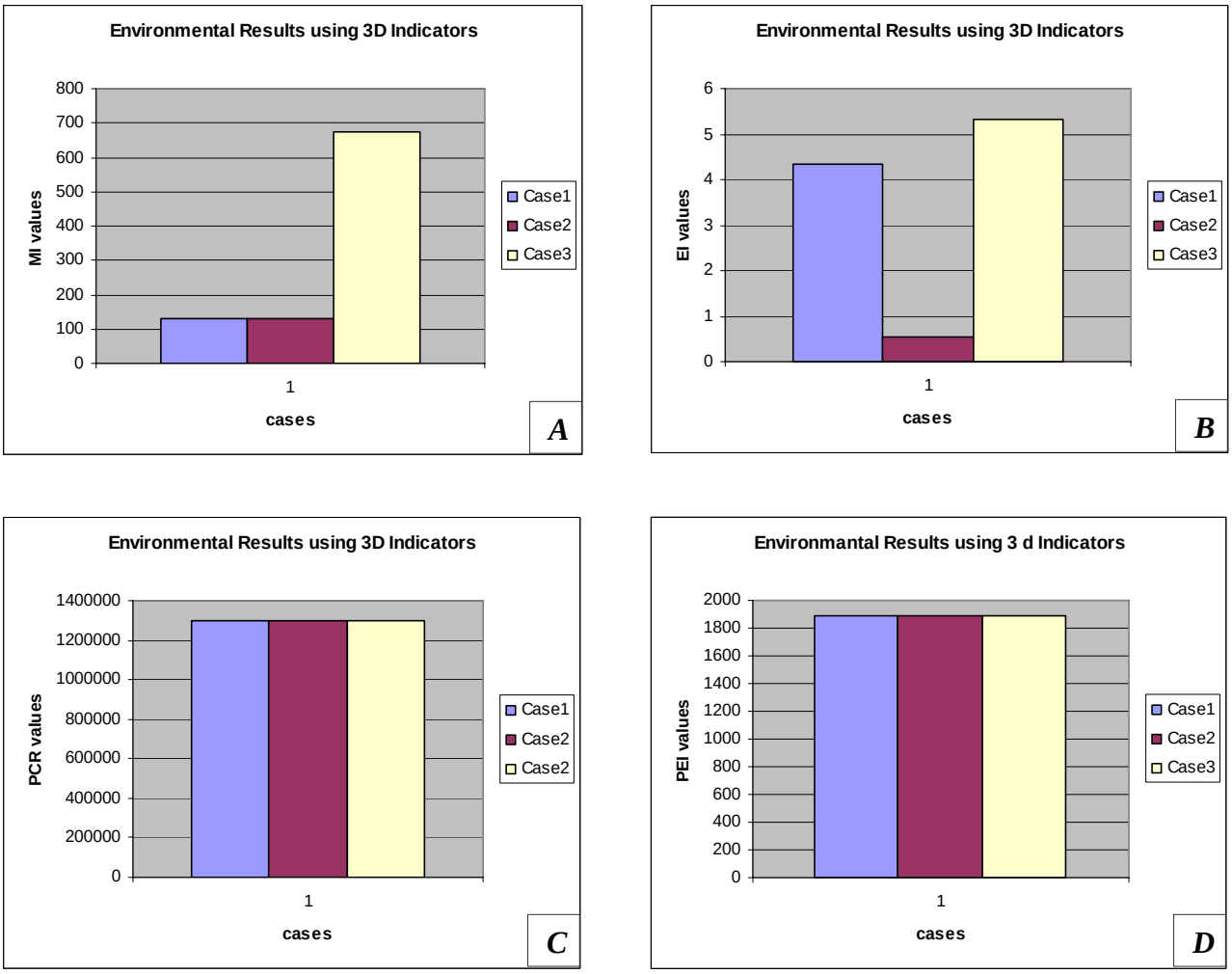


Figure 7.34 3D Indicators for R-134a production process A) MI; B) EI; C) PCR; D) PEI

For the same cases, WAR Algorithm has been applied. The CO Modules for 1D indicator (Proall and Proenergia) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.55.

Table 7.55 CO Modules specifications for 1D indicator for R-134a production process

CO MODULE NAME	**CO MODULES PARAMETERS**			**CONNECTED STREAM**
	PROCESS_TYPE	**CAPE_POSITION**	**CAPE_ID**	
CO1	0	0	1	S1
CO2	0	0	2	S6
CO3	0	1	3	S17
CO4	0	2	4	S19
CO5	0	2	5	R134A
CO6	0	1	6	S21
CO7	1	1	7	S32

The results obtained using 1D indicator, are reported in Table 7.56.

Table 7.56 Environmental Impact Indexes obtained in the R-134a production process using WAR Algorithm

CASE STUDY	**ENIVORONMENTAL INDEXES NAME**			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	532.25	0.2566	-10538.88	-5.091
CASE 2	489.99	0.2367	-10580.14	-5.111
CASE 3	479.89	0.2318	-10590.24	-5.116

CASE 3 is the most favorable. It can be noticed, from Table 7.56, that the difference between CASE 2 and CASE 3 is not so significant, so the two cases can be considered equivalent. Making the comparison between the same case studies in Table 7.54, a big difference between these two design alternatives can be noticed. In conclusion, CASE 2 is the most favorable design, taking into account 3D and 1D indicators. The results stress, once more, the necessity to use the complete PSP Framework.

The same results are presented in Figures 7.35.

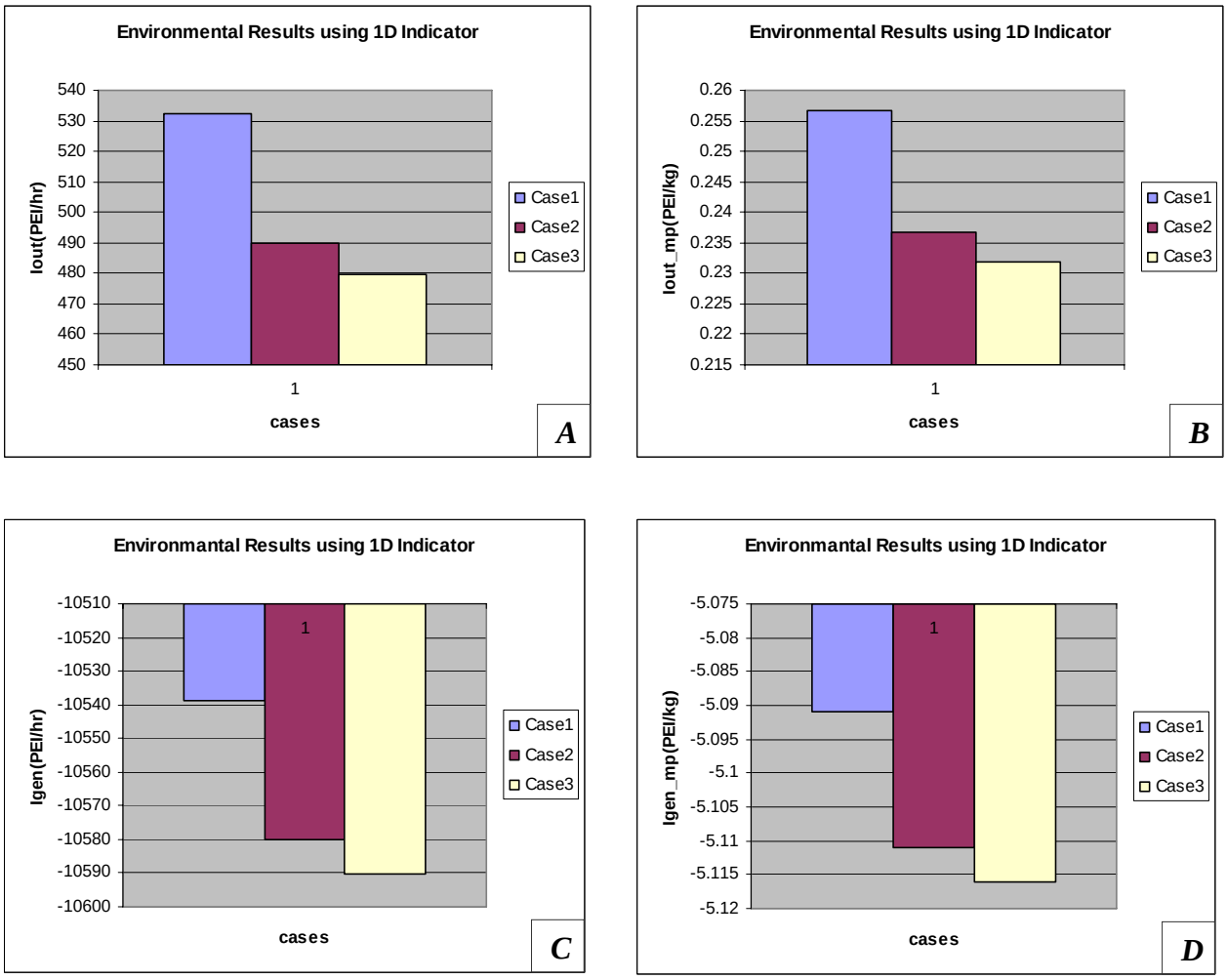


Figure 7.35 1D Indicators for R-134a production process A) Iout; B) Iout_mp; C) Igen; D) Igen_mp

Conclusions

The R-134a production process has been simulated using PROII process simulator. Three process alternatives are proposed and analyzed in order to choose the most environmentally friendly. The most environmentally friendly design is the second one, as it can be noticed from the results obtained using the 3D and 1D indicators of the PSP Framework. Making the heat integration fewer gasses are released into the atmosphere and a smaller quantity of energy has to be supplied from external sources.

7.2 Processes Correspondent to Chemical Plants Situated in Developing Countries

7.2.1 Fuel Ethanol Production from Sugar Cane Molasses

Introduction

After two centuries of almost absolute belief in technical and economic progress, human society is in a period of reconsideration and elaboration of new strategies for the ongoing new century. The progress made by our civilization, with an explosive rise in world population has led to an enormous consumption increase of resources and to an equal threat to the environment. In this context, biotechnology is considered to play a significant role. Notably the question of responsible use of resources for food, energy, and alternative products and production processes has created various reasonable solutions following the crisis in the early 1970s - new routes, but also rediscoveries of others which have been developed under different conditions in the past.

One of the examples discussed as possible alternative that has been investigated during the last few decades is the production of ethanol from various feedstocks (Roehr, 2001).

In the past decade, the use of inexpensive agricultural crops and residues for producing ethanol has received considerable attention (Rajagopalan *et al.,* 2002). Different raw materials such as: corn, potatoes, cellulose, sugar cane, artichokes, agricultural residues, municipal solid waste can be used to obtain ethanol. Development of liquid bio fuels based on low-cost agricultural raw materials has several benefits. First, fuels from renewable sources, such as agricultural crops, can reduce the dependence on imported oil. Second, oxygenated fuels, such as ethanol, burn cleaner than fossil fuels, alleviating environmental concerns such as the net atmospheric CO_2 content, the greenhouse effect, and noxious CO emissions. Other advantages include the development of the rural economy by creating employment opportunities and utilizing marginal lands to cultivate crops as feedstock for bio fuel production (Hohenstein and Wright, 1994; Yaccobucci and Womach, 2000).

In the process described below ethanol is obtained from sugar cane molasses. The process represents a real plant located in the central region of Cuba. The distillery can produce up to 70,000 litres of hydrated grade ethanol per day. It should be specified that the simulation of the present process was realized by Ing. Fidel Domenech López, from Cuban Institute for Research on Sugar Cane By-Products, National Cleaner Production Network of Cuba, Focal Point ICIDCA, during his fellowship training at ICS-UNIDO (18 July - 18 November 2005). After the simulation we have studied and analyzed the process applying the PSP methodology.

A brief description of the process is given below.

The process has been divided in four sections as follows:

1. Substrate preparation
2. Sugar conversion to ethanol
    a. Yeast propagation stage
    b. Alcoholic fermentation stage
3. Biomass separation
4. Ethanol separation
    a. Striping section

b. Rectification section

The most important reactions, which occur in the propagation stage, are:

$$\underset{sucrose}{C_{12}H_{22}O_{11}} + H_2O \rightarrow 2\underset{glucose}{C_6H_{12}O_6}$$

$$\underset{glucose}{C_6H_{12}O_6} + 6O_2 \rightarrow 6H_2O + 6CO_2$$

$$\underset{glucose}{122C_6H_{12}O_6} + \underset{urea}{48CH_4N_2O} + \underset{ammonium\ phosphate}{12H_9N_2O_4P} \rightarrow \underset{yeast}{12C_{65}H_{92}O_{30}N_{10}P} + 330H_2O + 69O_2$$

The conversion values are reported in Table 7.57.

Table 7.57 Conversion data for ethanol production process from sugar cane molasses (R-1)

REACTION NAME	**REFERENCE COMPOUND**	**CONVERSION** (%)
R 1	Sucrose	100
R 2	Glucose	14.38
R 3	Glucose	15.43

The following reactions take place in the fermentation stage:

$$\underset{glucose}{C_6H_{12}O_6} \rightarrow 2\underset{ethanol}{C_2H_5OH} + 2CO_2$$

$$\underset{sucrose}{C_{12}H_{22}O_{11}} + H_2O \rightarrow 2\underset{glucose}{C_6H_{12}O_6}$$

$$\underset{glucose}{C_6H_{12}O_6} \rightarrow 2\underset{acetaldehyde}{C_2H_4O} + 2CO_2 + 2H_2$$

$$\underset{ethanol}{C_2H_5OH} + \underset{acetic\ acid}{C_2H_4O_2} \rightarrow \underset{ethyl\ acetate}{C_4H_8O_2} + H_2O$$

$$\underset{glucose}{122C_6H_{12}O_6} + \underset{urea}{48CH_4N_2O} + \underset{ammonium\ phosphate}{12H_9N_2O_4P} \rightarrow \underset{yeast}{12C_{65}H_{92}O_{30}N_{10}P} + 330H_2O + 69O_2$$

The conversion values are reported in Table 7.58.

Table 7.58 Conversion data for ethanol production process from sugar cane molasses (R-2)

REACTION NAME	**REFERENCE COMPOUND**	**CONVERSION** (%)
R 1	Glucose	76.153
R 2	Sucrose	100
R 3	Glucose	0.11
R 4	Ethanol	1.84e-3
R5	Glucose	21.177

Yeast, produced in the fermentation stage, and the suspension solids are separated, using centrifugation, in the biomass separation phase.

In order to separate the ethanol and other volatile compounds from mash a distillation section is required. This represents the last step of the process. For distillation two sections are defined: striping section and rectification section. The ethanol is striped from the mash in the first section and is concentrated in the second section.

The simplified schema of the process is presented in Figure 7.36.

Simulation Goal

The goal of the present simulation is to analyze the process, to reduce the energy consumption and to identify the most environmentally friendly design from different process alternatives.

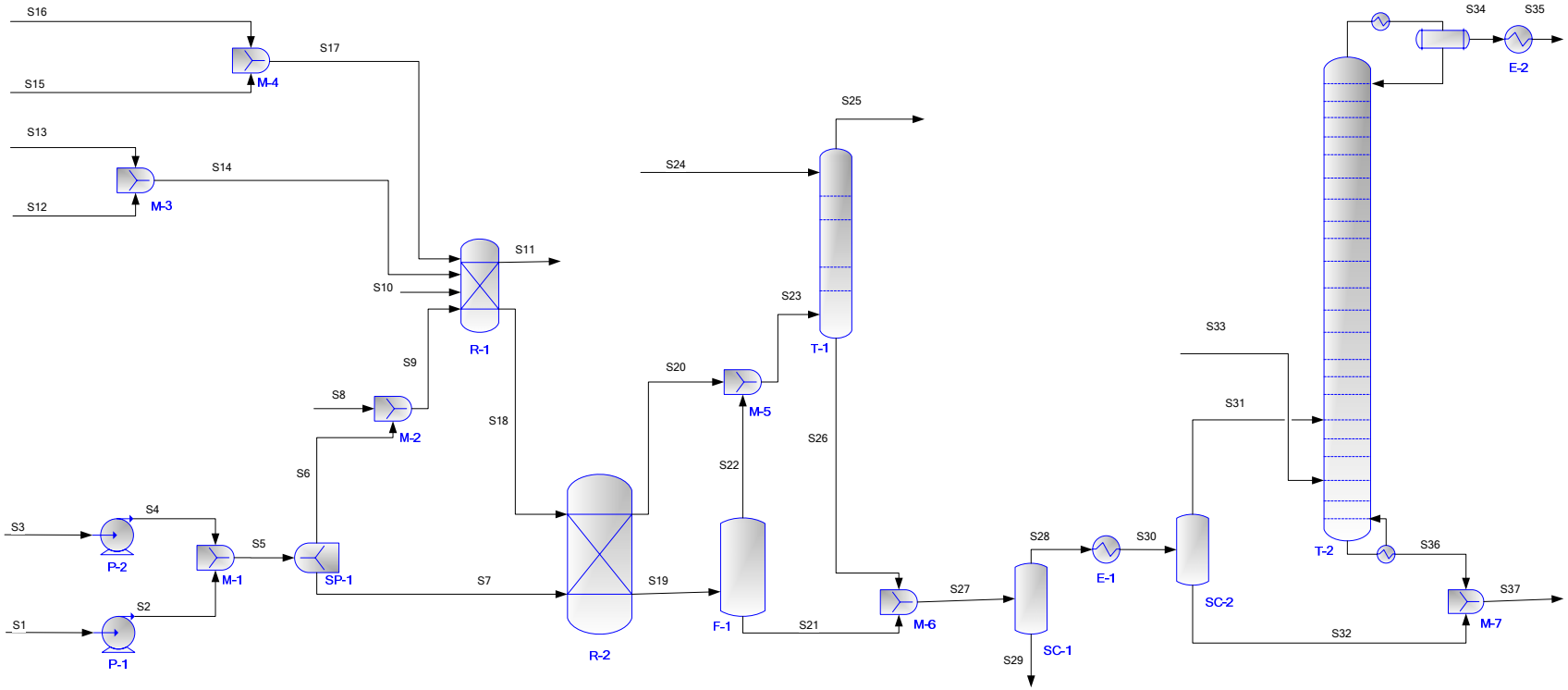


Figure 7.36 Ethanol production process from sugar cane molasses

Process Description

Molasses, S1, is mixed with water, S3. The resulting stream, S5, is split into two streams S6 and S7. Stream S7 is sent directly to the fermentator, R-2, while S6 is diluted once more with water, S8. The mixed stream S9 is sent to the propagator, R-1, where it meets other three streams, S10, S14 and S17. S14 is the diluted urea stream (formed by urea stream S12 and water stream S13). S17 is the diluted ammonium phosphate stream (formed by ammonium phosphate stream S15 and water stream S16). Urea and ammonium salts represent the nutrients for the fermentation process.

Yeast propagation represents the most important process stage. The final results of the fermentation depend on the yeast quality and on the contamination grade of inoculums. Yeast propagation takes place in the propagator, R-1. Stream S10, which is air, composed of oxygen 20.9% and nitrogen 79.1%, is fed in the propagator, R-1, as final acceptor of electrons in the aerobic yeast growth. The output R-1 streams, S18, containing yeast and water, is sent to the fermantator, R-2, while the other stream, S11, containing CO_2, nitrogen and unreacted oxygen is released into the atmosphere.

The next step is the fermentation process. This occurs in R-2. The product streams leaving the fermentator contain gasses products, S20, and liquid product, S19. Stream S19 is flashed in F-1 in order to separate the CO_2 dissolved in the mash. The gaseous streams, S22 and S20 are mixed and sent to the washing column, T-1. The goal of this column is to recover some ethanol. The absorption is made using water, S24. The T-1 output stream, S25, is released into the atmosphere while the bottom stream, S26, is mixed with the bottom flash stream, S21.

The next step is the biomass separation. The mash contained in S27 is separated by centrifugation in order to separate the yeast, S28, for other solid compounds, S29. Stream, S29, is heated up to 76° C in E-1 heat exchanger. The solid compounds, S32, are separated in SC-2. The liquid phase, S31, is sent to the separation system: T-2 distillation column. The top column stream, S34, contains ethanol which is cooled up to 76° C, S35.

The bottom stream, S36, is mixed with S32 in order to form S37 and it is sent to stillage.

Process Simulation

The process has been simulated using PROII process simulator.

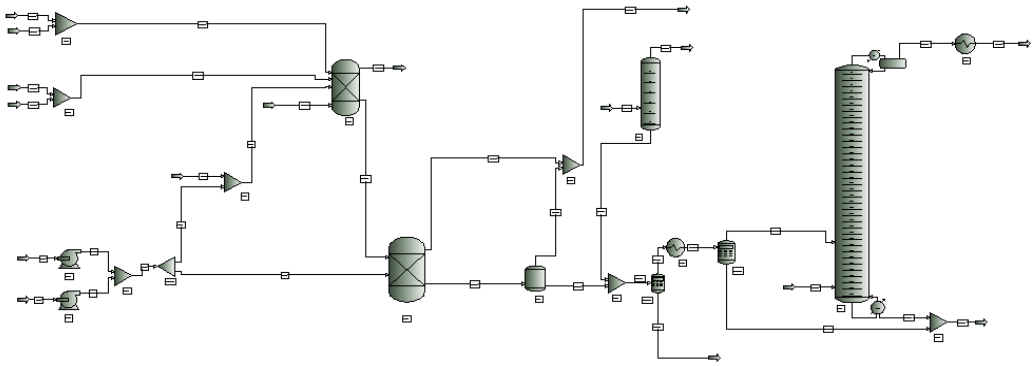


Figure 7.37 PROII schema of ethanol production process from sugar cane molasses

NRTL is the thermodynamic method used in the present simulation.

Table 7.59 Input streams specifications for ethanol production process from sugar cane molasses (base case)

STREAM NAME		**S1**	**S3**	**S8**	**S10**	**S12**	**S13**	**S15**	**S16**	**S33**
STREAM DESCRIPTION										
TEMPERATURE	C	28	28	28	30	28	28	30	28	124
PRESSURE	ATM	1	1	1	2	1	1	1	1	2.2
TOTAL MASS RATE	KG/HR	8391.439	38875.96	1691	598.54	100	62	50	79.50001	7950
TOTAL WIEGHT COMP.RATES	KG/HR									
H2O		2097.86	38875.96	1691	0	0	62	0	79.50001	7950
UREA		0	0	0	0	100	0	0	0	0
DAMPHOS		0	0	0	0	0	0	50	0	0
SUCROSE		2893.79	0	0	0	0	0	0	0	0
DEXTROSE		1644.72	0	0	0	0	0	0	0	0
GLUTAMIC		83.91	0	0	0	0	0	0	0	0
ACETACID		5.539999	0	0	0	0	0	0	0	0
PRPLALC		0.062	0	0	0	0	0	0	0	0
IBA		0.118	0	0	0	0	0	0	0	0
3M1BUALC		0.38	0	0	0	0	0	0	0	0
INERT1ASH		847.54	0	0	0	0	0	0	0	0
INERT2NOSUGAR		817.52	0	0	0	0	0	0	0	0
O2		0	0	0	94.26999	0	0	0	0	0
N2		0	0	0	504.27	0	0	0	0	0
ETHANOL		0	0	0	0	0	0	0	0	0
CO2		0	0	0	0	0	0	0	0	0
ACETALD		0	0	0	0	0	0	0	0	0
EOAC		0	0	0	0	0	0	0	0	0
HYDROGEN		0	0	0	0	0	0	0	0	0
YEAST		0	0	0	0	0	0	0	0	0

The output process streams are reported in Table 7.60.

Table 7.60 Output streams results ethanol production process from sugar cane molasses (base case)

STREAM NAME		**S11**	**S25**	**S29**	**S35**	**S37**
STREAM DESCRIPTION						
TEMPERATURE	C	36	36.00012	36	30	76
PRESSURE	ATM	1	1	1.338	1.12	1.338
TOTAL MASS RATE	KG/HR	629.1613	1318.516	2177.625	2008.794	51964.39
TOTAL WEIGHT COMP. RATES	KG/HR					
H2O		22.76774	32.52047	999.1815	245.4326	49704.57
UREA		0	0	1.25804	0	61.64402
DAMPHOS		0	0	0.592126	0	29.01422
SUCROSE		0	0	0	0	0
DEXTROSE		1.144967	1.28E-06	17.2883	0	847.1272
GLUTAMIC		0	0	1.678199	0	82.23181
ACETACID		0.003724	7.25E-07	0.109866	0.166447	5.216999
PRPLALC		0.00036	0.000567	0.001221	0.059851	7.58E-07
IBA		0.000661	0.000996	0.002327	0.114016	1.22E-06
3M1BUALC		0.003265	0.006019	0.007414	0.363301	3.02E-14
INERT1ASH		0	0	423.7701	0	423.77
INERT2NOSUGAR		0.004716	5.63E-19	16.35029	0	801.1651
O2		55.94178	23.90776	0.33416	0	0
N2		498.4622	5.762518	0.045257	0	0
ETHANOL		0	5.87219	17.85372	1762.574	4.945615
CO2		50.83187	1250.419	468.4321	0	0
ACETALD		0	0.007003	0.00079	0.038715	8.28E-16
EOAC		0	0.017236	0.000916	0.044881	8.04E-28
HYDROGEN		0	0.002008	0.00012	0	0
YEAST		0	0	230.7185	0	4.708537

Environmental Impact Results

Two design alternatives have been proposed and simulated for the process under study. The first case corresponds to the base case (Figure 7.36). In the second design the temperature of the flash and of the fermentator have been modified from 40 to 36°C.

Table 7.61 CO Modules specifications for 3D indicators for ethanol production process from sugar cane molasses

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	11	0	S1
CO2	2	0	11	0	S3
CO3	3	0	11	0	S8
CO4	4	0	0	11	S10
CO5	5	0	0	0	S12
CO6	6	0	11	0	S13
CO7	7	0	0	0	S15
CO8	8	0	11	0	S16
CO9	9	0	10	0	S33
CO10	10	1	10	10	S11
CO11	11	1	10	10	S25
CO12	12	1	10	10	S29
CO13	13	2	10	0	S35
CO14	14	1	10	0	S37
CO15	15	1	-	-	S19

The 3D indicators calculated using data from the process simulator and from the database are presented in Table 7.62.

Table 7.62 3D Indicators obtained in the ethanol production process from sugar cane molasses

CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	55215.98	3.355	355	8642.38
CASE 2	55223.08	3.387	355	8642.38

The case with the lowest MI and EI indicators is the first one, CASE 1. The reasons why PCR and PEI have equal values for both cases are explained below. All three processes are continuous processes, so the frequency class for the substances present in the process is the same (permanent use; > 6h/day- see Table 3.1) as well as the risk phrases. PEI has the same values for all three cases because the physical states of the substances involved in the process are the same and the receiving medium (air, water, soil) is also the same. In conclusion, CASE 1 represents the most environmentally friendly design, taking into account the 3D indicators. The same results are reported in Figures 7.38.

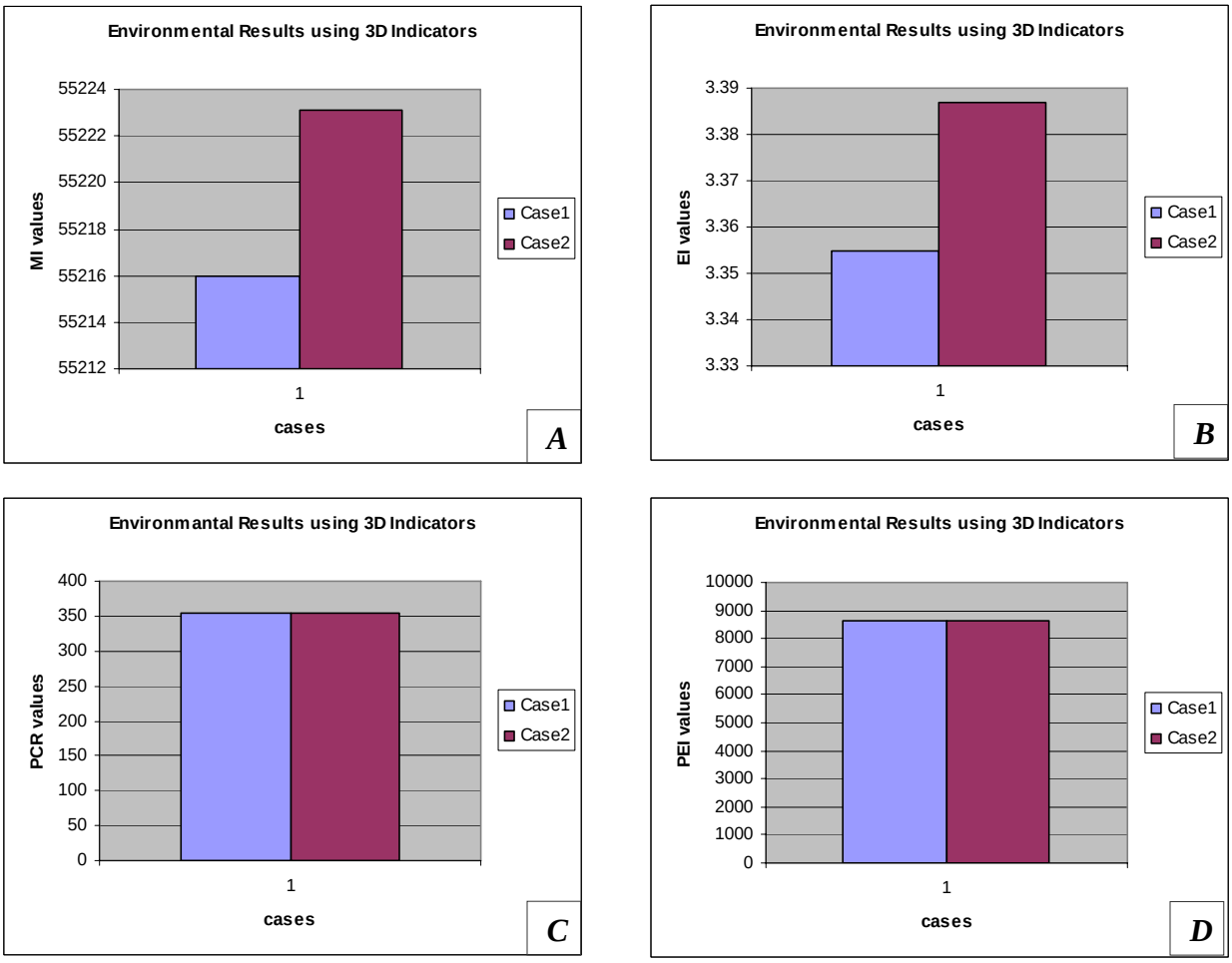


Figure 7.38 3D Indicators for ethanol production process from sugar cane molasses A) MI; B) EI C)PCR; D) PEI

For the same cases, WAR Algorithm has been applied. The CO Module for 1D indicator (Proall) has been inserted in the process flow-sheet. The CO Module parameters and the stream name linked to each module are presented in Table 7.63.

Table 7.63 CO Modules specifications for 1D indicator for ethanol production process from sugar cane molasses

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	0	2	S3
CO3	0	0	3	S8
CO4	0	0	4	S10
CO5	0	0	5	S12
CO6	0	0	6	S13
CO7	0	0	7	S15

CO8	0	0	8	S16
CO9	0	0	9	S33
CO10	0	1	10	S11
CO11	0	1	11	S25
CO12	0	1	12	S29
CO13	0	2	13	S35
CO14	0	1	14	S37
CO15	1	1	15	S40

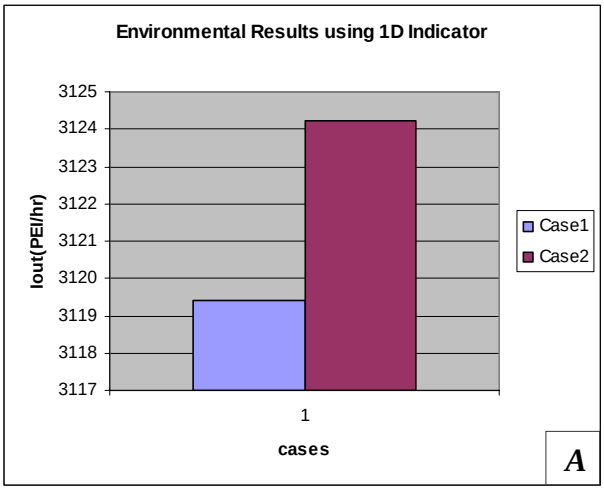
The results obtained using 1D indicator, are reported in Table 7.64.

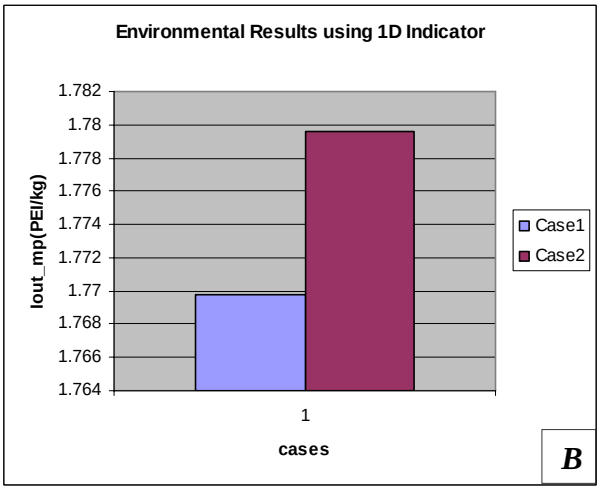
Table 7.64 Environmental Impact Indexes obtained in the ethanol production process from sugar cane molasses using WAR Algorithm

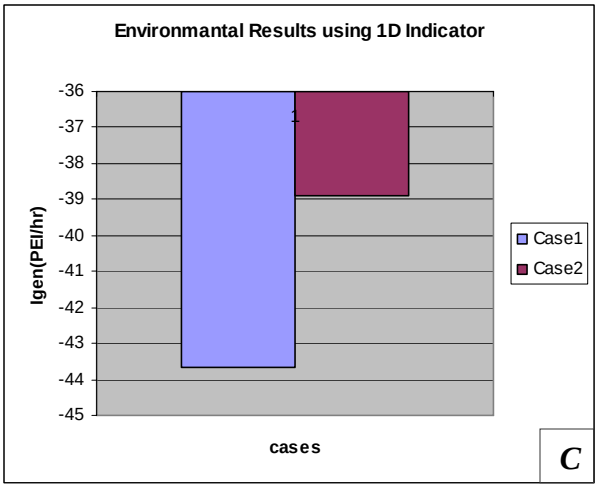
CASE STUDY	**ENIVORONMENTAL INDEXES NAME**			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	3119.42	1.77	-43.66	-2.47
CASE 2	3124.21	1.78	-38.88	-2.21

As it can be noticed, CASE 1 is the most favorable. In conclusion, CASE 1 is the most favorable design, taking into account 3D and 1D indicators. The results stress, once more, the necessity to use the complete PSP Framework.

The same results are presented in Figures 7.39.







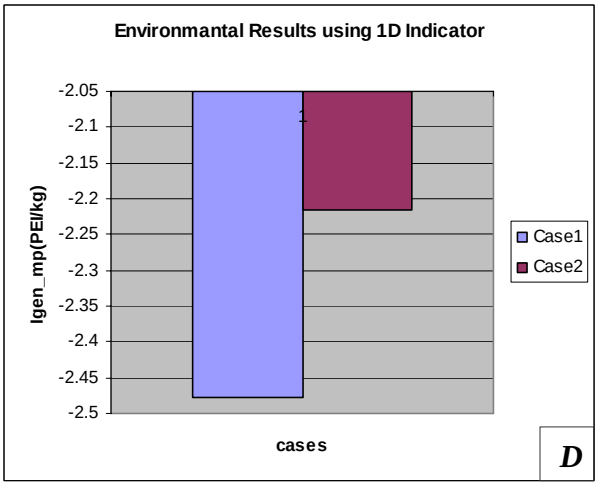


Figure 7.39 1D Indicators for ethanol production process from sugar cane molasses A)Iout; B) Iout_mp; C) Igen; D) Igen_mp

Conclusions

The ethanol production process from sugar cane molasses has been simulated using PROII process simulator. Two process alternatives are proposed and analyzed in order to choose the most environmentally friendly one. The most environmentally friendly design is the first one, as it can be noticed from the results obtained using the 3D and 1D indicators of the PSP Framework.

7.2.2 Multiple Effect of Sugar Cane Juice Process

Introduction

Sugar cane processing is focused on the production of cane sugar (sucrose) from sugar cane. Sugar cane is produced and harvested for two purposes: production of cane sugar and use as seed for subsequent plantings. Hand cutting is the most common harvesting method throughout the world, but some locations use mechanical harvesters for several years. After cutting, the cane is loaded by hand, mechanical grab loaders or by continuous loaders. Cane is transported to the mills using trailers, trucks, railcars, or a barge, depending upon the relative location of the cane fields and the processing plants. When the cane is cut, rapid deterioration of the cane begins. Therefore, sugar cane cannot be stored for later processing without excessive deterioration of the sucrose content. (U.S.EPA, 2007).

In the sugar cane industry, a substantial cost reduction can be achieved through efficient inventory management, reduction of the excess manufacturing capacity and rational use of resources. Heating processes are commonly employed in chemical plants in order to achieve product specific properties. In the specific case of sugar cane production, the juice is concentrated in evaporator units by heating until sucrose crystals are obtained. (Heluane *et al.,* 2007).

Norbert Rillieux has invented the multiple effect evaporators. Rillieux's invention allowed for the production of better quality sugar with less manpower and at reduced cost. Rillieux's great innovation was his understanding of how latent heat could be used repeatedly in processing sugar. The result was his Multiple Effect Evaporator under Vacuum, Rillieux utilized the latent heat produced from evaporating sugar cane juice by employing a series of three or four closed evaporating pans in which vapour was piped out of each pan to heat the juice in the next, with the vapours in the end going to a condenser. At the same time, pressure in the system was reduced by pumps, which created partial vacuums and lowered the boiling point of the liquid. A series of vacuum pans, or partial vacuum pans, have been combined together so as to make use of the vapour of the evaporation of the juice in the first pan to heat the juice in the second and the vapour from the second pan is used to heat the juice in the third one. The last pan is in connection with a condenser, the degree of pressure decreasing in the successive pans. The number of syrup-pans may be increased or decreased at pleasure so long as the last of the series is in conjunction with the condenser.

In the end, sugar manufacturers around the world in Cuba, Mexico, France, and Egypt, as well as the United States, adopted Rillieux's evaporator. Moreover, the device was not limited to sugar production but came to be recognized as the best method for lowering the temperature of all industrial evaporation and for saving large quantities of fuel. Multiple effect evaporation under vacuum is still used in sugar production as well as in the manufacture of condensed milk, soap, glue, and many other products (Sugar production and the multiple effect evaporator, 2007).

The multiple effect of sugar cane juice is described in the next pages. The process represents a real plant located in Mexico. It should be mentioned that the process simulation was realized by Ing. Cesar Romero Hernendez, from Regional Cleaner Production Center, Tabasco, Mexico during his fellowship training at ICS-UNIDO (20 February - 20 May 2007). After the simulation we have studied and analyzed the process applying the PSP methodology.

The simplified schema of the process is presented in Figure 7.40.

Simulation Goal

The goal of the present simulation is to analyze the process, to optimize the steam consumption and to identify the most environmentally friendly design from different process alternatives.

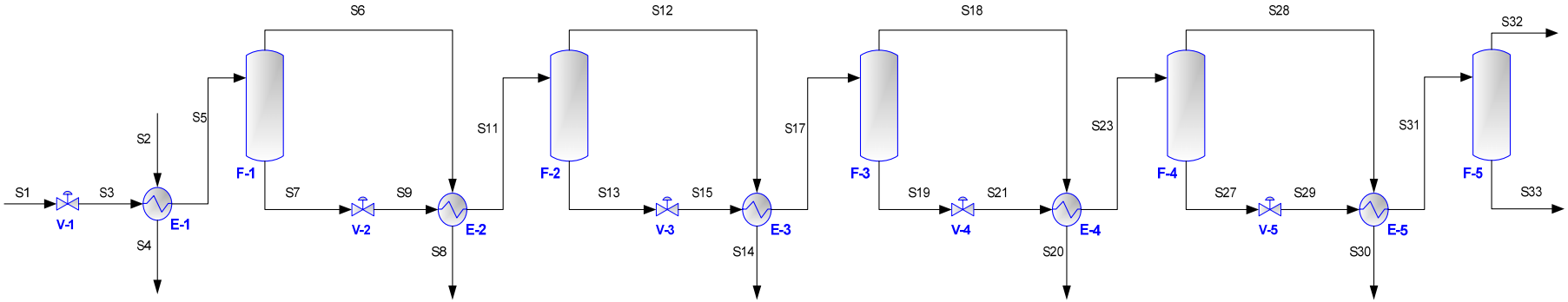


Figure 7.40 Multiple effect of sugar cane juice process

Process Description

The process consists of five flashes (F-1, F-2, F-3, F-4, and F-5), five heat exchangers (E-1, E-2, E-3, E-4, and E5) and five valves (V-1, V-2, V-3, V-4, and V-5). The juice is passed through heat exchangers to be preheated and then to evaporator stations. Evaporator station consists of a series of evaporators, termed multiple-effect evaporators: typically a series of five evaporators.

The input sugar cane juice stream, S1, contains water, sucrose and dextrose. Steam, S2, is used to heat the sugar cane juice stream. The hot process stream, S15, is sent to the first evaporator, F-1. This heat transfer process continues, in the same way, through the five evaporators. The temperature and the pressure decrease from one evaporator to another. This phenomenon allows the juice to boil at a lower temperature in the subsequent evaporator. The initial stream, S1, is evaporated till the final sucrose weight faction, coming out from F-5, reaches 47% in S33.

Process Simulation

The process has been simulated using PROII process simulator.

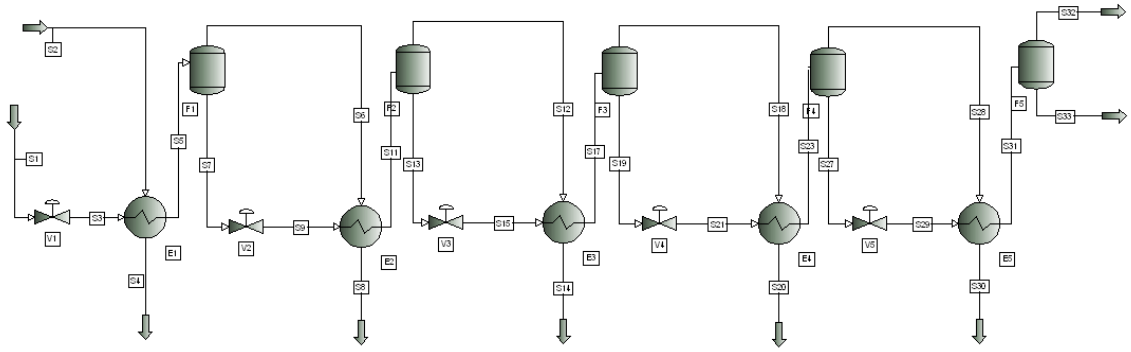


Figure 7.41 PROII schema of multiple effect of sugar cane juice process

NRTL is the thermodynamic method used in the present simulation.

Input data for juice - S1, and steam - S2, streams are presented in Table 7.65.

Table 7.65 Input streams specifications for multiple effect sugar cane juice process (base case)

STREAM NAME		**S1**	**S2**
STREAM DESCRIPTION			
TEMPERATURE	C	100.6	120
PRESSURE	KG/CM2	1.033	0.986
TOTAL MASS RATE	KG/HR	260000	37000
TOTAL WEIGHT COMP.RATES	KG/HR		
H2O		223600	37000
SUCROSE		33831.2	0
DEXTROSE		2568.8	0

Data reported in Table 7.66 represent the simulation results for waste streams: S4, S8, S14, S20, S30, and S32, and for the product process stream - S33.

Table 7.66 Output streams results for multiple effect of sugar cane juice process (base case)

STREAM NAME		**S4**	**S8**	**S14**	**S20**	**S30**	**S32**	**S33**
STREAM DESCRIPTION								
TEMPERATURE	C	68.6662	67.67557	67.00598	65.15778	61.12717	61.1307	61.13074
PRESSURE	KG/CM2	0.986	0.282	0.274	0.266	0.245	0.204	0.204
TOTAL MASS RATE	KG/HR	37000	186950.2	159.8217	62.93105	235.053	607.726	71984.23
TOTAL WEIGHT COMP. RATES	KG/HR							
H2O		37000	186950	159.8214	62.93097	235.0527	607.725	35584.5
SUCROSE		0	0.266897	0.000223	8.58E-05	0.0003	0.00067	33830.93
DEXTROSE		0	0	0	0	0	0	2568.8

Environmental Impact Results

Five design alternatives have been proposed and simulated for the process under study. The first case corresponds to the base case (Figure 7.40). The second case, CASE 2, is the base case with the pressure valves optimized. In the third case, CASE 3, the waste stream, S8, is sent to E-5 evaporator instead of sending it to E-3 like in the base case (see Figure 7.42). In the forth case, CASE 4, S8 and S14 waste streams have been used, together with the top flashes stream S12 and S18, to heat the flashes bottom streams S15 and S21(see Figure 7.43). The design of the fifth case, CASE 5, is similar to CASE 4, but, less amount of steam, 7400 kg/hr, instead of 370000 kg/hr utilized in CASE 1, has been used.

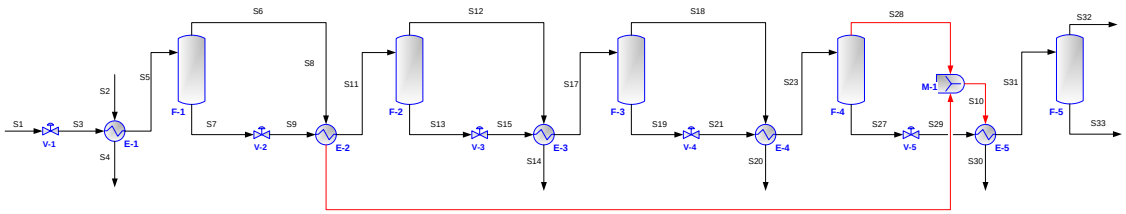


Figure 7.42 PROII schema of multiple effect of sugar cane juice process (CASE 3)

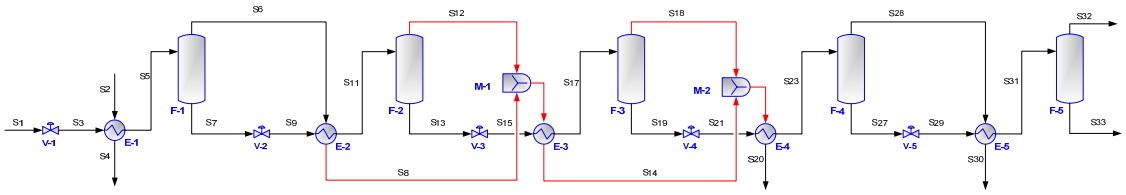


Figure 7.43 PROII schema of multiple effect of sugar cane juice process (CASE 4)

The CO Modules for 3D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.67.

Table 7.67 CO Modules specifications for 3D indicators for multiple effect of sugar cane juice process

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	10	0	S1
CO2	2	0	10	0	S2
CO3	3	1	10	0	S4
CO4	4	1	10	0	S8
CO5	5	1	10	0	S14
CO6	6	1	10	0	S20
CO7	7	1	10	0	S30
CO8	8	1	10	0	S32
CO9	9	2	10	0	S33
CO10	10	-	-	-	S31

The 3D indicators calculated using data from the process simulator and from the database are presented in Table 7.68.

Table 7.68 3D indicators obtained in the multiple effect of sugar cane juice process

CASE STUDY	3D INDICATORS			
	MI	EI	PCR	PEI
CASE 1	-518630.9281	15.42	0	0
CASE 2	-518630.8789	15.42	0	0
CASE 3	-518630.9245	15.42	0	0
CASE 4	-518630.9588	15.42	0	0
CASE 5	-518630.9590	3.084	0	0

The case with the lowest MI indicator is the fifth cases, CASE 5. EI indicator has also the lower value in CASE 5. PCR and PEI have zero values for all the cases because only natural compounds (water, sucrose, dextrose), which have no R-phrases are involved in the present process.

The same results are reported in Figures 7.44. It has to be specified that PCR and PEI being zero are not illustrated in the above mentioned figures.

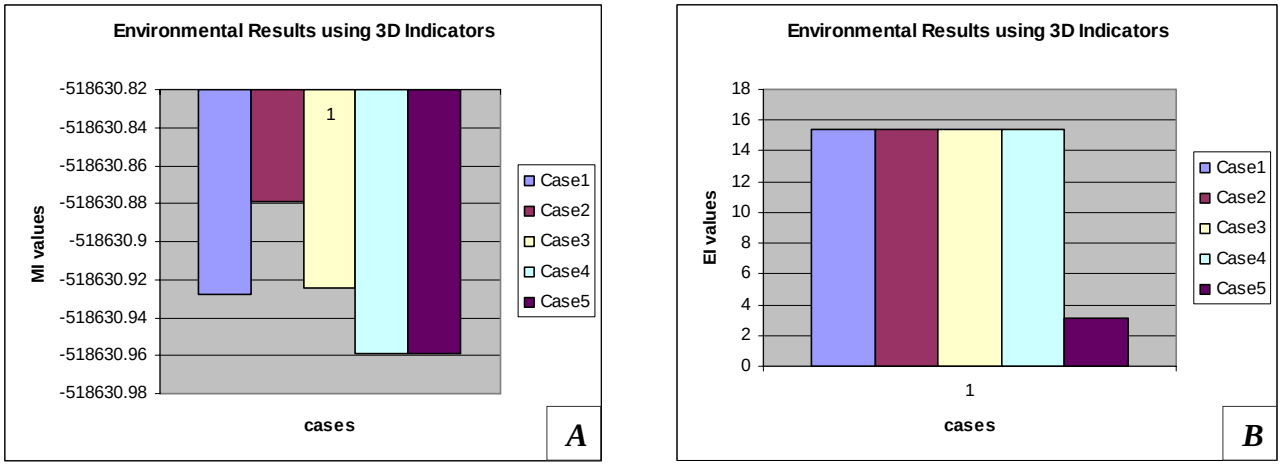


Figure 7.44 3D Indicators for multiple effect of sugar cane juice process A)MI; B) EI

For the same cases, WAR Algorithm has been applied. The CO Module for 1D indicator (Proall) has been inserted in the process flow-sheet. The CO Module parameters and the stream name linked to each module are presented in Table 7.69.

Table 7.69 CO Modules specifications for 1D indicator for multiple effect of sugar cane juice process

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	S1
CO2	0	0	2	S2
CO3	0	1	3	S4
CO4	0	1	4	S8
CO5	0	1	5	S14
CO6	0	1	6	S20
CO7	0	1	7	S30
CO8	0	1	8	S32
CO9	0	2	9	S33
CO10	1	1	10	S37

The results obtained using 1D indicator, are reported in Table 7.70.

Table 7.70 Environmental Impact Indexes obtained in the multiple effect of sugar cane juice process using WAR Algorithm

CASE STUDY	ENIVORONMENTAL INDEXES NAME			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	75.008	2.217e-3	-1461.88	-4.3211e-2
CASE 2	75.008	2.217e-3	-1461.88	-4.3211e-2
CASE 3	75.008	2.217e-3	-1461.88	-4.3211e-2
CASE 4	75.008	2.217e-3	-1461.88	-4.3211e-2
CASE 5	15.001	4.434e-4	-1521.84	-4.498e-2

The same results are presented in Figures 7.45.

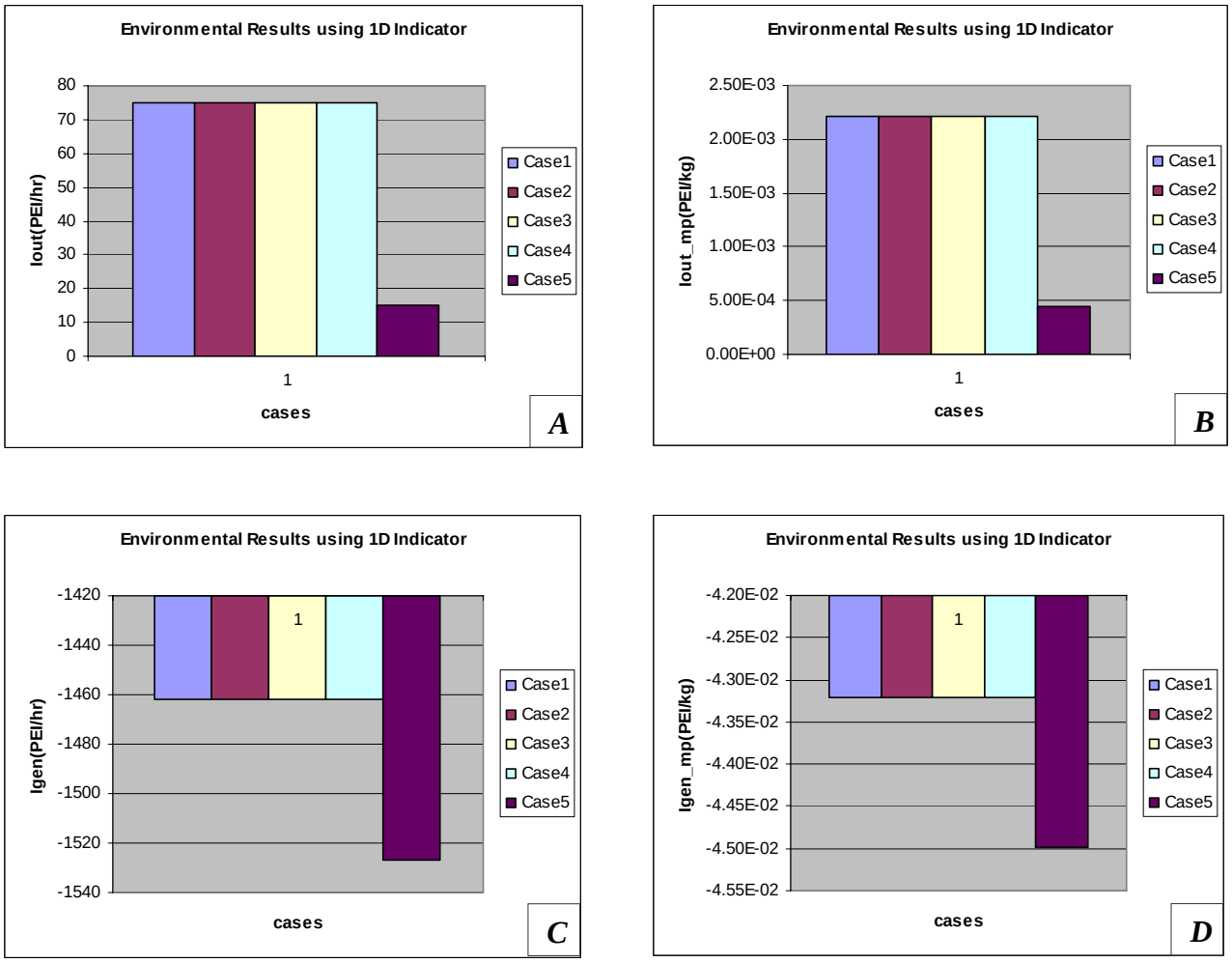


Figure 7.45 1D Indicators for multiple effect of sugar cane juice process A)Iout; B) Iout_mp; C) Igen; D) Igen_mp

As it can be noticed CASE 5 is the most favorable taking into account all 1D indicators (Iout, Iout_mp, Igen and Igen_mp).

Another factor that should be taken into account is the final product (sucrose) concentration. The sucrose concentration value for all five cases is presented in Table 7.71.

Table 7.71 Sucrose concentration in the output streams of multiple effect of sugar cane juice process

CASES	SUCROSE CONCENTRATION (weight %)
CASE 1	0.4700
CASE 2	0.5644
CASE 3	0.7662
CASE 4	0.8571
CASE 5	0.6505

The most favorable cases from productivity point of view, sucrose final concentration, is CASE 4, CASE 3, CASE 5. Another factor, which should be also considered, is the steam consumption. The steam quantities, S2, for all five cases are presented in Table 7.72.

Table 7.72 Steam consumption in the output streams of multiple effect of sugar cane juice

CASES	STEAM CONSUMPTION (kg/hr)
CASE 1	37000
CASE 2	37000
CASE 3	37000
CASE 4	37000
CASE 5	7400

The most favorable case, from steam consumption point of view, is CASE 5.

The final decision should be taken considering all the above presented factors (see Table 7.73).

Table 7.73 Most favorable cases and factors considered in the multiple effect of sugar cane juice process

FACTORS CONSIDERED		MOST FAVORABLE CASES
3D indicators	MI	CASE 5
	EI	CASE 5
1D indicator	Iout	CASE 5
	Iout_mp	CASE 5
	Igen	CASE 5
	Igen_mp	CASE 5
Sucrose final concentration		CASE 4; CASE 3; CASE 5
Steam consumption		CASE 5

A compromise should be made in this case. The case study with low environmental impact, using 3D and 1D indicators, and good technological performances (sucrose concentration and steam consumption) is CASE 5.

Conclusions

The multiple effect of sugar cane juice has been simulated using PROII process simulator. Five process alternatives are proposed and analyzed in order to choose the most environmentally friendly one. The example of the present process is very relevant because it takes into account technological (sucrose final concentration), economical

(steam consumption) and environmental impact (3D and 1D indicators) factors. The most environmentally friendly design and, at the same time, the technological and economical efficient one, is the fifth case, as it can be noticed from the results. This example can stress, once more, the necessity of having a complete view of the process and to consider all the elements of sustainability in order to make a high-quality engineering decision.

7.2.3 Electroplating Wastewater Discharge Process

Introduction

Electroplating is an electrochemical process in which a metal is deposited on a substrate using electrical current.

Usually there is an anode (positively charged electrode), which is the source of the material to be deposited; the electrochemistry which is the medium through which metal ions are exchanged and transferred to the substrate to be coated; and a cathode which is the substrate (the negatively charged electrode) to be coated.

Electroplating production is a widely used and most environmentally harmful industrial process, during which a large volume of wastewater containing heavy metal ions such as copper, zinc, nickel, cadmium, lead and chromium is generated. All these metals are very toxic and cause great environmental damage (Jansen *et al.*, 2002; Jütner *et al.*, 2000). In order to recover heavy metal and purify wastewater, closed-recycle system for water reuse, or so-called effluent-free technology, should be developed (Feng *et al.*, 2007).

The electroplating wastewater discharge process presented in the next section corresponds to real plant located in Russia. It should be mentioned that the simulation of this process was realized by Ing. Alena Chistikova, from North-Western International Cleaner Production and Environmental Management Centre UNIDO Saint-Petersburg, Russia, during her fellowship training at ICS-UNIDO (21 June – 15 October 2006). After the simulation we have studied and analyzed the process applying the PSP methodology.

There are two basic electroplating lines for the process under study: Nickel-plating line and Chromium-plating line.

The reactions that occur in this process are divided in two groups:

1. neutralization of chromium (VI) or polychromic acids to chromium (III) sulfate:

$$3H_2SO_4 + 6NaHSO_3 + 4CrO_3 \rightarrow 6H_2O + 3Na_2SO_4 + 2Cr_2(SO_4)_3$$

2. common reactions:

$$NiSO_4 + 2NaOH \rightarrow Ni(OH)_2 + Na_2SO_4$$
$$HCl + NaOH \rightarrow NaCl + H_2O$$
$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$$
$$6NaOH + Cr_2(SO_4)_3 \rightarrow 3Na_2SO_4 + 2Cr(OH)_3$$
$$H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$$

The simplified schema of the process is presented in Figure 7.46.

Simulation Goal

The goal of the present simulation is to analyze the process, to reduce the wastewater generation associated with rinsing operation involved in the plating process and to identify the most environmentally friendly design from different process alternatives.

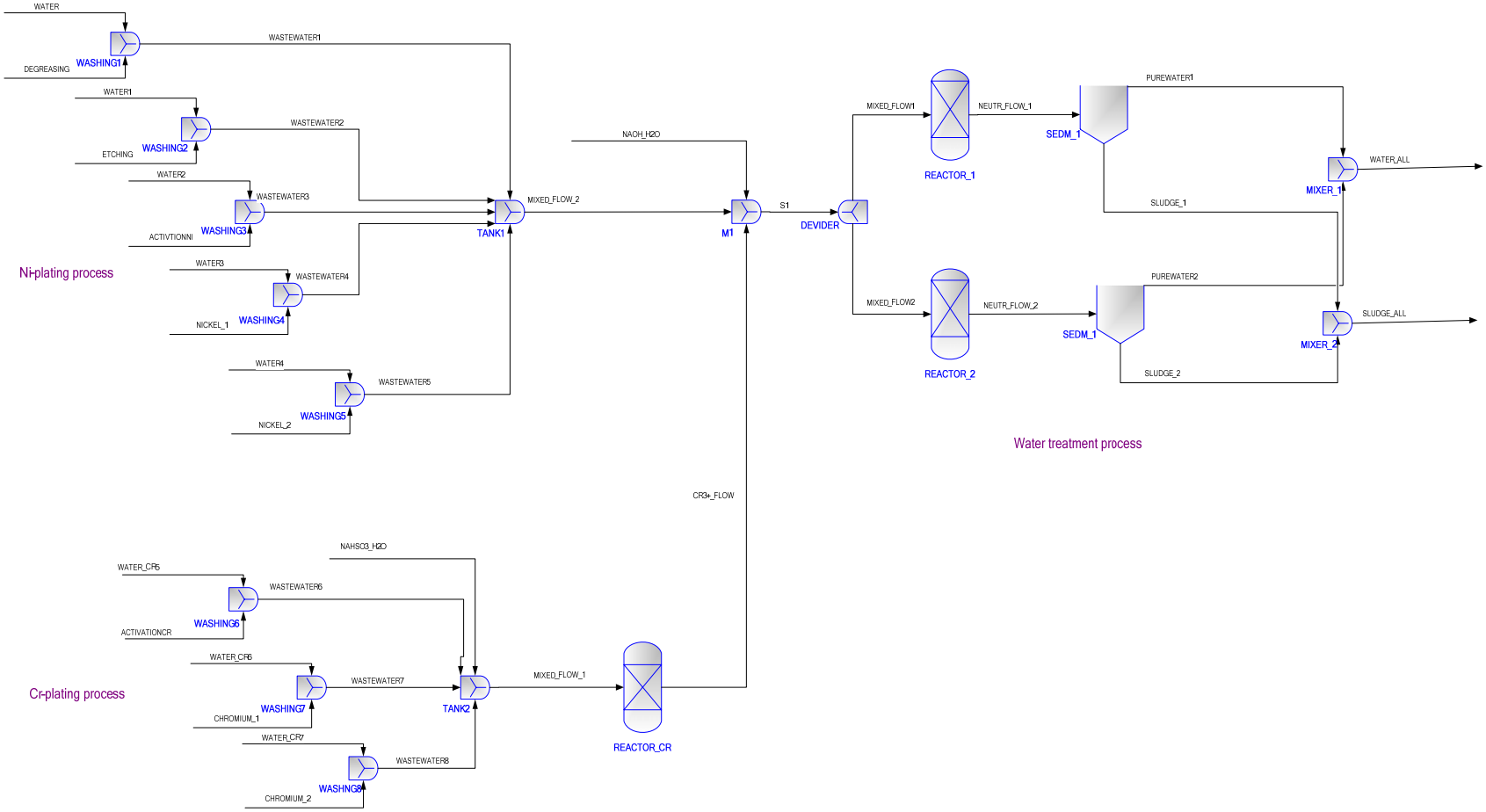


Figure 7.46 Electroplating wastewater discharge process

Process Description

The waste water discharge process can be separated in two parts:

1) Pre-plating operations, formed by:
   - Ni-plating process
   - Cr-plating process
2) Water treatment process

The Ni-plating process contains different waste streams: NICKEL_1, NICKEL_2. These are washed with WATER 3 and WATER 4 streams. The result streams are sent to THANK1. Here, other mixed streams come; they are formed of the DEGREASING (Na_3PO_4 solution), ETCHING (HCl, NaCl and H_2SO_4 solution), ACTIVATIONNI (HCl solution) streams, diluted with different water streams: WATER, WATER1, WATER2 come.

The Cr-plating process contains other waste streams: CHROMIUM_1, CHROMIUM_2. These are washed with WATER_CR6 and WATER_CR7 streams . The result streams are sent to TANK2. These are mixed with ACTIVATIONCR (HCl solution) diluted with WATER_CR5 water streams.

NaOH solution is feed to TANK 2 and $NaHSO_3$ solution to TANK 1.

The stream MIXED_FLOW_1, coming out from TANK2, is sent to the first reactor, REACTOR_CR, where the neutralization of chromium (VI) or polychromic acids to chromium (III) sulfate is done using $NAHSO_3$ solution. The output stream is mixed with MIXED_FLOW_2 coming from TANK1 and with the NaOH stream.

The next step is the water treatment process. This occurs in REACTOR_1 and REACTOR_2. The common reactions described in the previous part take place here. After neutralization, the output streams, NEUTR_FLOW_1 and NEUTR_FLOW_2 are sent to the sedimentation tanks, SEDM_1 and SEDM_2, to precipitate the solids. The streams coming out from the sedimentators are water in the top and sludge in the bottom.

Process Simulation

The process has been simulated using PROII process simulator.

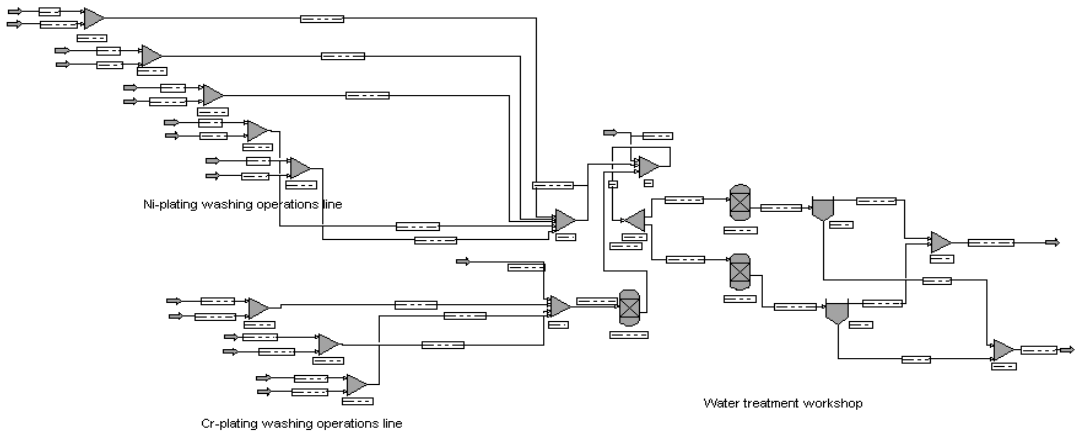


Figure 7.47 PROII schema of electroplating wastewater discharge process

NRTL is the thermodynamic method used in the present simulation.

Input data streams are presented in Table 7.74.

Table 7.74 Input streams specifications for electroplating wastewater discharge process (base case)

STREAM NAME		**WATER**	**DEGREASING**	**WATER1**	**ETHCHING**	**WATER2**	**ACTIVATIONNI**
STREAM DESCRIPTION							
TEMPERATURE	C	20	25	20	25	20	25
PRESSURE	ATM	1	1	1	1	1	1
TOTAL MASS RATE	KG/HR	62.41	0.125	62.41	0.125	62.41	0.125
TOTAL WEIGHT COMP. RATES	KG/HR						
HYCHLORD		0	0	0	0.0125	0	0.025
SULFURIC		0	0	0	0.0125	0	0
H20		62.4101	0.1188	62.4104	0.0989	62.4104	0.1
NAHSO3		0	0	0	0	0	0
NIOH2		0	0	0	0	0	0
NISO4		0	0	0	0	0	0
NACL		0	0	0	0.0011	0	0
NA2SO4		0	0	0	0	0	0
BORIC		0	0	0	0	0	0
NAOH		0	0	0	0	0	0
NITRIC		0	0	0	0	0	0
NANO3		0	0	0	0	0	0
TNAPHOS		0	0.0063	0	0	0	0
CROH3		0	0	0	0	0	0
CR2SO43		0	0	0	0	0	0
CRO3		0	0	0	0	0	0

(CONTINUED)

STREAM NAME		**WATER3**	**NICKEL_1**	**WATER4**	**NICKEL_2**	**NAOH_H2O**	**WATER_CR5**
STREAM DESCRIPTION							
TEMPERATURE	C	20	25	85	20	25	20
PRESSURE	ATM	1	1	1	1	1	1
TOTAL MASS RATE	KG/HR	62.41	0.125	62.41	0.125	30.144	62.41
TOTAL WEIGHT COMP. RATES	KG/HR						
HYCHLORD		0	0	0	0	0	0
SULFURIC		0	0	0	0	0	0
H20		62.4101	0.0786	62.4104	0.1137	24.1791	62.4104
NAHSO3		0	0	0	0	0	0
NIOH2		0	0	0	0	0	0
NISO4		0	0.0375	0	0.0075	0	0
NACL		0	0.0001	0	0	0	0
NA2SO4		0	0.0087	0	0.0037	0	0
BORIC		0	0	0	0	0	0
NAOH		0	0	0	0	5.9647	0
NITRIC		0	0	0	0	0	0
NANO3		0	0	0	0	0	0
TNAPHOS		0	0	0	0	0	0
CROH3		0	0	0	0	0	0
CR2SO43		0	0	0	0	0	0
CRO3		0	0	0	0	0	0

(CONTINUED)

STREAM NAME		**ACTIVATIONCR**	**WATER_CR6**	**CHROMIUM_1**	**WATER_CR7**	**CHROMIUM_2**	**NAHSO3_H20**
STREAM DESCRIPTION							
TEMPERATURE	C	25	20	50	85	25	25
PRESSURE	ATM	1	1	1	1	1	1
TOTAL MASS RATE	KG/HR	0.125	62.41	0.125	62.41	0.125	7.972
TOTAL WEIGHT COMP. RATES	KG/HR						
HYCHLORD		0.0164	0	0	0	0	0
SULFURIC		0	0	0.0037	0	0	1.8798
H20		0.1086	62.4104	0.0837	62.4104	0.1125	2.1032
NAHSO3		0	0	0	0	0	3.9892
NIOH2		0	0	0	0	0	0
NISO4		0	0	0	0	0	0
NACL		0	0	0	0	0	0
NA2SO4		0	0	0	0	0	0
BORIC		0	0	0	0	0	0
NAOH		0	0	0	0	0	0
NITRIC		0	0	0	0	0	0
NANO3		0	0	0	0	0	0
TNAPHOS		0	0	0	0	0	0
CROH3		0	0	0	0	0	0
CR2SO43		0	0	0	0	0	0
CRO3		0	0	0.0375	0	0.0125	0

Data reported in Table 7.75 represent the simulation results for water, PUREWATERALL, and waste stream, SLUDGE_ALL.

Table 7.75 Output streams results for electroplating wastewater discharge process (base case)

STREAM NAME		**PUREWATERALL**	**SLUDGE_ALL**
STREAM DESCRIPTION			
TEMPERATURE	C	25	25
PRESSURE	ATM	1	1
TOTAL MASS RATE	KG/HR	538.321	0.078
TOTAL WEIGHT COMP. RATES	KG/HR		
HYCHLORD		0	0
SULFURIC		0	0
H20		527.1034	0
NAHSO3		3.9112	0
NIOH2		0	0.0269
NISO4		0	0
NACL		0.0877	0
NA2SO4		2.9062	0
BORIC		0	0
NAOH		4.3059	0
NITRIC		0	0
NANO3		0	0
TNAPHOS		0.0063	0
CROH3		0	0.0514
CR2SO43		0.0001	0
CRO3		0	0

Environmental Impact Results

Four design alternatives have been proposed and simulated for the process under study. The first case corresponds to the base case (Figure 7.46). The second case, CASE 2, is the base case with controllers applied to the NaOH and $NaHSO_3$ streams. These streams should be controlled in order to neutralize the chromium stream and to avoid the secondary reaction:

$$Cr(OH)_3 + 3NaOH \rightarrow Na_3[Cr(OH)_6]$$

In the third case, CASE 3, the countercurrent and reuse of spent water methods have been utilized. These represent two advanced washing methods. This case is illustrated in Figure 7.48. In the forth case, CASE 4, membrane separation method has been simulated (see Figure 7.49).

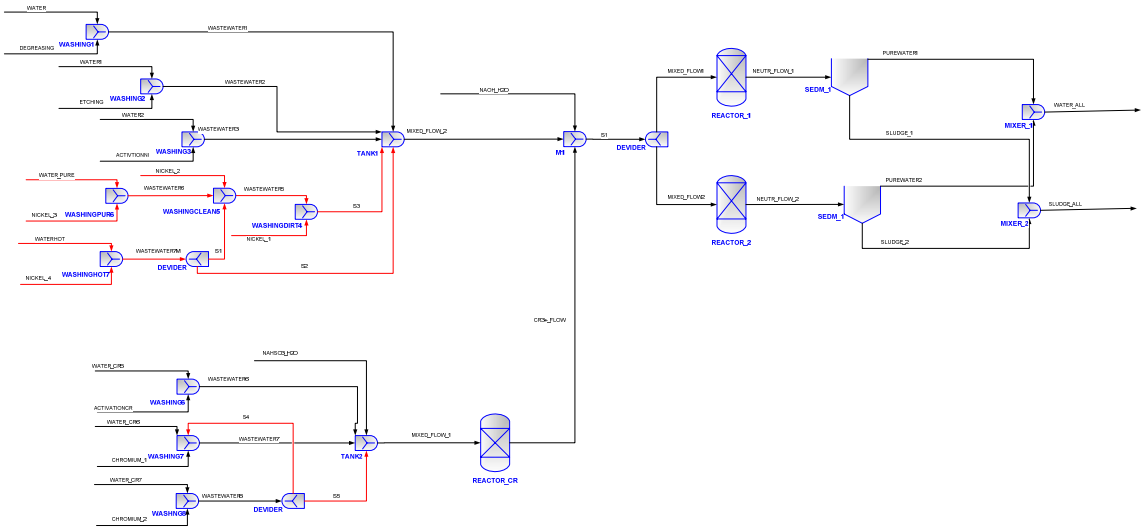


Figure 7.48 PROII schema of electroplating wastewater discharge process (CASE 3)

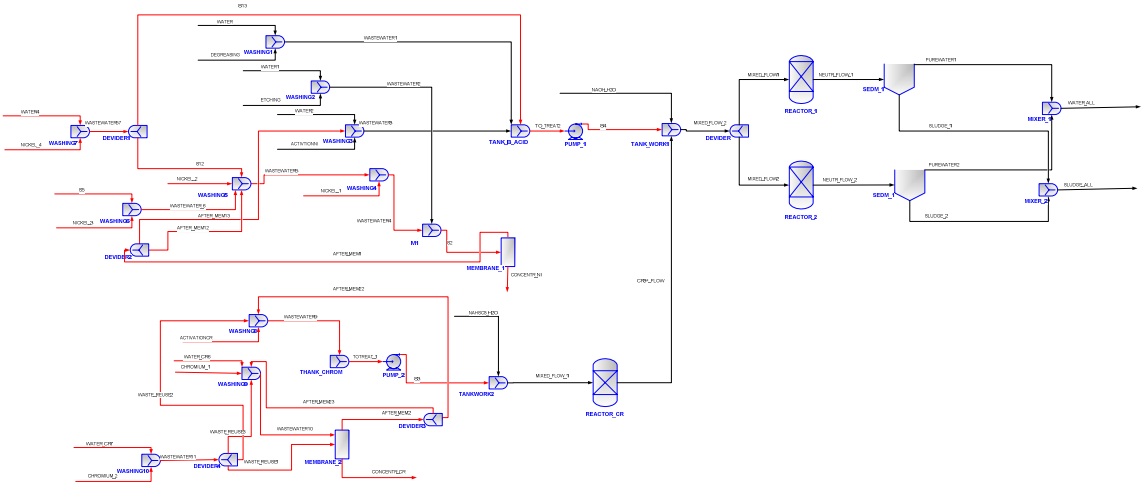


Figure 7.49 PROII schema of electroplating wastewater discharge process (CASE 4)

The CO Modules for 3D indicators (Promatrics and Pro_Point_Risk) have been inserted in the process flow-sheet. The CO Modules parameters and the stream name linked to each module are presented in Table 7.76.

Table 7.76 CO Modules specifications for 3D indicators for electroplating wastewater discharge process

CO MODULE NAME	CO MODULES PARAMETERS				CONNECTED STREAM
	NAME	CONNECTION	WATER_USAGE	AIR_USAGE	
CO1	1	0	10	0	WATER
CO2	2	0	10	0	DEGREASING
CO3	3	0	10	0	WATER1

CO4	4	0	10	0	ETCHING
CO5	5	0	10	0	WATER2
CO6	6	0	10	0	ACTIVATIONNI
CO7	7	0	10	0	WATER3
CO8	8	0	10	0	NICKEL_1
CO9	9	0	10	0	WATER4
CO10	10	0	10	0	NICKEL_2
CO11	11	0	10	0	NAOH_H2O
CO12	12	0	10	0	WATER_CR5
CO13	13	0	10	0	ACTIVATIONCR
CO14	14	0	10	0	WATER_CR6
CO15	15	0	10	0	CHROMIUM_1
CO16	16	0	10	0	WATER_CR7
CO17	17	0	10	0	CHEROMIUM_2
CO18	18	0	10	0	NAHASO3_H20
CO19	19	2	10	0	PUREWATERAL
CO20	20	1	0	0	SLUDGE_ALL
CO21	21	-	-	-	

The 3D indicators calculated using data from the process simulator and from the database are presented in Table 7.77.

Table 7.77 3D Indicators obtained in the electroplating wastewater discharge process

CASE STUDY	**3D INDICATORS**			
	MI	**EI**	**PCR**	**PEI**
CASE 1	-515.9778	0	616	5657.28
CASE 2	-503.5864	0	346	5657.28
CASE 3	-430.7012	0	346	5657.28
CASE 4	-254.2577	0	1516	7207.92

The case with the lowest MI indicator is the first one, CASE 1. EI indicator is zero because the processes do not need heat from external sources. PCR indicator has the lowest value in the second and the third case, CASE 2 and CASE 3. PEI has the lowest value for the first three cases, CASE 1, CASE 2 and CASE 3.

The same results are reported in Figures 7.50. It should be specified that EI values being zero are not represented in the above mentioned figures.

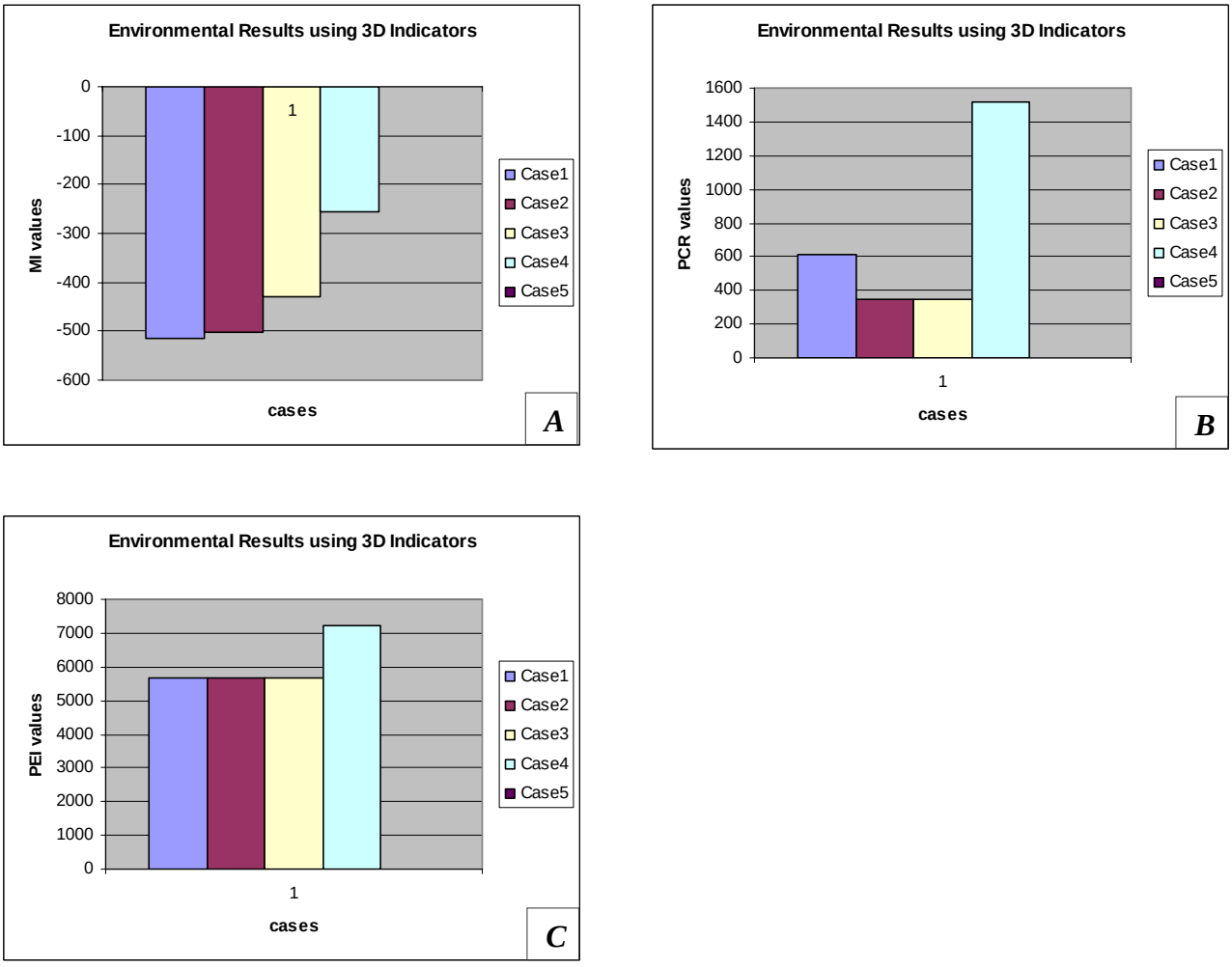


Figure 7.50 3D Indicators for electroplating wastewater discharge process A)MI; B) PCR; C)PEI

For the same cases, WAR Algorithm has been applied. The CO Module for 1D indicator (Proall) has been inserted in the process flow-sheet. The CO Module parameters and the stream name linked to each module are presented in Table 7.78.

Table 7.78 CO Modules specifications for 1D indicator for electroplating wastewater discharge process

CO MODULE NAME	CO MODULES PARAMETERS			CONNECTED STREAM
	PROCESS_TYPE	CAPE_POSITION	CAPE_ID	
CO1	0	0	1	WATER
CO2	0	0	2	DEGREASING
CO3	0	0	3	WATER1
CO4	0	0	4	ETCHING
CO5	0	0	5	WATER2
CO6	0	0	6	ACTIVATIONNI

CO7	0	0	7	WATER3
CO8	0	0	8	NICKEL_1
CO9	0	0	9	WATER4
CO10	0	0	10	NICKEL_2
CO11	0	0	11	NAOH_H2O
CO12	0	0	12	WATER_CR5
CO13	0	0	13	ACTIVATIONCR
CO14	0	0	14	WATER_CR6
CO15	0	0	15	CHROMIUM_1
CO16	0	0	16	WATER_CR7
CO17	0	0	17	CHEROMIUM_2
CO18	0	0	18	NAHASO3_H20
CO19	0	2	19	PUREWATERAL
CO20	0	1	20	SLUDGE_ALL

The results obtained using 1D indicator, are reported in Table 7.79.

Table 7.79 Environmental Impact Indexes obtained in the electroplating wastewater discharge process using WAR Algorithm

CASE STUDY	**ENIVORONMENTAL INDEXES NAME**			
	Iout (PEI/hr)	**Iout_mp** (PEI/kg)	**Igen** (PEI/hr)	**Igen_mp** (PEI/kg)
CASE 1	0.5691	1.0797e-3	-10.632	-2.0171e-2
CASE 2	0.5691	1.1220e-3	-3.3832	-6.6702e-3
CASE 3	0.6889	1.5878e-3	-3.0017	-6.9183e-3
CASE 4	0.7859	2.9200e-3	-13.5807	-5.0569e-2

The same results are presented in Figures 7.51.

The cases with the lowest Iout are the first and the second one, CASE 1 and CASE 2. The cases with lower Iout_mp values are also the first and the second one, CASE 1 followed by CASE 2. Igen and Igen_mp have the lowest value in the forth case, CASE 4.

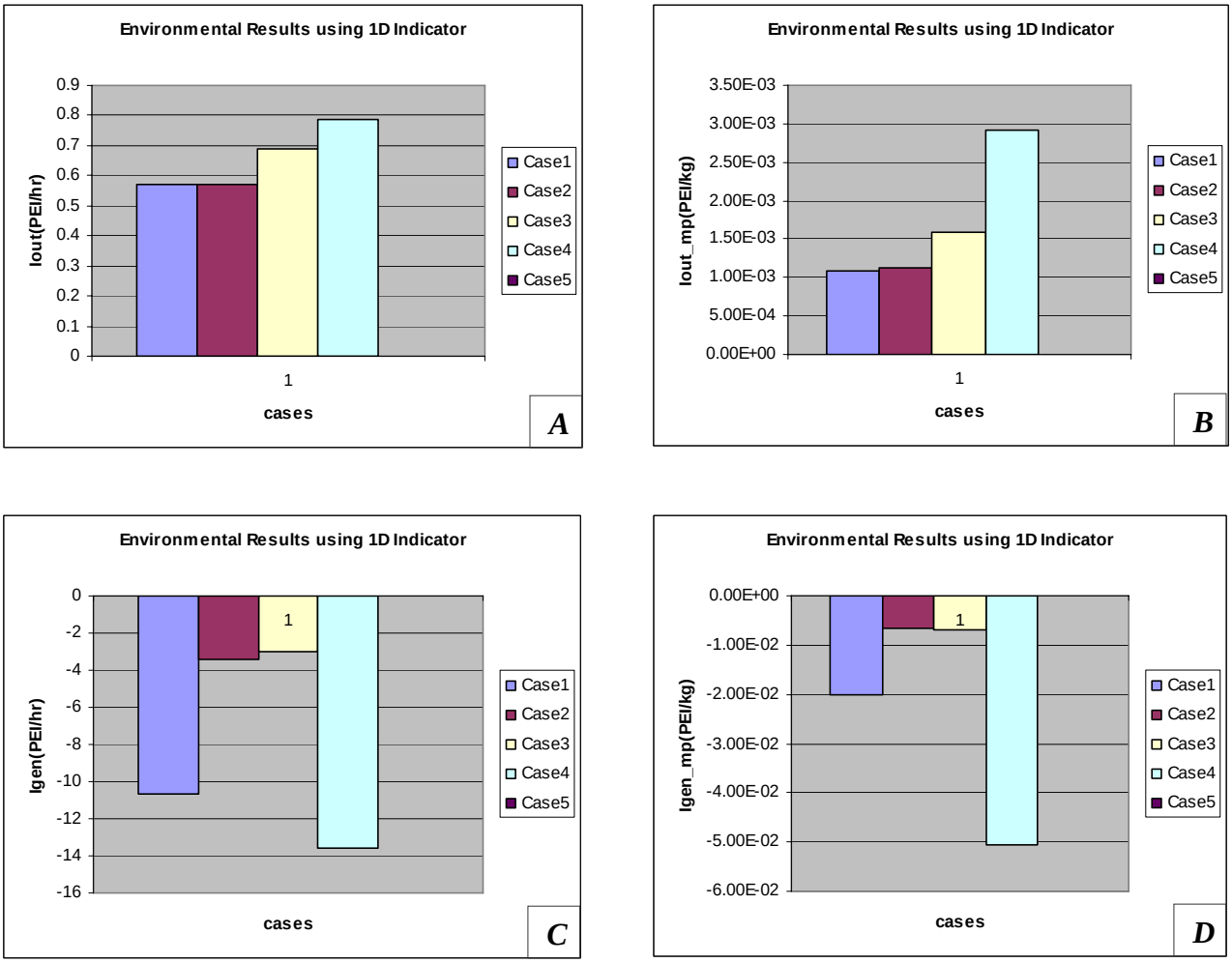


Figure 7.51 1D Indicators for electroplating wastewater discharge process A)Iout; B) Iout_mp; C) Igen; D) Igen_mp

An important factor, which should be also taken into account when deciding the most environmentally friendly solution, is the final purity of the water stream. The final purity results for the four cases under study are presented in Table 7.80.

Table 7.80 Final water purity in the electroplating wastewater discharge process

CASES	**WATER PURITY** (%)
CASE 1	97.92
CASE 2	99.20
CASE 3	99.17
CASE 4	94.97

The most favorable cases, from the purity point of view, are CASE 2 followed by CASE 3.

The quantity of water used for washing operations is also reported (see Table 7.81).

Table 7.81 Water used for washing operations in the electroplating wastewater discharge process

CASES	**WATER QUANTITY for NI-plating process** (kg/hr)	**WATER QUANTITY for Cr-plating process** (kg/hr)
CASE 1	312.5619	189.6392
CASE 2	312.5619	187.5360
CASE 3	260.7898	166.7325
CASE 4	267.7	55.1837

The most favourable cases, with low water consumption, are CASE 4 and CASE 3.

The final decision should be taken considering all the above presented factors (see Table 7.82).

Table 7.82 Most favorable cases and factors considered in the electroplating wastewater discharge process

FACTORS CONSIDERED		**MOST FAVORABLE CASES**
3D indicators	MI	CASE 1; CASE 2; CASE 3
	EI	-
	PCR	CASE 3; CASE 2
	PEI	CASE 3; CASE 2; CASE 1
1D indicator	Iout	CASE 1; CASE 2; CASE 3
	Iout_mp	CASE 1; CASE 2; CASE 3
	Igen	CASE 4; CASE 3
	Igen_mp	CASE 4; CASE 3
Final water purity		CASE 2; CASE 3
Water used for washing operations		CASE 4; CASE 3

A compromise should be made in this case. The case study with medium environmental impact, using 3D and 1D indicators, and high technological performances (water purity) is CASE 3.

Conclusions

The Electroplating wastewater discharge process has been simulated using PROII process simulator. Four process alternatives are proposed and analyzed in order to choose the most environmentally friendly. The example of the present process takes into account technological (final water purity), economical (water used for washing operations) and environmental impact (3D and 1D indicators) factors. The most environmentally friendly design and, at the same time, the technological efficient one is the third case, as it can be noticed from the results. This example can stress, once more, the necessity of having a complete view of the process and of considering all the elements of sustainability in order to make a high-quality engineering decision.

Chapter 8

PSP Framework Strategy Distribution

Summary

This chapter contains details regarding the PSP Framework strategy distribution and the main organizations involved in the distribution process.

"*Knowledge grows when shared.*"
Bhartrihari

Details regarding the distribution strategy of the developed tools toward small and medium enterprises in the developing countries are presented in Figure 8.1.

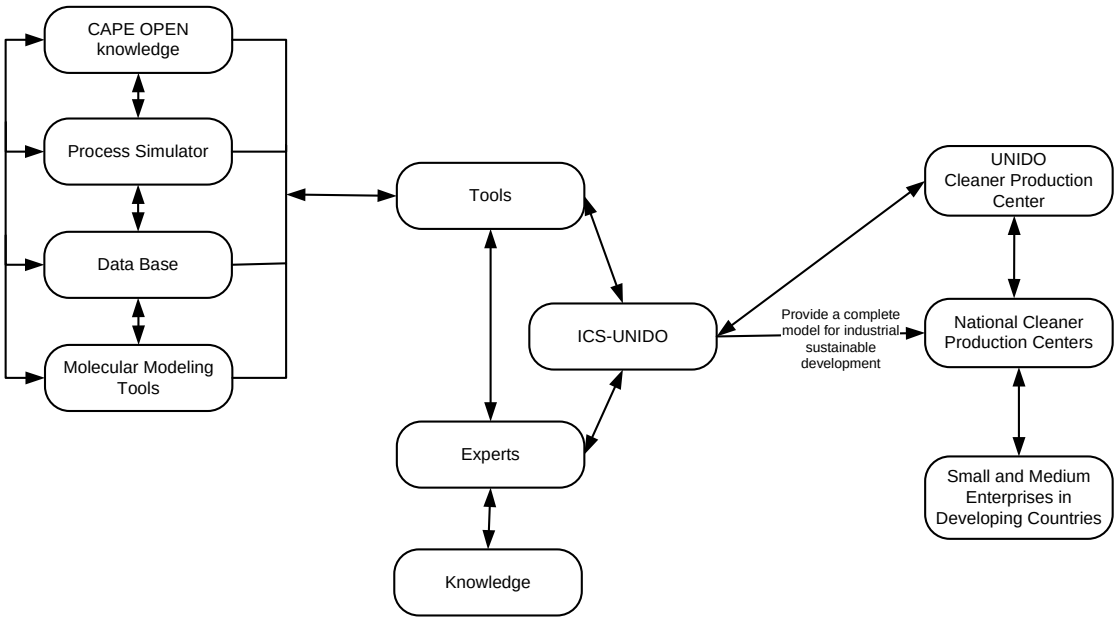


Figure 8.1 PSP Framework distribution toward developing countries

The main role is played by the International Centre for Science and High Technology (ICS-UNIDO), the institution where the PSP Framework software has been developed. ICS-UNIDO is an international technology centre of the United Nations Industrial Development Organization (UNIDO), created to assist countries in their industrial development through technology transfer programmes.

As part of UNIDO, the centre shares its broad goals: to create a better life for people by laying industrial foundations for long-term prosperity and economic strength. UNIDO and ICS have complementary programmes, expertise and instruments. To reach its beneficiaries, ICS works through its own channels, as well as UNIDO's global network of industries, governments, organizations, agencies and financial institutions (ICS-UNIDO, 2007). One of these centres is the UNIDO Cleaner Production Centre.

The UNIDO Cleaner Production (CP) programme aims at building national CP capacities, fostering dialogue between industry and government and enhancing investments for transfer and development of environmentally sound technologies. Through this programme, UNIDO is bridging the gap between competitive industrial production and environmental concerns. CP is more than just a technical solution. It has a widespread application at all decision-making levels in industry, with the chief focus on adopting cleaner technologies and techniques within the industrial sector. CP can only be sustained if capacity is in place to adopt and adjust it to local conditions. To make the

programme a reality and promote the application of CP by enterprises in developing and transition countries, UNIDO in cooperation with United Nations Environment Programme (UNEP) started, in 1994, to set up National Cleaner Production Centers (NCPCs) and National Cleaner Production Programmes (NCPPs). Since then, 34 NCPCs and NCPPs have been established, with others in the planning stage (UNIDO, 2007).

The Cleaner Production Assessment Methodology is used to systematically identify and evaluate the Cleaner Production opportunities and facilitate their implementation in industries. The purpose of a NCPCs is to promote and implement the Cleaner Production strategy in enterprises and government policies, in harmony with local conditions, and to develop local capacity to create and meet Cleaner Production demand throughout the country. The programme is based on the premise that Cleaner Production will only be truly integrated into a country's industries and policies if local capacity is in place to sustain it. A unique strength of the Centres is that they are considered neutral by both government and industry. The industries are therefore more open and forthcoming, as they do not have the fear of punitive or legislative follow-up actions. Thus, the Centres have to ensure high levels of competence to be able to be recognized as a Centre of excellence (UNEP, 2007). Collaborating with the medium and small enterprises in the developing countries the NCPCs have a crucial role in the sustainability promotion.

The PSP Framework examples and documentation will be periodically updated in the ICS-UNIDO web site (www.ics.trieste.it).

Chapter 9

Conclusions

Summary

This chapter represents a summary of the whole PhD research activity. The final conclusions of the present thesis are reported in this section.

"*Enough research will tend*
to support your conclusions."
Arthur Bloch

A methodology to quantify the environmental impact of a chemical or a biochemical process is presented in the present research work. The methodology, used in the early stages of project design, allows choosing the most environmentally friendly design among different process alternatives. The present research, organized in a systematic way, has been focused on some well-defined issues, in order to achieve the proposed goal. The most important statements covered in the present thesis are:

- Sustainable development concept analysis
- Identification of different indicators for sustainability evaluation
- Development and implementation of a specific software, PSP Framework, for industrial sustainability evaluation
- Development of a toxicological database
- Analysis and application of different molecular modelling techniques for evaluating the toxicity of chemical compounds
- PSP application in various case studies

The first two topics are necessary for understanding the background, the tools and the importance of such a research.

The software developed, the PSP Framework, contains interesting elements such as: i) CAPE OPEN Modules ready to be used in any process simulator which provides CO Interfaces, ii) a toxicological database, and iii) various support program codes developed in Visual Basic.

The connection between the process simulator and the environmental evaluation tools has been realized, for the first time, using a standard and innovative technique: CAPE OPEN. Four CO Modules, with different characteristics and aims have been developed in order to get automatically the necessary information from the process simulator. The modules have been tested successfully using different process simulators such as: PROII, Aspen Plus, COCO/COFEE.

Another important PSP Framework' element is the toxicological database. A relational database containing 4900 substances has been created and implemented. The database design phases (conceptual and logical design) are also described in detail.

Different thermo-physical properties correspondent to some toxicological data, such as the environmental impact categories (Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Inhalation or Dermal Exposure (HTPE), Terrestrial Toxicity Potential (TTP), Aquatic Toxicity Potential (ATP), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photochemical Oxidation or Smog Formation Potential (PCOP), Acidification Potential (AP)) for various chemical substances have been estimated using molecular modelling techniques. The molecular modelling techniques used are QSAR, GCM, QM and COSMO. For each estimated thermo-physical: octanol-water partition coefficient, lifetime, reaction rate with ozone, reaction rate with hydroxyl, representative results, discussions and interpretations are reported.

Another part of this research work is dedicated to the development of the support programs enclosed in the PSP Framework. The programs are able to:

- Set the weighting factors for the environmental impact categories according to local and political needs.
- To calculate the 3D indicators: Material Intensity (MI), Energy Intensity (EI), Potential Chemical Risk (PCR) and Potential Environmental Impact (PEI).
- To calculate the 1D indicators (WAR Algorithm) indexes: Iout (the total rate of PEI leaving the system), Iout_mp(the total rate of PEI leaving the system per mass of product, Igen (the total rate of PEI generated within a system) and Igen_mp (the total rate of PEI generated within a system per mass of product.

The case studies described in this thesis are of great importance to show the validity of the proposed software and to illustrate the incorporation of sustainability into chemical process design. Ten processes (described in the scientific literature and processes situated in the developing countries) have been simulated and analyzed from the environmental point of view. Different design alternatives, for each process, are proposed and through PSP Framework, the most environmentally friendly is chosen. Conclusions and arguments regarding the selected alternative are given at the end of the analysis of each single chemical process.

In conclusion, for the sustainable development of the chemical industry, it is essential that the chemical process designers use valid tools. The tool proposed in this research work is going to be used in developed, developing and emerging countries for a complete support to the global sustainability.

Chapter 10

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ANNEXES

NOMENCLATURE

Ab-Initio: from the beginning
AD: Average Deviation
ADO: ActiveX Data Objects
AM1: Austin Model 1
AP: Acidification Potential
ATP: Aquatic Toxicity Potential
CAS-Number: Chemical Abstract Service -Number
CAPE: Computer Aided Process Engineering
CBMC: configurational-bias Monte Carlo
CFC: chlorofluorocarbons
CFC-11: trichlorofluoromethane
CO: CAPE OPEN
CO-LaN: CAPE OPEN Laboratories Network
CORBA: Common Object Request Broker Architecture
COM - Microsoft's Component Object Model
COSMO: Conductor like Screening Model
COSMO-RS: Conductor like Screening Model for Real Solvents
COSMO-SAC: Conductor like Screening Model –Segment Activity Coefficient
CP: Cleaner Production
CSM: Continuum Solvation Model
1D indicators: one dimensional indicators
2D indicators: two dimensional indicators
3D indicators: three dimensional indicators
DOAS: Differential Optical Absorption Spectroscopy
DGA: dyglicol amine
DIPE: diisopropyl ether
DB: database
DFT: Density Functional Theory
dll: Dynamic Link Library
DME: dimethylether
DMF: dimethylformamide
EE: Expanded Ensemble
EI: Energy Intensity
EPA: Environmental Protection Agency
ep-g: gaseous output streams from the energy generation process
ep-s: solid output streams from energy generation process
EQS: Environmental Quality Standard
E-R Diagram: entity- relationship diagram
EU: European Union
FEP: free energy perturbation
GC-FID: Gas Cromatography-Flame Ionization detection
GC-MS: Gas Cormatography-Mass Spectrometry
PTR-MS: Proton Transfer Reaction Mass Spectrometry
RAD: Relative Absolute Deviation

GERA: Environmental Risk Assessment
GEMC: Gibbs ensemble Monte Carlo
GWP: Global Warming Potential
HCFC: hydrochlorofluorocarbons
HOMO: Highest Occupied Molecular Orbital
HTPE: Human Toxicity Potential by Inhalation or Dermal Exposure
HTPI: Human Toxicity Potential by Ingestion
ICIDCA: Cuban Institute for Research on Sugar Cane By-Products
ICSC: International Chemical Safety Cards
ICS-UNIDO: International Centre for Science and High Technology-United Nations Industrial Development Organization
IUPAC: International Union of Pure and Applied Chemistry
Kow: octanol-water partition coefficient
LC_{50}: Lethal Concentration
LD_{50}: Lethal Dose
MO: Material Object
MOOH: Molecular Orbital OH
MI: Material Intensity
MRAD:Mean Relative Absolute Deviation
MSDS: Material Safety Data Sheet
NCPCs: National Cleaner Production Centers
NCPPs: National Cleaner Production Programmes
NIST: National Institute of Standards and Technology
NRTL: Non-Random Two Liquid (activity coefficient model)
OEL: Occupational Exposure Limits
ODP: Ozone Depletion Potential
PEPA: Process Environmental Performance Assessment
PCOP: Photochemical Oxidation or Smog Formation Potential
PCRE: Potential Chemical Risk Evaluation
3PE: Processes-Product-Process Engineering
PEI: Potential Environmental Impact
PMCs: Process Modeling Components
PMEs: Process Modeling Environments
PPP: Physical Property Package
PS: Process Simulation
PSP Framework: Process Sustainability Prediction Framework
QM: quantum mechanics
QSAR: quantitative structure–activity relationship
RK: Redlich Kwong (Thermodynamic Equation)
R-phrases: Risk-phrases
R-133a: Trichlorotrifluoroethane
R-134a: Tetrafluoroethane
SMILES: Simplified Molecular Input Line Entry System
SRK: Soave Redlich Kwong (Thermodynamic Equation)
SVP: split valence polarization
TCE: Trichloroethylene

TTP: Terrestrial Toxicity Potential
TZVP: triple-zeta valence polarization
UNEP: United Nations Environment Programme
UNIDO: United Nations Industrial Development Organization
UNIFAC: Universal quasichemical Functional group Activity Coefficients
UNIQUAC: Universal quasi-chemical Activity Coefficient
URL: Uniform Resource Locator
UO: Unit Operation
UV: Ultra Violet
VB: Visual Basic
WAR: Waste Reduction Algorithm

ANNEX 1

Risk Phrases and significance

RISK PHRASES	RISK PHRASES MEANING
R1	Explosive when dry.
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition.
R4	Forms very sensitive explosive metallic compounds.
R5	Heating may cause an explosion.
R6	Explosive with or without contact with air.
R7	May cause fire.
R8	Contact with combustible material may cause fire.
R9	Explosive when mixed with combustible material.
R10	Flammable.
R2	Risk of explosion by shock, friction, fire or other sources of ignition.
R11	Highly flammable.
R12	Extremely flammable
R13	Extremely flammable liquefied gas. This code is no longer in use.
R14	Reacts violently with water.
R15	Contact with water liberates highly flammable gases.
R16	Explosive when mixed with oxidizing substances.
R17	Spontaneously flammable in air.
R18	In use, may form flammable/explosive vapour-air mixture
R19	May form explosive peroxides
R20	Harmful by inhalation.
R21	Harmful in contact with skin.
R22	Harmful if swallowed.
R23	Toxic by inhalation.
R24	Toxic in contact with skin.
R25	Toxic if swallowed.
R26	Very toxic by inhalation.
R27	Very toxic in contact with skin.
R28	Very toxic if swallowed.
R29	Contact with water liberates toxic gases.
R30	Can become highly flammable in use.
R31	Contact with acids liberates toxic gas.
R32	Contact with acids liberates Very toxic gas.
R33	Danger of cumulative effects.
R34	Causes burns.
R35	Causes severe burns.
R36	Irritating to eyes.
R37	Irritating to respiratory system.
R38	Irritating to skin.
R39	Danger of very serious irreversible effects.
R40	Possible risks of irreversible effects.
R41	Risk of serious damage to eyes.
R42	May cause sensitization by inhalation.

R43	May cause sensitization by skin contact.
R44	Risk of explosion if heated under confinement.
R45	May cause cancer.
R46	May cause heritable genetic damage.
R47	May cause birth defects.
R48	Danger of serious damage to health by prolonged exposure
R49	May cause cancer by inhalation.
R50	Very toxic to aquatic organisms.
R51	Toxic to aquatic organisms.
R52	Harmful to aquatic organisms.
R53	May cause long-term adverse effects in the aquatic environment.
R54	Toxic to flora.
R55	Toxic to fauna.
R56	Toxic to soil organisms.
R57	Toxic to bees.
R58	May cause long-term adverse effects in the environment.
R59	Dangerous for the ozone layer.
R60	May impair fertility.
R61	May cause harm to the unborn child.
R62	Possible risk of impaired fertility.
R63	Possible risk of harm to the unborn child.
R64	May cause harm to breastfed babies.
R14/15	Reacts violently with water liberating highly flammable gases.
R15/29	Contact with water liberates toxic, highly flammable gas.
R20/21	Harmful by inhalation and in contact with skin.
R20/22	Harmful by inhalation and if swallowed
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed.
R21/22	Harmful in contact with skin and if swallowed.
R23/24	Toxic by inhalation and in contact with skin.
R23/25	Toxic by inhalation and if swallowed.
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed.
R24/25	Toxic in contact with skin and if swallowed.
R26/27	Very toxic by inhalation and in contact with skin.
R26/28	Very toxic by inhalation and if swallowed.
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed.
R27/28	Very toxic in contact with skin and if swallowed.
R36/37	Irritating to eyes and respiratory system.
R36/38	Irritating to eyes and skin.
R36/37/38	Irritating to eyes, respiratory system and skin.
R37/38	Irritating to respiratory system and skin.
R39/23	Toxic: danger of very serious irreversible effects through inhalation.
R39/24	Toxic: danger of very serious irreversible effects in contact with skin.
R39/25	Toxic: danger of very serious irreversible effects if swallowed.
R39/23/24	Toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R39/23/25	Toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if

	swallowed.
R39/23/24/25	Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R39/26	Very toxic: danger of very serious irreversible effects through inhalation.
R39/27	Very toxic: danger of very serious irreversible effects in contact with skin.
R39/28	Very toxic: danger of very serious irreversible effects if swallowed.
R39/26/27	Very toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R39/26/28	Very toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R39/27/28	Very toxic: danger of very serious irreversible effects in contact with skin and if swallowed.
R39/26/27/28	Very toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R40/20	Harmful: possible risk of irreversible effects through inhalation.
R40/21	Harmful: possible risk of irreversible effects in contact with skin.
R40/22	Harmful: possible risk of irreversible effects if swallowed.
R40/20/21	Harmful: possible risk of irreversible effects through inhalation and in contact with skin.
R40/20/22	Harmful: possible risk of irreversible effects through inhalation and if swallowed.
R40/21/22	Harmful: possible risk of irreversible effects in contact with skin and if swallowed.
R40/20/21/22	Harmful: possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.
R42/43	May cause sensitization by inhalation and skin contact
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation.
R48/21	Harmful: danger of serious damage to health by prolonged exposure in contact with skin.
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed.
R48/20/21	Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.
R48/21/22	Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation.
R48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin.
R48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed.
R48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.

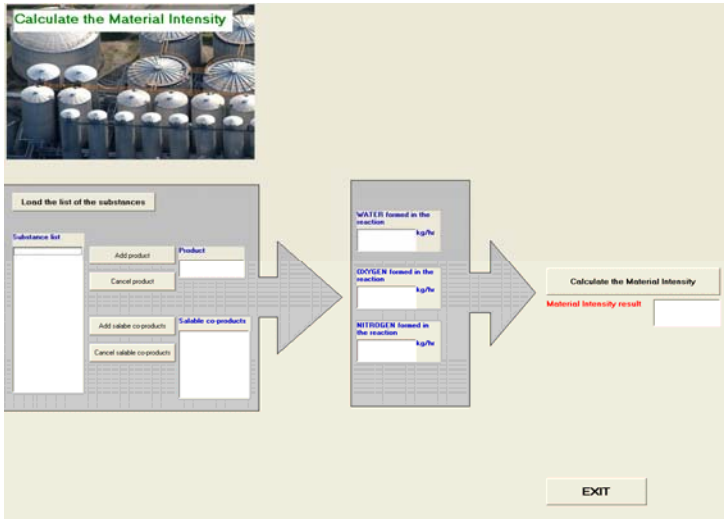
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R65	Harmful:may cause lung damage if swallowed
R66	Repeated exposure may cause skin dryness or cracking.
R67	Vapourus may cause drowsiness and dizziness
R68	Possible risk of irreversible effects

ANNEX 2

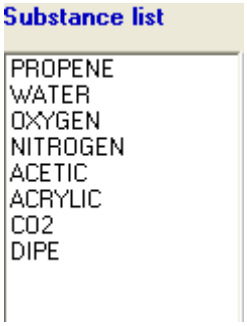
3D Indicators Software-User Manual

The present software, part of PSP Framework, is used for 3D indicators calculation.

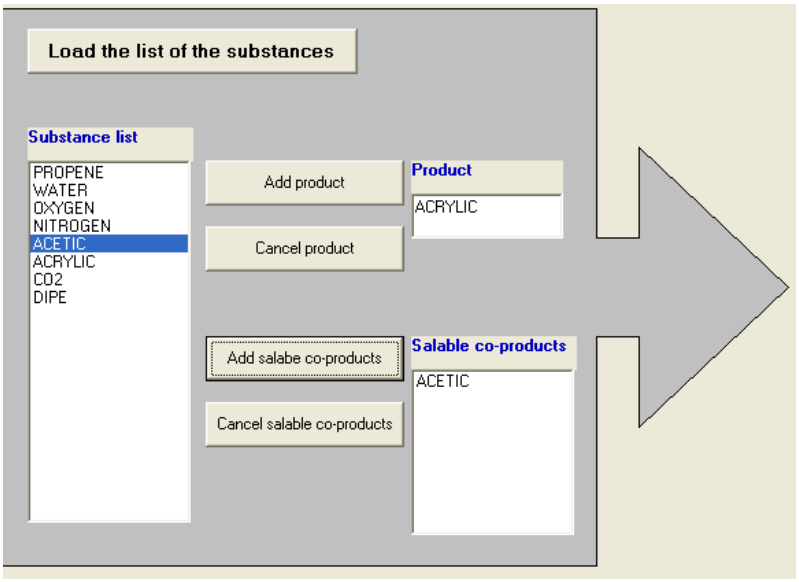
Step1: Calculate the Material Intensity (MI) Indicator



The user should click the button "**Load the list of the substances**". The list containing the substances involved in the process will appear in the "**Substances list**":



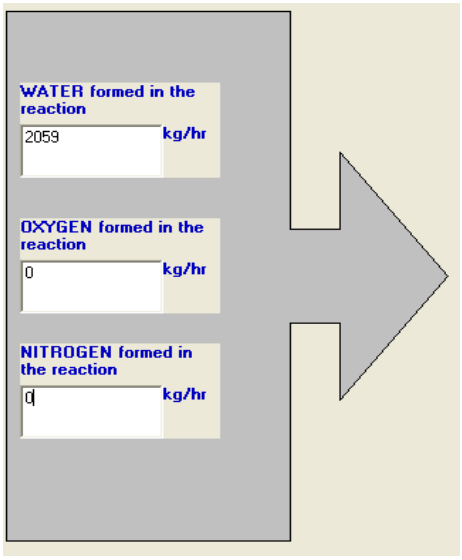
After this, a product sholud be chosen and added it in the "**Product**" filed. This can be done using the "**Add product**" button. The same procedure should be repeated for salable-co products (if they exist, otherwise, the "**Salable co-product**" filed will be empty). It is very important to know that the filed of the "**Product**" should have, at least, one component.



If the product or the salable co-products are not correct they can be removed in the following way:

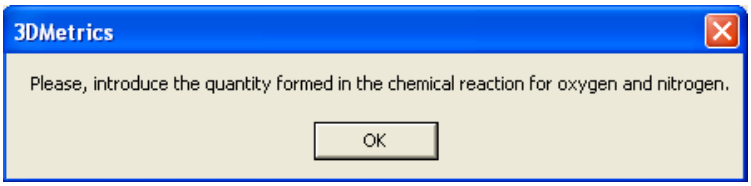
- Click the "**Cancel product**" button to remove the product
- Select a substance for the "**Salable co-products**" filed and press the "**Cancel salable co-products**" button. The selected co-product from the "**Salable co-products**" list will be removed.

One forward step is to introduce the quantities of the water, oxygen and nitrogen formed in the reaction(s). This information is taken from the process simulator by solving a simple mass balance equation.

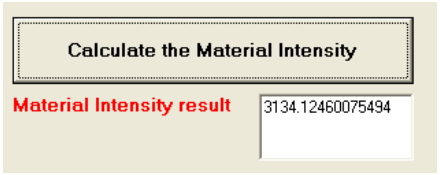


A quantity of 2059 kg/hr of water is formed in the present example. This value is introduced in the "**Water formed in the reaction**" filed. Oxygen and nitrogen are not formed in this case. For this reason the values introduced in the correspondent fields are 0. If one of the quantities for water, oxygen and nitrogen, is not introduced the user gets a warning message. For example if the values for oxygen and nitrogen are not introduced

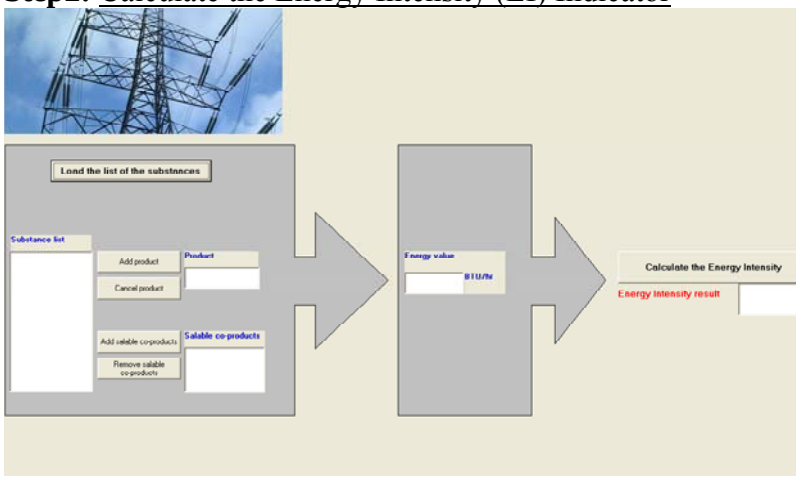
clicking the "**Calculate the Material Intensity**" button we will get the following warning message:



In this situation the inconvenience can be solved by introducing the value 0 in the required fields. Pressing the "**Calculate the Material Intensity**" button the Material Intensity indicator will be calculated and displayed on the interface:



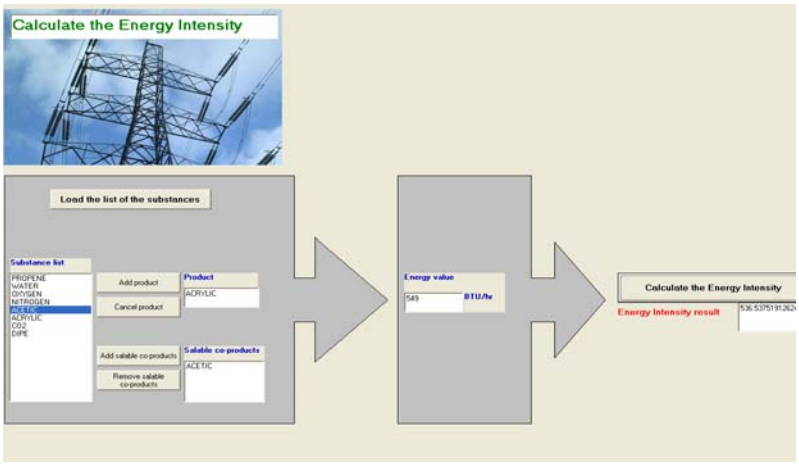
Step2: Calculate the Energy Intensity (EI) Indicator



As in the previous step, the user should click the "**Load the list of the substance**" button. The list of the substance, used in the simulation of the process, will appear on the interface. From this list the user should choose the product and the salable co-products of the process (in the same way it has been done for **Step1:** Calculate the Material Intensity). Click the command buttons "**Add product**" and "**Add salable co-products**" to set up the product and the salable co-products.

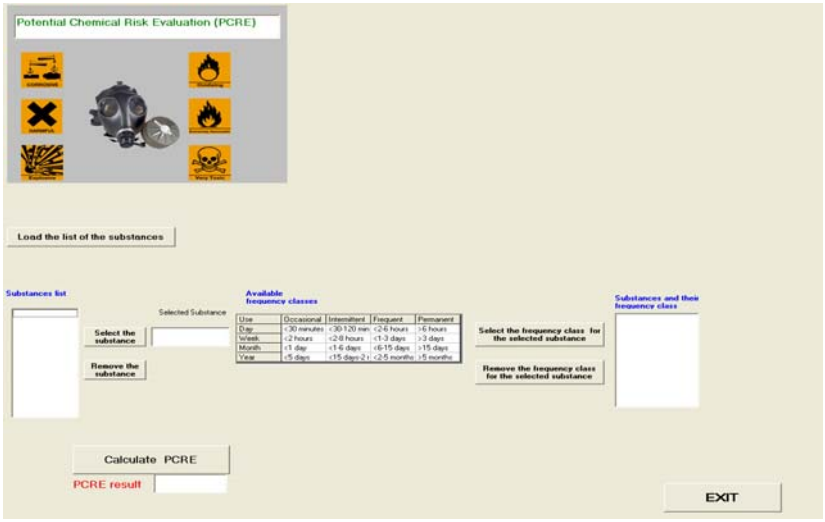
The value of the energy necessary for the process is required too. This value is calculated by the process simulator.

With those data, pressing the "**Calculate the Energy Intensity**" button the value of the Energy Intensity indicator will be calculated and displayed in the "**Energy Intensity result**" area.



Step3: Potential Chemical Risk Evaluation (PCRE)

The interface of this step is presented below.

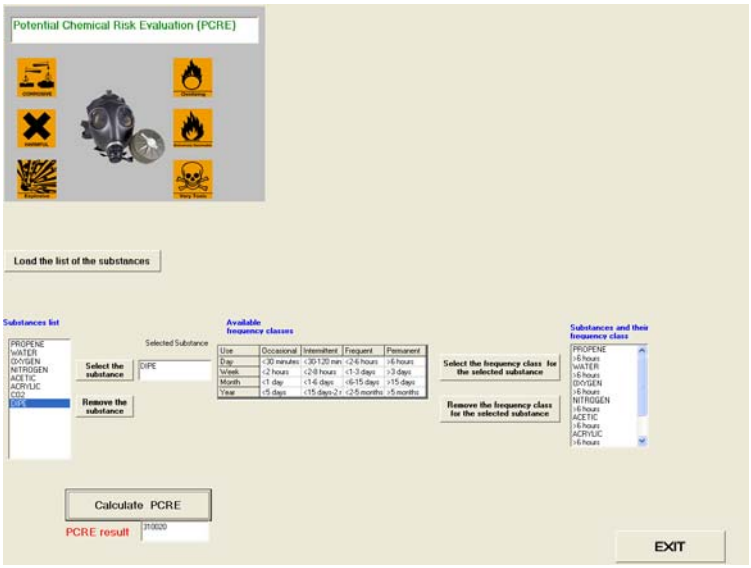


Clicking the "**Load the list of the substances**" button, the list of the substances used in the simulation of the process will appear on the interface. For every substance present in the "**Substances list**" the user should introduce the frequency class. The frequency class is an indicator which characterizes the use period of each chemical. The procedure is described in Table 1.

Table 1. Steps for the PCRE

STEPS	WHAT SHOULD THE USER DO?	WHICH IS THE RESULT OF THE ACTION?	WHY IS THE ACTION REQUESTED?
1	Press the command button **"Load the list of the substances"**	The list of the substance will be loaded.	Without loading the list of substances it is not possible to evaluate the potential chemical risk.
2	Click on one substance present in the **"Substances list"**	One component of the **"Substances list"** will be selected.	
3	Press the button **"Select the substance"**	The selected substance from the **"Substances list**" will be added in the **"Substance selected"** filed.	This action is necessary to choose the frequency class for each substance.
(Optional) If the substance present in the **"Substance selected**" filed is the wrong one	Press the button **"Remove the substance"**	The selected substance will be removed from the "Substance selected" filed.	This action permits to remove the substance from the **"Substance selected"** filed.
4	Click one value from the **"Available frequency class"** table	The clicked value of the frequency class is selected.	This action permits to attribute to each substance the correspondent frequency class.
5	Press the button **"Select the frequency class for the selected substance"**	The selected substance from the **"Substance selected**" filed and the selected frequency from the **"Available frequency class"** table will be added in the **"Substances and their frequency class"** list The final result will be a list containing each substance and the correspondent frequency class.	This action permits to display the substance and the correspondent frequency class in the **"Substances and their frequency class"** list.
(Optional) If the substance or the frequency present in the **"Substances and their frequency class"** list filed are not correct	-Click a substance from the **"Substances and their frequency class"** list -Press the button **"Remove the frequency class for the selected substance"**	The selected substance from the **"Substances and their frequency class"** list and the correspondent frequency will be deleted	This action permits to delete a substance and its correspondent frequency class if one of the two components is wrong.
6	Click the button **"Calculate PCRE"**	The potential chemical risk will be evaluated and displayed on the interface	

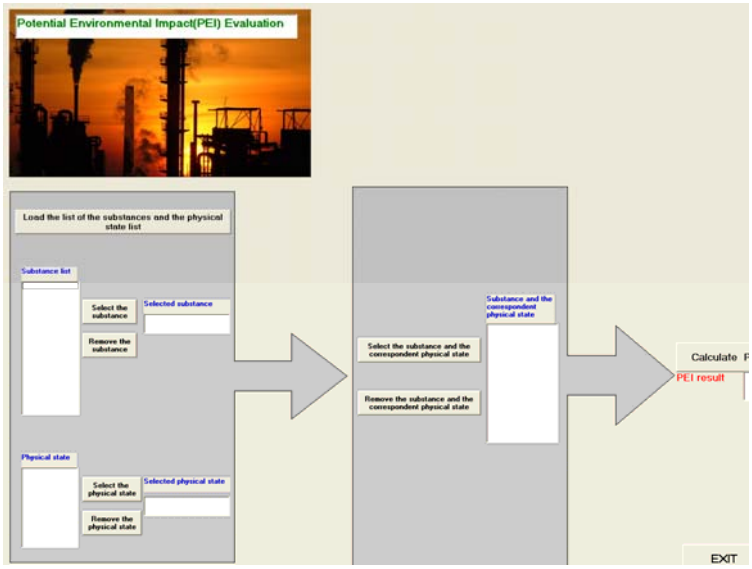
A complete view of this interface is displayed below.



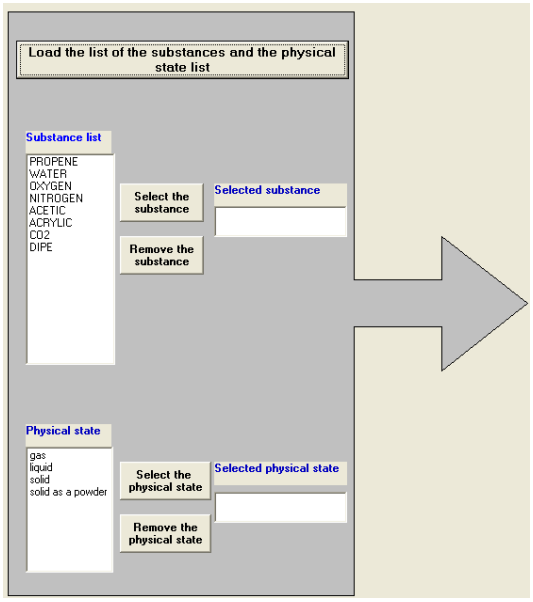
The final result is set in the "PCRE" field.

Step 4: Potential Environmental Impact (PEI) Evaluation

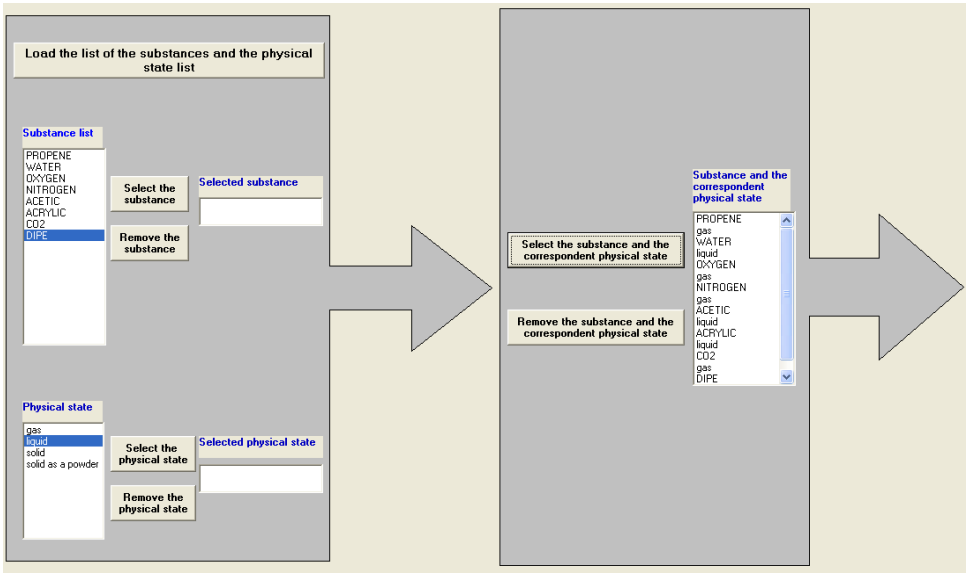
The last indicator which has to be calculated is the Potential Environmental Impact. A view of this interface is presented below.



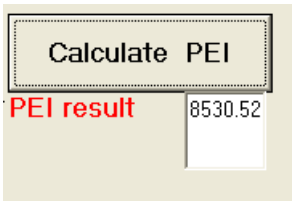
The user should press the command button "**Load the list of the substances and the physical state list**" to load the list of the substances and the available physical states.



For every substance present in the "**Substances list**" a physical state should be selected from the "**Physical state**" list. Pressing the command button "**Select the substance and the correspondent physical state**" this two information will be inserted in the "**Substance and the correspondent physical state**" list.



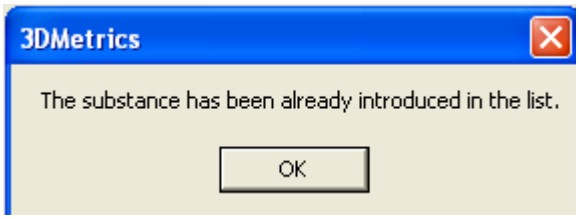
Pressing the command button "**Calculate PEI**" the Potential Environmental Impact is calculated and displayed on the interface.



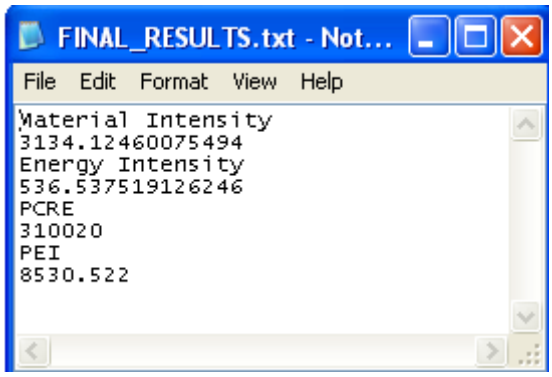
The program permits also to remove:

- the substance from the "**Selected substance**" list pressing the command button "**Remove the substance**"
- the physical state from the "**Selected physical state**" list pressing the command button "**Remove the physical state**".
- The substance and the correspondent physical state from the "**Substance and correspondent physical state**" list by selecting a substance from this list and after that pressing the command button "**Remove the substance and the correspondent physical state**".

If one substance has been already introduced in the "Substance and the correspondent physical state" list the user gets the following warning message when he tries to introduce once again the same substance:



All the results obtained in the 3D Indicators are displayed on each interface and they are also written in the txt file called: FINAL_RESULTS.txt:



ANNEX 3

COWAR development using the CAPE OPEN Unit Wizard

The following pages contain a description of the COWAR development (CO Module containing the equations of the WAR Algorithm).

Steps

The main steps for the development of a CO Unit Operation are:

1. Create the CO Unit Operation using the CAPE OPEN Unit Wizard
2. Write the VB Code
3. Install the Package
4. Test the CO Unit Operation using CAPE Tester

Required Tools

In order to develop a CO Unit Operation the following tools are required:

- CAPE OPEN Unit Operation Wizard Cape (it can be downloaded from CO-LaN web site: www.colan.org)
- Microsoft Visual Basic (VB version 6.0 was used in this case)
- CAPE OPEN Tester (it can be downloaded from CO-LaN web site: www.colan.org)
- Process Simulator software: Aspen Plus, PROII, COCO/COFE (other process simulator software programs which supports the CO interfaces).

All this tools are required to be installed on the machine were the CO Unit Operation is developed (development machine). To install a CO Unit Operation which has been already developed on the development machine the user needs only the dll.

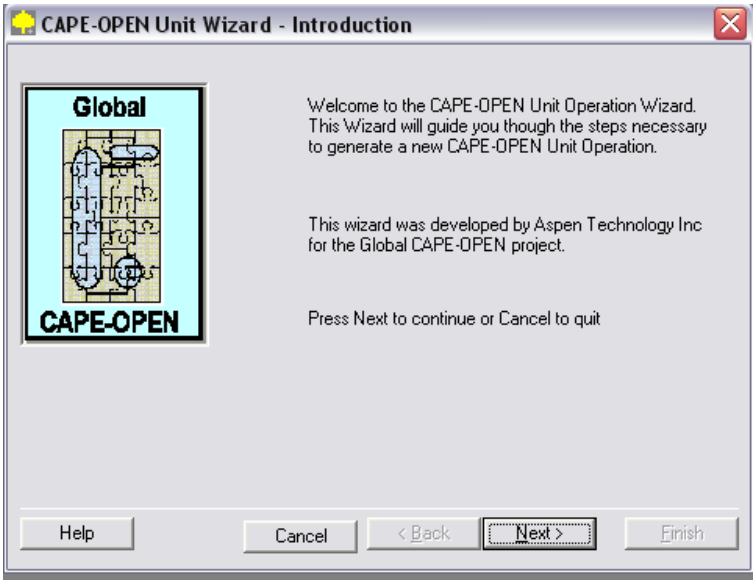
All the steps regarding the development of a CO Module are detailed in the next section.

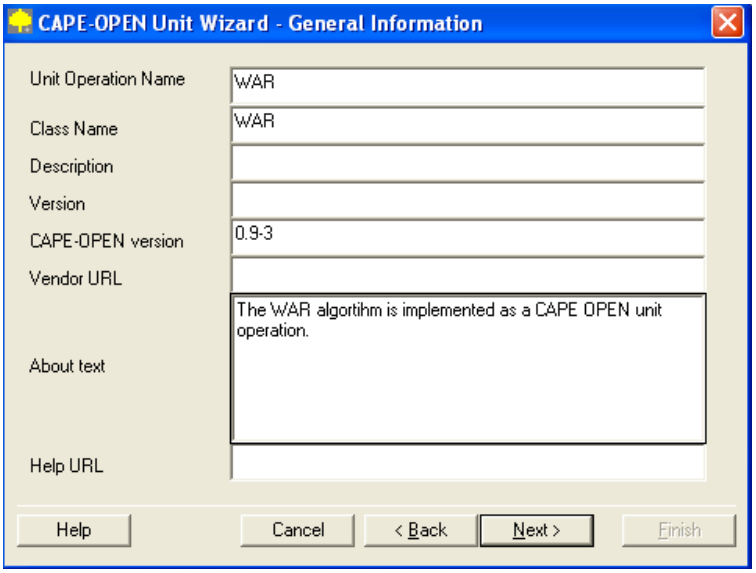
1. Create the CO Unit Operation Using CAPE OPEN Unit Wizard

The Wizard is an add-in for Visual Basic that allows a user to create a CO Unit Operation by filling in data on a sequence of forms. The objective of the wizard is to make it simpler and faster for an engineer to build a CO compliant unit operation using the Microsoft COM version of the interface standard. It is simpler- because the engineer using this tool will not need to know as much about COM as an engineer trying to develop a unit operation from scratch would. It is faster because the tool generates a complete Visual Basic project, to which the engineer only needs to add a user interface form, a calculation routine and a validation routine (CAPE OPEN Unit Wizard - Help).

The main steps for the construction of the CO Unit operation are presented below:

Open the CAPE-OPEN Unit Wizard:





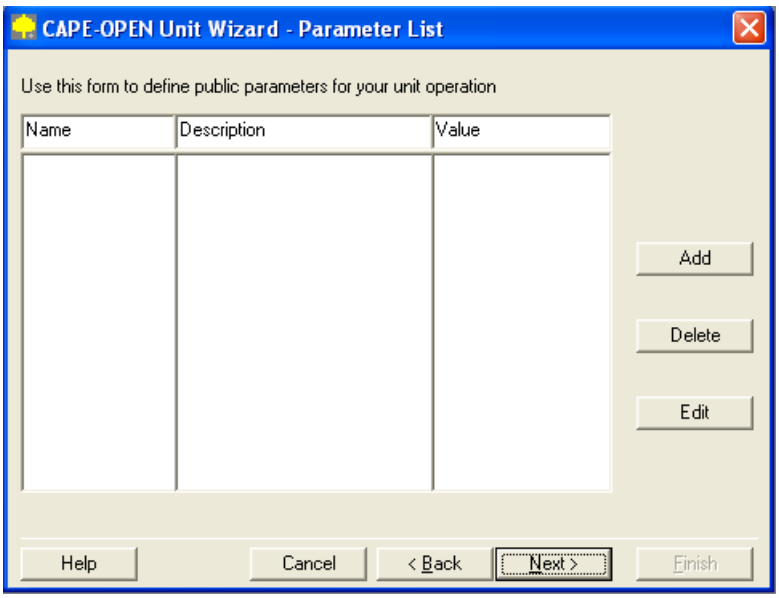
Write the necessary information on the fields:

- Unit Operation Name: type the name given to the unit operation. This will be the name that the user will see when he will choose the unit operation (required information).
- Class name: type the class name. This is a short name for the Visual Basic class. The class name is listed under the Class Modules folder in the VB Project Explorer (required information).
- Description: brief description of the unit operation. This will typically be displayed together with the unit operation name to help the user (additional information).

- Version: version of the unit operation. The user can develop many times the same unit operation and saved it with the same name. This information is useful to identify the version of the unit saved with the same name (additional information).
- CAPE-OPEN version: the version of the CAPE-OPEN Unit Wizard used for the development of the unit operation (required information).
- Vendor URL: web address containing the vendor of that specific unit operation. This might include contact addresses and telephone numbers (additional information).
- About text: Enter e brief description of the vendor of the unit operation. This might include contact addresses and telephone numbers (additional information).
- Help URL: a web address where the user can find more information regarding the unit operation or can ask for support (additional information).

(CAPE OPEN Unit Wizard - Help)

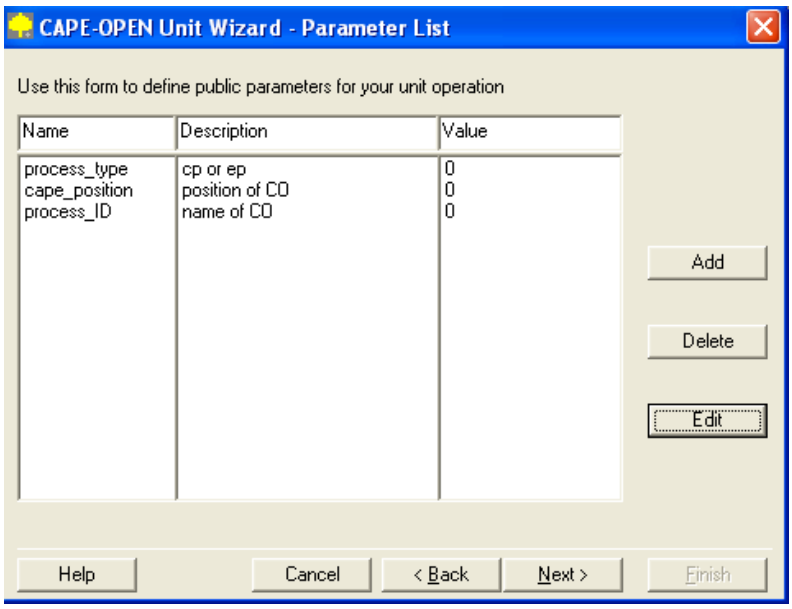
Clicking the next button the following window appears.



A parameter is a specific characteristic of the unit operation.
Click the "Add" button to add a new parameter, "Delete" button to cancel a parameter or the "Edit" bottom to modify a parameter, previously defined (added).
Clicking on "Add" causes the Parameter Details dialog to be displayed. This dialog contains the following data entry fields:

- Name: A short name for the parameter
- Description: contains the description of the parameter
- Type: contains the type of parameter: Real, Integer, Option

In the present module developed three parameters were defined.



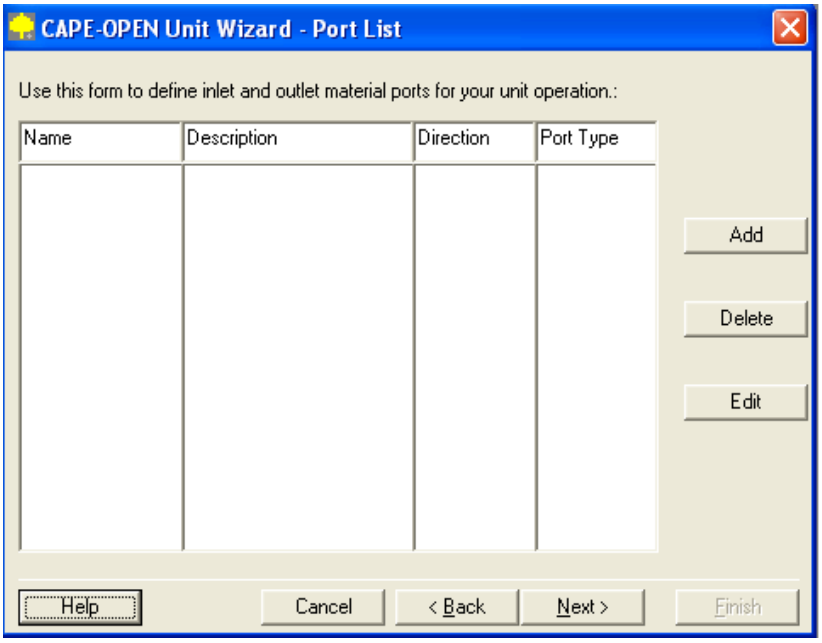
With regard to the necessity of using three parameters, it should be specified that: the process type parameter is used to identify the type of process (chemical or energy generation process); the position parameter is needed for the location detection of the CO in the flow sheet (the CO could be on an input, output, intermediary or waste stream of the process); and the name parameter is needed to find the CO units which were first classified using the position parameter.

Example: Parameters Values for a chemical process with four input streams the value of the *process type* parameter is zero (the parameter is set to zero for chemical process and to one for the energy generation process)

- the value of the *position parameter* for all the input streams is assumed to be zero (the parameter is set to zero for the input streams, one for the waste streams, two for the product streams and three for an internal stream of the process), so for this example there are four zero values (one for each input stream).
- to know which CO unit corresponds to each stream the *name* of the CO was introduced as a parameter too. In the example presented here there are four names for the units operation (CO1, CO2, CO3, CO4) correspondent to the four streams.

Click next to define the ports.

Unit operations must be able to provide the simulator executive with the number and the properties of allowable stream connections. This is done through the mechanism of "ports" (Conceptual Design Document, CAPE OPEN Team, 2000).



Click the "Add" button to add a new port, "Delete" button to cancel a port or the "Edit" bottom to modify a port, previously defined (added).

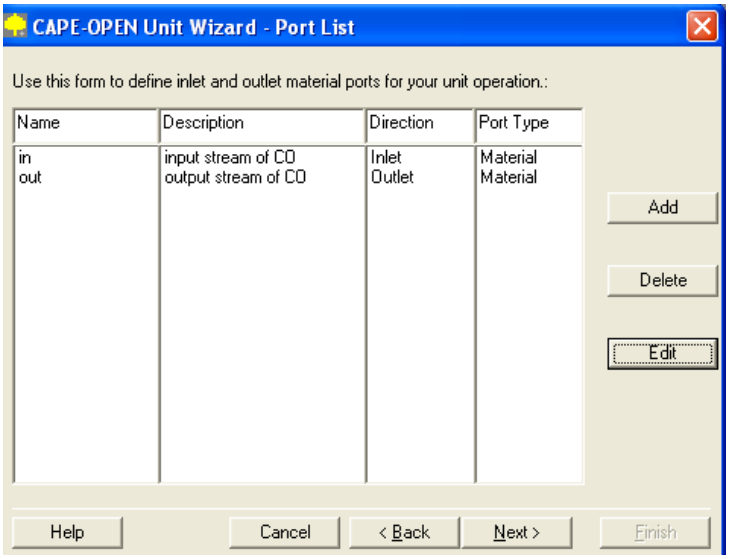
The name can indicate the location within the unit operation to allow the user to make a proper connection. For example for a distillation column the name could be: "column feed", "top product", "bottom product", "reflux ratio" or for a mixer the name could be: "input1", "input2", ..., "input n", "output1", "output2",…, "output". Any name can be chosen for the name of the ports. Any number of input or output ports can be defined.

A brief description for the port can be introduced too.

The port has also a direction which can be inlet or outlet. The direction attribute defines whether a port delivers information to a unit operation (input port) or receives information from a unit operation model (output port) (Conceptual Design Document, CAPE OPEN Team, 2000).

The connections type (material, heat or work) should be specified too. The three ports type corresponding to the three classes of information are MaterialPort, EnergyPort and InformationPort.

In the example reported here the unit operation has one input port and one output port. The ports will be used in the design stage of the process, for connecting the streams with the CO Module.



Before finishing, the project has to be saved on the computer. The user can choose the directory where the unit operation will be created and saved it. In this example the CO Unit Operation is saved in C:\CAPE_OPEN\Proall.

2 Write the VB Code

The Wizard generates a VB6 Project containing the source code for the new unit operation, and it also generates an installation package, so that the unit operation can be installed and uninstalled on the machine different from the development machine (CAPE-OPEN Unit Wizard-Help). In the present example the directory is called Proall. It contains a sub-directory called PackProall containing the Installation Package.

CAPE OPEN Unit Wizard does not generate all the code needed for a complete unit operation. In this context the ICapeUnit_Calculate subroutine of the Visual Basic code should be modified. This is the place where the WAR Algorithm equations 3.5-3.11 have been implemented. The COWAR Module is able to attribute the input stream properties to the output stream. In other words, the output stream is equal to the input stream (flow-rate, temperature, pressure, composition).

The subroutine reads from the database the normalized values of the potential environmental categories of the substances involved in the chemical or in the energy generation process. The subroutine ICapeUnit_Calculate generated by the Wizard was replaced with the code containing the WAR Algorithm equations. After typing this code in the ICapeUnit_Calculate, three modifications have been made in the Visual Basic program.

- The first one is in the Private Sub Class_Terminate(). Put as comment the statement Set myForm=Nothing.

```
Private Sub Class_Terminate()
    Set ATCOError = Nothing
    'Set myForm = Nothing
    Set myPorts = Nothing
    Set myParameters = Nothing
    Set mysimContext = Nothing
'MsgBox "Terminating"
End Sub
```

- The second modification is in the Icape_Parameter_Value.

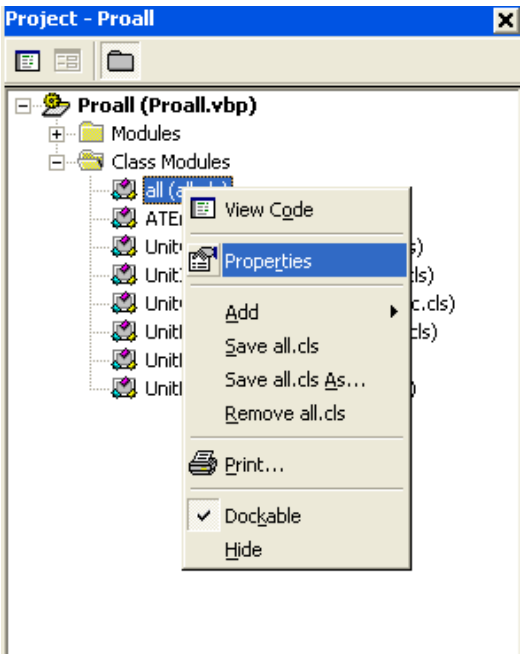
```
Private Property Let ICapeParameter_value(ByVal LHS As Variant)
    If MySpec.Type = CAPEOPEN093.CAPE_INT Then
        If VarType(LHS) <> vbLong And VarType(LHS) <> vbInteger Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not an integer number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_REAL Then
        If VarType(LHS) <> vbDouble And VarType(LHS) <> vbSingle Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a double number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_OPTION Then
        If VarType(LHS) <> vbString Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a string"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    Else
        myValue = LHS
        myOwner.SetStatus = CAPEOPEN093.CAPE_NOT_VALIDATED
        myStatus = CAPEOPEN093.CAPE_NOT_VALIDATED
    End If
End Property
```

Put the End If statement after Else.

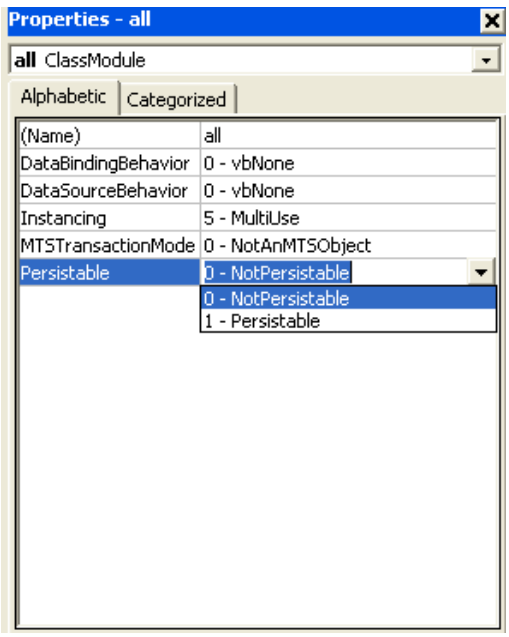
```
Private Property Let ICapeParameter_value(ByVal LHS As Variant)
    If MySpec.Type = CAPEOPEN093.CAPE_INT Then
        If VarType(LHS) <> vbLong And VarType(LHS) <> vbInteger Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not an integer number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_REAL Then
        If VarType(LHS) <> vbDouble And VarType(LHS) <> vbSingle Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a double number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_OPTION Then
        If VarType(LHS) <> vbString Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a string"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    Else
      End If
        myValue = LHS
        myOwner.SetStatus = CAPEOPEN093.CAPE_NOT_VALIDATED
        myStatus = CAPEOPEN093.CAPE_NOT_VALIDATED

End Property
```

- The third modification is in the properties of the module.



In order to modify the values of the parameters the notpersistable property should be selected.



With these modifications the program is ready to be compiled.

ANNEX 4

CO Module containing the energy generation process. Development using the CAPE OPEN Unit Wizard

The following pages contain a description of the CO Module containing the energy generation process.

The main steps for the development of a CO Unit Operation are:

1. Create the CO Unit Operation using the CAPE OPEN Unit Wizard
2. Write the VB Code
3. Install the Package
4. Test the CO Unit Operation using CAPE Tester

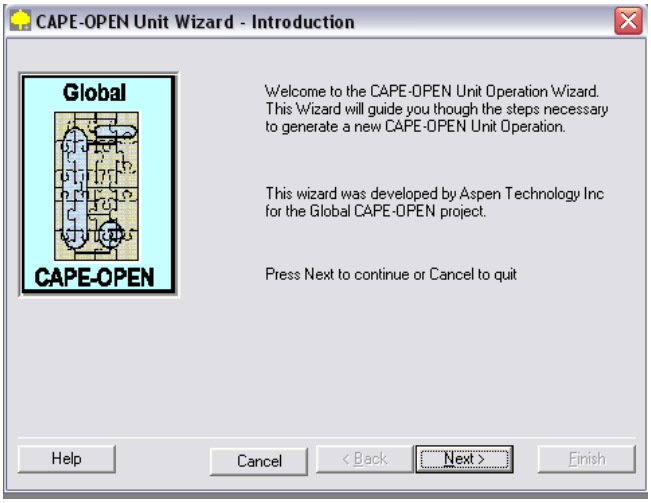
Required Tools

In order to develop a CO Unit Operation the following tools are required:

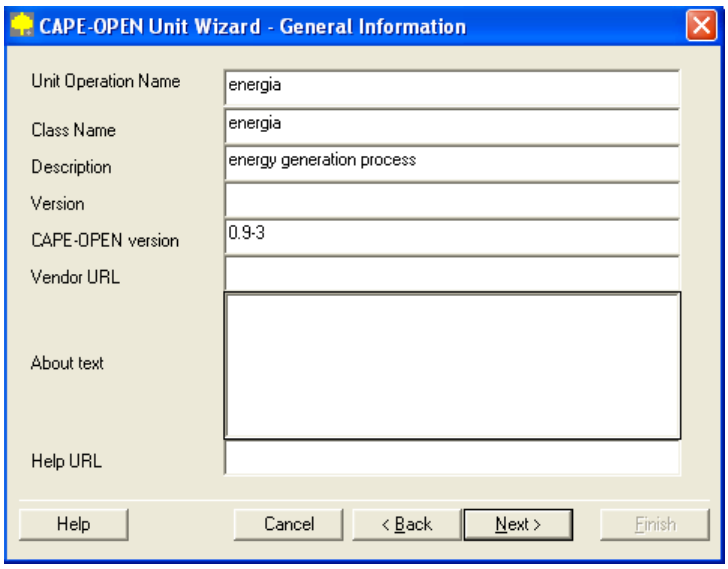
- CAPE OPEN Unit Operation Wizard Cape (it can be downloaded from CO-LaN web site: www.colan.org)
- Microsoft Visual Basic (VB version 6.0 was used in this case)
- CAPE OPEN Tester (it can be downloaded from CO-LaN web site: www.colan.org)
- Process Simulator software: Aspen Plus or PROII.

1 Create the CO Unit Operation Using CAPE OPEN Wizard

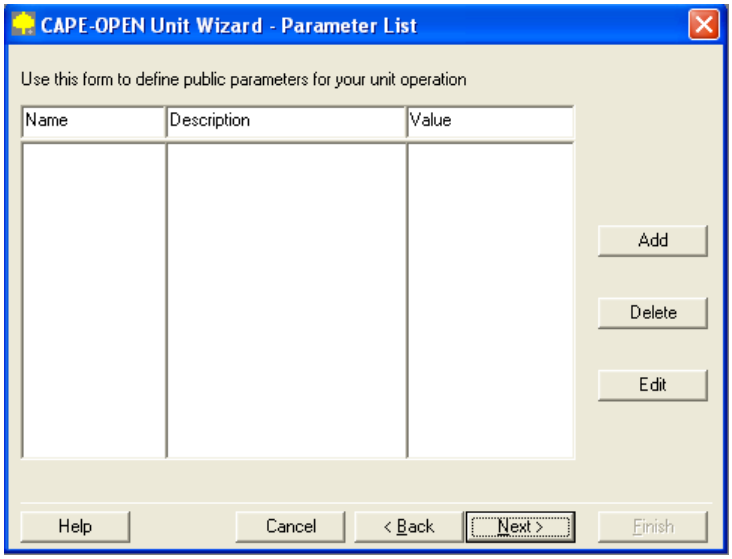
Open the CAPE-OPEN Unit Wizard:



Write the necessary information on the fields:

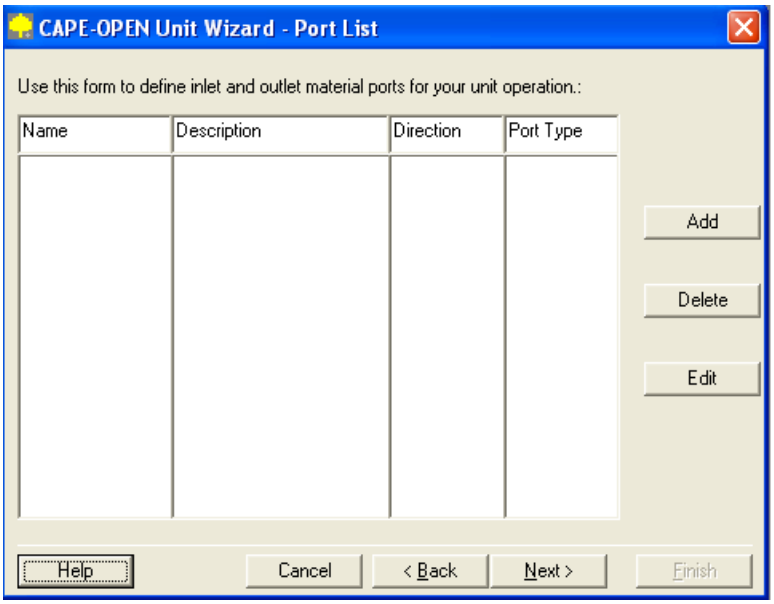


Clicking the next button the following window appears.



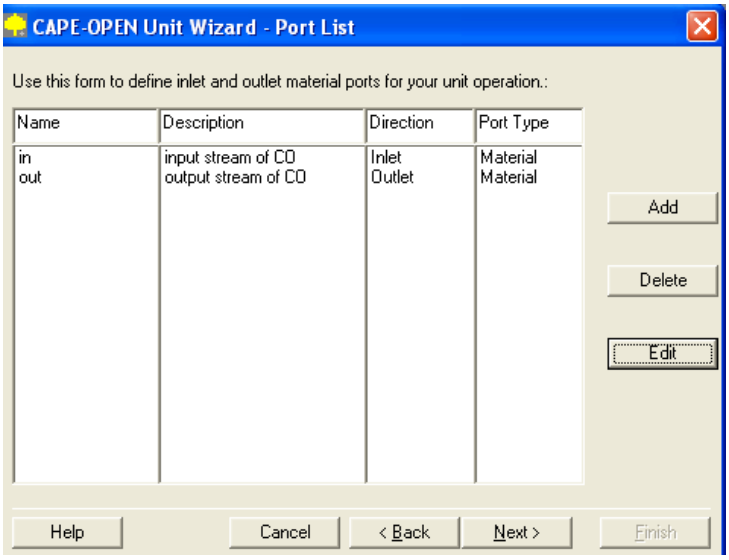
In the present module no parameters were defined.

Click next to add the ports.



Click the "**Add**" button to add a new port, "**Delete**" button to cancel a port or the "**Edit**" bottom to modify a port, previously defined (added). On the port details the user can enter a name and a description for the port, the direction (inlet or outlet), and the type of connections (material or information). Any name can be chosen for the name of the ports. Any number of input or output ports can be defined.

In the present example developed the unit operation has one input port and one output port. The ports are used later, in the design stage of the process, for connecting the streams to the CO Unit Operation.



Before finishing, the project has to be saved on the computer. The user can choose the directory where the unit operation will be created and saved. In this example the CO Unit Operation is saved in C:\CAPE_OPEN\energia.

2 Write the VB Code

As it was specified, the Wizard generates a VB6 Project containing the source code for the new unit operation, and it also generates an installation package, so that the unit operation can be installed and uninstalled on a different machines. In the example presented here the directory is called Proenergia. It contains a sub-directory called PackProenergy containing the Installation Package.

The ICapeUnit_Calculate subroutine of the Visual Basic code was modified. The equation of the coal combustion was implemented here. The output stream of the CO Unit Operation contains all the gases obtained by burning the coal. This module is connected with the COWAR Module and, in this way, the impact of the energy generation process is calculated too. After inserting the code the first two modifications presented in ANNEX 3 should be made in the Visual Basic program, for the energy module too.

- The first one is in the Private Sub Class_Terminate(). Put as comment the statement Set myForm=Nothing.

```
Private Sub Class_Terminate()
    Set ATCOError = Nothing
    'Set myForm = Nothing
    Set myPorts = Nothing
    Set myParameters = Nothing
    Set mysimContext = Nothing
'MsgBox "Terminating"
End Sub
```

- The second modification is in the ICape Parametrer_Value.

```
Private Property Let ICapeParameter_value(ByVal LHS As Variant)
    If MySpec.Type = CAPEOPEN093.CAPE_INT Then
        If VarType(LHS) <> vbLong And VarType(LHS) <> vbInteger Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not an integer number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_REAL Then
        If VarType(LHS) <> vbDouble And VarType(LHS) <> vbSingle Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a double number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_OPTION Then
        If VarType(LHS) <> vbString Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a string"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    Else
        myValue = LHS
        myOwner.SetStatus = CAPEOPEN093.CAPE_NOT_VALIDATED
        myStatus = CAPEOPEN093.CAPE_NOT_VALIDATED
    End If
End Property
```

Put the End If statement after Else.

```
Private Property Let ICapeParameter_value(ByVal LHS As Variant)
    If MySpec.Type = CAPEOPEN093.CAPE_INT Then
        If VarType(LHS) <> vbLong And VarType(LHS) <> vbInteger Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not an integer number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_REAL Then
        If VarType(LHS) <> vbDouble And VarType(LHS) <> vbSingle Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a double number"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    ElseIf MySpec.Type = CAPEOPEN093.CAPE_OPTION Then
        If VarType(LHS) <> vbString Then
            Set ATCOError = New ATError
            ATCOError.SetUserCode CAPEOPEN093.ECapeInvalidArgumentHR
            ATCOError.SetUserInterfaceName "ICapeParameter"
            ATCOError.SetUserOperation "set_Value"
            ATCOError.SetUserDescription "The input value is not a string"
            Call Err.Raise(CAPEOPEN093.ECapeInvalidArgumentHR)
        End If
    Else
      End If
        myValue = LHS
        myOwner.SetStatus = CAPEOPEN093.CAPE_NOT_VALIDATED
        myStatus = CAPEOPEN093.CAPE_NOT_VALIDATED

End Property
```

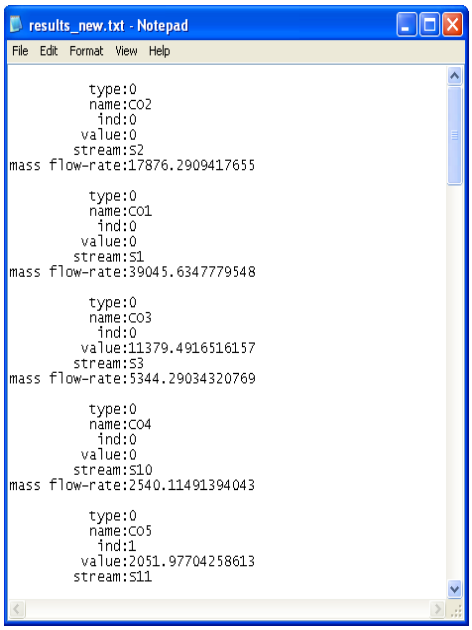
It should be specified that, in this case, the third modification (set the properties to nonpersistable) was not necessary because no parameters were defined for this module.

ANNEX 5

Final Interface- User Manual

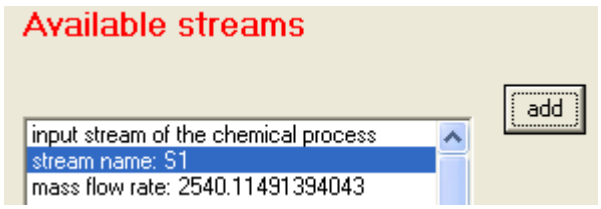
The next pages represent a description and a user manual for the Final Interface for Environmental Impact Indexes calculation

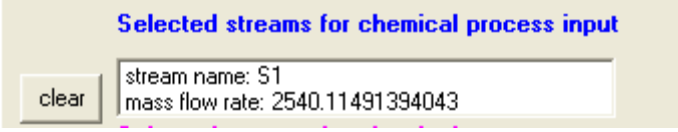
The first step that the user should do is to introduce manually the stream name in the resuls.txt. The new file should be saved with the name results_new.txt. This is the format of the results_new.txt file:



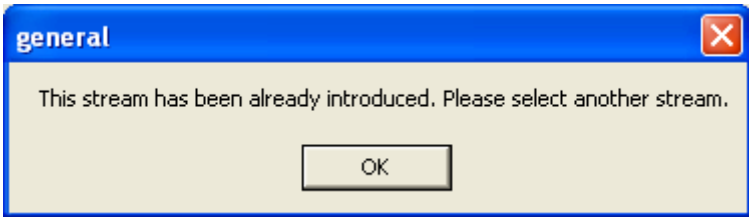
Opening the program **Final_interface.exe** the application loads automatically the content of results_new.txt and stream_name_and_composition.txt files and creates the test.txt and the display.txt files. The content of display.txt containing comments regarding the stream types, the stream names and the mass flow-rates (kg/hr) are displayed on the interface. The streams, present in the available streams list, should be added on the right place on the available lists. For example the first stream is an input stream of the chemical process. Selecting that stream and pressing the command button "**add**"

the name of the stream and the correspondent quantity are automatically introduced in the list "**selected streams for chemical process input**".

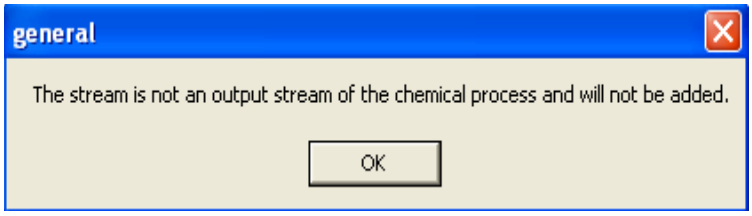




If the user tries to introduce a stream, which has been already introduced in the list, the program gives the following warning message:



If the user tries to introduce a stream from the "**available streams**" list to the "**selected streams**" list and the selected streams list is not correct the program gives another warning message. For example the user tries to introduce an input stream of the chemical process in the output streams of the chemical process list. The message received is:

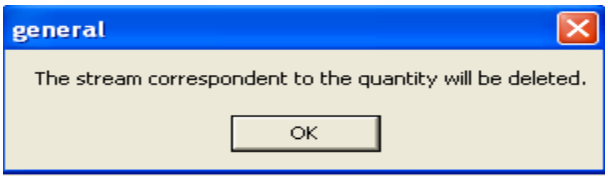


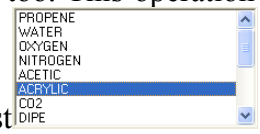
It is possible to delete a stream using the clear button

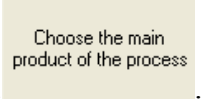
.

The user can select from the "**selected streams**" list the stream name he wants to delete. Pressing the "**clear**" bottom the stream and its correspondent quantity will be deleted.

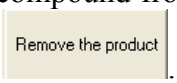
The user can also select the quantity and not the stream name. In this case the following message comes out:



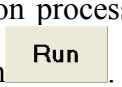
The main process product(s) should be selected too. This operation can be made by choosing from the "**Available Compounds**" list 

the desired one. 

.

The user has, also, the possibility to remove the compound from the selected list by pressing the command button "**Remove the product**" 

.

After all the fields (for input, output, waste for the chemical process and input and output for the energy generation process) are completed and the product(s) was (were) selected press the "**Run**" button 

.

The program creates some text files (Iin_cp.txt, Iout_cp.txt, Iin_ep.txt, Iout_ep.txt, test.txt, display.txt and ENVIRINDEXtot.txt) in the same directory where the simulation (in PROII or Aspen Plus) was run. The most important file, which contains the final results you have on the interface too, is ENVIRINDEXtot.txt

It contains:

Iout - The total rate of PEI leaving the system (units of PEI/time)

Iout_mp0- The total rate of PEI leaving the system per mass of product (main product of chemical process) (units of PEI/time)

Iout_mp1- The total rate of PEI leaving the system per mass of product (total products of chemical process) (units of PEI/time)

Iout_mp2- The total rate of PEI leaving the system per mass of product (products of chemical process + energy generation process) (units of PEI/time)

Igen- The total rate of PEI generated within a system (units of PEI/time)

Igen_mp0- The total rate of PEI generated within a system per mass of product (main product of chemical process) (units of PEI/mass of product streams)

Igen_mp1- The total rate of PEI generated within a system per mass of product (total products of chemical process) (units of PEI/mass of product streams)

Igen_mp2- The total rate of PEI generated within a system per mass of product (products of chemical process + energy generation process) (units of PEI/mass of product streams)

The results of environmental indexes, values and graphical representation, are also displayed in footer part of the interface.

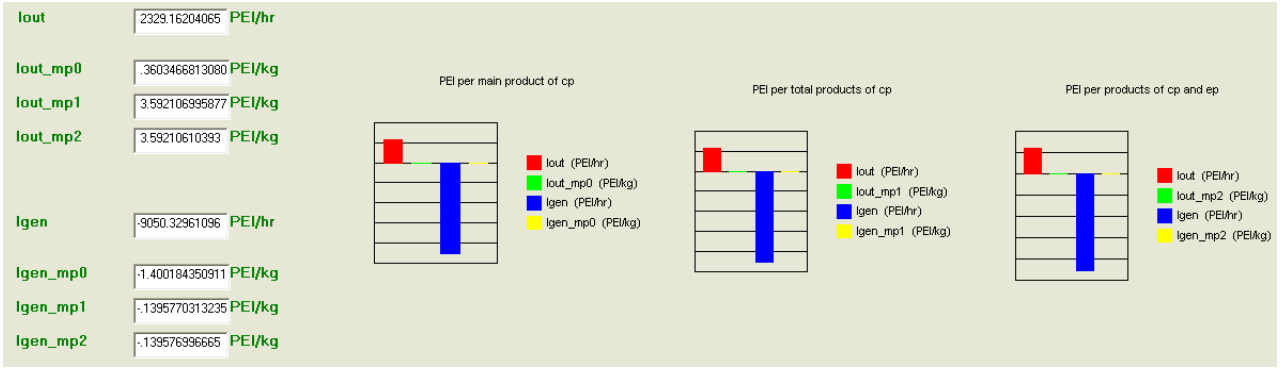


Figure1. Numerical values and graphical representation of PEI

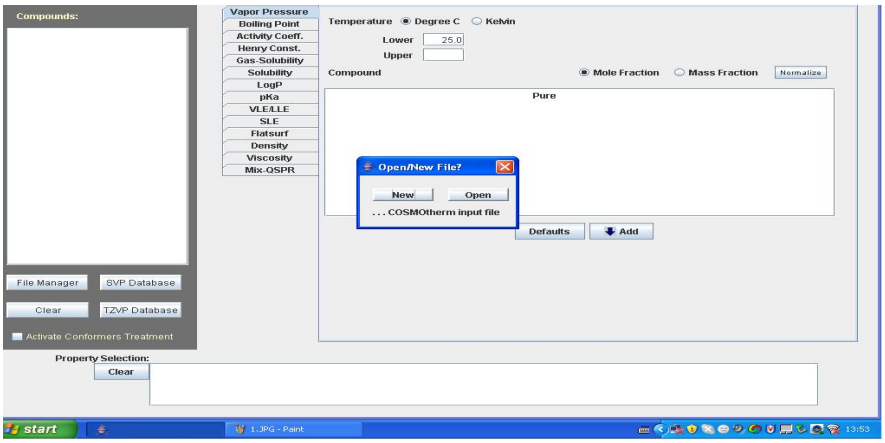
ANNEX 6

Octanol water partition coefficient, Kow, calculation using COSMO*Therm* software

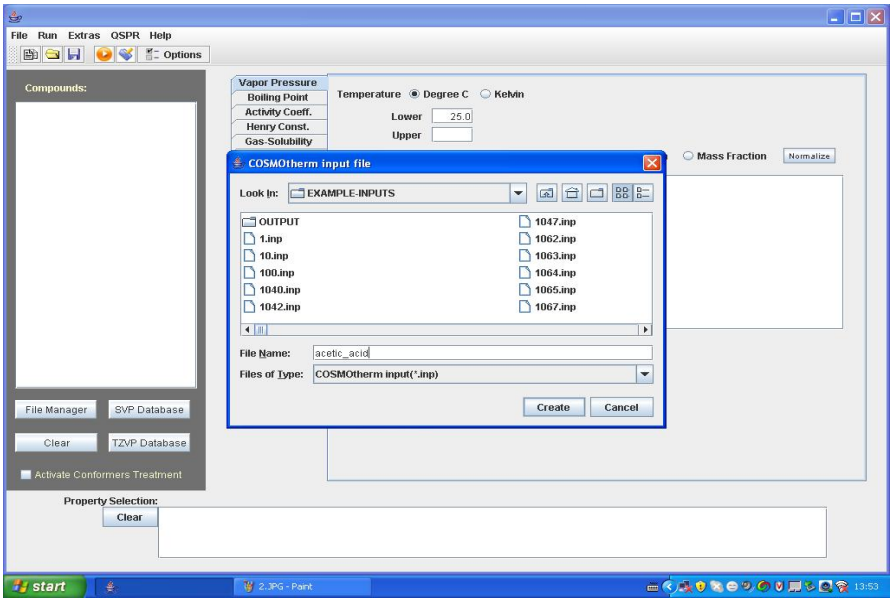
This section describes the procedure used for Kow calculation.

The cosmo files generated with TURBOMOLE and Materials Studio softwares have been used for octanol-water partition coefficient Kow calculation, using COSMO*Therm* (version 2.01.06) Software. The Steps for calculating Kow using COSMOTherm (version 2.01.06) Software are described below.

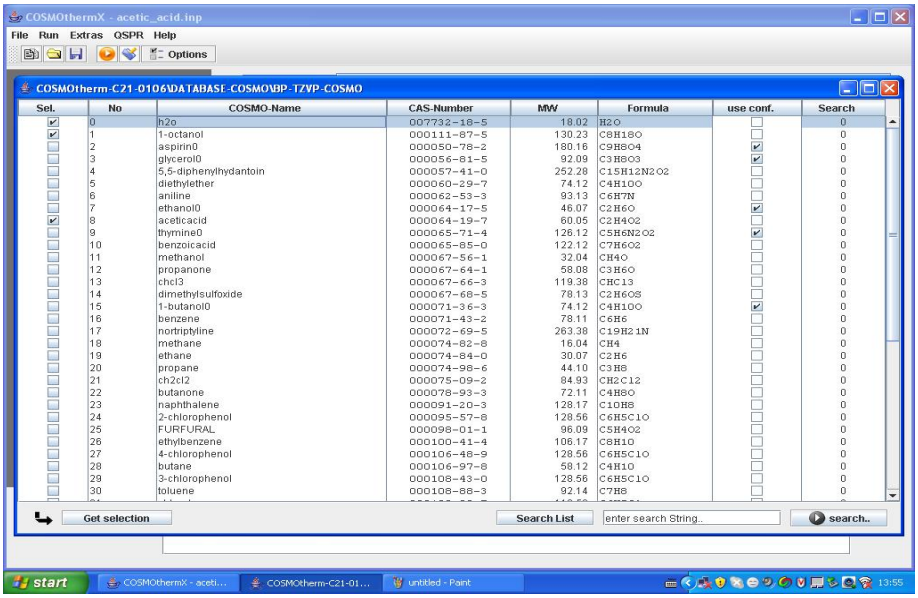
Open a new project



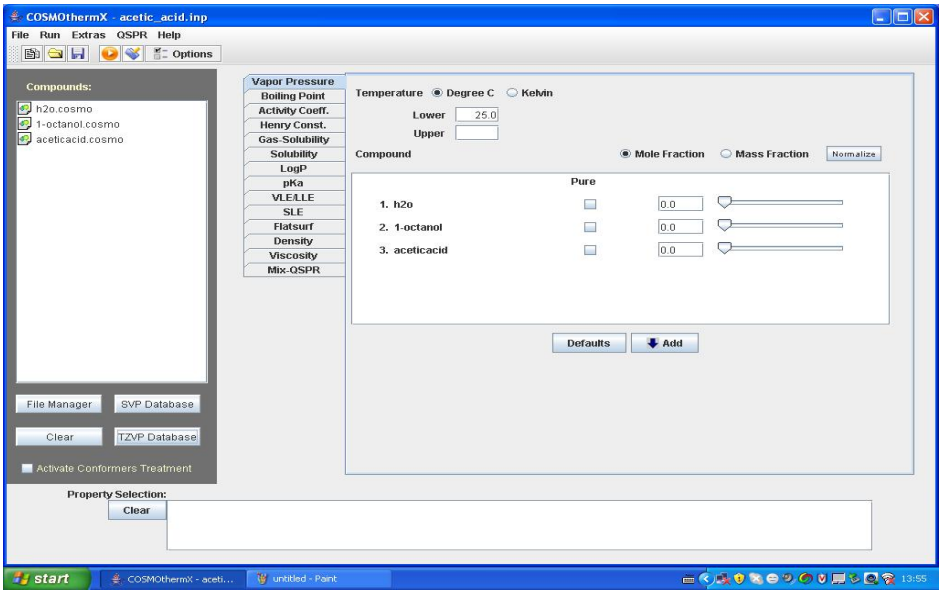
Give a name to the new project



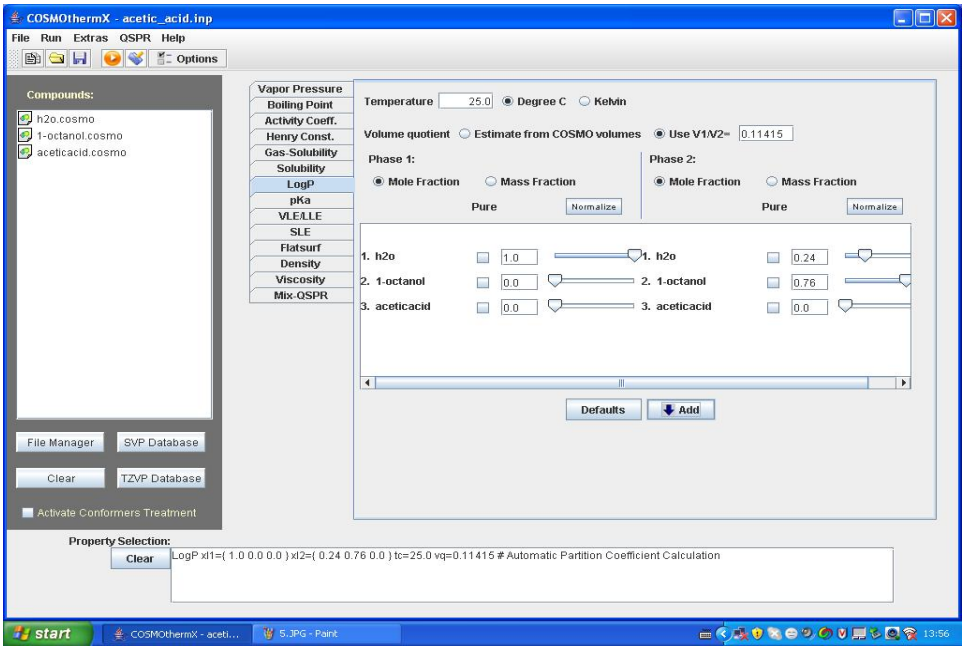
Select the substances from COSMOTherm database (TZVP or BVP databases)



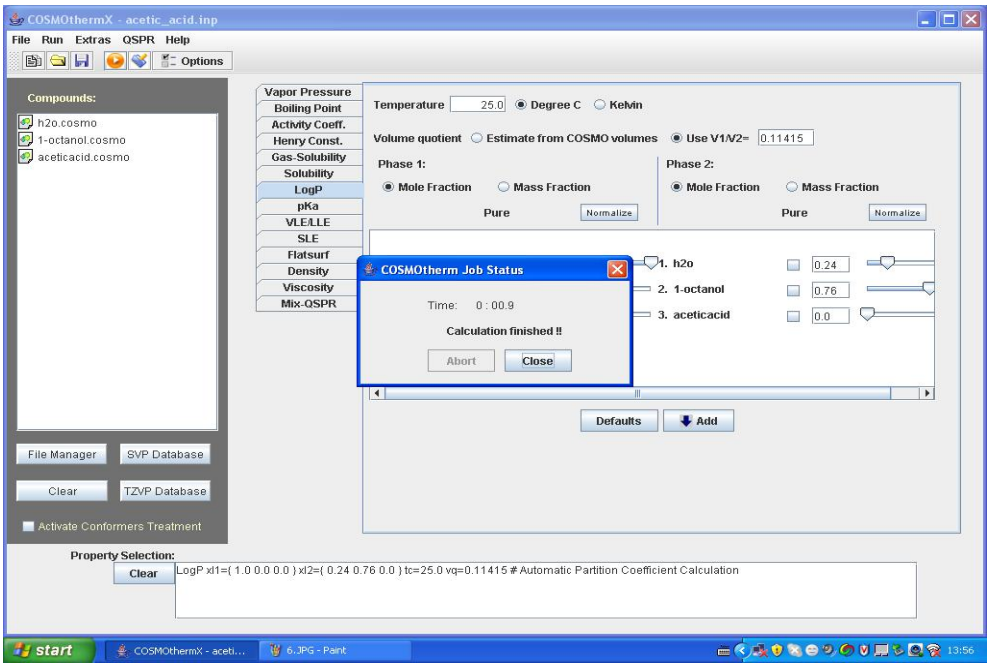
The selected substances are listed in the Compounds list



Press "LogP" button and fill the data (volume, mole fraction)

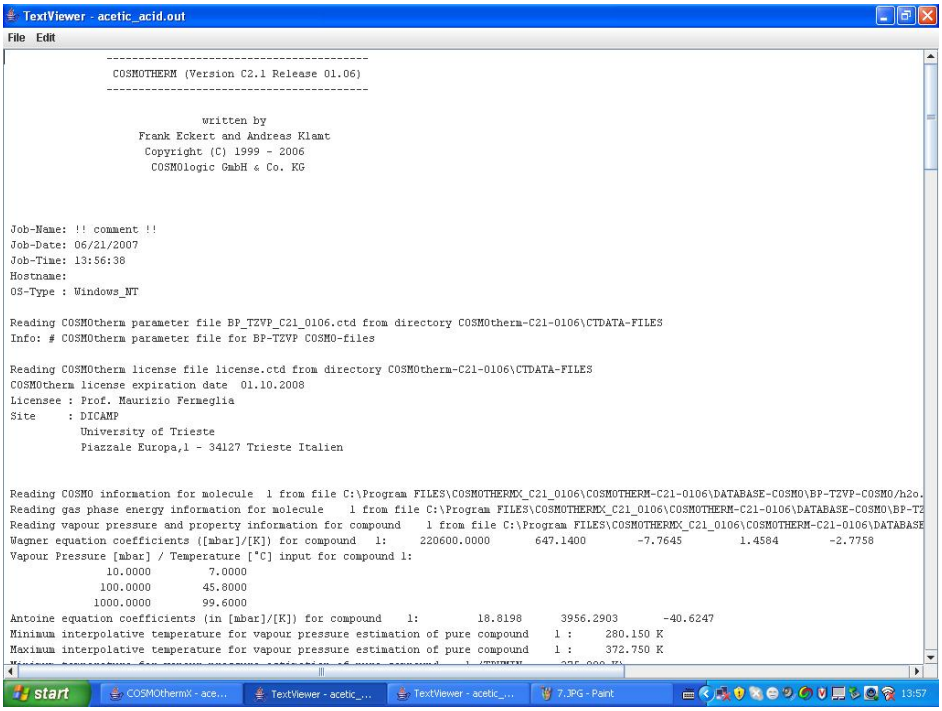


Run the simulation

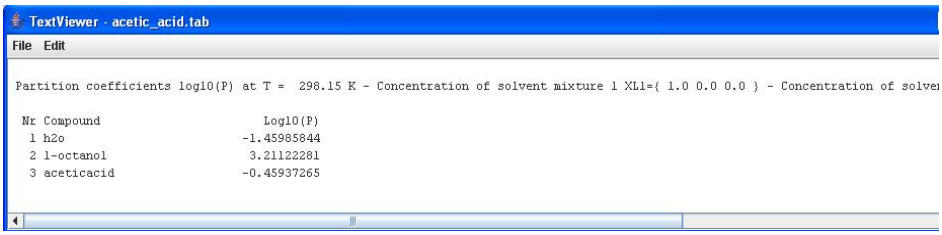


Analyze the results

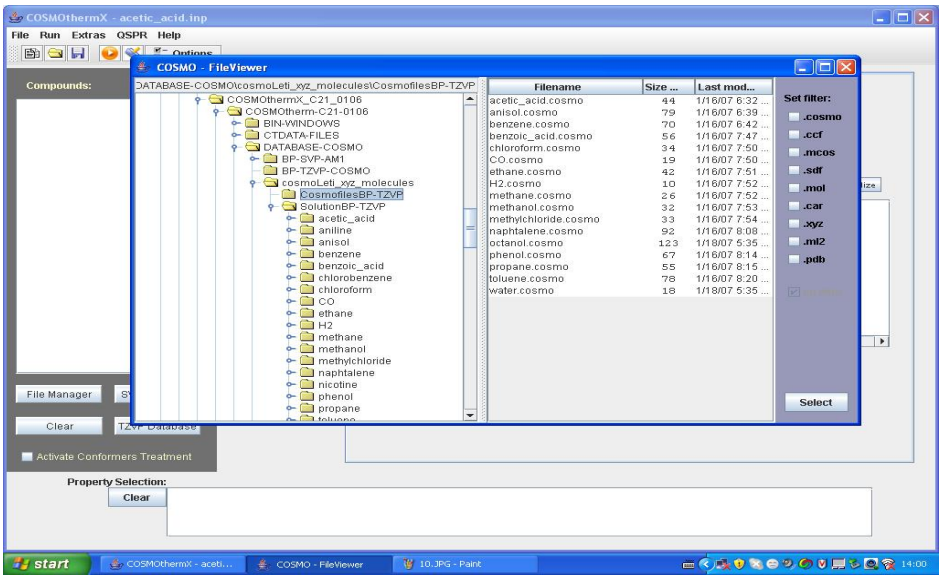
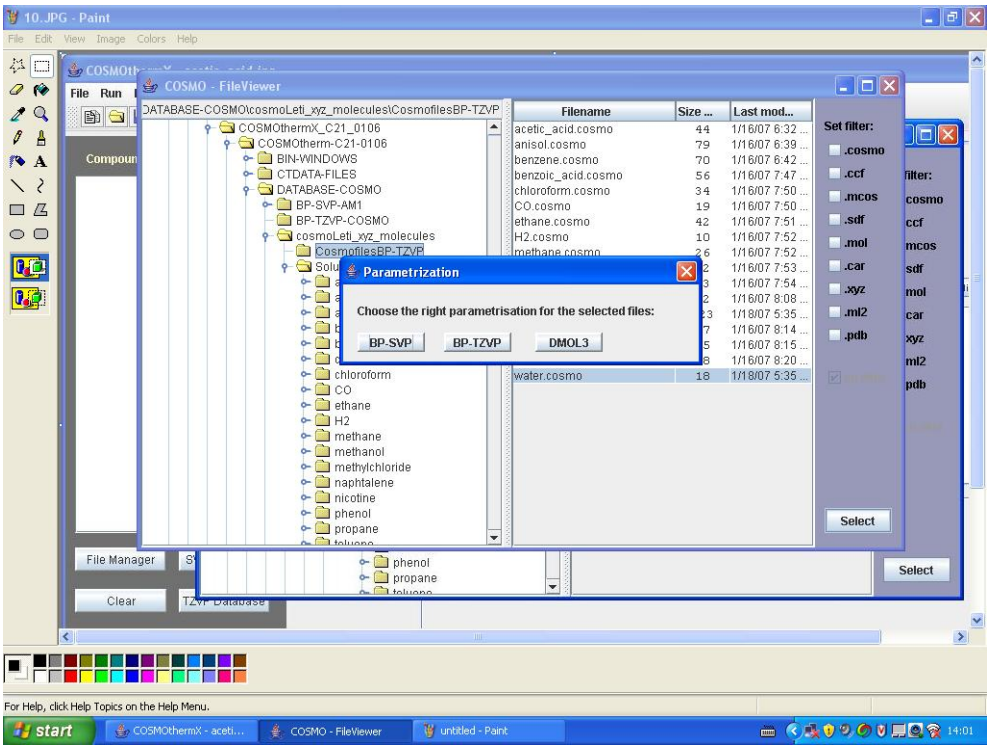
*.out file



*.tab file



If the substances (*.cosmo files) are not present in the software data base they should be generated using other softwares and imported in COSMOTherm. In the following example the cosmo files have been generated using TURBOMOLE and Materials Studio softwares.



Choose the right basis set