

Impact of technological development, market and environmental regulations on the past and future performance of chemical processes

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

For the degree of
Doctor of Technical Sciences

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Zurich 2003

Diss. ETH No. 15159

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Prof. Konrad Hungerbühler for giving me the opportunity to conduct doctoral studies under his supervision. It has been a great pleasure to work and develop as a person under his supervision.

I must also thank Prof. Gregory J. McRae because without his support I would have not started an international carrier. I would also like to thank him for letting me participate in nearly one year of great experiences at MIT and introducing me to Prof. Hungerbühler.

I thank Dr. Ulrich Fischer for the time he spent helping me, not only with the writing of my thesis but solving many bureaucratic issues as well.

I would like to express my gratitude to Prof. Masahiko Hirao for his help and significant input in environmental assessment. I must also thank him for the great and fruitful time spent when I visited Japan.

If I look back on all my colleagues I have to thank Dr. Laurent Cavin, Dr. Eric Uerdingen and Dr. Volker Hoffmann for fruitful and interesting discussions about almost any kind of subject, but especially for their friendship and support. I must also thank Joana Martinez and Antonio Manen for their excellent job carrying out their diploma thesis and whose effort is also expressed as a result in this thesis; Fabio Wegmann and Dr Andreas Zogg for all their many environmental arguments, and Shailesh Shah for reminding me of some safety issues about hot food.

If I look back on my friends I would like to thank Oscar Carrillo for always keeping in touch and for the good times we have spent in Barcelona, Pep Vicente for being able to live with me during the time I lived in Barcelona, Sergio Vinagre, Luis Miguel Santiso, Juan Solis and many others. I would also like to thank Dr. Anny Rosell for her help when I first arrived at ETH.

But in particular I want to thank Agnes Knorr for all her help, support, friendship and love we have shared while completing this thesis. I truly think that without her support it would have been very difficult to finish this thesis.

Finally I want to acknowledge my parents and sisters, their total support and understanding allowed me to be able to develop as a person and to meet this entire group of interesting people

ABSTRACT

With its products used by virtually every other manufacturing industry, the chemical industry is one of paramount importance. In recent years, numerous changes have affected the way business is carried out in the chemical industry. New regulatory requirements, globalization, shorter product life cycles, and emerging technologies, among others, are forcing this industry to re-establish its statements and objectives. Chemical industry in the past has been characterized by static and inflexible responses to external influences. The effect of economy of scale converted many specialty chemicals into commodities thereby forcing a reduction of manufacturing cost and shrinking profits. This had a dual effect: only those technologically competitive processes would prevail and from that moment on their flexibility to affront external influences was reduced. This combined effect forced the chemical industry to act reactively to change, thereby losing the competitive advantage of acting proactively.

This thesis aims to study the influences of technology, market situation, and environmental regulations upon a chemical process during its lifetime. With knowledge of the major driving forces, resources can be allocated more wisely, and a traditionally reactive action can be transformed into a proactive one. Of course no one can predict the future, but proactive action based on the knowledge and experience gathered to current date will better position the chemical industry to face incoming and unknown events. This study was based on three major aspects: On a first level, the evolution of the technology for the production of hydrogen cyanide and its precursors was studied. On a second level, the evolution of the market situations regarding prices and demand along with the evolution of environmental regulations were studied. A new Dynamic Life Cycle Analysis (DLCA) method was developed to obtain the evolution of the environmental performance. The evolution of prices was used to obtain the economic performance of the process over time.

Results allowed investigating the relationship economy-environment and the influence of environmental regulations and the market situation on the chemical process of study. These investigations resulted in the conclusion that technological improvements in the process, besides improving the economic performance, also produce a higher impact on the environmental performance of the process than the environmental regulations.

As a final step, the information obtained from the evolution of the economic and environmental performance was used in addition to state of the art retrofit methodologies to identify potential process improvements. The combined information obtained from the retrofit analyses and the evolution of the process allowed identification of possible process alternatives better positioned towards future changes in market or in environmental legislation.

ZUSAMMENFASSUNG

Mit dem Breiten einsatz chemische Produkte in allen Produktionssektoren kommt der Chemischen Industrie eine besondere. Eine grosse Anzahl von Veränderungen haben in den letzten Jahren die Geschäftsabwicklung der chemischen Industrie beeinflusst. Unter anderem zwingen neue regulatorische Anforderungen, die Globalisierung, kürzere Produktlebenszyklen und neu aufkommende Technologien diese Industrie dazu, ihre Aussagen und Ziele neu zu formulieren. Die Reaktion der chemischen Industrie auf äussere Einflüsse wurde früher als statisch und unflexibel charakterisiert. Der Effekt der erhöhten Wirtschaftlichkeit durch Massenproduktion zwang die Spezialitätenchemie zu tieferen Produktionskosten und zu sinkenden Gewinnen. Dies hatte eine doppelte Wirkung: es könnten sich nur die technologisch konkurrenzfähigen Herstellungsprozesse durchsetzen, aber deren Flexibilität, externen Einflüssen zu trotzen, wurde gleichzeitig reduziert. Dieser kombinierte Effekt zwang die chemische Industrie, reaktiv auf Veränderungen zu reagieren, unter Verlust des wettbewerblichen Vorteils der proaktiven Handlung.

Diese Doktorarbeit will den Einfluss der Technologien, der Marktsituation und der Umweltgesetzgebung auf einen chemischen Prozess während dessen Lebensdauer untersuchen. Ressourcen können mit dem Wissen der hauptsächlichen Triebkräfte effektiver verteilt werden und eine traditionell reaktive Handlung kann in eine proaktive umgewandelt werden. Natürlich kann die Zukunft nicht vorhergesagt werden, aber eine proaktive Handlung, basierend auf dem bis heute gesammelten Wissen und der Erfahrung, wird der chemischen Industrie eine bessere Ausgangslage geben, zukünftige und wenig bekannte Herausforderungen anzugehen. Diese Studie basiert auf drei Aspekten: In einer ersten Stufe wird die Technologieentwicklung der Herstellung von Blausäure und dessen Vorläufern untersucht. In einer zweiten Stufe wird die historische Entwicklung der Marktsituation in Bezug auf Preise und Bedarf zusammen mit der Entwicklung der Umweltgesetzgebung untersucht. Eine neue *Dynamic Life Cycle Analysis* (DLCA) Methode wurde entwickelt um die Evolution der Effizienz von Umweltschutz-Massnahmen zu untersuchen. Die Preisentwicklung wurde verwendet, um die ökonomische Leistung des Prozesses während der betrachteten Zeit zu beurteilen.

Die Resultate erlauben die Untersuchung der Ökonomie-Umwelt-Beziehung und des Einflusses der Umweltgesetzgebung sowie der Marktentwicklung auf den betrachteten chemischen Prozess. Diese Untersuchungen resultierten im Befund, dass technologische Fortschritte des Herstellungsprozesses zu Verbesserungen der ökonomischen Leistung einen höheren Einfluss auf die Verringerung der Umweltbelastung durch den Prozess ausübten als die Umweltgesetzgebung.

Schlussendlich wurden die Informationen der ökonomischen und ökologischen Effizienz zusammen mit modernsten *Retrofit* Methoden

angewendet, um potentielle Prozessverbesserungen zu identifizieren. Die kombinierten Erkenntnisse der *Retrofit* Analyse und der Prozessentwicklung erlaubten, mögliche Prozessalternativen zu identifizieren, die gegenüber kommenden Veränderungen des Marktes oder der Umweltgesetzgebung Vorteile bieten.

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1.1 Current challenges and opportunities in modern chemical industry

In recent years numerous changes have affected the way business is done in the chemical industry. New regulatory requirements, globalization, shorter product life cycles, and emerging technologies among others are forcing this industry to re-establish its statements and objectives. Buy-outs and mergers have in some cases resulted in considerable staff reductions. Simultaneously, there has been a drive to increase productivity and reduce costs. Now more than ever, there is a need for tools which enable chemical manufacturers to meet increasingly complex and stringent regulatory requirements while keeping material, staff and equipment costs low and overall productivity high.

On the other hand, there has been a persistent decline in the favorability of the chemical industry over the past 20 years despite efforts by the industry to improve environmental performance. The chemical industry assumes that the facts on their improved environmental performance speak for themselves, but this is not the case.

The chemical industry must deliver continuous improvement in environmental performance and must ensure that it captures the reputational benefits of that improved performance. In the 20th century it was enough for the chemical industry to show that its activities were legal and profitable. In the 21st century the industry needs to prove to society that it can be legal, profitable, and environmentally and socially responsible, and so far it has not completely succeeded in this task.

It seems clear that in order to meet all these evolving challenges, innovation is required. Technological change must be the driving force of the evolution of chemical processes introducing proactively and responsibly environmental, social and economic objectives.

1.2 Facing decision making

Decision making is a fundamental design activity. Exploring needs, setting requirements, and evaluating designs all depend on translating complex information into a form that will result in successful decisions. Achieving sustainable decisions is a very difficult task, not only because trade-offs between different objectives (economic, environmental, and social) must be made, but also because sustainable decisions must also to remain sustainable in a near future. The lack of tools available aiding decision makers to achieve present and future sustainable decisions has been the major motivation of this study. Decision making is critically affected by the information available; this work aims to develop a methodology that provides information about the economic and environmental performance of a production process over time in the past, and its potential improvements for the future.

1.3 Thesis statement

The objective of this thesis is to develop a methodology that will allow decision makers in the chemical industry to better allocate resources. This objective is achieved, first by providing a structured methodology to study the influences of market situation, environmental regulations and technological development on the environmental and economic performance. Figure 1.1 shows how the different driving forces of the chemical industry are related. In a second phase, this information used in concert with state of the

art retrofit methodologies serves to identify potential improvement parts of the chemical process.

The information obtained from the study of the influence of market, environmental regulations and technology on the evolution of chemical processes also shows the interaction between these three key aspects. This interaction and its results are of high value for policy makers since it shows the major influences on the performance of chemical processes. This issue later, discussed will show for example what was the real effect of environmental regulations and their role as a driving force for the environmental and economic performance of chemical processes.

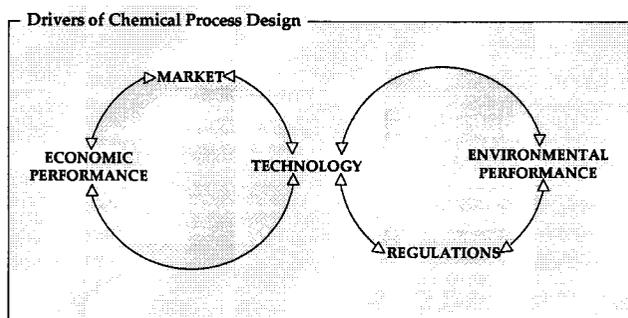


Figure 1.1: Relationship among the different driving factors of the chemical industry

1.4 Outline

Figure 1.2 shows how this thesis has been divided into two major parts and 9 chapters. After the introduction in chapter one, the first section of the thesis is presented. The objective of this section is to obtain the economic and environmental assessment of the hydrogen cyanide production by means of the BMA process over the period of study. First, the methodology proposed is introduced in chapter two. Chapters three, four, and five present the analysis of the evolution of technology, market, and environmental regulations.

Finally, in chapter six the results from the methodology are presented. This first section introduces a new method to obtain the environmental performance of a process over time, the dynamic life cycle assessment.

In the second section (chapter seven), the information obtained from the first section together with state of the art retrofit methodologies presents process alternatives and potential improvements to the BMA process.

Chapter eight presents the conclusions of the thesis and chapter nine indicates directions for future research.

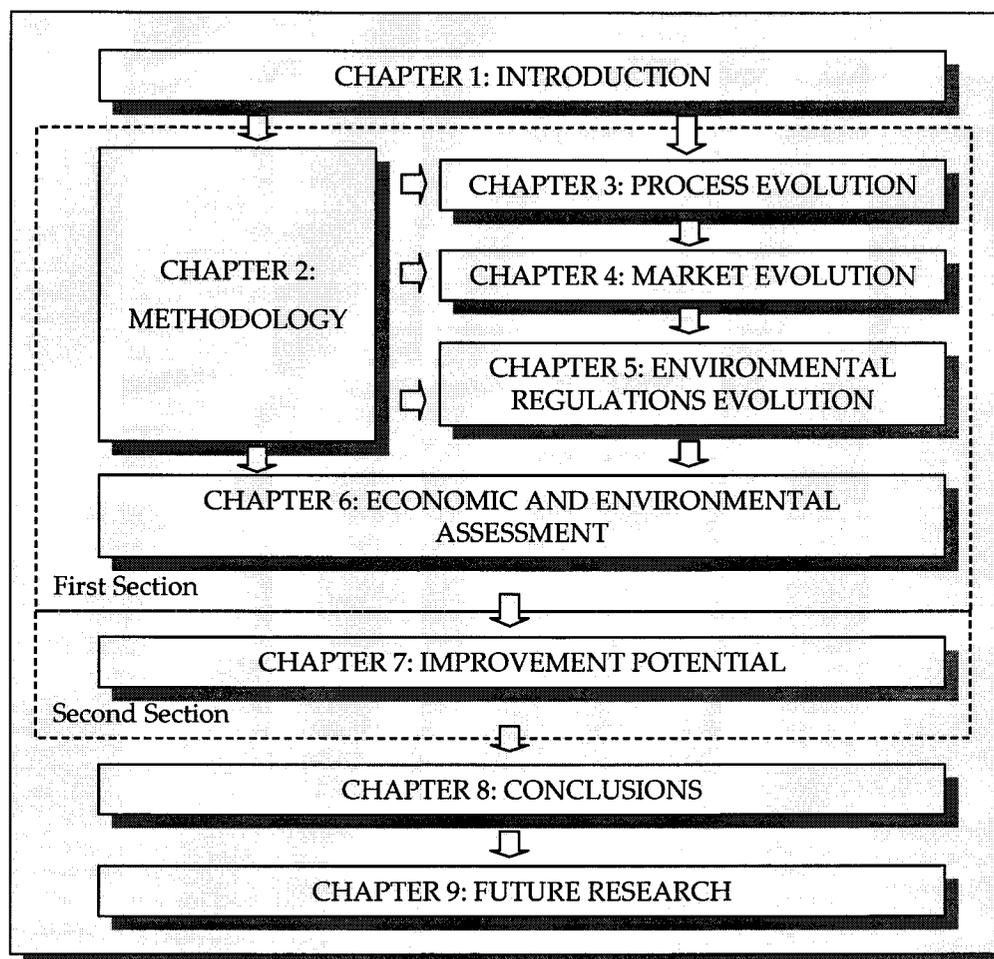


Figure 1.2: Outline of the thesis

1.5 Hydrogen cyanide production

The production of hydrogen cyanide is the case study chosen for this thesis. The selection of this case study was motivated by a number of factors. First, this process is of economic importance: HCN is a raw material for basic construction materials used in the housing and automotive industries. Second, the longevity of the hydrogen cyanide technology allows a historical study of the process. Third, the availability of the data, HCN is produced from basic materials that have been already documented in ecological databases. Fourth, the extreme toxicity of HCN provides a perfect framework for environmental studies, and, finally, the experience already gathered in the research group [1, 2], makes hydrogen cyanide a suitable case study for this research.

Besides the production of acrylonitrile in which hydrogen cyanide is produced as a by-product, there are three major processes for the production of HCN depending on how the heat required for the reaction is supplied, Andrussow, Fluhomic, and Bläusaure-Methane-Ammoniak (BMA).

Andrussow Process

The Andrussow process was developed around 1930 by L. Andrussow of I.G. Farben [3-6]. The Andrussow process is the most important process in terms of volume of production. In this process, an excess of natural gas is mixed with ammonia and air in specific proportions in order to combust this excess and provide the required heat for carrying out the reaction [7]:



The gas mixture is passed over a platinum–rhodium or platinum–iridium gauze [8] catalyst; temperature and upper flammable limit should be monitored carefully [9] [10]. The reaction takes place at 1000 °C, atmospheric pressure, and with a gas velocity through the catalyst zone of about 3 m/s. To avoid decomposition of HCN, the effluent gas from the reactor is quickly cooled in a waste-heat boiler, which produces the steam used in the process. Unreacted ammonia is absorbed by either sulfuric acid or a monoammonium/diammonium phosphate solution. The hydrogen cyanide is separated from methane, hydrogen and other gases by absorption with water and is finally distilled obtaining required purity.

Fluohmic and Other Processes

In the Shawinigan process, hydrocarbon gases react with ammonia in an electrically heated fluidized bed of coke. The process, sometimes called the Fluohmic process, was developed in 1960 by Shawinigan Chemicals [11] [12-14], now a division of Gulf Oil Canada. In a circular reaction cavity constructed from alumina and silicon carbide, the mixture of ammonia and hydrocarbon (N:C-ratio slightly > 1) passes through a fluidized bed of coke, heated by electrodes imbedded within. The chemical reaction is similar to the methane – ammonia process, but no catalyst is required and temperatures are kept above 1500 °C. Propane is usually the main feedstock. The reaction can be described as:

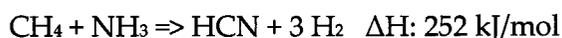


Unreacted feed gas is almost completely decomposed into its elements. The control of bed coke size is an important operating parameter. The gas is further cooled and enters the absorption equipment where HCN is removed. The residual gas, mostly hydrogen, can be used for other chemical processes.

In practice, at least 85 % of the ammonia and up to 94 % of the hydrocarbon are converted to hydrogen cyanide. Other processes have been studied in the past, where no catalyst was used [15], [16], [17]. Recent patents concern the production of HCN using other type of raw materials such as methanol and nitrogen oxides, among others [18], [19], [15].

BMA Process

The basis of the Degussa BMA (Bläusaure-Methane-Ammoniak) process is the formation of hydrogen cyanide in the absence of oxygen [20-32].



The endothermic reaction requires temperatures above 1200 °C, and is performed in externally heated alumina tube bundles, which are coated with a thin layer of a special platinum catalyst [21, 29]. A mixture of ammonia and methane (natural or purified gas with a content of 50 – 100 vol % methane) is passed through the tubes and quickly heated to 1300 °C at normal pressure. After leaving the reaction tubes, the gas produced is cooled to 300 °C by passage through a water-cooled chamber made of aluminum. The subsequent reaction steps, ammonia absorption and hydrogen cyanide isolation, are similar to those of the Andrussow process.

Market Figures

Hydrogen cyanide production is primarily accomplished through either the Andrussow or the BMA process (Degussa). The Andrussow process accounts for 74 percent of the total U.S. HCN production [33, 34]. The BMA process is used at only one facility, which accounts for 3 percent of U.S. HCN

production. Hydrogen cyanide is also produced as a byproduct in the manufacture of acrylonitrile by the ammoxidation of propylene (Sohio technology). The Sohio process accounts for the remaining 23 percent of HCN production in the U.S. [33, 34]. In Western Europe these figures are similar although the BMA process market share increases up to 15% due to the fact that Degussa's main plants are located in Europe.

In Table 1.1 hydrogen cyanide production facilities in the US and their capacities are listed according to data obtained from Chemexpo [33]. In the USA only one plant from Degussa is producing hydrogen cyanide by means of the BMA process.

November 23, 1998	
PRODUCER	CAPACITY*
BP Chemicals, Green Lake, Tex. (B)	100
BP Chemicals, Lima, Ohio (B)	45
Ciba, St. Gabriel, La. (P)	90
Cyanco, Winnemucca, Nev.	48
Cytec Industries, Fortier, La. (P)	65
Degussa, Theodore, Ala. (P) BMA	76
Dow, Freeport, Tex. (P)	20
DuPont, Beaumont, Tex. (B)	60
DuPont, Memphis, Tenn. (P)	220
DuPont, Orange, Tex. (P)	320
DuPont, Victoria, Tex. (P)	400
FMC, Green River, Wyo. (P)	33
Rhone-Poulenc, Institute, W.Va. (P)	15
Rohm and Haas, Deer Park, Tex. (P)	200
Solutia, Alvin, Tex. (B)	60
Sterling, Texas City, Tex. (B)	75
Total	1,827

Table 1.1: US hydrogen cyanide producers.

*Millions of pounds per year of HCN as primary product(P) and as a byproduct of acrylonitrile production(B) [33].

Consumption [35], [36], [37], [38]

Overall demand of hydrogen cyanide increases at a rate of about 2% in the period of 1990-1999. Due to its toxicity, hydrogen cyanide is usually consumed at its site of production. Figure 1.3 shows major hydrogen cyanide uses.

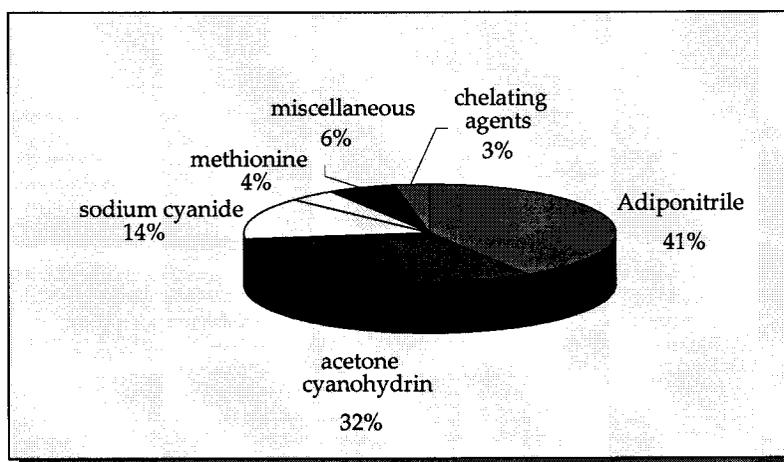


Figure 1.3: Major hydrogen cyanide consumption in 1994 in the US.

- Adiponitrile

About 41% of the hydrogen cyanide consumed in the US is used in the manufacture of adiponitrile. Adiponitrile is manufactured in the US by DuPont and Monsanto, however, the DuPont process is the only one that uses hydrogen cyanide with on-site HCN production facilities. All the adiponitrile produced is used in the manufacture of nylons.

-Acetone cyanohydrin

Acetone cyanohydrin represents the second largest US end use for hydrogen cyanide consuming around 32%. Acetone cyanohydrin is used for methacrylate production.

-Sodium cyanide

US sodium cyanide manufacture was the third largest consumer of hydrogen cyanide in 1994. Sodium cyanide is the cheapest product that can be obtained from hydrogen cyanide so its production depends on the price of the other products.

-Methionine

About 4% of the hydrogen cyanide consumed in 1994 was used to produce methionine and analogs. Methionine is the largest synthetic amino acid in commercial production in the US. Methionine is used for poultry feeds.

-Chelating agents

Chelating agents of the polyamine-polybasic acid type are made from amine, formaldehyde and hydrogen cyanide. Major markets for chelating agents are in industrial water treatment, soaps and cleaning formulations.

-Cyanuric chloride

Cyanuric chloride is produced from cyanogens chloride, which is made from hydrogen cyanide and chlorine. About 3.5% of the hydrogen cyanide produced in the US in 1994 was used for the manufacture of cyanuric chloride. It is used for herbicides, dyestuffs and optical brighteners. The chlorine agents may create health problems that may result in an uncertain future for this end use of hydrogen cyanide.

-Other

Other end uses of hydrogen cyanide are nitrilotriacetic acid salts used as detergents, synthetic lactic acid, analgesics such as ibuprofen and naxopren.

Summary

This chapter serves as an introduction to the current situation of the chemical industry. It states the problem situation and explains the methodology proposed to tackle this problem. A general introduction to the production and uses of hydrogen cyanide is presented to establish a framework for the BMA case study.

CHAPTER 2 -METHODOLOGY

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2.1 Introduction

Decision making is a fundamental design activity. Exploring needs, setting requirements, and evaluating designs all depend on translating complex information into a form that will result in successful decisions. Achieving sustainable decisions is a very difficult task not only because trade-offs between different objectives (economic, environmental, and social) have to be made. Sustainable decisions have also to remain sustainable in a near future. The lack of tools towards aiding decision makers to achieve present and future sustainable decisions has been the major motivation of this work. Decision making is critically affected by the information available; this work aims to develop a methodology that provides information about the economic and environmental performance of a production process over time in the past and combine it with state of the art retrofit methodologies to obtain the potential improvement of a chemical process.

Obtaining the economic and environmental performance of a process is a difficult task affected by the information available and the methods used for the evaluation. Economic performance evaluation tends to be a straight forward calculation based on prices that affect the cost/income economic functions. Environment evaluations on the other hand do not have a standard calculation procedure and results may vary depending on the method or the data used. In this direction Life Cycle Assessment (LCA) is a method to standardize the environmental evaluation of a process. This method is based on the overall emissions of all the processes involved in the production, in this case of a certain chemical. Figure 2.1 shows the LCA of the hydrogen cyanide production. These emissions can be classified into different groups depending on their specific impact (e.g. global warming or acidification) and are then aggregated into a single value that represents the environmental performance.

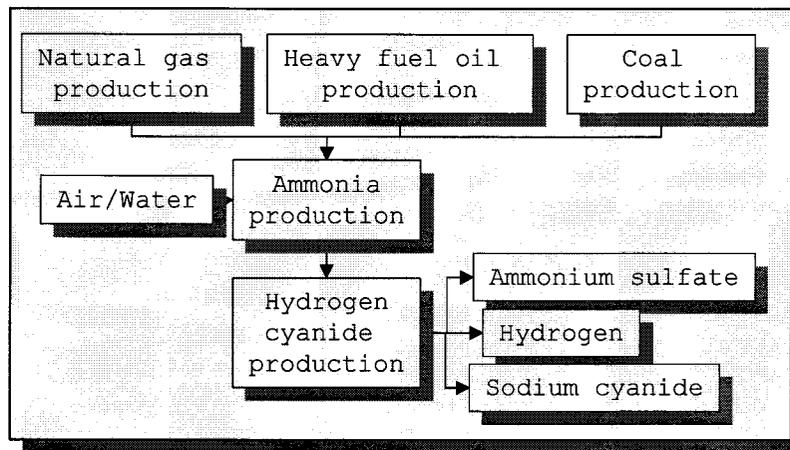


Figure 2.1: Processes involved in the production of hydrogen cyanide.

The introduction of time as a new variable makes evaluation even more complicated. Time influences economic calculations because the process technology changes over time and because prices are affected by the market situation. In order to obtain reliable comparisons of different time periods one should include the effect of inflation. These problems can be resolved because evolution of prices and inflation rates can be found in literature, and the technological performance can be obtained from process data by using process simulators such as ASPEN PLUS[®] from ASPENTECH. Environmental performance evaluation is even more complicated. Although emissions can easily be obtained from mass and energy balances in a similar way, a special problem arises when trying to aggregate the different emissions into one single score, since these aggregations are based on a subjective perception of environmental problems and this perception changes over time.

2.2 Methodology overview

The methodology proposed to obtain the potential improvements of a process is based on four steps (see Figure 2.2). The first three are required to obtain the economic and environmental performance of a chemical process. The fourth step, then, is the combination of state of the art retrofit methodologies and the evolution of the economic and environmental performance to obtain potential improvements of the process.

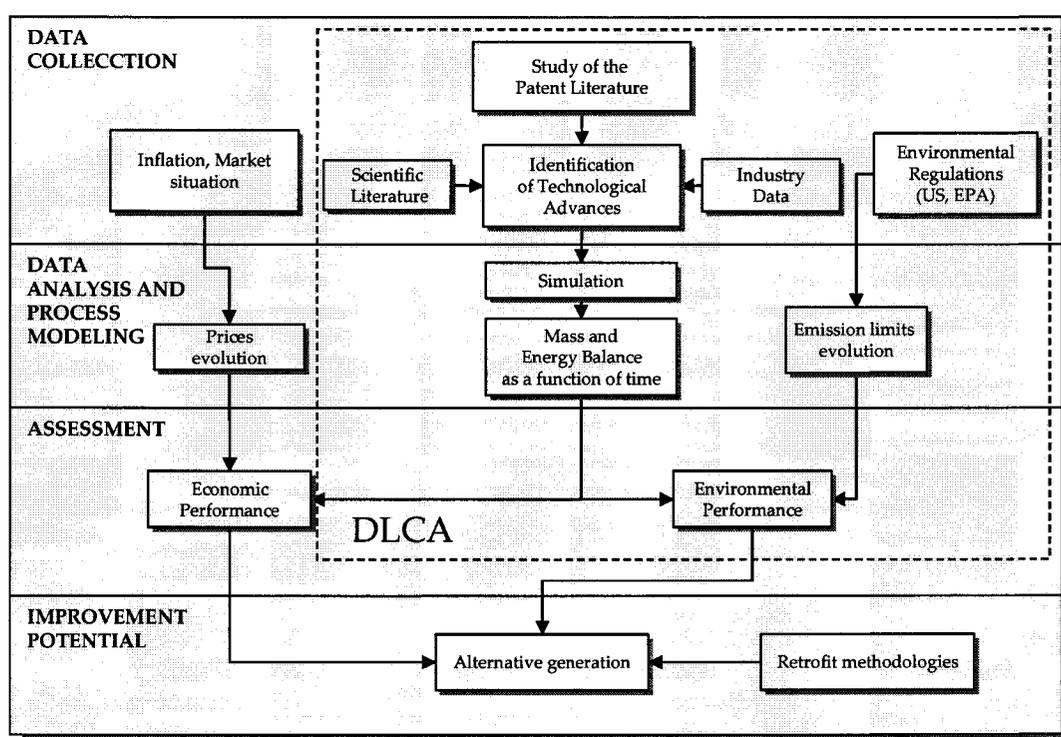


Figure 2.2: Methodology to obtain the economic and environmental performance of a process

In order to obtain the evolution of the environmental and economic performance, there are three steps and three inputs that must be taken into account. The inputs are the evolution of the environmental regulations, the evolution of the market and the evolution of the technology of the process. The steps are data collection, data analysis, and assessment. The data collection step identifies the technological advances of the processes involved

in the Life Cycle (LC) of the process from the study of patents, scientific literature and other sources of information such as industry data or personal communications. In this step, an analysis of the market situation based on the evolution of demand and inflation is also performed together with a study of the evolution of environmental regulations. In the data analysis and modelling step the technological advances are introduced into ASPEN PLUS® obtaining the evolution of mass and energy balances of the process LC over time. During this step emission limits are calculated and the evolution of the different prices affecting the economic calculations is obtained. During the assessment step emission limits, prices, and mass and energy balances over time are used to calculate the economic and environmental performance of the process over time. As a result of this methodology, one can define the Dynamic Life Cycle Assessment (DLCA) of a chemical process as the process to obtain the evolution of the environmental performance of a process over time.

In a final step the process is analyzed with state of the art retrofit methodologies and combined with the information obtained from the evolution of the environmental and economic performance to obtain potential improvements of the process.

For the study of the performance of a process there is a need to define the indicators that will give an idea of how profitable/non-profitable (in the case of economy) or how environmentally benign/malign (in the case of environment) a chemical process is. In order to evaluate the economic performance, indicators such as the net present value or the total income/cost per kilogram of product can be used, among others. These economic indicators are based on the mass and energy balances and the price of raw materials/products.

The evaluation of the environmental performance is more complicated: Although all indicators are based on the emissions produced, a problem arises when trying to aggregate emissions that have different effects on the environment. Aggregation is a very important step because it provides an absolute value of the environmental performance of a process instead of fractionating the results into different values that correspond to the different emissions. In the importance of aggregation resides its weakness. To this date, only scientific methods to aggregate emissions that have the same effect (the global warming potential index) exist. Subjective decisions must be made when aggregating the effect of different impact categories such as acidification or global warming. These subjective weightings are influenced mainly by the importance of the different effects during the period of study or the awareness of public opinion towards such environmental problems. The problem becomes even more complex when evaluating a process over time since the perception of the environment has dramatically changed over the last fifty years. It is required then to use the direct emissions as indicators since aggregation only leads to arbitrary results.

The problem can even be more complicated if trying to aggregate economic and environmental results into one single score, since one indicator is measured in monetary units and the other in eco-points or kilograms of a specific emission. This would be very helpful when comparing different processes, but until now a non-subjective method for such aggregation has not been defined. We propose that in order to offer more consistent proposals in the future we must learn from the past. Preferences and its results can be observed studying the evolution of the process. These decisions may help to develop a methodology that will merge economy and environment in a more rational way. The work presented here is a first step in the direction of obtaining such a method.

It can be appreciated that both environmental and economic performances of a process are influenced by process-dependent variables (mass and energy balances) and external-dependent variables (prices and environmental legislation). In the case of external variables, prices are defined by the market situation and environmental regulations are defined by the government and the public opinion. The process-dependent variables are the link between environment and economy. These variables are affected by one single effect : the technological evolution of the process.

2.3 Environmental evaluation (DLCA)

LCA methodologies were originally developed to create decision support tools for distinguishing between products, product systems, or services from the perspective of environmental impact. In chemical process design, LCA is used as a tool to compare different process alternatives [39], [40], [2].

The performance of a chemical process is influenced by many variables during its lifetime. The introduction of new technologies, changes in the market situation, and new environmental regulations, among others, are continually affecting environmental and economic results. In order to achieve decisions that remain sustainable in the future one must utilize tools that introduce time as a variable taken into account. This is the reason why the LCA scope for environmental assessment must be extended. Many efforts have been made in the field of generation of future scenarios [41], [42], [43]. The data supplied to such scenarios must be dynamic, and thus the introduction of dynamic inventories is required. LCA methodology research efforts are focused on obtaining inventories and the following impact assessment. The concept of dynamic life cycle analysis is relatively new and unexplored [44],[45]. The methodology proposed together with efforts from Hirao and collaborators [46] aims to define DLCA as the life cycle analysis in which time

(future or past) is considered as a variable affecting the inventory analysis and/or the impact assessment of the LCA framework (Figure 2.3).

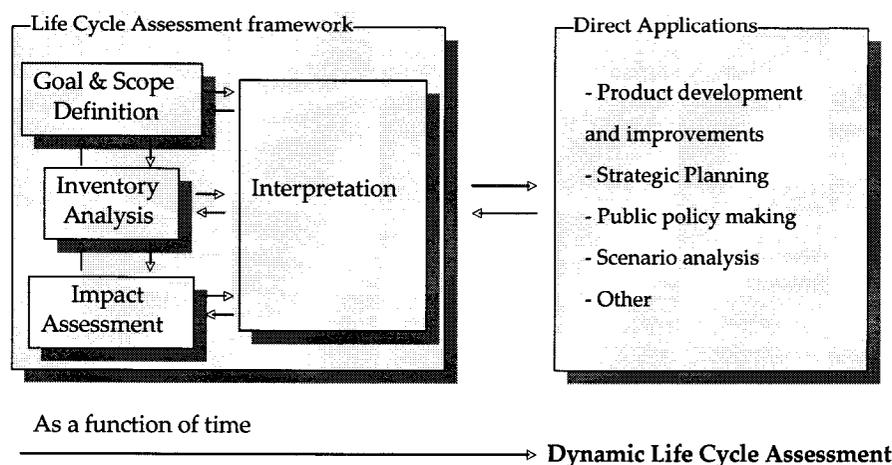


Figure 2.3: LCA framework and applications (according to ISO 14000)

The DLCA methodology as defined here is divided into four steps according to the LCA framework [47] (see Figure 2.4): goal and scope definition, inventory analysis, impact assessment, and interpretation. The goal of the study is to obtain the DLCA of the production of an intermediate chemical. During the inventory analysis, data regarding the technological evolution of the production process and evolution of the environmental regulations will be collected. The collected technical data of the process is analyzed using the process simulator software ASPEN PLUS®, obtaining an evolution of the mass and energy balances of the process. The emissions produced in the process are calculated from the mass and energy balances and the limits posed by the evolution of the environmental regulations. This evolution of emissions represents the inventory used. The impact assessment step analyzes this inventory and produces environmental indicators that can be used for further applications.

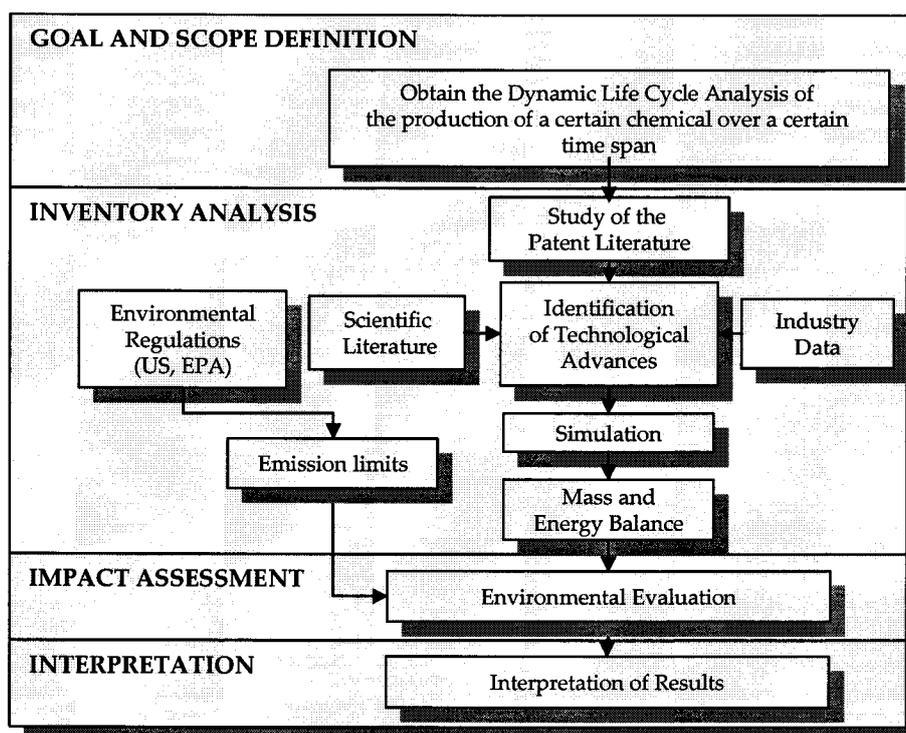


Figure 2.4: Methodology of the Dynamic Life Cycle Analysis (DLCA).

Goal and Scope Definition

The goal of the study is to obtain the DLCA of the production of hydrogen cyanide. Figure 2.1 shows a simplified process tree for the production of hydrogen cyanide. The figure demonstrates how the production of raw materials and energy are taken into account for life cycle calculations.

Inventory Analysis

For the inventory analysis of hydrogen cyanide production by means of the BMA process, the mass and energy balances as well as emissions must be considered. The mass and energy balances are obtained from the technological assessment over time of the processes involved, while emissions data are obtained from the evolution of environmental regulations.

The technological assessment of processes is a methodology that consists of two major steps: data collection and data analysis (see Figure 2.2). The data collection step contains three basic sources of information: patents, publications and industry data. As a result the major technological advances of a process as a function of time will be obtained. These advances serve as an input for the second step, the data analysis. During data analysis, technological advances are identified. The resulting evolution of technical parameters can be used for modeling the different process variants. These technological advances are assumed to be implemented as soon as they are discovered. This means that there is no time gap between discovery and implementation. In this study, the process simulator ASPEN PLUS® was used to model the process variants. As a result, mass and energy balances were obtained as functions of time. Mass and energy balances along with the emissions limits obtained from imposed environmental regulations serve as a basis for the environmental assessment of the production of hydrogen cyanide.

When studying the Dynamic Life Cycle Analysis of chemical processes, system boundaries and assumptions must be defined. In this study the analyses will be limited to the chemical processes themselves and no impact due to auxiliary processes such as transportation will be considered.

In the case of hydrogen cyanide, basic raw materials and energy sources are required. Natural gas is used as a raw material and as an energy source. Ammonia is obtained from air and from energy carriers (natural gas, coal or oil). This leads to the assumption that every major emission is related to the combustion of fossil energy carriers, in this case to the combustion of natural gas, coal and oil. It is also assumed that the combustion processes of coal, oil and natural gas themselves have not changed over time. What did change

were end of pipe technologies to achieve the regulations that appeared over the time period of study.

Hydrogen cyanide is quite a dangerous chemical but direct emissions to water or air were not considered due to the fact that they have always been minimal. Environmental impact as considered in this study will only come from the energy consumption and the raw material production which again requires energy consumption. Production of energy also requires certain energy consumption. It is assumed that this energy comes from the respective energy source produced. This means that for the production of natural gas the energy source is natural gas, and that the emissions from natural gas production are considered to come from natural gas combustion.

The final assumption is that to avoid complicating the problem, only air emissions will be considered. The reason for this assumption lies in the simplicity of obtaining air emissions data from simple calculations. Water emissions on the other hand would require further analysis that would complicate calculations considerably.

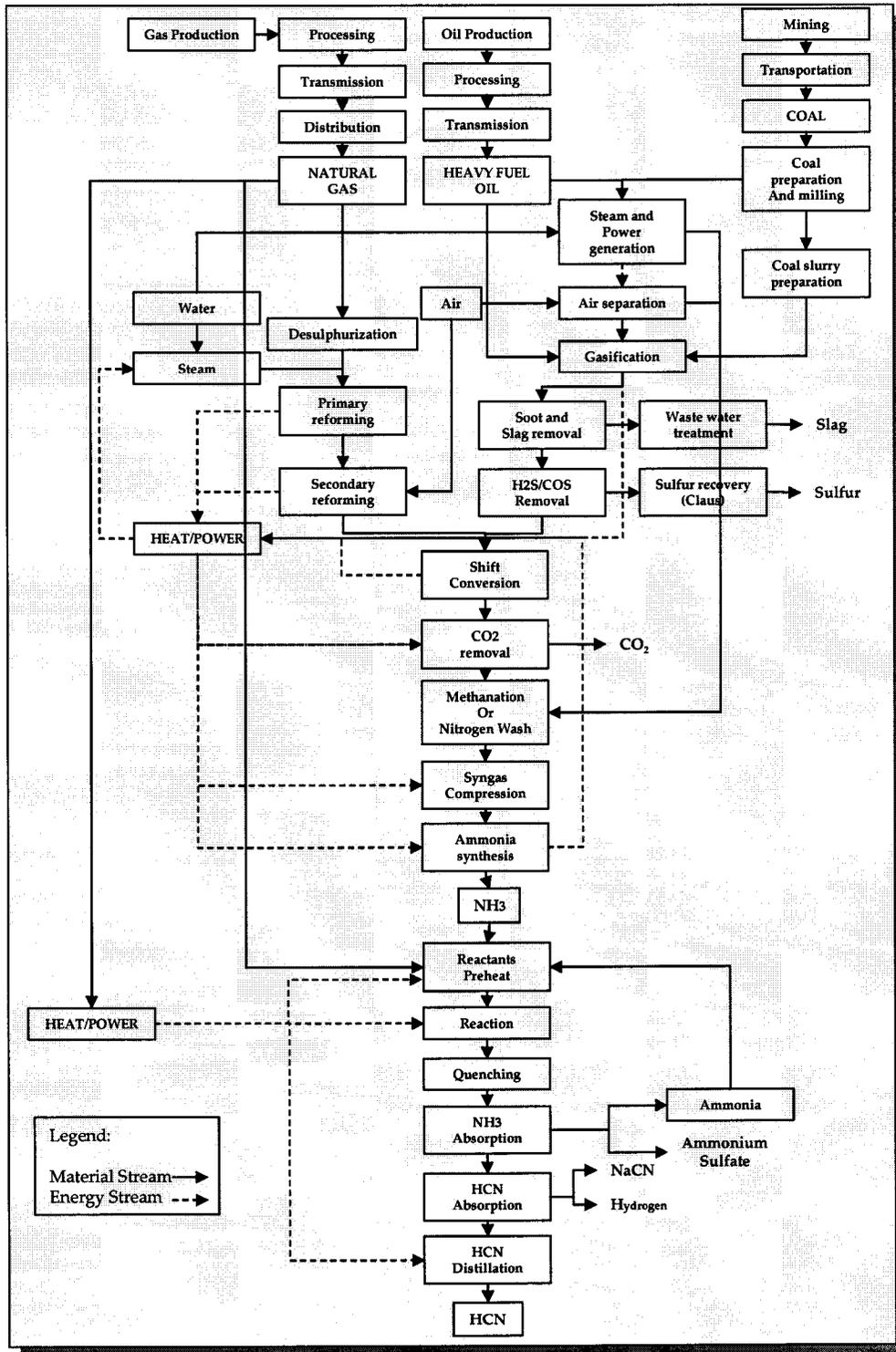


Figure 2.5: Processes considered within the DLCA of hydrogen cyanide production by means of the BMA process.

Once it is decided that only air emissions from the combustion of energy are to be considered, one should decide which indicators must be studied. For the emissions of energy combustion by means of natural gas, oil, and coal one should consider indicators that can be compared amongst themselves. For this study the indicators considered comprise nitrogen oxides (NO_x including N₂O), carbon monoxide (CO), carbon dioxide (CO₂), volatile organic compounds (VOCs, including CH₄), sulfur dioxide (SO₂), and particulate matter (PM) [48-51].

Impact Assessment

Environmental assessment is a critical procedure which is sensitive to the data used for its calculations. The problem increases when trying to evaluate processes over time. Current environmental evaluation tools only provide data for current processes. Changes in the perception of the environment over time generate a secondary problem: Since aggregation of all indicators into a single value based on scientific methods is complicated, direct emissions were used for the evaluation process.

Amounts of energy and raw materials required for each process are employed to obtain the emissions data and are added up to obtain the overall emissions of hydrogen cyanide production. Emissions of CO₂, NO_x and VOC are aggregated into one impact category, the global warming potential (GWP) gases. This aggregation is possible due to the fact that it is based on purely scientific methods that define equivalences between the compounds.

Interpretation

The results from the impact assessment are obtained in two forms; on the one hand emissions represented by different indicators and on the other hand the aggregation of some of these indicators into a single value, the global

warming potential. These results are obtained as an evolution of time in the period of study and represent the dynamic life cycle analysis of the process. These results reflect the influence of technology and environmental regulations on the environmental performance of the process.

2.4 Economic evaluation

In order to obtain an objective view of the historical evolution of chemical processes, one must bear in mind the influence of the market evolution. In contrast with environmental evaluation, market evaluation has always played a very important role in the performance of chemical processes. Many methodologies towards economic evaluation have been developed [53, 54]. Time has always been included looking towards the future as a factor to adjust the payback of the investment. In this study time plays a different but similar role. The role of the interest rate used for future calculations is replaced by the role played by the inflation-demand. Inflation rates on the oil prices are available in several sources of literature [53, 54] and can easily be extrapolated to the hydrogen cyanide case study. Simultaneously there exist fluctuations in price due to offer-demand of raw materials, products and energy. This price information can be obtained from several sources such as consulting companies [34, 57-60], governments, major producer associations [55-59] and public institutions such [60-65]. The inflation factor allows translation of the market fluctuations into monetary units of today which allows comparison between processes at different points in time.

Once the market analysis has been performed one must face the economic assessment of the process. There are several appropriate indicators available for performing economic evaluations; most of them include the fixed investment cost such as the net present value described in Turton [52] or

Biegler [66]. Net present value is an economic indicator that analyzes the whole lifetime of the investment in order to compare alternatives. The net present value does not adjust to analysis of the economic performance since the plant and most of the equipment remains the same when a technological improvement is introduced. A different indicator must be established. The economic indicators used for this evaluation are expressed as the total annualized cost per kilogram, TACK; total annualized income per kilogram, TAIK; and total annualized profit per kilogram, TAPK.

The TACK comprises the direct manufacturing costs and the costs of investment. Direct manufacturing costs considered are: raw materials, utilities, wastewater treatment, maintenance, personnel and catalyst cost. The fixed costs include all costs associated with the construction of a facility for the production of the required amount of hydrogen cyanide at certain point in time. Maintenance and depreciation are finally added to obtain the final TACK value. The Total Annualized Income per Kilogram TAIK is obtained by addition of sales of the main product and byproducts at their respective market price.

Net present value will be used to evaluate the alternatives generated in the potential improvement step. This is due to the fact that time (as does interest rate) starts playing an important role due to the fact that new equipment may need to be purchased.

2.5 Improvement potential

Chemical process design currently focuses on the improvement of the performance of chemical processes. It seems clear that the starting point for possible improvements is the state of the art of existing technology. Several

efforts have been made to develop structured methodologies for the retrofit of existing processes with different objectives [67-72]. These methods analyze the existing process and come up with different alternatives or possible improvement potential. As described in previous sections, the technological evolution of processes is a very important source of information that should be included in retrofit process. This chapter aims to merge information obtained from the technological assessment with the existing retrofit methodologies. Information obtained from chapters 3 to 6 will be combined with a novel retrofit methodology developed by Uerdingen [73] in order to obtain further improvement potential of the BMA process.

Summary

This chapter describes the methodology proposed to introduce time as a new process design variable. The methodology is divided into two major parts, the first part is oriented to extract the maximum information of the evolution of the technical, environmental and economic performance of the process. The second part focuses on the evaluation and generation of retrofit alternatives. This chapter serves as a link between the different chapters of the thesis.

CHAPTER 3 PROCESS EVOLUTION

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3.1 Introduction

In this chapter the assessment of the processes involved in the production of hydrogen cyanide is presented. As a first step the technological assessment of each specific process is performed. Major technological advances are identified as an evolution of process parameters. The resulting evolution of process parameters can be used for modeling the different process variants. These technological advances are assumed to be implemented as soon as they are discovered. This means that there is no time gap between discovery and implementation. In this study the process simulator ASPEN PLUS® was used to model the process variants. As a result mass and energy balances as functions of time are obtained.

3.2 Hydrogen cyanide process (BMA)

The basis of the Degussa BMA process is the formation of hydrogen cyanide in the absence of oxygen [74-77]. Figure 3.1 shows the major steps in the BMA process.

The endothermic reaction requires temperatures above 1200 °C, and is performed in externally heated alumina oxide tube bundles which are coated with a thin layer of a platinum catalyst [21, 28, 32]. A mixture of ammonia and methane (natural or purified gas with a content of 50 – 100 vol % methane) is passed through the tubes and quickly heated to 1300 °C at normal pressure. After leaving the reaction tubes, the product gas is quenched to 300 °C by passing through a water-cooled chamber made of aluminum. After quenching the reaction gases, rapid absorption of ammonia must be performed to avoid polymerization. Ammonia absorption can be performed by using of a monoammonium phosphate solution, where the ammonia reacts to form

diammonium phosphate [78, 79]. To complete the ammonia loop the absorption solution is boiled and the released ammonia is condensed and recycled to the reactor, while the monoammonium phosphate solution is regenerated and reused. A second process option is to employ a solution of sulfuric acid which reacts with the ammonia to produce ammonium sulfate [80], which in turn is crystallized and sold as a by-product.

Hydrogen cyanide is separated from methane, hydrogen, and other gases by absorption with water and is finally distilled to its required purity (99%). The mixture of non-absorbed gases (methane, hydrogen and hydrogen cyanide) is passed through a solution of caustic soda to remove the remaining hydrogen cyanide, thereby obtaining sodium cyanide as a by-product. Hydrogen can then be combusted or further purified for other uses.

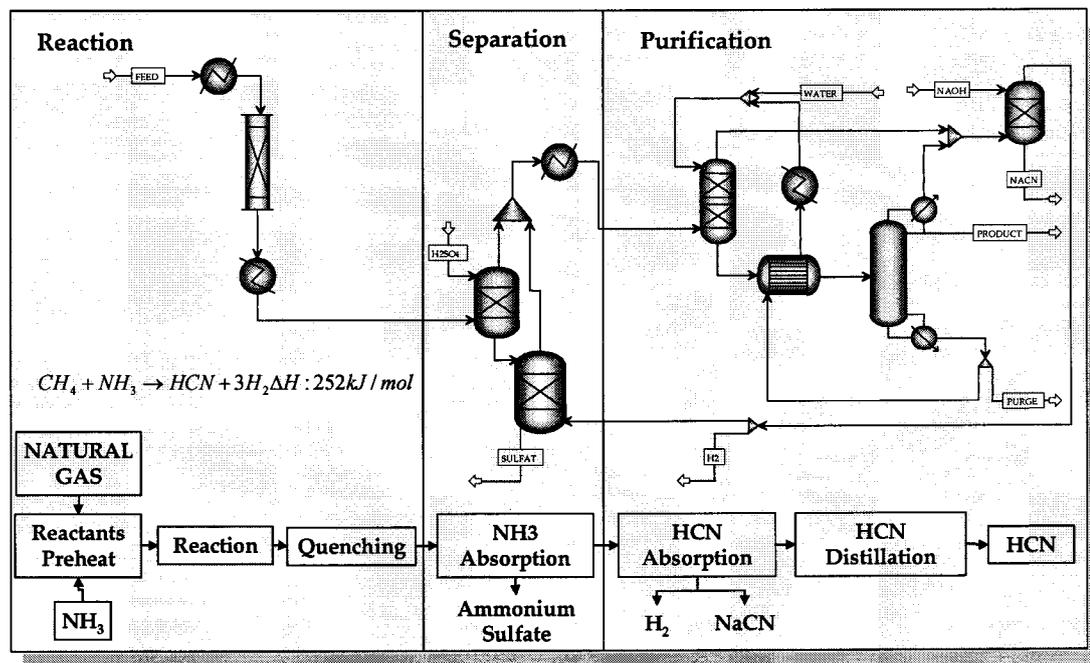


Figure 3.1: Process diagram of the BMA process.

The technological evolution of the BMA process has focused on the reactor and the following aspects: furnace, tubes and catalyst, raw materials, and finally energy. Other separation techniques were also studied but discarded because of technical or economic infeasibility.

3.2.1 Technology evolution

In order to perform the technological assessment of the BMA process several sources of information were considered. Patents, scientific publications and industry data were used to describe the chronological evolution of this chemical process. The study of patent literature was of high importance due to the required technical information and due to the fact that in this study there is no time lap between the discovery and implementation of new technological developments. It is assumed that the date of the patent is the date at which the technical improvement was implemented. There were approximately 350 patents found related to the production of hydrogen cyanide. These patents were sorted into families to facilitate the analysis and to structure the information.

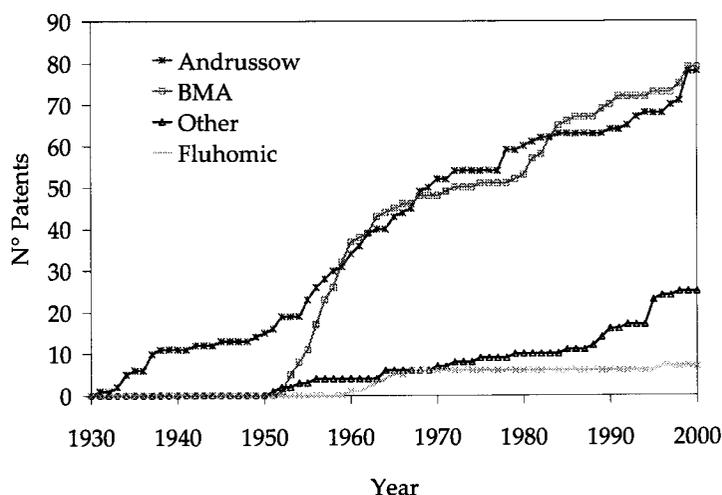


Figure 3.2: Accumulated number of patents for the production of hydrogen cyanide.

Figure 3.2 shows the accumulated number of patents concerning the different chemical processes for the production of hydrogen cyanide, Andrussow, BMA Fluhomic and others.

There are patents specifically attached to each production process such as type of reaction, nature of the catalyst or specification of the process. There are also patents that are common for each production process such as separation or environmental patents. Figure 3.3 shows the different BMA subfamilies, Reaction, Catalyst, Process, Separation, and Environmental patents.

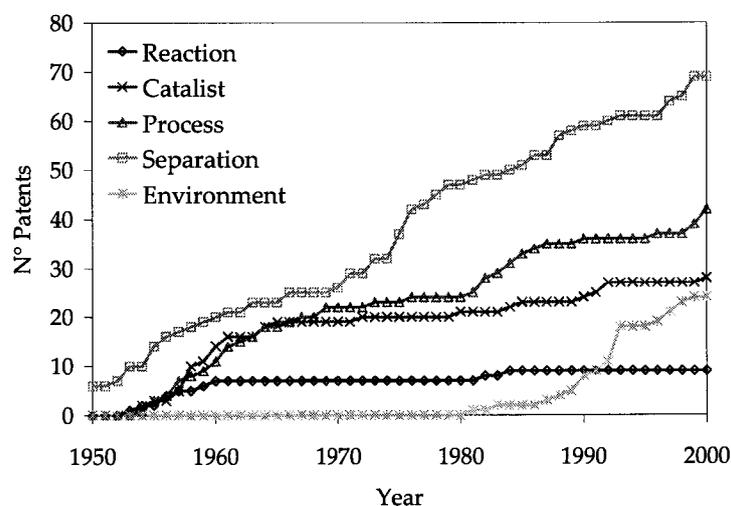


Figure 3.3: Accumulated number of BMA patents sorted by subfamilies.

By analyzing information regarding the BMA-process-specific patents it was discovered that the technological evolution of the BMA process focused on the reactor and the following additional aspects: furnace, tubes and catalyst, raw materials and finally energy consumption. These aspects were simulated in the process as the following parameters, lifetime of the tubes, number of tubes per chamber, and energy consumption per kilogram of hydrogen

cyanide produced. Figure 3.4 shows the evolution of the most important process parameters of the BMA process. One can observe how the information obtained from each patent was directly implemented as soon as the patent was filed. One can also observe how the information is based mainly on the patent evolution and industry data.

The furnace is the physical support for the tubes and for the combustion of the energy source (see Figure 3.5). It has been studied in depth mainly because it highly influences energy consumption and production capacity. The first furnace (1955) was constructed with 8 chambers and 13 tubes per chamber, [32] with a production capacity of 6 tons per tube and year [81]. Subsequently, after increasing the number of chambers to 10, efforts were made to increase the number of tubes while maintaining the old furnace structure. The number of tubes increased over the years to 65 tubes per chamber in 1984 [82] as described in Figure 3.4.

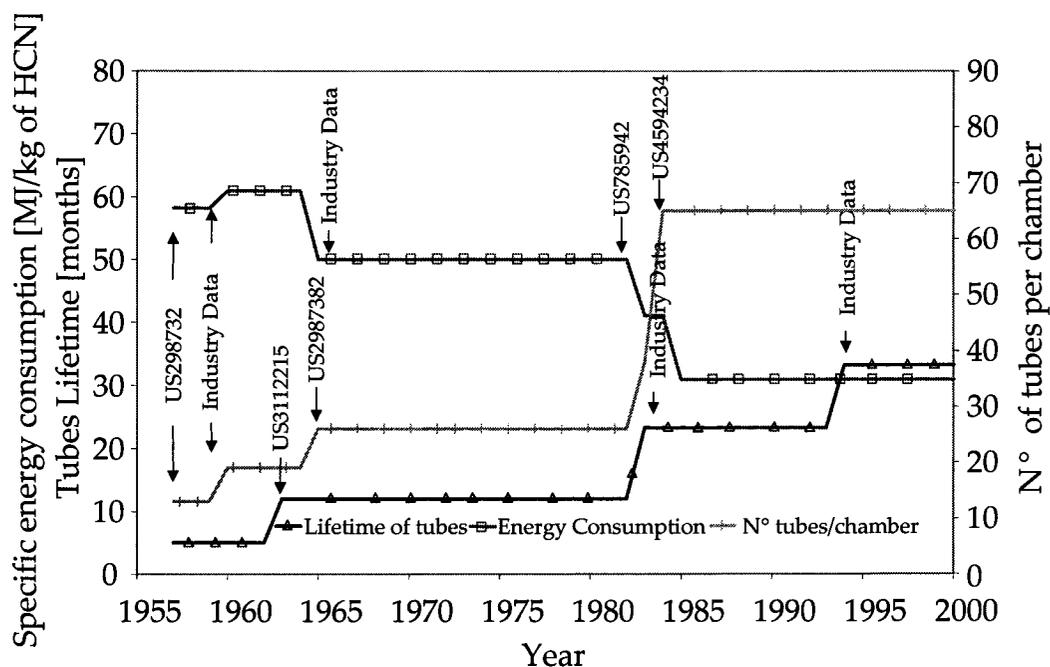


Figure 3.4: Evolution of technical parameters of the BMA process.

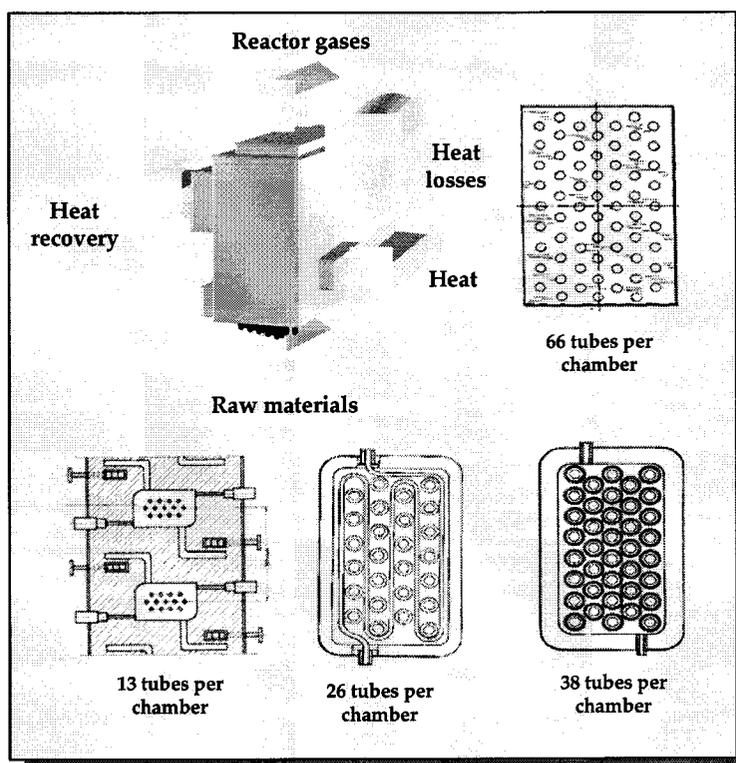


Figure 3.5: Representation of the reactor scheme and number of tubes per chamber [84].

The increase in the number of tubes is reflected by a higher production rate. The fact that there are more tubes in one bundle also means that the energy lost, which accounts for about 15 % [83] of the total energy supplied for the reaction, is reduced per kg of HCN produced. A second parameter manipulated in the reactor was its temperature. In 1960 the temperature was raised from 1300°C to 1400 °C in order to increase the yield of the reaction, but results were not as good as expected and this variable was later discarded [84].

Tubes and catalyst developments have also been studied; new coating methods and new ceramics improved tube lifetime as well as the selectivity of the catalyst [85]. Many catalysts were analyzed but those showing best results

were based on platinum. Due to the extreme reaction conditions (900-1300°C) the ceramic tubes (physical support of the catalyst) suffered continuous breakages during start-up and normal operation times. Production is normally stopped when capacity has decreased by 10 % due to tube breakage. At that moment the plant must stop production for at least 5 to 7 days to change all the tubes [81]. Current plants with more than one reactor are operated in a way that only one reactor is stopped at a time with a complete shutdown every two years. This parameter affects the economic performance because of the price of the tubes itself, and because of the loss of productivity during the time the plant is not operating. Other aspects such as a decrease of the start-up time and an increase of the overall lifetime of the catalyst, as well as increase of the operating time per year were also taken into consideration. As a result the capacity of one BMA reactor has increased over the period of study from 400 tons per year in 1955 to almost 3500 tons per year in current reactors.

Another aspect of the process studied is the separation of un-reacted ammonia to avoid polymerization. Two major process alternatives were implemented; the simplest and oldest is the absorption with a solution of sulfuric acid in different concentrations [80]. This option is also the cheapest and has been widely used by most producers; the only drawback is that a byproduct being ammonium sulfate is generated. Ammonium sulfate can be sold as fertilizer but its market is unreliable and there is not a large demand for it. In several occasions it was dumped or sold at no gain.

A second alternative is the use of a monoammonium phosphate solution, in which the ammonia reacts to form diammonium phosphate [78, 79]. To recover the ammonia the absorption solution is boiled and the released ammonia is condensed and recycled to the reactor, while the monoammonium phosphate solution is regenerated and reused. This alternative is licensed by Dupont and

is widely used in the Andrussow process where quantities of un-reacted ammonia are higher. In the BMA process licensing and operation costs made this alternative less attractive than the sulfuric acid absorption.

There have been studies on the implementation of other separation alternatives, but there were proven economically unfeasible in comparison to both mentioned above. Figure 3.6 represents the accumulated number of separation patents. Figure 3.6 shows how sulfuric acid and ammonium phosphate appear to be the most studied. Other ammonia separation technologies such as the use of zeolites [86], ketones [87] or other acids [88] can also be found in Figure 3.6.

Environmental patents concerned purification of waste gas and waste water [89], [90]. Around 30 patents were studied with the conclusion that these patents are end-of-pipe technologies not affecting the core technology of the BMA process.

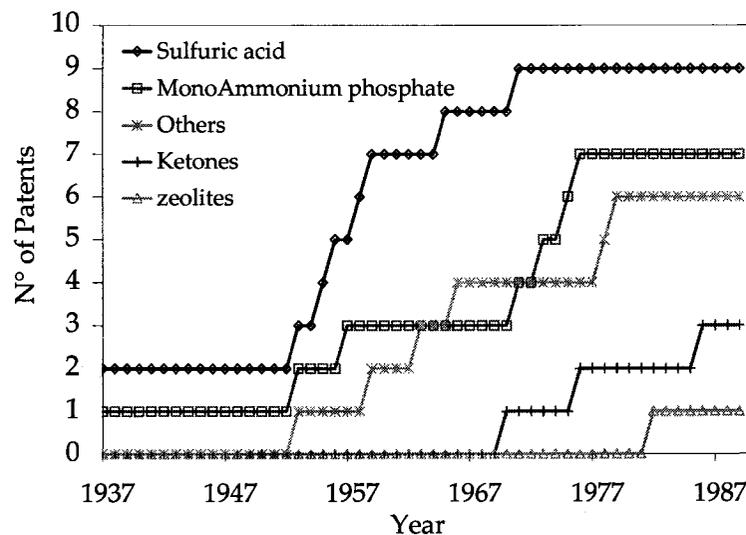


Figure 3.6: Evolution of the accumulated number of ammonia separation patents.

3.2.2 Simulation

The BMA process as described in Figure 3.1 can be divided into three parts, reaction, separation, and purification. Simulation was conducted using the process simulator ASPEN PLUS ®. Models and assumptions for the three parts are also described in the appendix A and in [81].

Reaction

The reaction part was simulated with a plug flow reactor model using kinetic information from scientific literature [91]. The BMA reactor consisted of a furnace of 10 chambers (the first reactor only had 8 chambers) with a number of tubes per chamber that varied over time (see Figure 3.5). The heat required for the reaction was obtained from the external combustion of natural gas. Assumptions for energy requirements and further heat recuperation are shown in Figure 3.7. Plant capacity for one reactor per year is the basis taken for the calculation of mass and energy balances. The number of operating days was calculated, taking into account average tube lifetime, the time needed for rebuilding the reactor [83] and the start-up time. It was further assumed that tubes had a linear lifetime (tube breakage), and that the reactor had to be stopped when capacity dropped to 80% (see Table 3.1).

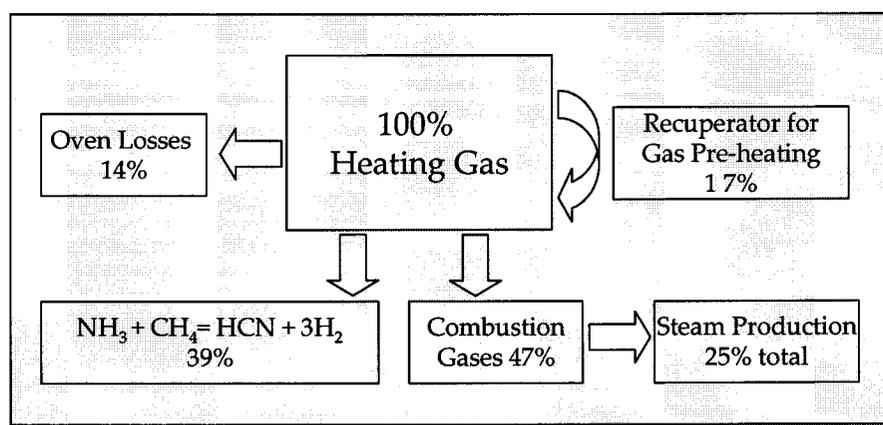


Figure 3.7: Distribution of heat in the BMA reactor per kilogram of HCN [84].

The reaction yield of hydrogen cyanide remains constant over time and accounts for approximately 83% based on ammonia [81]. The average off-gas composition of the reactor in percentage was: 23% hydrogen cyanide, 2.4% methane, 3.2% ammonia, 70.8% hydrogen and 0.6% nitrogen [81]. Since the yield is constant over time, ratios between products and reactants remained constant and differences found resided in the increase of reactor capacity and energy consumption. The major contribution to both parameters is clearly the increase in the number of tubes per reactor. A second parameter affecting capacity is the increase of operating days per year due to smaller start-up times and new materials that allowed longer catalyst lifetime.

Year	Lifetime catalyst (months)	Number of tubes per chamber	Energy consumption (MJ /kg HCN)	Start-up time (hours)	Operating time per year (days)	Capacity loss for changing tubes (%)
1957	5	13	58.1	220	300	20
1960	5	19	61	220	300	20
1965	18	26	50	24	355	20
1983	18	38	41.1	24	355	20
1984	23.3	65	31	24	357	20
1994	33.3	65	31	24	360	10

Table 3.1: Simulation parameters used for modeling the evolution of the BMA reactor [81].

According to Figure 3.7 twenty-five per cent of total energy per kilogram of HCN provided for the reactor, can be reused for steam production. Efficiency is already included in these 25% for later calculations [84]. The co-generated steam is used to run the separation and purification parts. A detailed description of the calculations can be found in [81].

Separation

Separation part was simulated using the electrolytes thermodynamic package (ELECNRTL) available in ASPEN PLUS[®]. The equipment analyzed in this part consists of an ammonia absorber, followed by a hydrogen cyanide stripper and ending with the ammonium sulfate crystallizer. First two units were modeled using the rigorous RadFrac model available in ASPEN PLUS[®]. The ammonium sulfate crystallization was modeled using the crystallizer model available in ASPEN PLUS[®].

In order to simplify calculations and to avoid convergence problems the models of separation part were considered as ideal separators (SEP) in the overall flowsheet analysis (see Figure 3.1) taking into account results from the rigorous simulation shown in Figure 3.8.

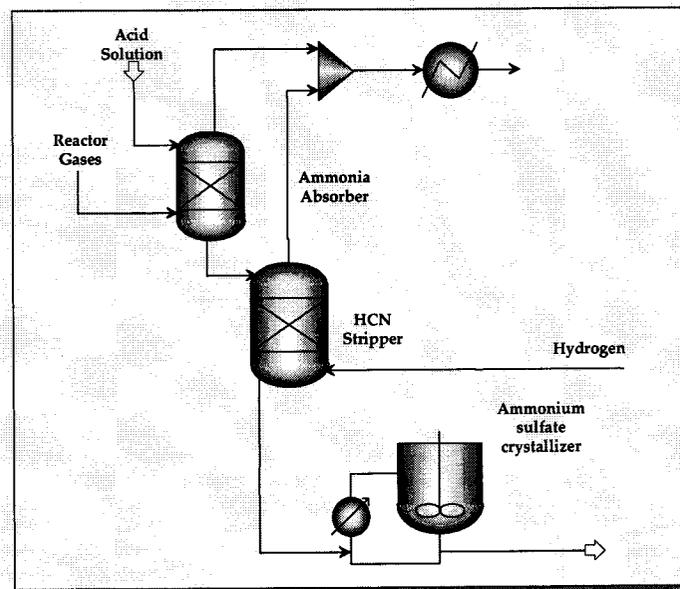


Figure 3.8: Separation as simulated with ASPEN PLUS[®].

Purification

Purification part was modeled using the NRTL thermodynamic package fitted with experimental vapor-liquid equilibrium data [92] (see Figure 3.9). The HCN absorption and distillation were modeled using the rigorous RadFrac model available in ASPEN PLUS®.

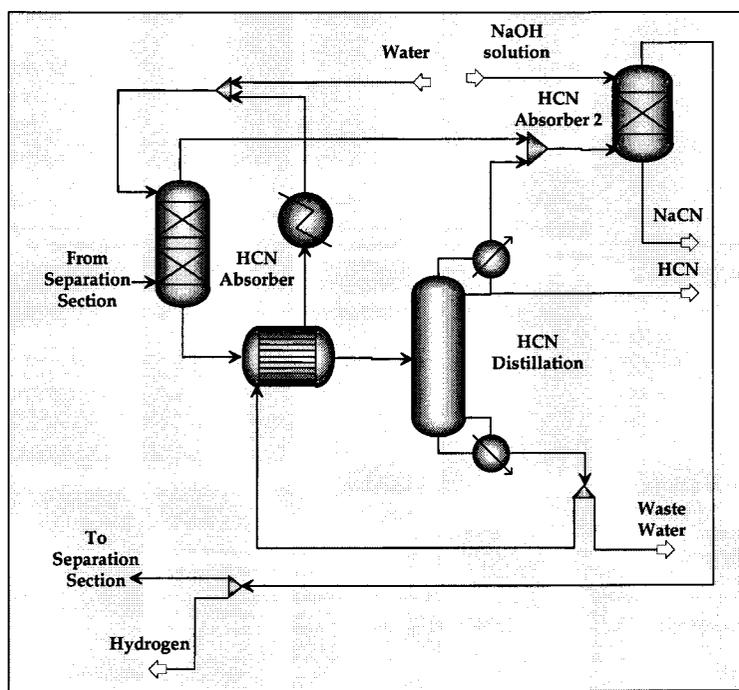


Figure 3.9: Purification as simulated with ASPEN PLUS®.

The heat exchanger was modeled using the rigorous model HeatX available in ASPEN PLUS®. The second absorber was modeled using an ideal separator with the stoichiometrical amount of caustic soda solution.

3.2.3 Mass and energy balances

Figure 3.10 shows the evolution of the reactor capacity and the energy consumption per kilogram of HCN considered in the calculations. The mass and energy balances obtained from simulation are illustrated in Figure 3.11

and Figure 3.12. These figures show how natural gas is used as a source of energy to supply the heat requirements of the reactor and as a raw material providing the methane required for the reaction.

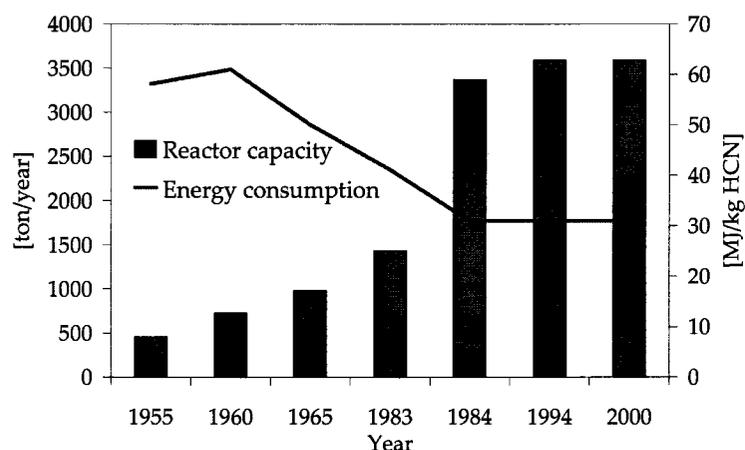


Figure 3.10: Evolution of reactor capacity and energy consumption per kilogram of HCN.

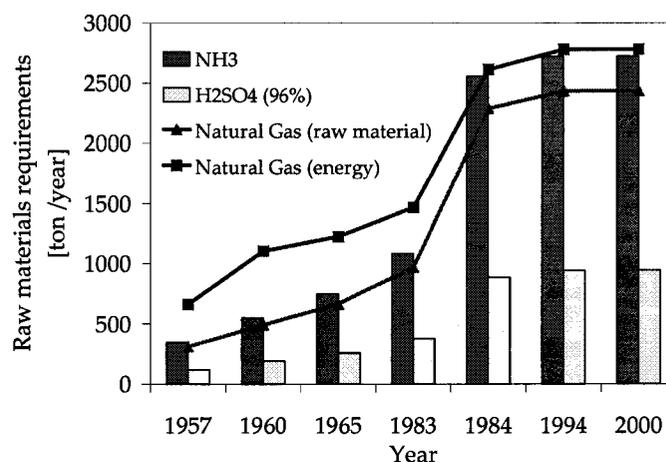


Figure 3.11: Calculated raw materials and energy requirements in BMA process as a function of time.

There are several alternatives for the hydrogen produced; among others purification or methanation could be studied. In order to simplify calculations in this study the hydrogen produced was combusted and used for heating

purposes decreasing thereby the amount of natural gas required. Figure 3.13 represents the energy consumption, the steam production and evolution steam demand from the separation and purification parts.

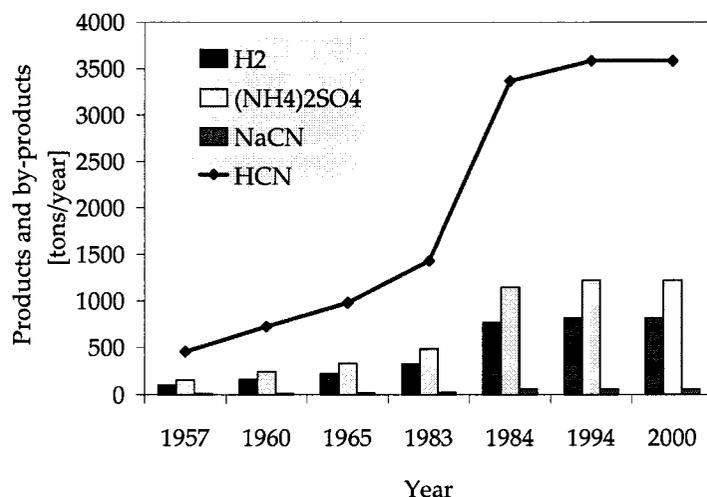


Figure 3.12: Calculated production in the BMA process as a function of time.

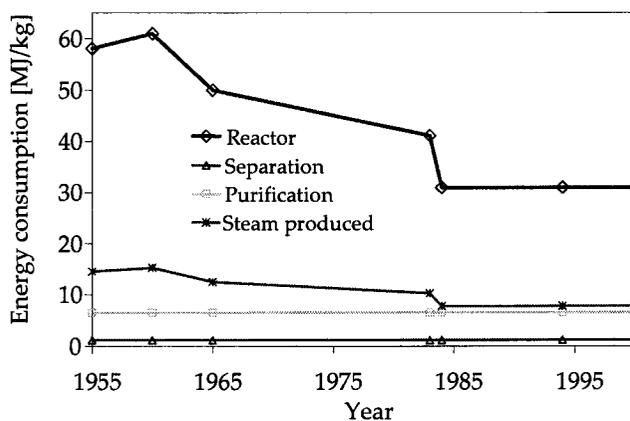


Figure 3.13: Evolution of the steam production and energy consumption of the BMA process.

3.3 Ammonia process

The ammonia process can be divided into three parts, synthesis gas production, carbon dioxide separation, and the ammonia loop [93]. A detailed evolution of the technological evolution can be obtained from [94]. In contrast with the analysis of the hydrogen cyanide production the ammonia required is obtained from an average of all processes and technologies available at a certain time (see Figure 3.14). The classical Haber-Bosch plant employed coal as a source of hydrogen [95] (first plant built in 1940, Oppau, Germany). To avoid the expensive coking step, direct gasification of coal was explored [96]. Around 1940 natural gas became cheap in huge quantities in North America [97] and ten years later in Europe as well [98]. During the period of European delay ICI (Imperial Chemical Industries) succeeded with steam-reforming light naphtha. The first plant went on stream in 1959 [99]. By 1952 about 80% of the synthetic ammonia in the USA was produced by plants using the methane-steam reactions. All these plants operated at essentially atmospheric pressure [100].

At the same time, oil producers (Texaco and Shell) developed partial oxidation processes. It is used for the gasification of heavy feedstocks such as residual oils and coal. Extremely viscous hydrocarbons and plastic wastes could also be used as fractions of the feed [101]. An air separation unit is required for the production of oxygen in the partial oxidation step. Nitrogen is added to the liquid nitrogen washing step to remove impurities from the synthesis gas and to obtain the required hydrogen/nitrogen ratio. When compared with steam reforming of natural gas, partial oxidation of fuel oil consumes 20% more energy. Figure 3.14 shows the evolution of the different raw materials used in ammonia production.

An important aspect of partial oxidation is gasification at elevated pressures, which takes advantage of the volume expansion from feedstock to product gas. This constitutes considerable savings in compression energy. It is even more effective if the feedstock is available at an elevated pressure, as is the case for natural gas. For this reason, in 1953, reforming process designers began to raise the operating pressure. The extent, to which this could be done, however, was limited by the tube material. For equilibrium reasons, the residual methane content in the product gas increases with rising pressure, which can be compensated by higher temperature or, less economically, by a higher steam-to-carbon ratio [96, 102].

The steam/air reforming concepts (conventional, unconventional and autothermal reforming) [103, 104] based on natural gas and other light hydrocarbons are considered to be the dominating technologies from the economic and environmental point of view. The performance of the three alternatives is similar. In this study only the evolution of conventional steam reforming was investigated. For heavy feedstocks, partial oxidation is considered to be the best production process.

Figure 3.14 shows the major steps of the ammonia production processes. In the reforming step (primary and secondary reformer) the natural gas reacts to produce the hydrogen and nitrogen required for ammonia synthesis, along with carbon monoxide and carbon dioxide. Reforming is equivalent to the gasification process used for the coal and oil processes. The heat for the reforming process is supplied by burning natural gas or other gaseous fuel, and the flue-gas is one of the main sources of emissions from the plant. These emissions are mainly CO_2 , and NO_x , with small amounts of SO_x and CO , depending on the energy source.

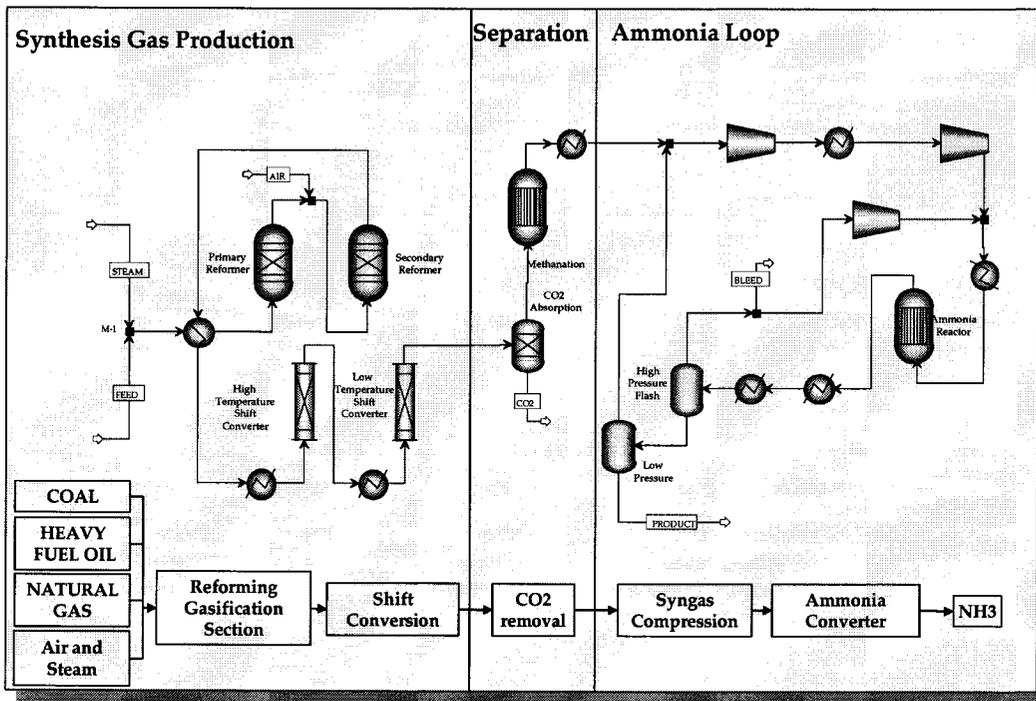


Figure 3.14: Scheme of the ammonia production processes.

Due to its superior energy performance and because of known resources of fossil raw materials, natural gas dominated and will dominate as the feedstock for ammonia for the next 50 years at least. In the long run, one might expect coal to take over, based on world reserves and consumption rates. Figure 3.15 shows how coal is slowly increasing its market share, which is due to the fact that China is basing its ammonia production on this feedstock.

Heavy oil may be attractive under special environmental concerns, when natural gas is not available and the partial oxidation process could solve a waste problem (heavy residues, plastics recycle).

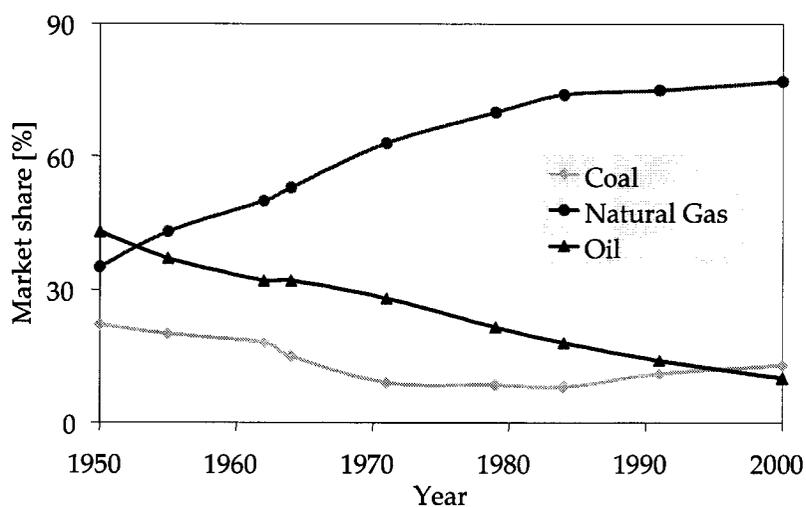
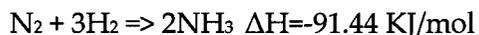


Figure 3.15: Evolution of the feedstock in worldwide ammonia production [96, 103-106].

The outlet from the reforming/partial oxidation steps leads to the shift converter zone where carbon monoxide reacts with water to carbon dioxide, producing more hydrogen. The CO_2 is removed in a chemical or a physical absorption process. The small amounts of CO and CO_2 remaining in the synthesis gas are poisonous for the ammonia synthesis catalyst and must be removed by conversion to CH_4 in the methanator.

Dried synthesis gas consists of nitrogen and hydrogen in stoichiometrical proportions (1:3). Inert gases, argon and methane are also introduced into the ammonia loop. The equilibrium reaction that takes place in the loop converter yields 20% to 28% in ammonia [93].



The ammonia is then liquified and separated from the non-reacted synthesis gas. Since inert gases are introduced into the loop a purge is required.

3.3.1 Technology evolution

In order to perform the technological assessment of the ammonia process several sources of information were considered. A detailed evolution of the technological evolution can be obtained from [94]. Patents, scientific publications and industry data were used to describe the chronological evolution of this chemical process. In difference to the BMA process the ammonia process is widely known and studied. The impressive amount of patents required searching for other sources of information such as technical journals. There are several sources of technical literature available, the most important being which was mainly used for this thesis was the technical journal "Nitrogen" edited by "British Sulfur Corp. LTD". As patents for the BMA process reports published in this journal served as a source of technical and chronological information.

The technological assessment of the ammonia process was focused on four main aspects. On one hand the capacity of the average ammonia plant is important due to the economy of scale. On the other hand the three main parts of the process were studied, synthesis gas generation, carbon dioxide separation, and the ammonia loop.

Size

The growing demand for fertilizers due to an increase in world population generated a necessity for ammonia which when combined with the economy of scale resulted in an increment in the size of ammonia plants [107] [96]. First plants produced 250 t.p.d. in 1916 [96]. Converters only produced 50-60 t.p.d. [96] of ammonia per converter, and the only way to increase production was by using converters in parallel.

In 1954 Monsanto's Luling ammonia plant increased production adding two new compressors to a 300 t.p.d. plant, arriving at 525 t.p.d. [108]. In 1963 a REPESA plant increased production to 325 t.p.d. of ammonia [109]. Production was limited by the size of the reciprocating compressors.

The development of radial converters [103] and centrifugal compressors [110, 111] during the mid-sixties propagated a new concept of ammonia plant. During this period improvements in construction technology resulted in the large ammonia plant concept propagated by Kellogg. Figure 3.16 shows the evolution of the ammonia plant capacity over time.

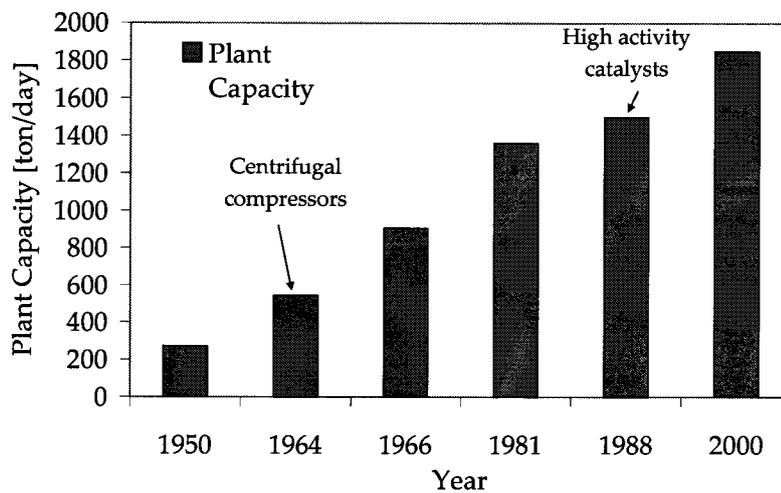


Figure 3.16: Technical evolution of an ammonia plant capacity over time.

Synthesis gas production

As shown in Figure 3.15 the synthesis gas production consists of a reforming step and a shift reaction step.

Reformer

The technological advances achieved in the reformer step focused on reducing the overall energy consumption of the plant [98, 111-113]. For this reason, an increment in the operating pressure of the reformer took place to reduce the operating costs of the loop compressors. As shown in Figure 3.17 the development of centrifugal compressors [110, 111] allowed working at higher pressures with lower costs.

A second important parameter in the reforming part is the steam to carbon ratio. A high ratio favors conversion but increases operating costs. The tendency has been to reduce the steam to carbon ratio while increasing the temperature of the reforming part to obtain equivalent conversion. In order to make this option economically feasible reactants were preheated [108, 109, 114-211].

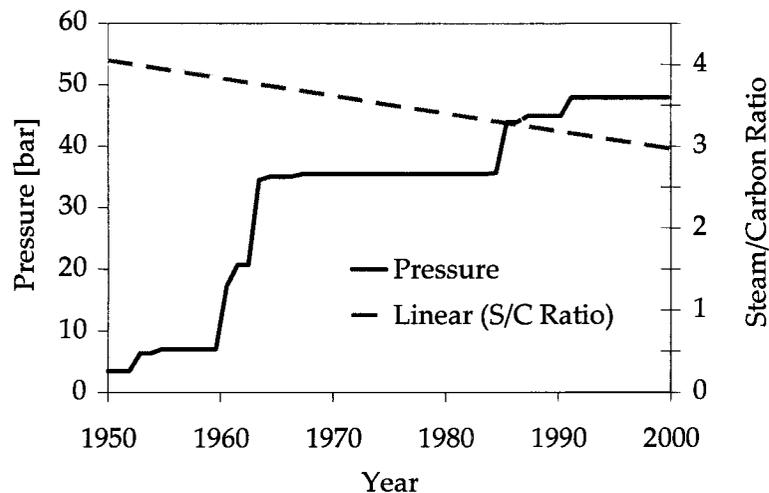


Figure 3.17: Evolution of reforming pressure and steam (S) to carbon (C) ratio in the synthesis gas production part [108, 109, 114-211].

Shift converter

From the very beginning, only one stage of high temperature shift converter (HTSC) was used [100]. Beginning in 1962 two stages of HTSC were used [95, 101, 102, 212, 213]. In 1963 the low temperature shift converter (LTSC) appeared. In 1966 47% of plants used LTSC. In 1971 the Selectoxo process appeared. A detailed description of this process can be obtained from [94]. . In this study a conversion of 90% of carbon monoxide in one stage of HTSC [214] was assumed, while 96% of conversion was assumed for a LTSC.

Carbon dioxide separation

After shift converters most of the carbon monoxide is converted to carbon dioxide. Its removal is critical for the proper operation of ammonia plants. The gas mixture that enters the CO₂ removal system mainly of nitrogen, hydrogen, and carbon dioxide, along with low quantities of carbon monoxide and other minor components. Removing carbon dioxide not only decreases the amount of inert gases in the ammonia loop, it also removes a catalyst poison that affects the catalyst of the ammonia converter. Therefore the content of carbon dioxide in the synthesis gas must be reduced to less than 5 to 10 ppm by volume.

The carbon dioxide removal system is one of the major energy consumers in ammonia plants. In this part the evolution of the different removal methods are performed in order to obtain the best available technology during the period from 1950 to today.

The carbon dioxide removal can be divided into two major families, chemical and physical absorption. In the chemical absorption process the acidic carbon dioxide reacts with a base solution that is later regenerated, obtaining carbon dioxide gas. The regeneration of the base solution is performed via stripping

requiring high amounts of steam. The physical absorption on the other hand absorbs carbon dioxide by dissolving it under high pressure requiring mechanical energy for the compression; no additional heat is required due to the fact that carbon dioxide is recovered by simple flash evaporation.

- Chemical absorption

Chemical absorption has been widely used by the ammonia industry since the very beginning and major changes have led to great improvements in this process. A detailed evolution of its technological evolution can be obtained from [94]. Chemical absorption can also be divided into two categories; the first category is generally referred to as the aqueous amine process in which relatively concentrated amine solutions are employed during absorption. A second category is formed by processes that use potassium carbonate solutions and similar process equipment.

Amine solutions have been widely employed by the ammonia industry; the first commercial plant using monoethanolamine (MEA) began operation in 1929 [102]. The main advantage of this type of solutions is that they could achieve low residual carbon dioxide with simple and inexpensive installation. The major disadvantage of this kind of solutions is the formation of carbamate instead of carbonate; carbamates are highly corrosive especially affecting the hotter parts of the units. This fact led to the usage of amines that form less stable products with carbon dioxide such as diethanolamine (DEA) [213].

In the early 1970s Union Carbide developed a corrosion inhibitor known as "Amine Guard" that allowed MEA concentrations above 20% and also decreased the energy necessary for amine solution regeneration. Following products such as Amine Guard II, III IV were released achieving higher concentrations of MEA [215]. During the beginning of the 80's BASF

developed a new process based on Methyl-diethanolamine (MDEA or aMDEA) [215, 216]. The major advantage of MDEA is that it requires lower temperatures, far less energy to decompose, and does not form carbamates or other corrosive products. Most of the MEA units can be revamped to utilize MDEA with small investment. Recently, BASF introduced a highly activated MDEA solution to increase carbon dioxide recovery. The first activated MDEA (Activated MethylDiethAnolamine aMDEA) plant went on stream in 1971 with BASF's ammonia plant n° 3 in Ludwigshafen [217], and in 1982 started licensing the process to other companies. The advantage of such a process is that at high loads it acts as a physical solvent as well. Much of the carbon dioxide can be released just by depressurizing the liquor. By increasing the activator concentration the character of the solvent can be shifted. The aMDEA can be used in the revamping of old MEA units by simply switching the solvent.

Carbonate solutions have been widely employed by ammonia producers due to their low energy requirements for absorbent regeneration. The major problem was that the concentration of carbon dioxide in the synthesis gas was not low enough and therefore required another complementary method for final "cleaning", such as MEA solutions. Additives that increased the absorption capacity and decreased the corrosion were developed, Benfield 1959 [218], Cartacarb 1961 [219-221], Giammarco-Vertrocoke 1962 [222], started using highly toxic arsenic activators, changing later on to glycerin based activators which are less toxic. New process configurations for these processes were developed [223] that increased the energy efficiency of the process.

- Physical absorption

Physical absorption has been implemented lately in some ammonia plants [224]. The physical absorption dissolves the CO₂ under pressure without

reacting with the solvent. The CO₂ is then recovered by flashing without any other heat requirement.

Since physical absorption is involved, the amount of circulating solvent is proportional to the quantity of feed gas, inversely proportional to the pressure, and almost independent of the concentration of carbon dioxide in the feed gas. This process has been economically favored by the fact that ammonia plants have increased their operation pressure over the last 50 years. The lack of further heat requirements makes physical absorption a very interesting technology, although designers must bear in mind the mechanical energy required for the recirculation of the solvent.

Among the different solvents that can be used one can find products such as Estasolvan, Purisol, Rectisol, Sepasolv-MPE, Fluor solvent and Selexol. Fluor solvent and Selexol are studied in depth here due to the high vapor pressure of Rectisol (mainly composed by methanol) and the relatively poor CO₂ solubility of Estasolvan for example. A detailed evolution of these processes can be obtained from [94].

The Selexol process is a patented process invented by Allied Chemical Corporation in 1969, although first studies began in the mid 1950s [225]. In 1982 Allied Chemical Corporation was bought by Norton Co. Currently, Dow Chemicals is registered as the sole assignee of the patent and the trademark for the Selexol process. Selexol is a mixture of different polyethylene glycol dimethyl ethers.

The advantage of the Selexol process is that this solvent is non-corrosive, non-toxic, stable, biodegradable and non volatile. General advantages are that no heat for solvent regeneration is required thereby saving high pressure steam.

The non-corrosive solvent makes the use of simple carbon steel for equipment construction adequate. Lower humidity of the synthesis gas required less energy for its compression before entering into the ammonia loop.

Among other physical solvents tested propylene carbonate has proven particularly effective, [226,227]. In general this process is best suited for cases where the partial pressure of carbon dioxide is above 60 psi and in cases when the heavy hydrocarbon content is low. Since the solvent capacity is increased at lower temperatures, operating conditions are usually under ambient temperature. In 1979 three ammonia plants used this absorption process.

Ammonia Loop

Changes observed in the technological development of the ammonia loop were focused on obtaining catalysts with higher activity and converters with lower pressure drop and higher conversion [112, 227, 228]. According to Figure 3.18, the development of new compressors highly influenced the operating pressure of the ammonia loop as well as the capacity of the plant (described in prior parts). It is evident that centrifugal compressors influenced the ammonia loop pressure operation because the economic optimum of centrifugal compressors was around 150 bar [229, 230].

After this time period, pressure increased slowly to obtain higher yields until the introduction of new highly active catalysts in the late 1980s allowed pressure reduction [94]. The development of low pressure converters with smaller pressure drop in addition to the higher conversion catalysts during the 1980s also justified a lower working pressure in the ammonia loop [231, 232].

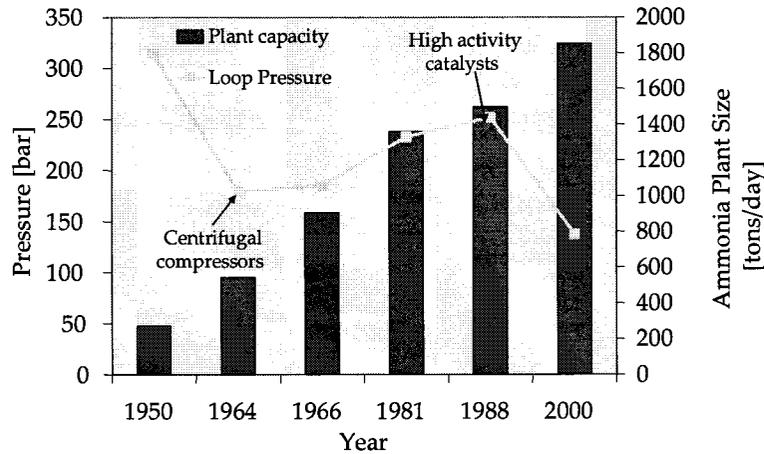


Figure 3.18: Evolution of the ammonia plant capacity and loop pressure.

Inert gases purge

In a typical ammonia plant the purge of inert gases represents 4-6% of the total synthesis gas [104]. Before 1950, the purge exited the process without any treatment. In 1952 the purge was used as combustion gas in the reformer because of its high hydrogen content. In 1964 cryogenic separators for the recovery of hydrogen became available. In 1971 a new technology based on semi-permeable membranes competed with the cryogenic separators. Efficiencies in hydrogen recovery are 85-95% in membrane recovery and 90-95% in cryogenic recovery [233]. Both technologies are improving and it is difficult to consider one better than the other. It is also possible that membrane technology purge treatment is worthwhile in ammonia plants with a production lower than 600 tons per day [106]. In energy terms a cryogenic purification represents an energy saving of up to 0.7 GJ per ton ammonia [234] as compared to having a purge. Nowadays, membrane purge technology has similar energy consumption.

Waste Heat recovery

In 1965 surplus heat from a reformer produced 1.2 tons of steam at a pressure higher than 100 bar per ton of ammonia produced [230]. This heat could be used in different parts of the ammonia plant. As an effect of the oil crisis a higher integration (integrated auxiliary boilers) of the different parts of the plant was conducted. In 1976 about 85% of the total energy demand of the plant was supplied by waste heat [96]. The steam generated provides most of the power required for synthesis gas compression (85% in 1976) [96]. During the early 80's waste heat recovery was conducted in such a way that the generated surplus of energy was exported outside the ammonia plant [235].

3.3.2 Simulation

The production of ammonia as described in Figure 3.12 can be divided into three major parts: synthesis gas production, carbon dioxide separation, and ammonia loop. In order to avoid convergence problems the three parts were first simulated rigorously and separately and then merged into a single simplified simulation. A typical

The first task is selecting the property method for the simulation. After studying the problem it was decided to use one property method for the whole plant except the carbon dioxide absorption where a specific property method for each solvent was chosen [236].

The property method chosen for the ammonia plant is the RKS-BM [237-239] property method that uses the Redlich-Kwong-Soave (RKS) cubic equation of state with Boston-Mathias alpha function for all thermodynamic properties [238, 239]. This property method is comparable to the Peng-Robinson-Benson-Mattias (PR-BM) property method. It is recommended for gas-processing,

refinery, and petrochemical applications. Example applications include gas plants, crude towers, and ethylene plants. For more accurate results in VLE calculations the use of binary parameters for the different components is required although for the ammonia case study this was not necessary since models predicted a correct behavior.

The RKS-BM property method can be used for non-polar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide, and hydrogen. From this point of view reasonable results at all temperatures and pressures are expected. The RKS-BM property method is consistent in the critical region, although results are least accurate in the region near the mixture critical point [238, 239]. A detailed flowsheet simulation is specified in Appendix A.

Synthesis gas production

The production of synthesis gas is an important and interesting part of the overall process of synthesizing ammonia. Desulfurized natural gas, which is the source of hydrogen in the example, is reformed in a conversion reactor (reformer) where it is combined with steam. Air is added to the second reactor at a controlled flow rate such that the desired ratio of $H_2:N_2$ in the synthesis gas is attained.

The oxygen from the air is consumed in an exothermic combustion reaction while the inert nitrogen passes through the system. The addition of steam as shown in Figure 3.19 serves the dual purpose of maintaining the reactor temperature and ensuring that the excess methane from the natural gas stream is consumed.

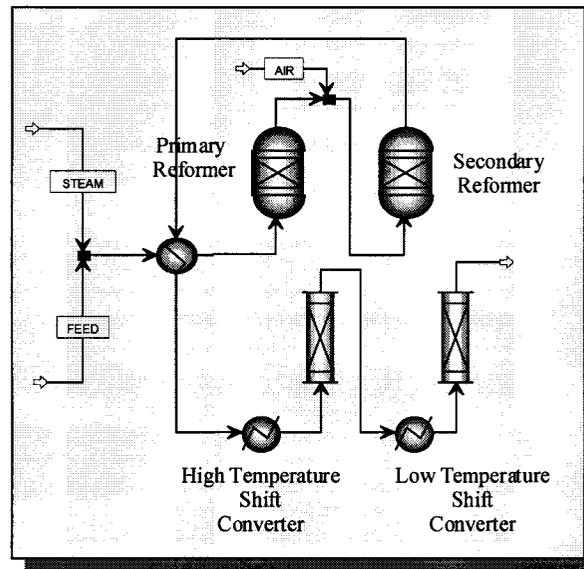


Figure 3.19: Synthesis gas production part in the ammonia process.

The primary and secondary reformers were modeled using a conversion reactor or RGIBBS [240]. RGIBBS uses Gibbs free energy minimization with phase splitting to calculate equilibrium. RGIBBS does not require the reaction stoichiometry to be specified. The reason why RGIBBS was chosen for the simulation is that this type of reactor gives the required accurate information without the need of kinetic information.

Data used to simulate the reformer performance can be observed in Table 3.2. Process variables considered were: Feed temperature (T_{feed}), primary reformer temperature (T_{prim}), primary reformer temperature outlet (T_{mid}), secondary reformer temperature outlet (T_{out}), steam on carbon ratio (s/c_{rat}), air feed temperature inlet (T_{Air}), dry methane concentration secondary reformer inlet (CH_4_{mid}), number of the technical journal "Nitrogen" ($\#_{\text{nitro}}$) and the page of reference (pag).

Year	Pres.bar	T feed	T prim	T mid.	T Out	s/c rat	T Air	CH4mid	#nitro	page
1950	3.4	661	660	700	861	4.0	200	7.7	39	25
1953	6.3	686	657	861	869	4.0	227	8.0	16	35
1955	7.0	700	655	857	875	4.0	245	8.2	152	91
1961	17.2	371	704	845	892	3.8	371	8.0	11	35
1962	20.7	737	648	843	894	3.8	227	9.0	16	35
1964	34.5	732	815	839	943	3 - 6,5	245	11.5	29	32
1965	35.0	747	645	837	903	3.7	299	9.3	152	91
1968	35.5	753	642	831	911	3.7	308	9.6	52	30
1986	35.7	450	800	780	961	3.6	326	11.5	164	36
1987	44.0	580	804	804	983	3.2	335	11.6	167	36
1989	45.0	800	800	790	970	3.2	362	11.8	182	25
1993	48.0	663	617	815	964	3.2	524	12.2	206	32
2000	48.0	663	617	815	964	3.2	524	12.2	206	32

Table 3.2: Reformer process variables used for simulation.

Preheating process air temperature represent 8% of savings since the 1950s and since there is no data found in BAT references, linear increasing will be considered from 200°C in 1950 to 650°C in 2000 [102]. Preheating combustion air is another variable to consider. Nowadays it is preheated to 260°C and in the 1950s it was introduced at 25°C.

In the High and Low Temperature Shift Converters (HTSC, LTSC), the water-gas shift equilibrium reaction takes place. Kinetic information was found and two RPLUG [237, 241] reactors were chosen for the simulation. First shift converters consisted in only one stage of HTSC. Beginning in 1962 two stages of HTSC was implemented. In 1963 a Low Temperature Shift converter appeared. In 1966 47% of plants used LTSH, sometimes improved. In 1971 the Selectoxo process appeared. It is considered a conversion of 90% of carbon monoxide in one stage of HTSC. It is considered a 96% of conversion in a LTSC. Table 3.3 describes the different process variables taken into account: temperature in the HTSC, temperature in the LTSC and % composition of dry carbon monoxide at LTSC outlet.

Year	Temperature °C		% CO out
	HTSC	LTSC	
1950	450		
1955	438		
1962	434	450	1
1964	434	450	1
1972	433	240	0.20
1979	429	239	0.17
1984	423	235	0.12
1991	411	229	
1999	398	222	

Table 3.3: Shift converter process variables used for simulation.

Carbon dioxide separation

After shift converters most of the carbon monoxide is converted to carbon dioxide and its removal is critical for the proper operation of ammonia plants. The process gas that enters the CO₂ removal system consists in a major mixture of nitrogen, hydrogen and carbon dioxide together with low quantities of carbon monoxide and other minor components [93]. Removing carbon dioxide from these gases not only decreases the amount of inert gases in the ammonia loop it removes a catalyst poison that affects the catalyst of the ammonia converter. Therefore the content of carbon dioxide in the synthesis gas must be reduced to less than 5 to 10 ppm by volume [93]. Table 3.4 represents all the carbon dioxide absorption processes simulated and the comparison to literature results obtained from Nitrogen.

The methanator has the function of removing all the carbon monoxide before entering the loop due to its poisonous characteristics towards the ammonia production catalyst. The reaction takes place at a fixed temperature and the influence of its heat duty is relatively small. Kinetics were not considered because reactants are totally converted to products. For these reasons the reactor chosen is a stoichiometric reactor RSTOIC [240] at a given temperature with a fractional conversion of 1.

Type of absorption process	Energy Demand		Year
	Simulated kJ/mol of CO ₂	Literature kJ/mol of CO ₂	
MEA	210		1960
MEA	190	209	1970
Amine Guard II	120	140	1972
Amine Guard III	95	107	1976
Amine Guard IV	80	88	1979
aMDEA (single)	80	73	1980
aMDEA (double)	40	28-30	1991
Benfield (single stage)	180	107	1959
Benfield (double stage)	120		1971
Benfield (single stage + ejector)		88	1972
Benfield (double stage + ejector)		76	1974
Benfield (double stage + compr)		63	1979
Benfield (LowHeat)		36-41	1987
Selexol90%	45.3*	45.6*	1975
Selexol 100%	35.1*	37.1*	1984

*Assuming a conversion factor of 15.3 kJ/kwh [28]

Table 3.4: Carbon dioxide absorption processes.

Ammonia loop

The ammonia loop is based on the ammonia reactor; simulations were run using a RGIBBS [240] reactor because of insufficient kinetic data available to execute a plug flow reactor simulation. This is due to the proprietary rights on the catalyst and their resulting kinetic data. Figure 3.20 shows the ammonia loop flowsheet. A detailed flowsheet simulation of the ammonia process is described in Appendix A.

As shown in previous figures the most important equipment in the ammonia loop are the compressors and the ammonia converter. Major changes of the ammonia loop technology reside on its operating conditions and the use of the purge stream.

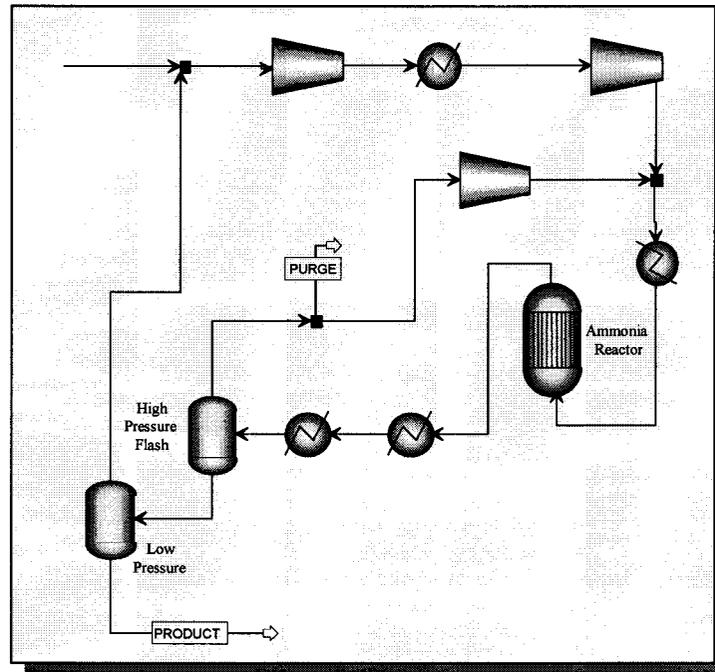


Figure 3.20: Ammonia loop configuration

Ammonia loop pressure chosen for Aspen simulation it is shown in Table 3.5. Its evolution represents the initial increasing pressure from the very beginning because pressure in 1950s went down from higher pressures used in previous years. It is possible to see how centrifugal compressors influenced ammonia loop pressure operation because the economic optimum of centrifugal compressors was at 150 bar.

Year	P [bar]
1950	370
1955	290
1962	175
1964	145
1972	170
1979	190
1984	210
1991	180
1999	90

Table 3.5: Ammonia loop working pressure.

Purge represents 4-6% of the total synthesis gas [242] in a typical ammonia plant. In 1952 purge has been simulated as a combustion gas into the reformer because of its high hydrogen content. From 1964 until nowadays the purge gases were recovered and separated for reuse. Further information about the simulation of the purge recovery and heat recovery can be found in [94]

3.3.3 Mass and energy balances

Mass and energy balances can be observed in Figure 3.21, Figure 3.22, and Figure 3.23. Figure 3.21 shows the evolution of the average feedstock for the production of one kilogram of ammonia. These values include the average amounts of natural gas, coal and oil required for the reaction (based on Figure 3.15), and the amount of these materials required as energy. It was assumed that processes consume the same feedstock as an energy source. This means that a process based on natural gas as a raw material uses natural gas as a source of energy. Figure 3.21 represents mass and energy balances for the ammonia production using a feedstock mix at every point in time. Results obtained in Figure 3.22 show requirements in terms of energy for the production of one ton of ammonia.

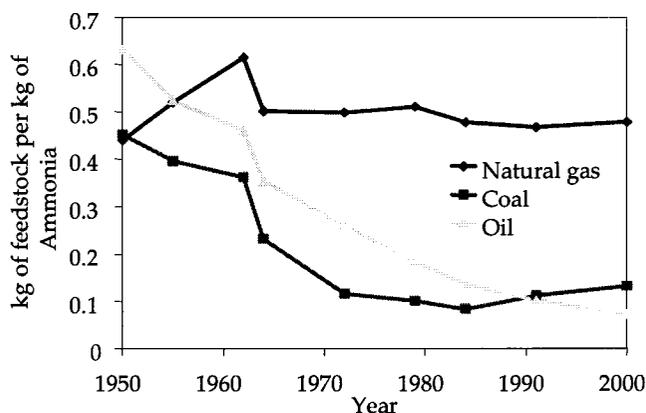


Figure 3.21: Calculated feedstock mix requirements per kilogram of ammonia as a function of time.

Figure 3.22 shows four major aspects of energy consumption in ammonia production: The heat required for running the plant (mainly reformer part), the requirements for carbon dioxide absorption, the requirements for running the compressors before the loop and the surplus generated beginning in the early nineties.

It is also interesting to view the results of carbon dioxide absorption and its evolution over time. The energy consumption for solvent regeneration has always been the major driving force of technological improvement in the CO₂ absorption process. Chemical absorption processes, beginning with Methylethanolamine (MEA), followed by Benfield, and finally with activated-methyldiethanolamine (aMDEA) have periodically decreased their steam requirements. Physical absorption processes such as the Selexol process resulted in a large technology leap when higher overall operating pressures were achieved; although nowadays hybrid processes such as aMDEA can be considered the process with lower energy requirements [215-222, 245-249]. A further interpretation of the results presented in Figure 3.22 can be found in [94].

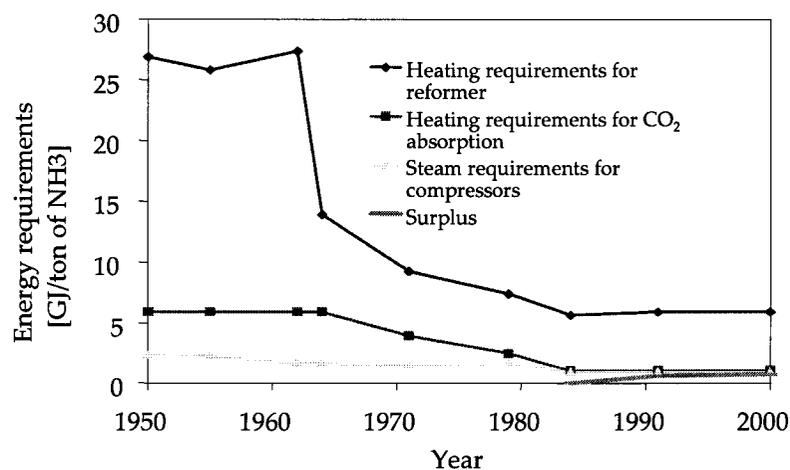


Figure 3.22: Calculated energy requirements in ammonia production as a function of time.

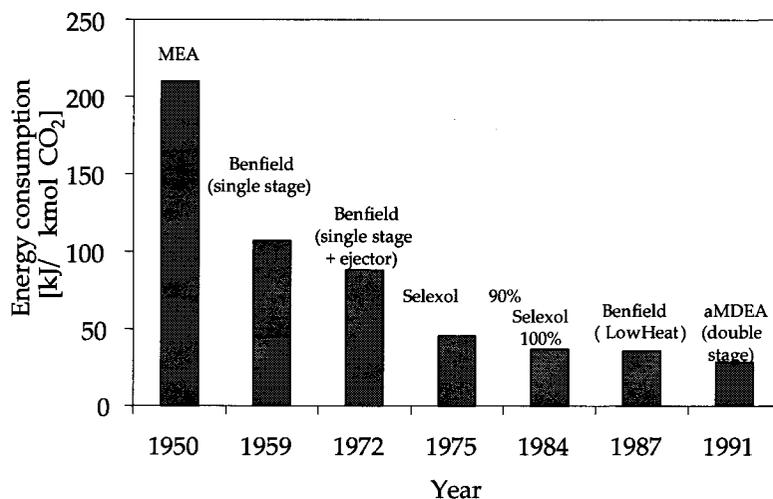


Figure 3.23: Evolution of the calculated energy consumption for the CO₂ absorption process in ammonia production.

Figure 3.23 shows the energy consumption per kmol of CO₂ absorbed for the different separation processes. The major barrier in the evolution of these processes was the high cost of switching to a different technology. For example, at a certain point in time it may have been cheaper to change the additives of a chemical absorption process instead of switching to a physical absorption. After purification the carbon dioxide produced can be sold.

These results show that ammonia production has dramatically changed over the last fifty years. Changes in feedstock, but most importantly changes in technology, have led to a more efficient process in which energy consumption has been reduced to half of the requirements in 1950.

3.4 Energy and feedstock

The technological evolution of the oil and gas industry has been focusing during the past two decades on improving exploration and production technology [244-246]. Efficiency improvements in oil refineries are limited mainly by the lack of competitive financial conditions [246]. Due to the low price of oil, capital investments in refinery upgrades often would not provide a competitive economic return. The same is true for coal processing upgrades. Low prices of fossil fuels are consequences of many traditional policies like direct and indirect subsidies, non-inclusion of external costs associated with their production and use (environmental and social costs), large scale of consumption and long time presence in the market. These factors allowed the creation of an optimized production, transportation and commercialization structure.

Later regulations on methane emissions forced the coal, oil and gas industries to reduce these losses. Due to several EPA (Environmental Protection Agency) programs the natural gas industry has been reducing methane emissions over the last 10 years (1992 to the present) in the US. Similar efforts have been made in the coal and oil production [247].

These small changes and the low impact of the production of natural gas itself have led to discarding a study in depth or simulation of its production. Similar scenarios can be found in the oil and coal sectors where the production itself did not suffer dramatic changes over the last fifty years.

Summary

In this chapter the assessment of the processes involved in the production of hydrogen cyanide is presented. As a first step the technological assessment of

each specific process is performed. Major technological advances are identified as an evolution of process parameters. The resulting evolution of process parameters can be used for modeling the different process variants. These technological advances are assumed to be implemented as soon as they are discovered. This means that there is no time gap between discovery and implementation. In this study the process simulator ASPEN PLUS® was used to model the process variants. As a result mass and energy balances as functions of time are obtained. The information obtained in this chapter is used as an input for the following chapters in which this mass and energy balances are evaluated to obtain the environmental and economic performance of the hydrogen cyanide production by means of the BMA process.

CHAPTER 4 -MARKET EVOLUTION

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4.1 Introduction

In order to obtain an objective view of the historical evolution of chemical processes, one must have in mind the influence of the market evolution. The fact that hydrogen cyanide and ammonia production require very basic raw materials simplifies this study. In the following sections the market and historical prices of products, raw materials, and energy will be analyzed with the aim for obtaining a detailed framework towards performing further economic calculations.

4.2 HCN Demand

When studying the evolution of hydrogen cyanide over time one should consider the market influence and the relationship between production and demand. In Figure 4.1 the evolution of US production for the period of 1955 to 2000 can be observed [248]. An increasing demand of this commodity has been observed during the last 20 years [249]. These figures present hydrogen cyanide as an important commodity with a promising future.

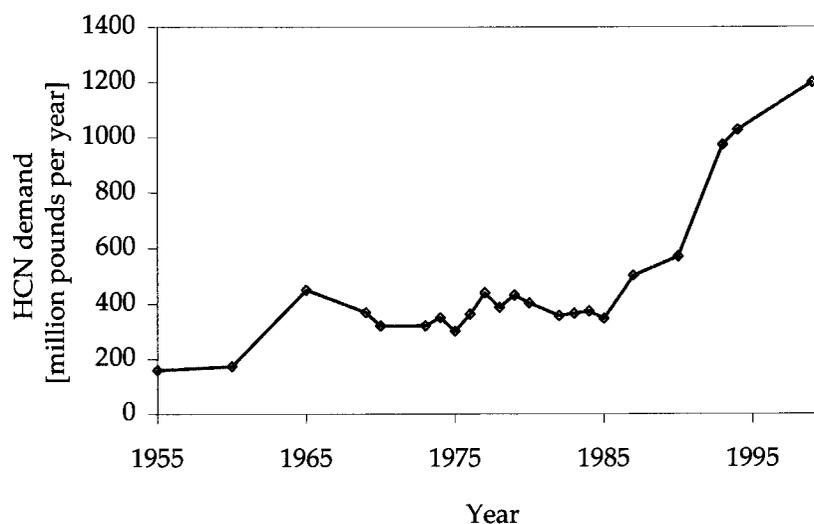


Figure 4.1: Hydrogen cyanide demand in the US [249].

4.3 Inflation

It seems obvious that when performing an economic analysis that the inflation rate should be taken into account. Its importance increases when analyses are used to compare different processes over a long period of time. The inflation rate is a sustained increase of the overall level of the prices. One of the most applied measurements of inflation is the consumer price index (CPI). The CPI measures the cost of a fixed basket of goods relative to the cost of the same basket of goods in a base year.

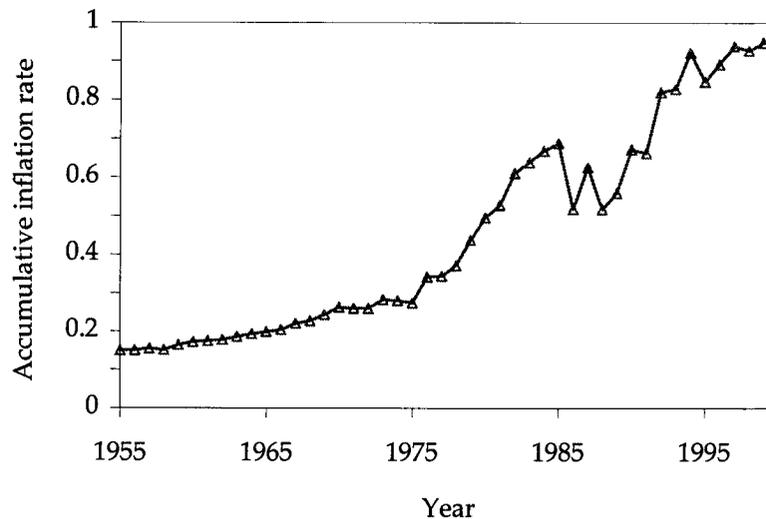


Figure 4.2: Accumulative inflation rate of oil [53, 54].

For evaluation purposes it is necessary to translate all the economic calculations into monetary units of today. This fact will introduce the inflation factor and will allow comparing processes that have a large time lap between each other. Finally, this translation will provide a normalized basis towards economic performance evaluation of processes over time. In accordance with that fact, all prices found have been translated into a same monetary unit, 1999\$ (dollars of 1999).

One of the most important sources of change for inflation is energy price and specifically oil price. Figure 4.2 shows the accumulated inflation rate applied to the price of a barrel of oil since 1950 [53, 54]. One can see how the accumulated inflation rate varies exponentially with time for the period from 1950 to 1975. During the oil crisis of the 70's inflation performed differently due to the great increase of oil prices during that period of time.

For this study, due to the great importance of energy consumption for hydrogen cyanide production, the accumulated inflation rate based on crude oil market price [246] is used to perform further economic calculations. This inflation will mainly be reflected in the price of hydrogen cyanide and the different raw materials.

4.4 Evolution of prices

Market studies, are of greater importance when facing costly investments. There are many consulting companies focusing on market studies of fine chemicals, energy and commodities, [34], [57-60]. Most of these companies have available information of historical prices on their websites. Ammonia as a main raw material for the fertilizer industry and ammonium sulfate as a fertilizer itself have been studied in depth by governments and major fertilizer associations [55-59]. Energy studies can be obtained from public institutions such as the Energy Information Administration (EIA) [60-65] and annual reports from oil companies such as BP-Amoco [54].

4.4.1 Hydrogen cyanide price

Total world production of hydrogen cyanide is averaged in 1.5 million metric tons per year [93]. Major producers are Dupont, Degussa-Hüls, and Rohm and

Haas [249]. As described in prior sections, there are three main production processes, Andrussow, BMA, and Fluhomic, and these processes represent 75% of the total capacity and the balance is co-product material from acrylonitrile production.

Major end uses for hydrogen cyanide include acetone cyanohydrin, adiponitrile, sodium cyanide, methionine, cyanuric chloride and chelating agents [250]. Overall demand of hydrogen cyanide linearly increased over the last 15 years, [250] (see Figure 4.2). Its increasing demand has been ruled by the market demand of downstream products such as adiponitrile (41%), sodium cyanide (32%) and methionine (14%).

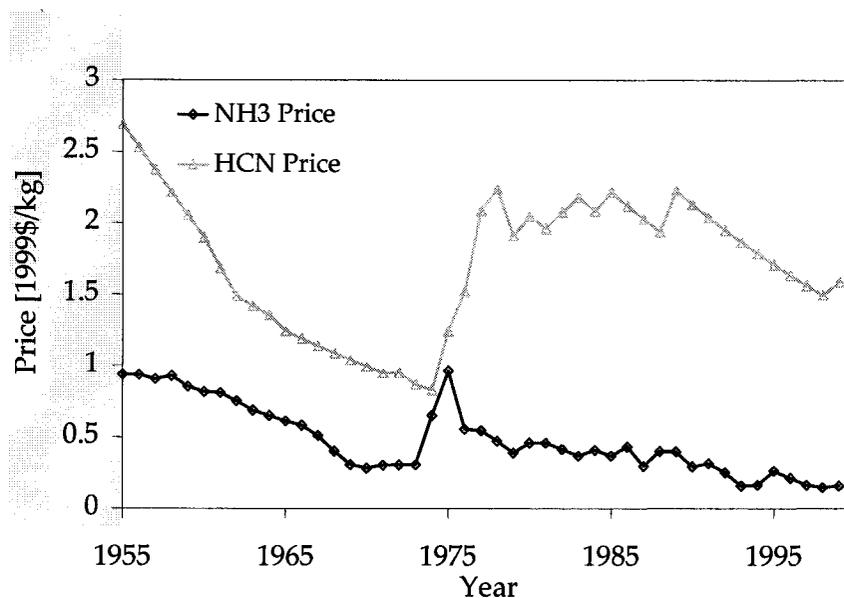


Figure 4.3: Ammonia and hydrogen cyanide price evolution [251, 252].

Due to its high toxicity hydrogen cyanide is commonly internally consumed, causing that only relatively small amounts go into the market trade and that is the reason why it is very difficult to estimate a market price. In Figure 4.3 one can observe the evolution of prices for 99.5% liquid hydrogen cyanide [251].

4.4.2 Ammonia price

Ammonia is the basic raw material of the world fertilizer industry [59], [252], [55], [58]. Fertilizers account for an estimated 85-90% of the end-use market for ammonia [93]. Major downstream fertilizer products include urea, ammonium nitrate, ammonium sulfate, and ammonium phosphates. Industrial uses for ammonia and its derivative products account for the remaining 10-15% of the world market. These include animal feed, explosives and the production of polymers. World ammonia production in 1999 was approximately 107 million metric tons and its demand is expected to increase by 3% per year, [57], [55]. Figure 4.3 shows the evolution of the ammonia price during the period of study.

4.4.3 Natural gas, coal, and heavy oil prices

Natural gas is generally defined as a characteristic mixture of gaseous minerals containing both hydrocarbon and non-hydrocarbon gases, methane being its major component (typically 85–96% by volume) [93]. Natural gas also contains ethane, propane, butanes, pentanes, hexane (known as natural gas liquids (NGLs)) and non-hydrocarbon gases such as nitrogen, helium, carbon dioxide and hydrogen sulfide. Dry natural gas (used as a raw material in the hydrogen cyanide process) contains mainly methane (up to 96%) and small quantities of NGLs and nitrogen.

Worldwide natural gas reserves (recoverable with present technology) are estimated at 5,100 trillion cubic feet (33% of the world total), [55, 56, 65, 67, 69,259]. The increasing demand and the following construction of pipelines and infrastructure, is turning natural gas into one of the most important sources of energy.

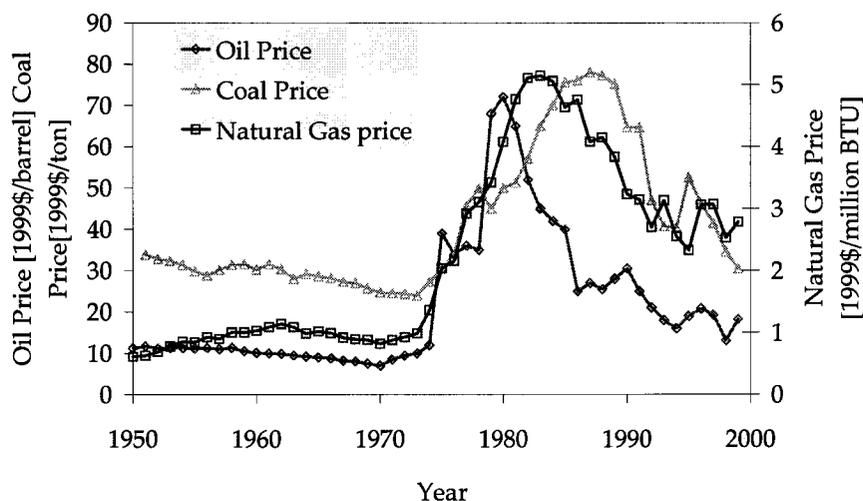


Figure 4.4: Natural gas, coal and oil price evolution in 1999\$ [55, 56, 65, 67, 69,259].

Figure 4.4 shows the evolution of prices for natural gas, coal and oil in the US over the last fifty years [56, 65, 68]. The importance of natural gas in the production of hydrogen cyanide relies on the fact that it is used for heating purposes and as a source of methane for the reaction with ammonia.

4.4.4 By-products and other raw materials prices

Among other chemicals, ammonium sulfate [253] and sodium cyanide [250] as by-products, sulfuric acid [261,262], and caustic soda [255] have been taken into account (see Figure 4.5). The option of selling hydrogen obtained from the process requires pressure swing adsorption for further purification. In the scenario described in this work, the hydrogen produced is burned to obtain heat required in the reactor; this means that the evolution of the hydrogen price is not required for further economic evaluation.

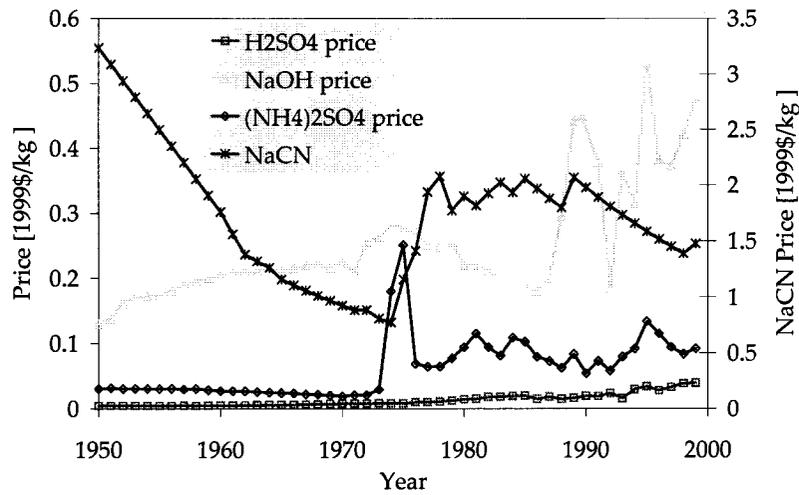


Figure 4.5: By-products and other raw materials price evolution.

Summary

This chapter shows the influence of the market evolution on the evolution of the economic performance of the BMA process. The market and historical prices of products, raw materials, and energy were analyzed obtaining a detailed framework towards performing further economic calculations.

CHAPTER 5 -ENVIRONMENTAL REGULATIONS EVOLUTION

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5.1 Introduction

The performance of a chemical process is influenced by many variables during its lifetime. The introduction of new technologies and changes in the market situation are continually affecting environmental and economic results. In previous chapters the evolution of the technology and market situation was studied. It is clear that besides technology and market, environmental regulations also play an important role in both, the economic and environmental performance of chemical processes.

In this chapter the study of the evolution of the environmental regulations is performed. After an initial analysis of the emissions produced in the production of hydrogen cyanide by means of the BMA process, a framework for the analysis of the environmental regulations is presented.

5.2 Framework

Hydrogen cyanide is a quite a dangerous chemical. Direct emissions to water or air were not considered due to the fact that emission limits during the entire period of study were considered extremely low. The production of hydrogen cyanide requires very basic raw materials and energy sources. Natural gas is used as a raw material and as an energy source. Ammonia is obtained from air and from energy carriers (natural gas, coal, or oil). This leads to the assumption that every major emission is related to the production and combustion of energy, in this case natural gas, coal, and oil. As described in previous chapters the production of natural gas, coal, and oil has not dramatically changed. It is also assumed that the combustion processes of coal, oil and natural gas themselves have not changed over time. What did

change were the end of pipe technologies to comply with the regulations that appeared over the time period of study.

Energy production also requires certain energy consumption. It is assumed that this energy will come from the respective energy source produced. This means that for the production of natural gas the source of energy is natural gas and the emissions from natural gas production are considered to come from natural gas combustion.

The final assumption is that in order to not complicate the problem, only air emissions will be considered. Indicators considered comprise nitrogen oxides (NO_x including N₂O), carbon monoxide (CO), carbon dioxide (CO₂), volatile organic compounds (VOCs, including CH₄), sulfur dioxide (SO₂), and particulate matter (PM) [48-51].

5.3 Evolution of Legislation

Environmental regulations define the emission levels for the different indicators of study over time which is why no technological assessment of combustion is performed. The regulations followed in this study are the US regulations obtained from the Environmental Protection Agency (EPA) [256]. The evolution of the environmental regulations can be described as follows.

In 1955 [257], after many state and local governments had passed legislation dealing with air pollution, the federal government decided that this problem needed to be dealt with on a national level. This was the year Congress passed the Air Pollution Control Act of 1955, the nation's first piece of federal legislation on this issue. The language of the bill identified air pollution as a national problem and announced that research and additional steps to

CHAPTER 5 ENVIRONMENTAL REGULATIONS EVOLUTION

improve the situation needed to be taken. It was an act to make the nation more aware of this environmental hazard.

Eight years later, Congress passed the nation's Clean Air Act of (CAA) 1963[258]. This act dealt with reducing air pollution by setting emission standards for stationary sources such as power plants and steel mills. Amendments to the Clean Air Act were passed in 1965 [259], 1966[260], 1967[261], and 1969[262]. These amendments authorized the Secretary of Health, Education, and Welfare (HEW) to set standards for auto emissions, expanded local air pollution control programs, established air quality control regions (AQCR), set air quality standards and compliance deadlines for stationary source emissions, and authorized research on low emissions fuels and automobiles.

By 1970 [262, 263], the issue needed to be addressed again. Although important legislative precedents had been set, the existing laws were deemed inadequate. Although technically an amendment, the Clean Air Act of 1970 was a major revision and set much more demanding standards. It established new primary and secondary standards for ambient air quality, set new limits on emissions from stationary and mobile sources to be enforced by both state and federal governments, and increased funds for air pollution research. It was soon discovered that the deadlines set were overly ambitious (especially those for auto emissions). To reach these standards in such a short period of time, the auto industry faced serious economic limitations and seemingly insurmountable technological challenges. Over the next decade, the legislation was once again amended to extend these deadlines and to mandate states to revise their implementation plans. Congress did not amend the Clean Air Act during the decade of the 1980s, in part because President Reagan's administration placed economic goals ahead of environmental goals.

In 1990[264], after a lengthy period of inactivity, the federal government believed that they should again revise the Clean Air Act due to growing environmental concerns. The Clean Air Act of 1990 addressed five main areas: air-quality standards, motor vehicle emissions and alternative fuels, toxic air pollutants, acid rain, and stratospheric ozone depletion. In many ways, this law set out to strengthen and improve existing regulations.

In summary, the Clean Air Act of 1970 established a major air regulatory role for the federal government. The act was further extended by amendments in 1977 [263] and, most recently, in 1990 [264]. The 1990 Clean air amendment is one of the most complex and comprehensive pieces of environmental legislation ever written. It authorized EPA to establish standards for a number of atmospheric pollutants, including SO₂ and NO_x. Two major portions of the CAA relevant to SO₂ and NO_x control are Title I and Title IV. The effect of this legislation over the combustion emissions of natural gas, coal and oil is going to be observed in the following sections.

5.4 Evolution of emission limits

SimaPro 5.0 data for oil [51], coal [49] and natural gas [50] combustion were used as a basis for calculating the emissions over time. Restrictions produced by environmental regulations were applied to these emissions to obtain an evolution of the emission limits per GJ over time. Emissions not considered as pollutants by the Clean Air Act have remained constant over time (e.g. CO₂). According to the SimaPro 5.0 database, 54MJ [50] of energy are obtained assuming 100% efficiency from the combustion of 1 kg of natural gas. Simple natural gas combustion produces low SO_x and NO_x emissions. Natural gas combustion is considered always to be below the emission limits regulated by legislation.

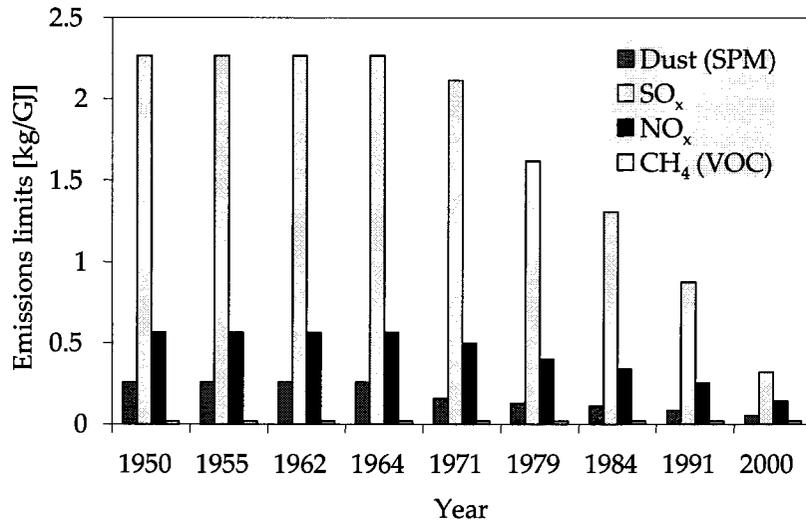


Figure 5.1: Evolution of coal combustion emission limits.

Information about emissions for the production of natural gas, coal, and oil can be found in the literature [49-51, 265, 266]. As an assumption all the emissions from the production of these sources of energy will be considered to come from the combustion of the respective energy sources. As a result 2.7 MJ, 1.465 MJ, and 5.41 MJ of energy are required for the production of 1 kg of natural gas, coal and oil respectively. A major criticism of coal as a fuel source for energy generation is that it produces large amounts of pollutants, primarily sulfur dioxide (SO₂), nitrogen oxides (NO_x), and small particulate matter (SPM), as well as carbon dioxide (CO₂), which is implicated in global climate change.

According to the SimaPro 5.0 database from the combustion of 1 kg of coal and oil 29.3 MJ and 41 MJ of energy are obtained respectively assuming 100% efficiency [265], [266]. Over the last fifty years advanced technologies have dramatically improved the environmental performance of flue-gas desulphurization systems for SO₂ control and NO_x reduction technologies

[267]. The evolutions of the resulting emissions due to changes in environmental regulations in coal and oil combustion are shown in Figure 5.1 and Figure 5.2.

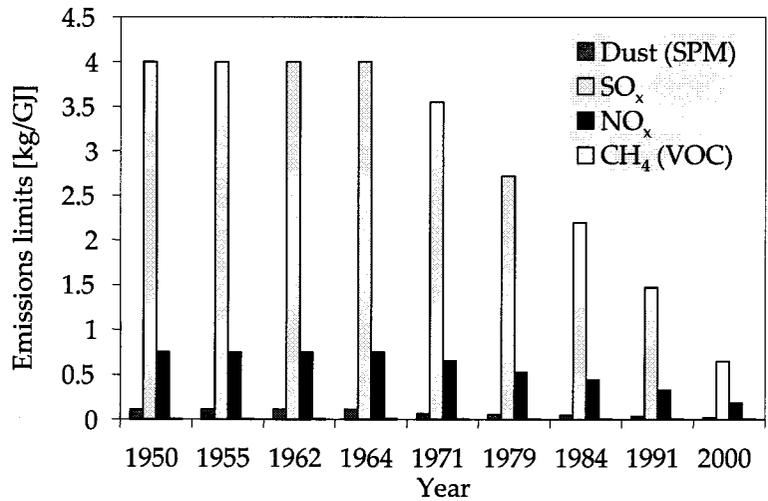


Figure 5.2: Evolution of oil combustion emission limits.

Summary

In this chapter the study of the evolution of the environmental regulations is presented. Since hydrogen cyanide is a very toxic chemical emissions of this product have always been minimum. The major sources of emissions have always been then the combustion of energy carriers. The information obtained in this chapter then, is related to the evolution of the emission limits for the combustion of energy carriers

CHAPTER 6 - ECONOMIC AND ENVIRONMENTAL ASSESSMENT

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6.1 Introduction

This chapter introduces the results of the assessment of the BMA process. This chapter emerges as the result of combining the analysis of the technological evolution with the evolution of market and environmental regulations.

6.2 Economic assessment

As described in prior sections, there are several indicators appropriate to perform economic evaluations; most of them include the fixed investment cost such as the net present value described in Turton [52] or Biegler [66]. Net present value is an economic indicator that analyzes the whole lifetime of the investment to compare between alternatives. The net present value does not apply to the current case study since the plant and most of the equipment remains when a technological improvement is introduced. A different indicator has to be introduced. The economic indicators used for this evaluation are expressed as the total annualized cost per kilogram, TACK; total annualized income per kilogram, TAIK; and total annualized profit per kilogram, TAPK. A detailed description of the indicators can be found in Appendix B.

The TACK comprises the direct manufacturing costs and the costs of investment. Direct manufacturing costs considered are: raw materials, utilities, wastewater treatment, maintenance, personnel and catalyst cost. The fixed costs include all the costs associated with the construction of a facility for the production of the required amount of hydrogen cyanide at certain point in time. Maintenance and linear depreciation for a plant lifetime of 25 years are finally added to obtain the final value of TACK. The Total Income per Kilogram TAIK is comprised by the addition of selling the main product

and byproducts at their respective market price. The TAPK is equal then to the TAIK minus the TACK. Results are shown in Figure 6.1 for ammonia and Figure 6.2 for hydrogen cyanide.

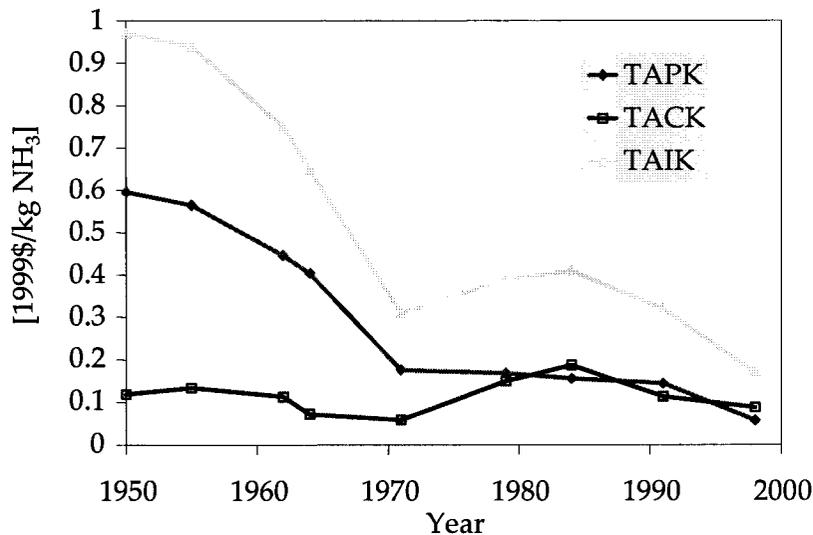


Figure 6.1: Evolution of economic indicators for the ammonia technology.

Figure 3.22 showed the evolution of the energy consumption per ton of ammonia during the last fifty years. Energy consumption evolution is of high importance due to the fact that for the production of ammonia raw materials and energy usually come from the same source. There has been a steep descent of the energy consumption in this process for two main reasons, the energy crisis of the seventies and the influence of the economy of scale of the sixties. A detailed description of the results can be found in Appendix B.

So it is obvious that any technological change influencing the energy consumption would also influence the economic performance of the process. As discussed in Chapter 3, most of the improvements related to the reforming part were of high importance. Followed by those energy savings due to

CHAPTER 6 ENVIRONMENTAL AND ECONOMIC ASSESSMENT

improvements in other parts such as carbon dioxide absorption and compressor duty were of second importance.

The total annualized income per kilo has been decreasing over time due to the fact that the price ammonia has not consequently increased with the raise of the natural gas price. This has been due to the influence of the economy of scale, and the fact that bigger plants were constructed and the market reached a saturation point in which the demand was lower than the production. This phenomenon can also be observed in the total annualized cost per kilogram that in spite of the increase of the price of natural gas did not change dramatically over time. High cost of raw materials was modulated by the construction of larger ammonia plants. Focusing now on the hydrogen cyanide production (see Figure 6.2), during the first years of existence (1957-1965) fixed costs highly influenced the economic performance of the BMA process. The small capacity of the reactor was associated with a big investment cost. The demand and the high price of hydrogen cyanide resulted in a positive economic result.

The period from 1965 to 1970 is characterized by the appearance of large improvements in the ammonia production. Bigger and better operating ammonia plants produced a certain over-capacity of ammonia and therefore a large drop in its price. The economy of scale created the consequent drop of the hydrogen cyanide price. In order to maintain a profitable process the efficiency of the plant was optimized by increasing the number of tubes in the reactor. Fixed costs per kilogram of hydrogen cyanide decreased but profitability dropped due to a insufficient price of the chemicals produced.

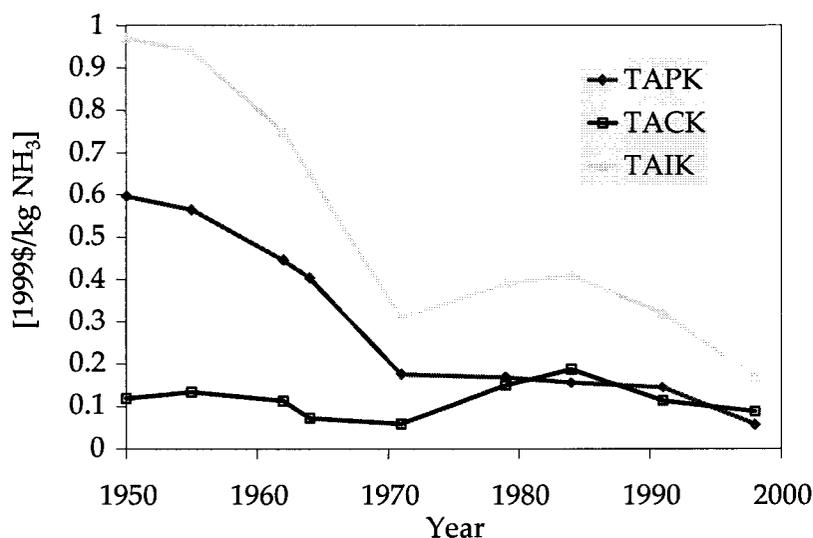


Figure 6.2: Evolution of economic indicators for the BMA technology.

The 1970-1983 decade was a period of economic instability. The energy crisis affected in particular the basic chemicals. Natural gas and ammonia doubled their price in a short period of time. The hydrogen cyanide price slowly increased with a certain time delay. During this period the profitability decreased to a loss. This fact forced the implementation of new solutions. New reactor designs with higher numbers of new-generation tubes were implemented. A higher operational time and a larger plant capacity with lower energy consumption were achieved.

In 1983 new tube technology allowed a significant increment in the number of tubes per reactor and consequently of its capacity. This resulted in great improvement of the economic performance of the process. Further changes affected the lifetime of the tubes, but the BMA technology remained similar to how it is known today. During these last two decades the price of raw materials stabilized and its slow descent produced quite a substantial and stable profit.

6.3 Environmental assessment

In this study the environmental assessment of hydrogen cyanide production was based on the total energy consumption of the BMA process and its upstream processes. Combustion of natural gas, coal, and oil was considered as direct source of emissions. As described in prior sections natural gas has been used as the energy source in the BMA reactor. Figure 6.3 describes the evolution of energy consumption per kilogram of hydrogen cyanide.

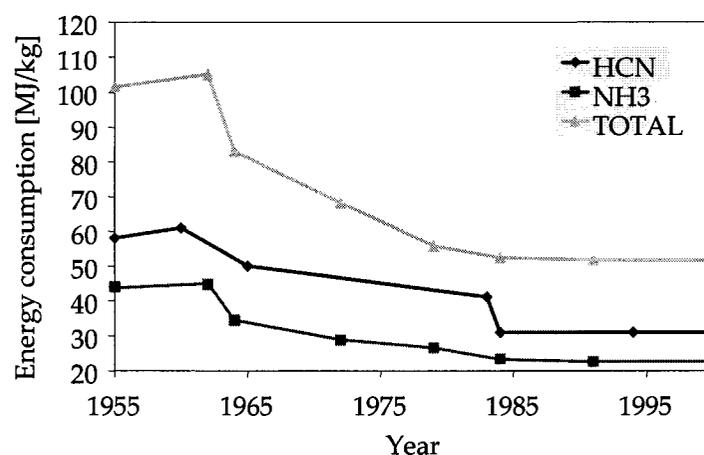


Figure 6.3: Model based evolution of energy consumption in the hydrogen cyanide production.

The total energy consumption is calculated from the direct requirements of energy in the BMA process, the energy consumed for the production of the required ammonia and the energy demanded for energy carrier production. The production of one kilogram of hydrogen cyanide today requires almost half the energy required fifty years ago. The energy consumption of ammonia production also decreased from 60 MJ to 28 MJ per kg.

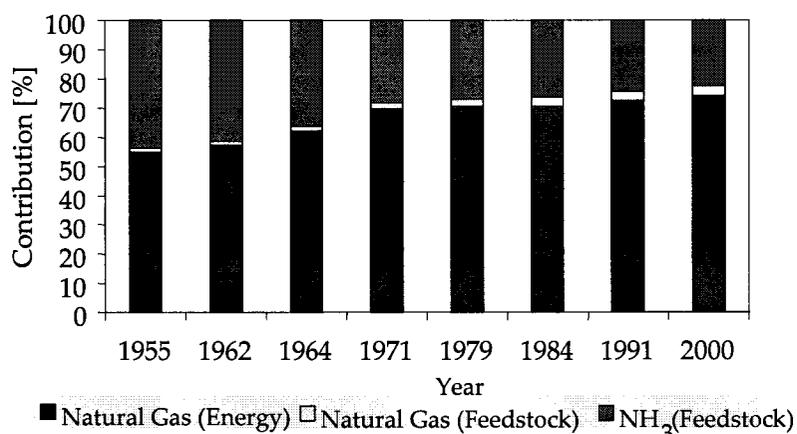


Figure 6.4: Relative contribution to the overall CO₂ emissions of hydrogen cyanide production resulting from ammonia, natural gas and hydrogen cyanide technologies.

Figure 6.4 shows how the ammonia production highly contributed the overall emissions of the hydrogen cyanide process in 1955. The contribution of ammonia production continuously decreased from 45% in 1955 to 22% in 2000 to CO₂ emissions. The production of natural gas accounted for less than 2% over the period of study. If the technologies of hydrogen cyanide and ammonia production are compared, one finds different evolutions. Ammonia production has shown a faster technological improvement as displayed in Figure 6.3 and Figure 6.4. Reasons for this are based on the importance of ammonia itself. After sulfuric acid the second largest chemical produced in the world. A second reason is that due to its extreme reaction conditions the BMA process is technically rather complicated. This fact slowed down the research for further improvements. A last reason that can be formulated is the ownership of the technology. There are several companies that license ammonia technology such as ICI, Kellogg, Topsoe, Uhde, and Ammonia Casale, while the BMA process is owned by Degussa and is only licensed to Lonza. This may restrict the efforts towards further development of the BMA process.

The emissions of the ammonia production are influenced by two factors, the evolution of its technology and the feedstock production. Figure 6.5 displays that current CO₂ emissions have decreased more than 80% as compared to the 1950's while overall energy consumption has decreased 45%. During the first ten years studied, the most important factor affecting the emissions was only the feedstock mixture used. During this period a slight descent in the emissions can be observed due to the introduction of natural gas as the main raw material.

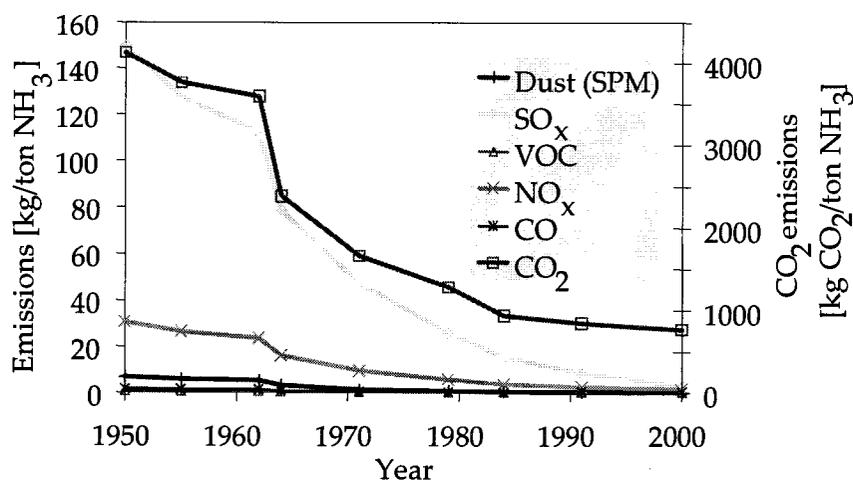


Figure 6.5: Model based evolution of emissions from ammonia production.

The trend to increment the reformer working pressure during the following years increased the overall energy demand due to a higher steam to carbon ratio. Emissions did not increase during this period due to the continuous introduction of natural gas as the main feedstock. The development of centrifugal compressors around 1960 allowed the raising of loop and reformer working pressures at a lower energy cost and decreased the overall energy consumption of the plant.

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Emissions kept decreasing during the following years due to the combined effect of operating conditions and the feedstock mixture. The development of centrifugal compressors also allowed the Kellog and Topsoe concept of larger ammonia plants. This concept permitted higher energy efficiency thus decreasing the emissions per kilogram of ammonia produced. The 1970-1980 period was highly influenced by the energy crisis and many actions were taken to increase energy efficiency. Heat integration and improved CO₂ absorption systems along with the continuous introduction of natural gas as the preferred feedstock decreased the overall energy consumption and thus the total emissions. Finally, the development of new catalysts with higher yield at lower pressure combined with the introduction of high capacity and low pressure drop converters during the last part of the eighties nearly shaped ammonia processes to those known today.

CO₂, SO_x and NO_x emissions evolved similarly until the beginning of the seventies (see Figure 6.5). Since then, two factors affected the different behavior of the curves, the feedstock mixture and legislation. Cleaner natural gas increased its market share in comparison to coal or oil and highly affected the emissions of SO_x. The Clean Air Act introduced in 1971, 1979, and 1984 controlled NO_x and SO_x emissions. The effect of legislation can be observed in the steeper descent of the SO_x and NO_x curves versus the CO₂ curve, since CO₂ was not regulated.

The overall case of hydrogen cyanide production (see Figure 6.6) is more complicated due to the fact that it is also affected by the production of precursors. The SO_x emissions are completely related to the ammonia production due to the fact that natural gas combustion (mainly used in the BMA process) emits low amounts of SO_x. The CO₂ emissions come from the hydrogen cyanide process, the ammonia process and the natural gas

production. On the other hand, the steam produced is reused in the plant, the excess obtains an environmental credit equal to the emissions required to produce such amount from natural gas.

The major influence in the environmental performance of the BMA process has been the increment of the reactor capacity that allowed higher energy efficiency per kilogram of hydrogen cyanide produced. As described in prior sections the capacity continuously increased due to the increment of the number of tubes and their longer lifetime. Due to the low price of natural gas the reactor temperature was increased to obtain higher yields. This event (later discarded), and changes in ammonia production during these years increased the total energy consumption (see Figure 6.3).

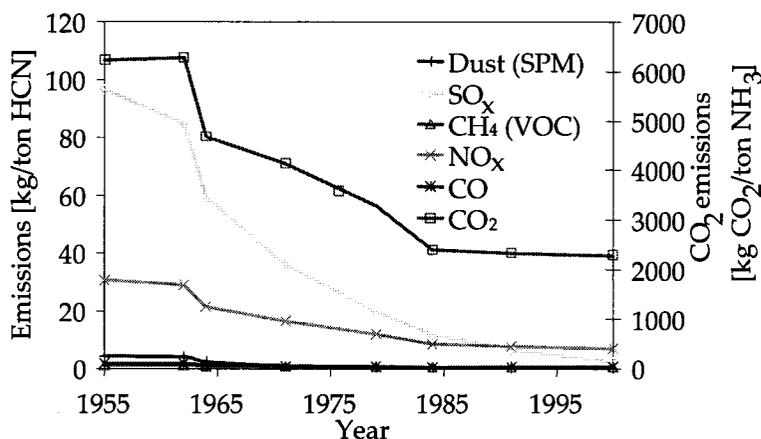


Figure 6.6: Model based evolution of emissions from hydrogen cyanide production.

SO_x and CO₂ emissions trigger completely different environmental effects (acidification and global warming). CO₂ emissions, for example, were considered as non pollutant in the past and were not restricted by any environmental regulation.

The aggregation problem is partially solved by the Global Warming Potential index (GWP). This indicator is used to translate the level of emissions of various gases that have the same effect into a common measure. GWPs are calculated as the ratio that would result from the emission of one kilogram of a greenhouse gas to that from the emission of one kilogram of carbon dioxide. The impact of greenhouse gases is expressed in terms of Carbon Dioxide Equivalent. The International Panel on Climate Change (IPCC) has presented these GWPs and regularly updates them in new assessments [268].

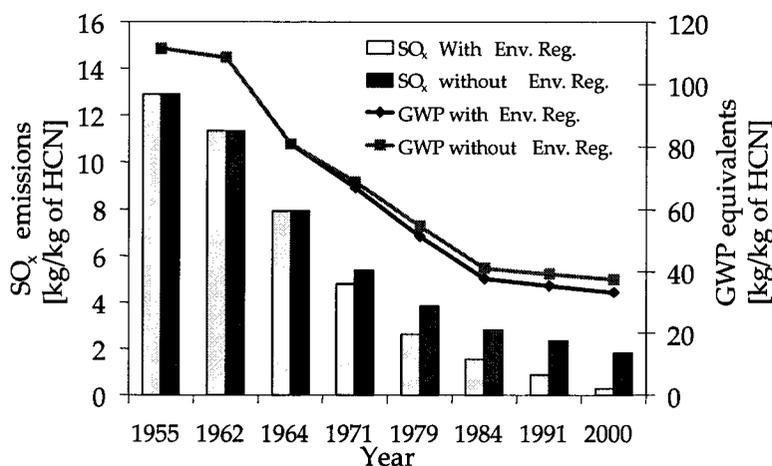


Figure 6.7: Evolution of emissions of SO_x and GWP gases resulting from hydrogen cyanide production.

Figure 6.7 shows the evolution of the GWP emissions and the SO_x emissions with and without the effect of environmental regulations. The results of not having environmental regulations were obtained by using the emissions from 1950 during the whole time of study. A difference between the curves can be observed as soon as the clean air act of 1971 was introduced. SO_x emissions are directly related to the production of ammonia, while the GWP gases

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emissions are more influenced by the production of hydrogen cyanide. Natural gas is mainly used in the production of hydrogen cyanide, compared to coal or oil it is a cleaner raw material and source of energy. A higher influence of regulations can therefore be observed in SO_x emissions, since these emissions are generated mostly in ammonia production which also uses coal and oil.

From the environmental point of view Figure 6.7 shows that emissions have decreased as a result of the technological improvements and environmental regulations. Some of the reductions are due to the combined effect of technology and regulations such as for NO_x, SO_x and VOC. In the case of CO₂ the reduced emissions were only due to the effect of technological change which resulted in a more efficient use of energy.

It is evident that hydrogen cyanide production has dramatically changed over the last fifty years. The introduction of the Clean Air Act began to restrict the amounts of air pollutants released from combustion of energy carriers. Nevertheless, energy savings have been the major driving force for the reduction of emissions. Since only emissions from energy consumption are taken into account it is difficult to establish a trade-off between energy and emission reduction. The scenario might have changed if emissions of hydrogen cyanide itself would have been considered. A trade-off between energy consumption and emission limits could have been established. It is possible that in such a case the role of environmental regulations would have increased.

6.4 Conclusions

After reviewing the economic and environmental results, one can state that the environmental performance of the BMA process is correlated to its economic performance. Results show a general trend; the higher the technological development of a process the better its economic and environmental results.

It is clear that a chemical process is not usually on the cutting edge of its technological development when it starts production. Chemical companies are governed by the market situation, when there is an urgent need of a certain product. In such a case time is the constraint, possibly because other processes inside the company require this product as a raw material or simply because the first to make the move will later obtain a larger market share. On the other hand, certain technological advances are not available at the time production starts, such as new materials (new ceramics for tubes in the BMA process) or development of more efficient process equipment (centrifugal compressors in the ammonia production).

If we look back on our process of study of the BMA process, it is very easy to now say (looking at its evolution) that several decisions were not the most appropriate. Among others, the reactor configuration and its constraints have been leading the technological evolution of the whole process. Obviously that there was more room for improvement in that reactor but this statement is not attempting to criticize decisions made by engineers at that time. Who forgot to tell them that hydrogen cyanide would become a commodity chemical dropping quickly its price, or that there would be an energy crisis or environmental regulations would appear sooner or later? Clearly the BMA reactor is technologically highly complicated and consequently very

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expensive. By learning from this example, future designs should include flexibility and environmental motivations among others, apart from economic motivations. The continuously changing situation and the long lifetime of chemical plants are reasons enough to invest time and resources into developing small and flexible processes that can easily adapt to new regulations and market needs.

At this point it seems clear that technology is a major driving force of the environmental and economic performance of a process but what have the effects of environmental regulations been? The introduction of the clean air act began restricting the amounts of air pollutants released from combustion of energy carriers. Environmental regulations improved end of pipe technologies such that they allowed remaining at the established emission limits. Nevertheless, energy savings at the core process have been the major driving force for the reduction of emissions. But looking at the results from Figure 6.7 one can see that two indicators have been chosen, SO_x and GWP. On one hand SO_x emissions are directly affected by the emission limits established by environmental regulations. On the other hand GWP, are only affected by the limits established for NO_x emissions SO_x emissions clearly were reduced further than GWP but major reductions have been achieved by improvements of the energy efficiency of the process and not by the effect of regulations. A critical market situation highly influenced the technological improvements of the process and with it the environmental performance of the process. It is not surprising to discover that an economically more efficient process improved at the same time as its environmental performance. It is time to question whether reactive modes of legislation such as those represented by environmental restrictions are more effective than proactive solutions such as inducing technology development by introducing tax benefits for those companies that invest in research and development. When

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facing the possible imposition of a CO₂ tax, the question would be which proactive solutions can be formulated? The appearance of environmental regulations in the past provoked the use or improvement of end of pipe technologies.

It was stated that improvements in the core process technology had a higher influence in the environmental performance. Promoting the investment on research and development to develop the core technology of the processes would be a way to obtain better environmental "AND" economic performance. This option, together with responsible environmental regulations will help to merge economic and environmental concerns into a single objective of tackling the problem from a proactive point of view.

Summary

This chapter introduces the results of the assessment of the BMA process. In this chapter the information obtained from previous chapters regarding the evolution of mass and energy balances, market, and environmental regulations is combined to obtain the economic and environmental performance evolution of the BMA process.

CHAPTER 7 -POTENTIAL IMPROVEMENT

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7.1 Introduction

Chemical process design is currently focused on the improvement of the performance of chemical processes. It seems clear that the starting point for possible improvements is the state of the art of existing technologies. Several efforts have been made to develop structured methodologies for the retrofit of existing processes with different objectives [67-72]. These methods analyze the existing process and come up with different alternatives or possible improvement potential. As described in previous sections the technological evolution of processes is a very important source of information that should be included in the retrofit process. This chapter aims to merge the information obtained from the technological assessment and the existing retrofit methodologies. Information obtained from chapters 3 to 6 will be combined with a novel retrofit methodology developed by Uerdingen [73] in order to obtain potential improvements of the BMA process.

7.2 Performance evolution

Boundaries must be defined in order to limit the flow of information. For economic studies, only prices of raw materials of upstream processes are needed. These prices can be easily obtained from data bases, publications, or governmental organizations. On the other hand for the environmental analysis a deeper study of the upstream processes is required in order to obtain an evolution of the life cycle emissions. In previous chapters, analysis of the evolution of the production of raw materials, such as ammonia, was performed to produce the inventory required for further environmental calculations.

The first problem is encountered; retrofit methodologies are process oriented, and this means that only the process of study is analyzed. This is due to the belief that the process can only be improved by changing the core process technology. This is correct when only economic objectives are taken into account because the price of raw materials and energy is fixed by the market. When attempting to minimize the total environmental impact, one should take into account the entire life cycle of the product of study. At times, an alternative with a better environmental and economic performance from the core process point of view is not the best from the life cycle point of view.

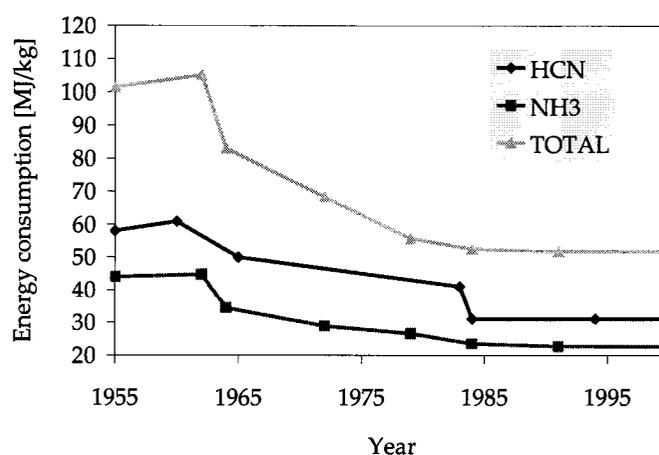


Figure 7.1: Calculated energy consumption per kilogram of hydrogen cyanide produced.

Figure 7.1 represents the evolution of the total energy consumption for the production of hydrogen cyanide. As shown, approximately half of the energy requirements come from raw materials and energy production, especially ammonia.

The BMA process has dramatically improved its performance during its fifty years of lifetime. Figure 7.1 shows that the total energy consumption per

kilogram of hydrogen cyanide produced has been cut by nearly half. Most of this reduction has been achieved by more efficient energy consumption in the reactor, more efficient production of raw materials, and rational use of the energy recycled. This affected the economic and environmental performance as discussed in chapter 6. A second and also related issue is increase in capacity; the BMA reactor has more than doubled its capacity in less than fifty years. This fact directly associated with the economy of scale allowed more efficient use of downstream equipment such as absorption or distillation columns.

7.2.1 State of the art

This section introduces an analysis of the evolution of the state of the art of the BMA process. In order to structure the information gathered in chapter three, the BMA process is divided again into three parts: reaction, separation, and purification (see Figure 7.2).

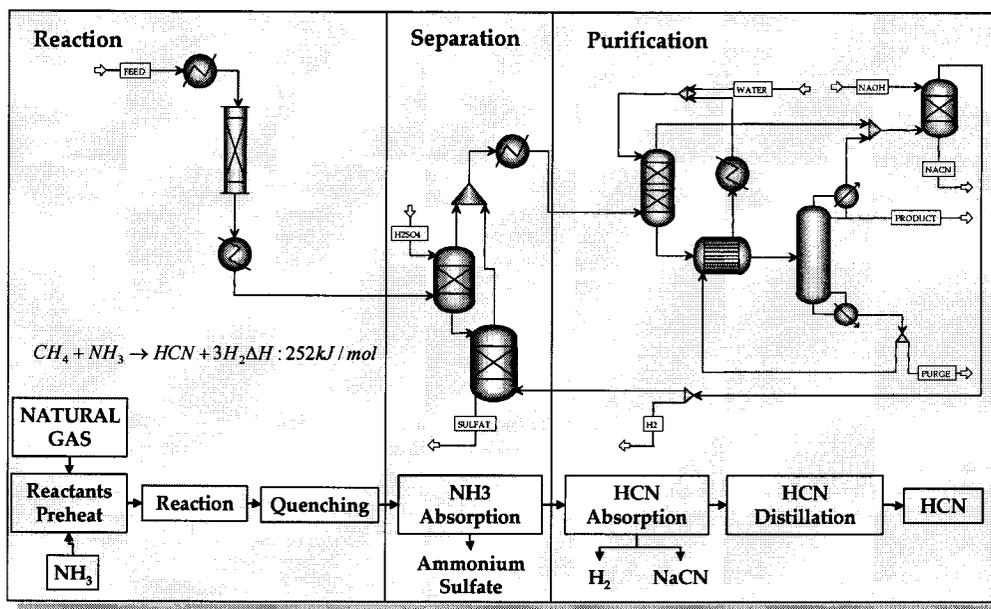


Figure 7.2: BMA process parts

Indicators used for the assessment consist of the Net Present Value (NPV) for the economic evaluation and carbon dioxide emissions for the environmental evaluation. Previous section used indicators based on annuities such as the total annualized profit per kilogram due to the fact that there was no large change in equipment or fixed cost investment. Alternatives generated in this section deal with large process changes and high investment in equipment that forced choosing net present value as a more appropriate indicator for economic evaluation. Figure 7.2 represents the base case, where for the production of 10,000 ton per year of hydrogen cyanide a NPV of 22 million dollars and 2.4 kilograms of carbon dioxide per kilogram of hydrogen cyanide are obtained. A detailed description of the flowsheet can be found in Appendix A.

Figure 7.3 represents the NVP and its major parts. The cost of the equipment is represented by the Bare Module Cost (BMC), the operating costs are represented by the Manufacturing Costs (MC) and the income by the Profit (P).

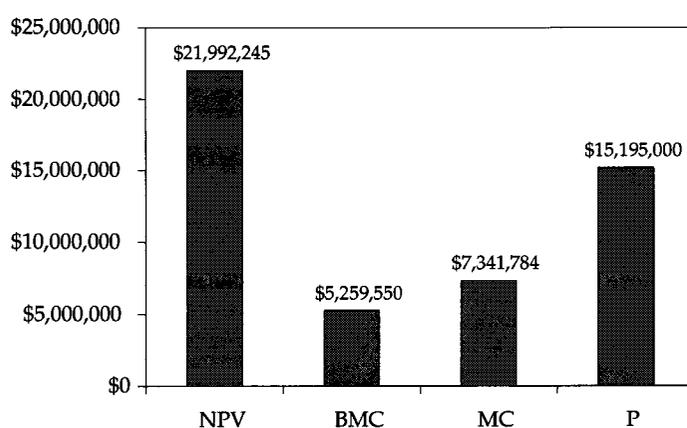


Figure 7.3: Net present value and parts of the base case.

Figure 7.4 illustrates the contribution of each process part to the operating costs, fixed costs and carbon dioxide contribution.

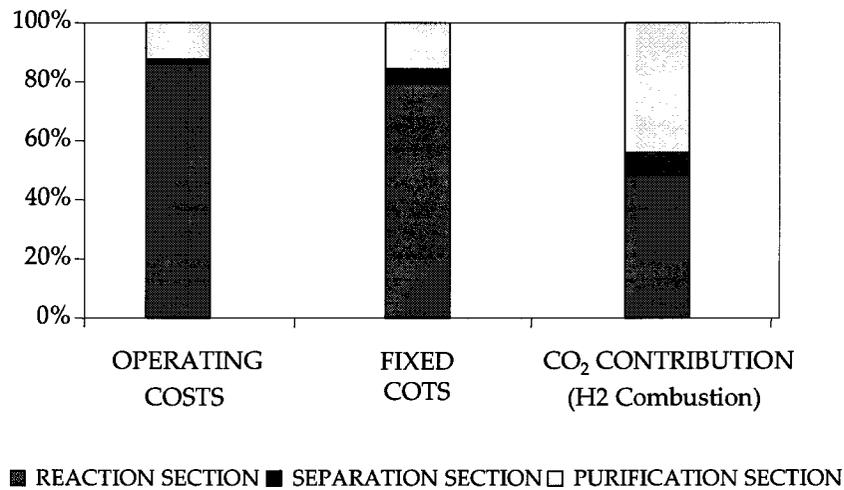


Figure 7.4: Contribution of each part to the economic and environmental performance.

Figure 7.5 represents the contribution of each raw material and energy carrier to the total carbon dioxide emissions. Natural gas has a double impact, as energy carrier (Nat Gas) and as a raw material (CH₄).

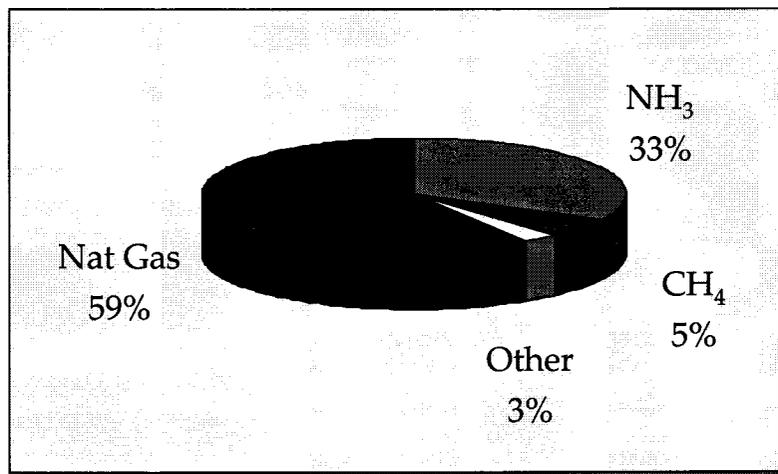


Figure 7.5: Contribution to the carbon dioxide emissions.

7.2.2 Process evolution

As mentioned before the BMA process is divided into three parts for further analysis. The reaction part consists of the preheating, reactor, and quenching parts. The separation part consists of the ammonia absorber, hydrogen cyanide stripper and crystallization parts. Finally, the purification part consists of the hydrogen cyanide absorber, heat exchanger, hydrogen cyanide distillation, and sodium cyanide absorber parts. This division was made to study the improvement efforts done in each part and to better identify improvement potentials.

From the economic point of view, a first analysis of the different parts was performed using the operational and fixed cost contributions. This analysis provides an idea of which part consumes most resources and which are the most expensive parts of equipment. Figure 7.6 represents the calculated evolution of the contribution of the different parts to the operational cost of the BMA process.

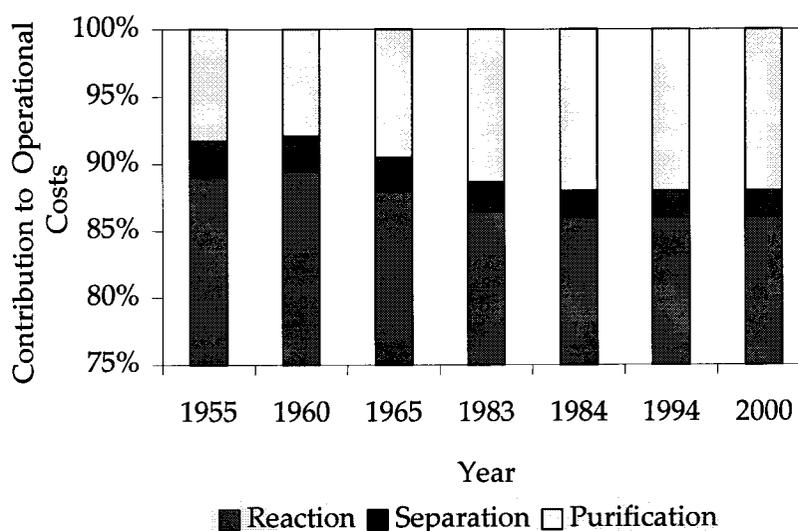


Figure 7.6: Calculated contribution to the operational costs of the BMA process.

Figure 7.6 shows that the reaction part had the highest cost contribution over the whole period of study. The separation part remained almost constant and the purification part increased its contribution from 8 to 12 per cent. This is an expected result since the endothermic reaction of hydrogen cyanide formation requires high energy consumption. Part of the energy recovered from the reactor is used for operating the rest of the plant, mainly lowering the contribution of the purification part.

The evolution of the contribution to the total fixed costs was considered second economic indicator. Figure 7.7 shows the contribution to the investment cost of the different parts of the plant. As soon as the reactor increases in number of tubes and higher production is achieved, the separation and purification parts contribute to a lower extent.

In this case tubes contribute to the fixed cost of the reactor although they have influence on the operational costs since they are replaced the plant stops for maintenance.

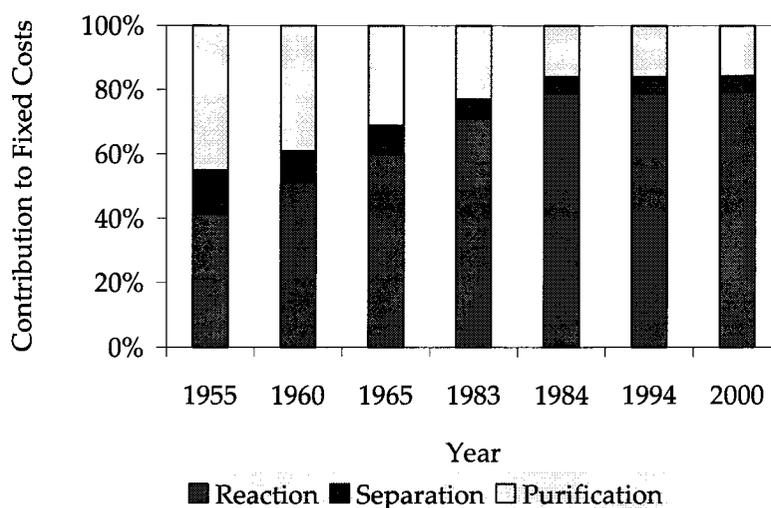


Figure 7.7: Calculated contribution to the fixed costs of the BMA process.

In order to obtain the environmental evolution of the different parts of the process one must define several assumptions. If the life cycle methodology is used, it is difficult to define the contribution of each part to the total environmental impact of the process. As a first assumption a division is performed, the impact from the ammonia production is separated from the specific emissions of the hydrogen cyanide process. Figure 7.8 represents the contribution to carbon dioxide emissions for the production of one kilogram of hydrogen cyanide of the ammonia and BMA technologies.

It can be observed how the improvements of the ammonia technology resulted in a decrease in the total carbon dioxide contribution per kilogram of hydrogen cyanide. This reduction is attachable only to technological improvements since the yield of the hydrogen cyanide reaction remained constant over the whole period of study.

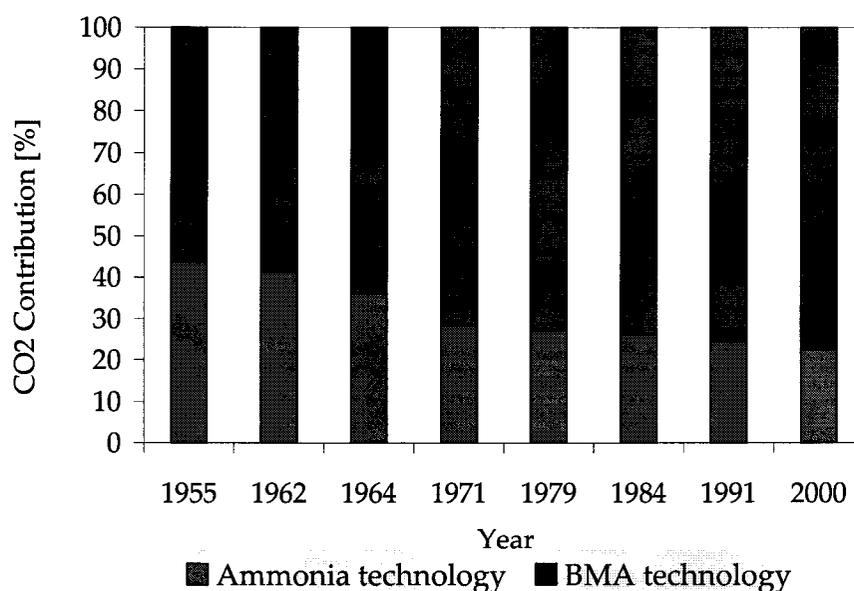


Figure 7.8: Calculated contribution to the production of hydrogen cyanide of the ammonia and BMA technologies.

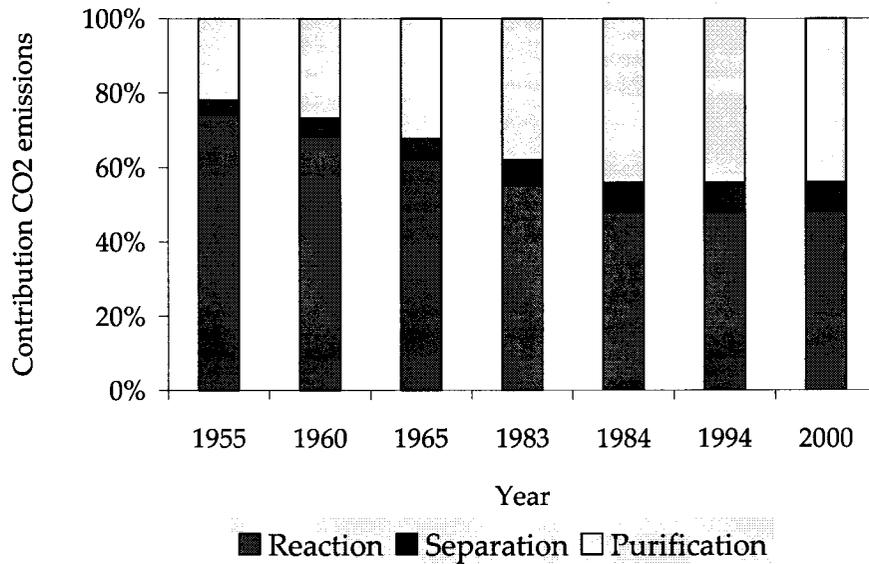


Figure 7.9: Calculated CO₂ contribution to the production of hydrogen cyanide by the different process parts.

Once the BMA technology contribution has been defined one can divide it into the contribution of the different parts of the process. Figure 7.9 represents the contribution of the reaction, separation and purification parts to the overall carbon dioxide emissions of the production of one kilogram of hydrogen cyanide by the BMA process.

This figure was plotted under several assumptions. As a first assumption the hydrogen produced is not purified and is reused for heating purposes. The different parts of the process interact amongst one another, meaning for example, that the steam produced by the heat recovered from the reactor can be reused in different parts. For economic evaluations this does not suppose a problem because steam can be sold/bought at a market price. On the other hand for the environmental calculations one should keep in mind that the steam should get some credit or bonus. In order to avoid problems with steam bonus and allocation it was assumed that the steam recovered was re-used in

each part. This means that there was no interaction between parts and the environmental impact is directly related to the energy consumption of each part.

Figure 7.9 shows how the improvements in the reaction part decreased its relative contribution to the carbon dioxide emissions. On the other hand the purification part suffered no technological change maintaining its emission levels constant but increasing its relative contribution to the overall emissions of the process.

7.2.3 Process technology outlook

In the previous section an analysis of the evolution of the state of the art in the production of hydrogen cyanide by the BMA process was performed. The process was divided into three parts and was evaluated regarding three indicators, contribution to the operational cost, fixed cost and emissions. In this part an analysis of these results is performed. This analysis aims to obtain guidelines for future improvements before using more methodological retrofit tools.

Observing Figure 7.6, Figure 7.7 and Figure 7.9 one can see that the reaction part is the most critical part of the process. As described in previous chapters it has also been the one subjected to the most technological changes. A small improvement in the reaction part supposes a large impact on the economic and environmental performance of the process. As a drawback the development of the reactor was based on the increase of number of tubes per chamber. At the same time this increase was subject to the discovery of new and stronger ceramic materials that could bear more extreme conditions. It seems that from the engineering point of view one should either develop new

ceramics or develop an entirely new concept of reactor. The development of a new reactor is a very expensive and risky procedure that requires a lot of R&D resources. On the other hand development of ceramics is more basic research than engineering studies.

Figure 7.10 shows that the best reactor configuration is the one that approaches the thermodynamic minimum of the reaction. The BMA process continuously decreased in total energy consumption during the period of study approximately to this minimum. Around 85 per cent of the total energy requirements are related to the reaction part (see Figure 7.4). This means that around 31 MJ of energy are required for the production of one kilogram of hydrogen cyanide. This is still far from the 7 MJ per kilogram required by the thermodynamic minimum, but there is less room for improvement than in 1955.

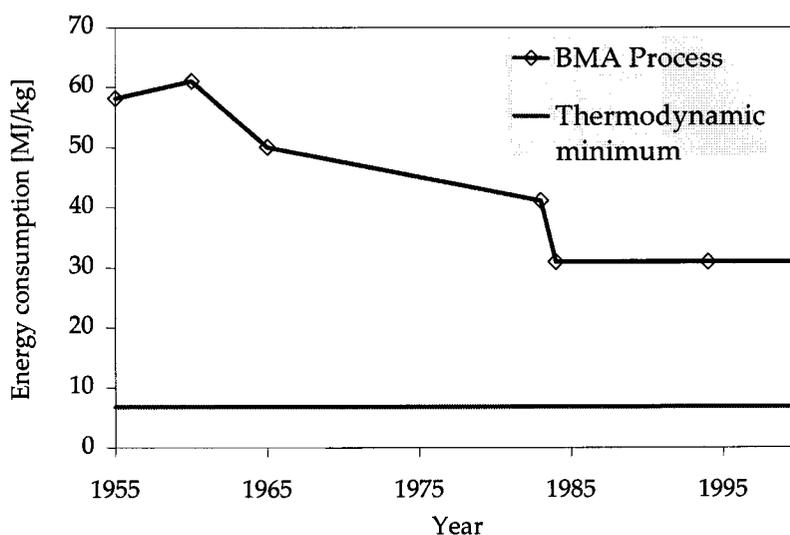


Figure 7.10: Calculated evolution of the energy requirements for the production of hydrogen cyanide by means of the BMA process.

It is not possible to achieve the thermodynamic minimum and the more a solution approaches it the more technological complications engineers must face.

On the other hand the closer the reaction part is to the thermodynamic minimum, the higher its contribution is to the other parts. This means that the separation and purification parts will start playing a more important role in overall economic and environmental performance. In difference with the reaction part, there are several existing process alternatives to the separation and purification and they can be improved by structured retrofit methodologies. One must keep in mind that these parts remained the same since the beginning of the process so there must be high potential improvement.

The separation process was highly investigated during the first years of existence of the BMA process. Analogies to other processes for the production of hydrogen cyanide (such as Andrussow) were implemented. Absorption of un-reacted ammonia with a solution of sulfuric acid was the first option implemented. The production of ammonium sulfate sold as a fertilizer favored this option. Changes in the fertilizer market forced the exploration of other alternatives such as absorption with a phosphate solution and then recovery of ammonia. This option was implemented and licensed by DuPont in the Andrussow process. However the lower content of un-reacted ammonia in the BMA process, along with the high operational cost per kilogram of ammonia recovered, including the license, led to discarding this option. Other separation methods were studied such as the zeolites adsorption later discarded due to undesirable polymerization. It is clear that the separation process can be improved if a new absorption method is discovered but information from Figure 7.6, Figure 7.7 and Figure 7.9 show

that the overall impact on the economic and environmental performance is relatively low.

In contrast, the purification part has remained totally unchanged during the whole period of study. Figure 7.6, Figure 7.7 and Figure 7.9 show that the influence on the overall performance has increased over the whole period of study. Its 12 per cent contribution to overall operational costs may drive wrong decisions when taking into account that it represents 40% of the carbon dioxide emissions. The difference in behavior between these two contributions is due to the fact that steam generated in the reaction part is mainly reused for running the distillation column of the purification part. Technology in the separation of gases has had a major breakthrough during the last fifty years. Technologies such as membrane separation or partial condensation discarded earlier can represent a good alternative for potential improvements.

7.3 Retrofit methodology

There are several retrofit methodologies based on two general principles on how to approach the retrofit problem [67-72]. The practice-based and the system based approach. The practice based approach focuses on specific parts of equipment and uses the experience gathered in daily plant operation as well as heuristic methods to obtain design alternatives. On the other hand system-based approaches focus on the overall process tending to simplify the problem in order to be able to use algorithmic and thermodynamic methods.

A good retrofit design method should include elements of both practice-based and system based approaches. The practice based approach shows clear advantages for the pre-selection of promising retrofit alternatives. System-

based approaches are well suited for the decision process when only few alternatives remain. The screening method applied in this thesis is a combination of both approaches developed by Eric Uerdingen during his PhD thesis [73].

Figure 7.11 shows an adapted version of the methodology proposed by Uerdingen [73]. It is divided in two major parts, base case analysis, and generation of alternatives.

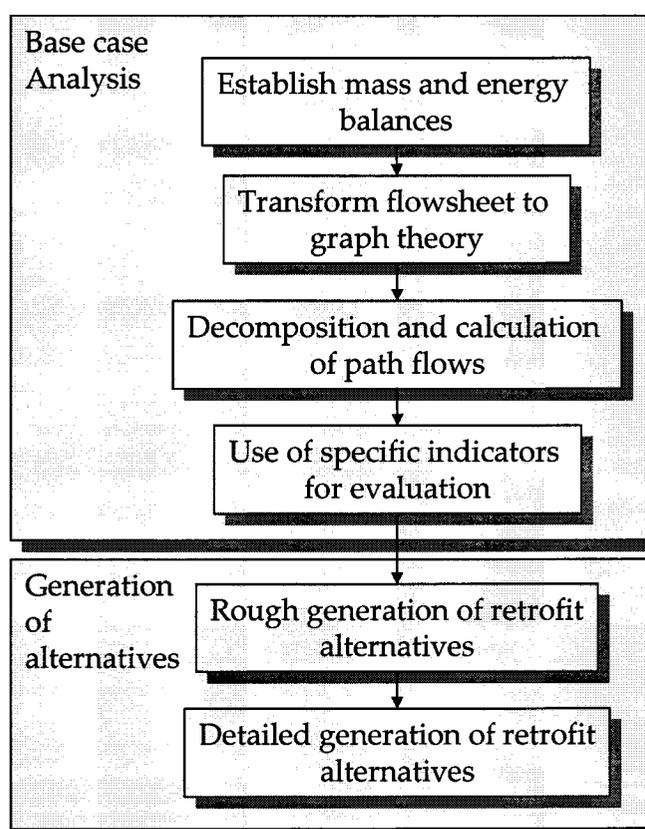


Figure 7.11: Structure of the retrofit methodology [73].

The base case analysis part is structured into 4 steps. First, mass and energy balances are obtained from the process simulator package ASPEN PLUS[®] using the base case defined in Figure 7.2.

Once mass and energy balances are obtained the process is transformed and represented according to graph theory (see Figure 7.12). In a third step the process is decomposed into open and cycle path flows. Open path flows of a component originate either in an external feed or by reaction in a vertex and are terminated either in a process output or by consumption in a reaction. Cycle path flows instead are idealized representations of the specific flow-rate of a component that circulates endlessly inside the process. In the last step the indicator framework developed by Uerdingen [73] is used to evaluate the process.

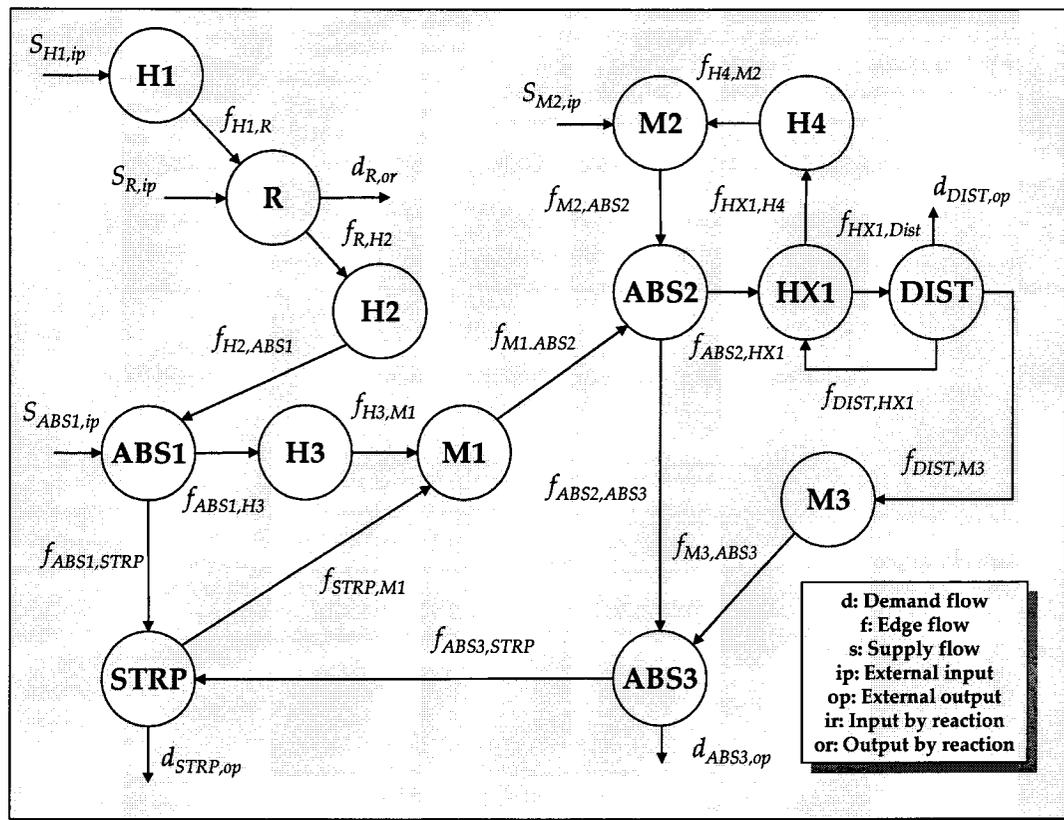


Figure 7.12: Process graph for the production of hydrogen cyanide by means of the BMA process.

The last step of the first section is the analysis of the different paths using specific indicators. Figure 7.13 describes an overview of the assessment procedure and the different indicators used. The different path flow rates depending on whether they are open, or cycle path flow they are assessed by different indicators. For the open path flows the first indicator is the material-value added (MVA). It calculates the difference of the demand flows and the value they represent outside the process boundaries, as well as the costs in raw material consumption they caused. Negative values can represent losses of material or consumption inside reaction, and it can represent potential for improvement.

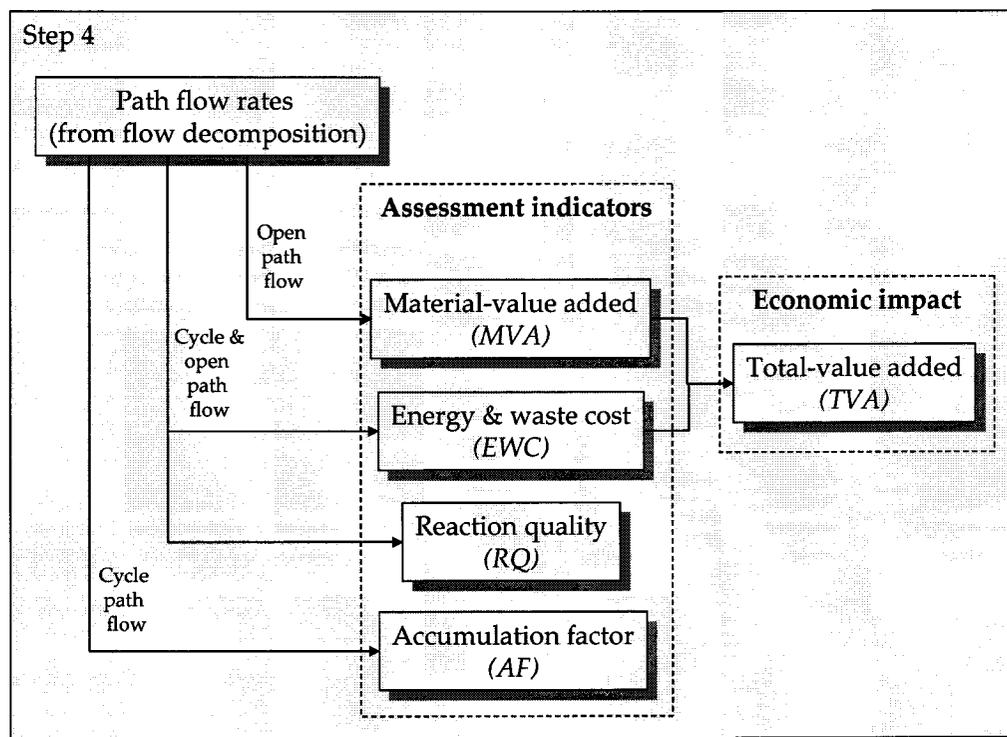


Figure 7.13: structure of indicators used for the path flow assessment [73].

The energy and waste cost (EWC) is applied to open and cycle path flows. It represents cost related to utility consumption and waste treatment to a component path flow. Results indicate potential costs reduction for every

specific component path flow. The reaction quality (RQ) is applied to open and cycle path flows, and measures the effect of a component path flow upon reactions that occur along its path. Positive RQ values indicate a positive effect on overall plant productivity.

The accumulation factor (AF) is applied to cycle path flows, and indicates the accumulative behavior in recycle streams. A large accumulation factor often indicates unfavorable build-up in a cycle and can be caused by non optimal separation systems or too low reaction conversions. The total value added (TVA) describes the economic impact of a given component path flow on the variable process cost. Negative numbers represent process improvement potentials.

Results obtained from the assessment of the base case for the production of 10.000 ton hydrogen cyanide per year can be viewed in Table 7.1 and Table 7.2. For the calculation retrofit-pro, a software tool developed by Andersen [269] based on Uerdingen's method was used.

Indicators for open paths

Open path #	Component	Flowrate (kg/hr)	RQ	MVA (103 \$/yr)	EWC (103 \$/yr)	TVA (103 \$/yr)
O1	NH3	16.16	0.004	-176.17	63.84	-240.01
O2	H2O	315.00	0.000	-0.11	1.12	-1.23
O3	H2	356.88	0.004	11219.52	220.30	10999.22
O4	CH4	123.98	0.004	-1053.94	115.22	-1169.16
O5	N2	272.42	0.004	0.00	0.09	-0.09
O6	HCN	77.53	0.004	2460.35	53.48	2406.87
O7	H2O	171.30	0.000	-0.06	0.00	-0.06
O8	H2O	269.96	0.000	-0.09	6.09	-6.19
O9	HCN	0.41	0.004	4.55	0.28	4.27
O10	HCN	1254.15	0.004	53884.42	866.95	53017.46
O11	H2O	6.30	0.000	0.00	0.14	-0.14

Table 7.1: Assessment of the open path flows.

The analysis of the open path flows shows how the consumption of raw materials represents most of the negative TVA numbers. It can also be observed that un-reacted ammonia represented by O1 has a negative value suggesting that better separation systems should be investigated.

On the other hand the assessment of the cycle path flows show there is a large accumulation of water in C5 obtaining extremely high values for AF and EWC. These values represent a high cost as shown by the negative TVA. C5 represents the purification part of the BMA process and results obtained from the assessment encourage further analyses to obtain process alternatives.

Indicators for mass cycle paths

Cycle path #	Component	Flowrate (kg/hr)	AF	RQ	EWC (103 \$/yr)	TVA (103 \$/yr)
C1	H2	18.3498	0.0514	0.0038	0.1467	-0.1467
C2	CH4	6.3746	0.0514	0.0000	0.0768	-0.0768
C3	N2	14.0071	0.0514	0.0038	0.0001	-0.0001
C4	HCN	49.6387	0.0373	0.0038	0.3409	-0.3409
C5	H2O	33053.1983	43.3452	0.0000	687.9462	-687.9462

Table 7.2: Assessment of the cycle path flows.

The second part of the simulation is the generation of retrofit alternatives and is divided into a first rough alternative generation followed by deeper evaluation of the most promising alternatives. This section is based on simultaneous identification of important process parameters (referred to as optimization parameters) and generation of promising structural modifications of the process (referred to as structural retrofit alternatives). In the last phase a detailed economic and environmental evaluation of the alternatives is performed in order to identify those most promising.

Results obtained from the assessment of the open and cycle path flows show possible targets for potential improvement to be the separation and

purification parts. They also show that the reaction part represents the most critical part of the process. Retrofit alternatives are presented in next part.

7.4 Process alternatives

As Figure 7.11 showed the last and also important part of the retrofit methodology is the generation of alternatives. In this section several process alternatives focused on the objectives obtained from the analysis of the base case as well as the information obtained from the process assessment over the period of study are presented.

As previously discussed the process and its alternatives will be assessed in its economic and environmental aspects.

Reaction

The information obtained from the technological assessment in addition to the data regarding reaction quality observed in Table 7.1 and Table 7.2 show that any improvement in the reactor will have a high impact on the economic and environmental performance of the process. The problem resides in the fact that in order to improve the reactor basic science has to provide with new ceramics, high activity catalyst or a totally new reactor configuration. In this section this three hypothetical alternatives are studied and compared to the base case.

As a first case (Case 1) the hypothetical development of a new ceramic tube that allows higher average lifetime and increasing the number of tubes per chamber from 65 to 75 is analyzed. The second alternative analyzed (Case 2) is obtained from US patent *US5980838* which describes the development of a new reactor configuration. A third hypothetical alternative (Case 3) is

presented as the development of a new catalyst that allows improving the yield by 1 per cent. The reactor consists of a monolithic arrangement of heating and reaction channels. The fuel gas and a gas containing oxygen pass through the heating channels and the reactants pass through the reaction channels (with internal walls coated with catalyst.). The fuel gas is burned in the heating channels.

The monolithic structure is a heating and reaction channel in intimate contact. The heating and the reaction channels may be arranged in alternating layers, reaction gases may pass through them co- or counter-currently.

Figure 7.14 and Figure 7.15 represent the schematic longitudinal and sectional view of the reactor. The main improvement in this kind of reactor, in comparison with the previous one, is that it has a substantially lower energy input per kg of hydrocyanic acid produced and an improved space-time yield. Depending on the pilot-model of the patents 10 to 20 MJ per kg HCN produced can be saved.

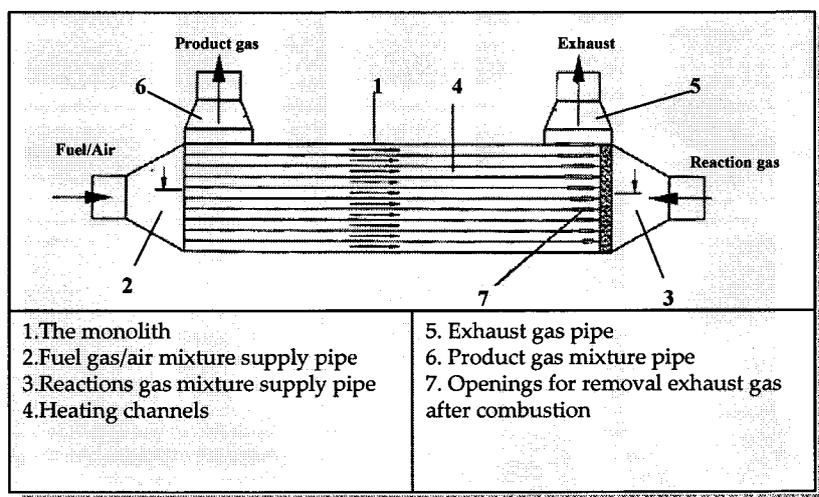


Figure 7.14: Schematic longitudinal view of the reactor.

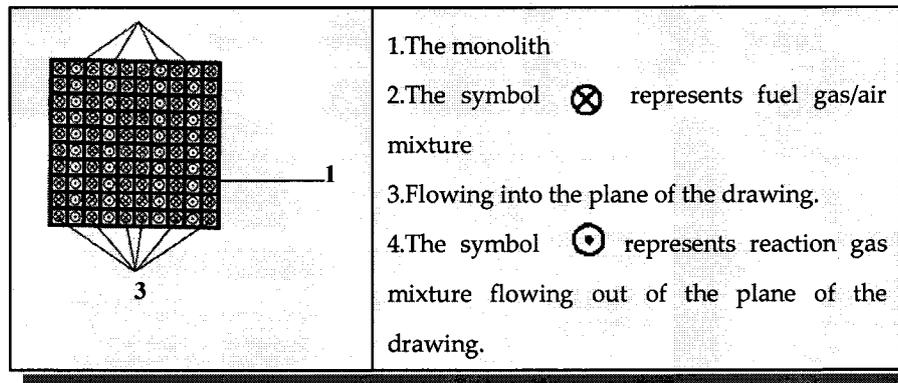


Figure 7.15: Schematic sectional view of the reactor.

The same yield and production per tube was assumed. No tube breakage was considered although the monolith must be replaced after a two year maintenance stop. Main improvement, then, is obtained from the energy consumption reduction.

Figure 7.16, Figure 7.17, and Figure 7.18 show the economic and environmental results together with the contributions to the different parts.

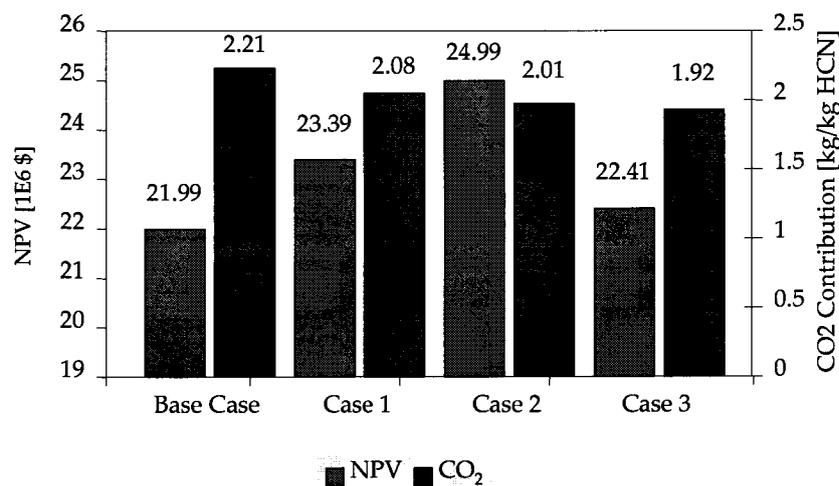


Figure 7.16: Economic and environmental performance of the different alternatives.

One can observe that the three alternatives have a higher net present value than the base case. This was expected due to the increment in production in Case 1 and 2, or the lower energy consumption experienced in Case 3. Case 1 and Case 2 produce higher amounts of carbon dioxide emissions than Case 3 due to the fact that steam has to be provided to the process. Amount of emissions might vary depending on the environmental credits that are given to the surplus of steam in Base Case and Case 3. Surplus of steam was considered as negative emissions required producing such steam from natural gas combustion.

Figure 7.18 shows the influence of raw materials and energy carriers to the total carbon dioxide emissions per kilogram of hydrogen cyanide produced. It can be observed how the reduction of energy consumption in the reactor produces a demand of steam that has to be provided to the process.

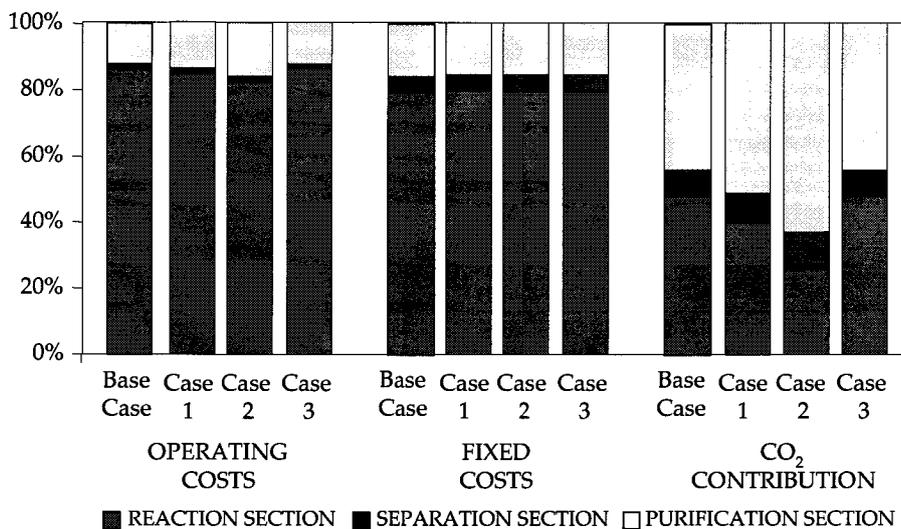


Figure 7.17: Contribution to the operating costs, fixed costs and Carbon dioxide emissions of the different alternatives and its parts.

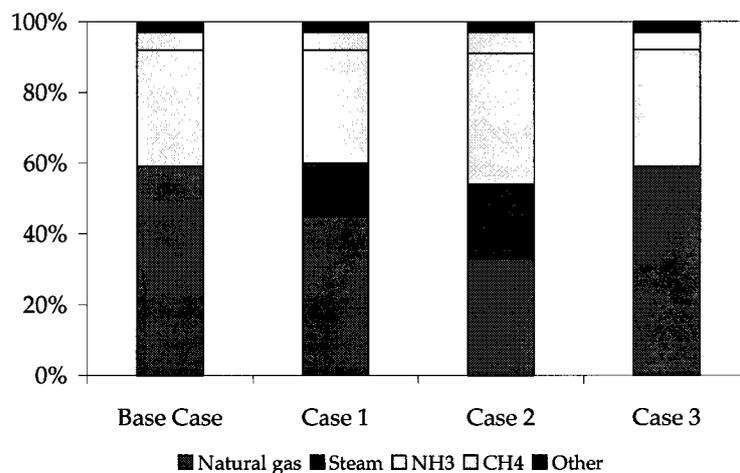


Figure 7.18: Contribution of the different raw materials and energy carriers to the CO₂ emissions.

Separation

Section 3.2.1 describes several processes explored for ammonia absorption. They are all based on similar operating conditions but the only two processes implemented were the sulfuric acid solution and the phosphate solution.

In the separation part the only alternative studied (Case 4) was the implementation of the Dupont's phosphate solution absorption system. The process was simulated using ASPEN PLUS ®. Figure 7.19 represents the flowsheet of the separation process analyzed. No license costs were introduced.

Results obtained from the simulation show that phosphate solution absorption has worse results when compared to the base case from the economic point of view (21.202 million \$). If compared to Andrussov process where this separation system is implemented the gases coming from the reactor have a lower content of ammonia in the BMA process.

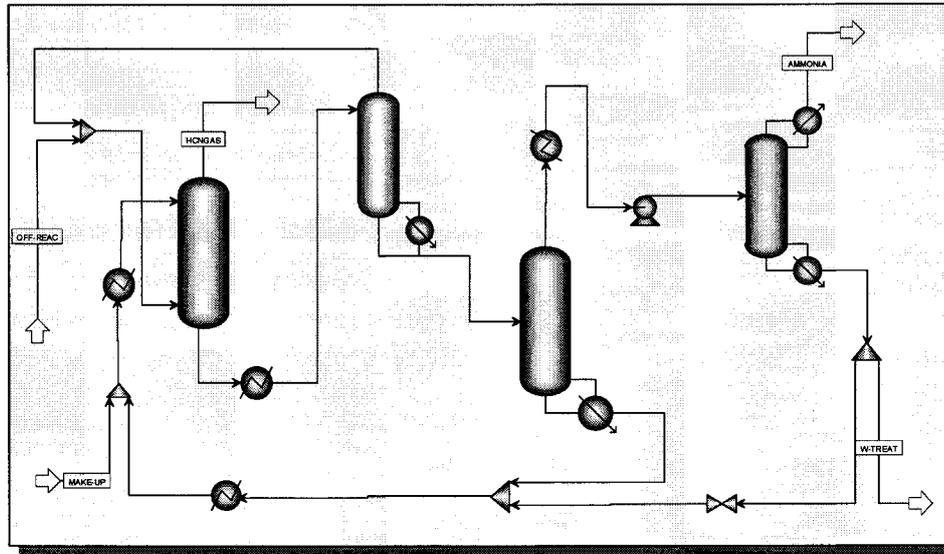


Figure 7.19: Ammonia absorption by means of phosphate solution.

The low amounts of ammonia to recover together with the small annual production considered as a base case (10,000 ton per year) make the investment and the operating cost per kilogram of ammonia recovered too high. The higher demand of steam also castigates the environmental performance (2.501 kg of carbon dioxide per kg of hydrogen cyanide produced). A different scenario would be to consider the ammonium sulfate as waste. This would penalize the environmental performance of the sulfuric acid solution absorption system. If this case were considered then it would be possible that the phosphate solution absorption system would show a better environmental performance having this way a trade-off between economic and environmental objectives. This option was not explored due to the fact that the environmental indicators used for evaluation are only based on air emissions. As explained in previous parts no aggregation of indicators was performed to avoid any subjective influence on the results.

Purification

The purification part has not changed over the last fifty years. BMA and Andrussow share the same purification part consisting in absorption of hydrogen cyanide with water and then separation by distillation. Processes only differ in the size of the equipment and the operation conditions. No other purification method applied to the hydrogen cyanide production was found in literature.

Results obtained from the analysis of the technology show that the more the reaction part was improved, the higher the influence of the purification part on the economic and environmental performance was. On the other hand, from the analysis of the path flows in the base case one can see that the accumulation factor of the recycle path flow is relatively high with a large associated cost. It seems clear, then, that this part has a high potential for improvement and other purification processes should be considered.

In opposition to classical absorption distillation two totally different processes are studied. Purification by membranes (Case 5) and condensation of the hydrogen cyanide (Case 2) are considered as process alternatives.

Membrane technology achieved a major breakthrough in the last 20 years. New and cheaper membranes have been developed. Figure 7.20 shows the membrane process simulated using ASPEN PLUS ®. Pressure drop is regenerated by the use of a compressor, and the membrane is simulated by an ideal separator. It is assumed that this system can separate 95 per cent of the total hydrogen cyanide introduced into the membrane.

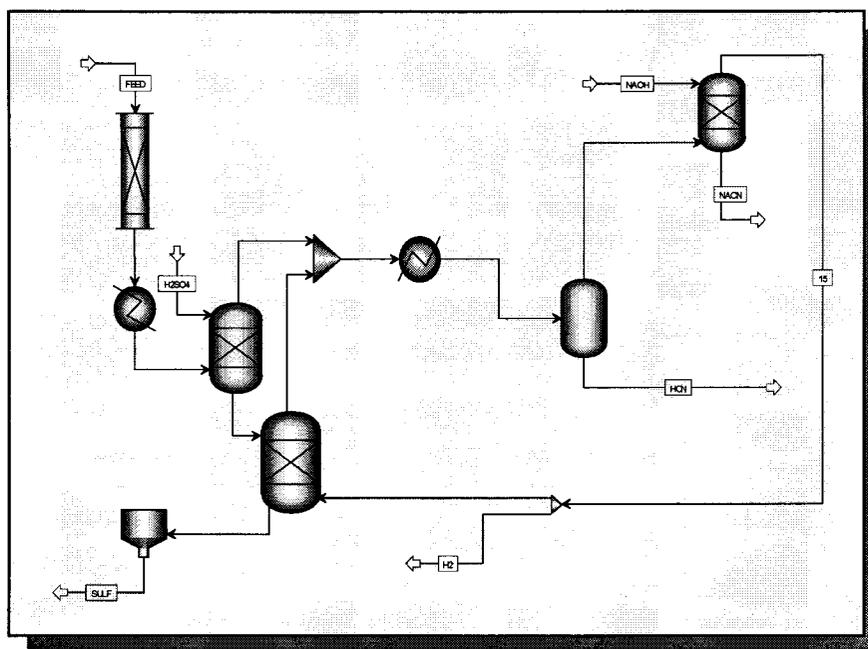


Figure 7.21: Membrane process simulated with ASPEN PLUS ®.

Figure 7.22 and Figure 7.23 represent the economic and environmental results of Case 5 and Case 6. The use of membranes with the assumptions presented above, show that both, the economic and the environmental performances were highly improved. Because less energy consumption is required to operate the membrane system.

The fixed cost of the membrane and auxiliary equipment was estimated in \$600.000. Expensive cost of membranes does not have a large influence on the results due to the fact that absorption and distillation columns are no longer required. On the other hand the fixed cost of the refrigeration equipment was estimated in \$300.000 but the high operational costs because of the extra steam required make this option not as attractive as case 5. In addition the steam required also produces a higher environmental impact than the base case.

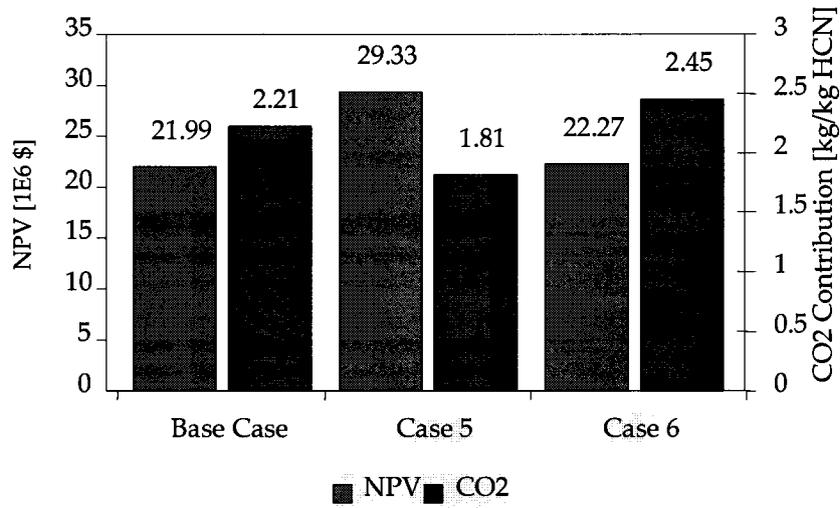


Figure 7.22: Economic and environmental performance of the different alternatives.

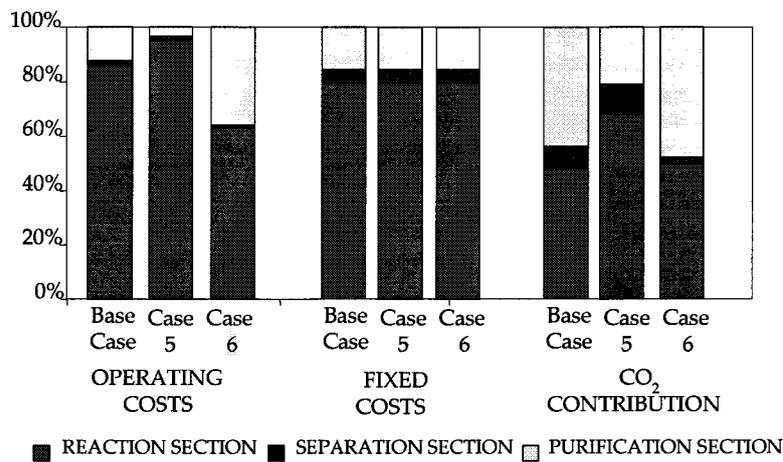


Figure 7.23: Contribution to the operating costs, fixed costs and Carbon dioxide emissions of the different alternatives and its parts.

On the other hand the high cost of cooling shows that the net present value does not have a high increment. Operating costs of the separation part increased due to a high demand of steam, producing slightly higher carbon dioxide emissions than the base case.

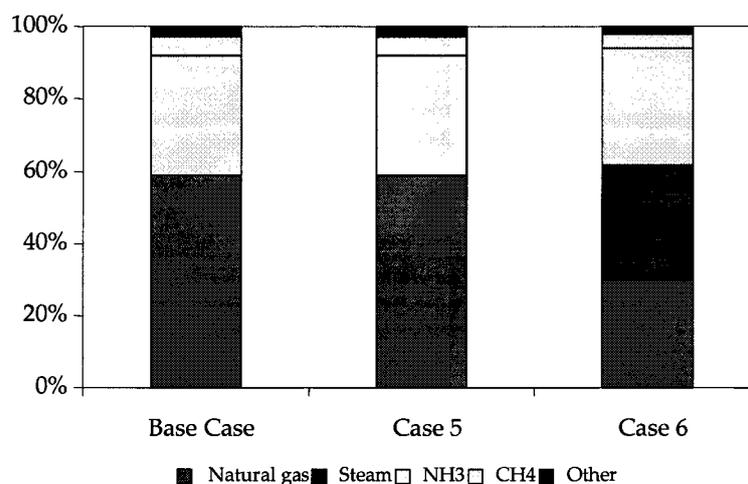


Figure 7.24: Contribution of the different raw materials and energy carriers to the CO₂ emissions.

Figure 7.24 shows that for Case 5 there is no contribution by steam since all energy requirements to operate the compressors are covered by the steam generated in the reactor. In contrast Case 6 shows how the extra steam requirements to operate the cooling system highly influence the contribution to the carbon dioxide emissions.

Summary

This chapter aims to merge the information obtained from the technological assessment and the existing retrofit methodologies. Information obtained from chapters 3 to 6 is combined with a novel retrofit methodology developed in order to obtain potential improvements of the BMA process.

CHAPTER 8 - CONCLUSIONS

Decision making is a fundamental activity defined as the process for arriving at a decision. Decision at the same time is defined as the removal of uncertainty with respect to a course of action to achieve certain objectives. Considering these two definitions one can conclude that decision making is the process of reducing uncertainty in order to choose a course of action to achieve an objective.

A decision maker is a subject who, after the decision making process, must choose a course of action. It is clear that with less uncertainty the decision will be the less subjective. It is of high importance then to define, study, and reduce the uncertainty in order to arrive at better decisions. The final objective of this thesis is to apply this principle to the chemical process design decision making situation.

Objectives of chemical process design can be divided into several dimensions; the most important being the economic dimension followed by ecological and social dimensions among others. Business is built on profits, without them no organization can survive. Success in business is based on how objectives of increasing importance such as environment or social aspects are integrated into the goal of obtaining profits.

Once objectives have been defined uncertainties must be reduced in order to achieve the least subjective decision as possible. Besides technical uncertainties, time is one of the most important sources of uncertainty. One can technically reduce all uncertainties to obtain the best current decision, but will it remain the best in the future? In the chemical process design decision making problem, in order to achieve stated objectives, decision makers should decide between chemical processes, and within each process between process configurations. In current approaches one studies each alternative carefully, reducing technical uncertainties. It is important to know for example, the yield of reaction, temperature of the reactor, recovery of a certain product on top of a distillation column or the composition of the waste water produced. These are all technical uncertainties that can be reduced by either experimentation or simulation. But when deciding to build a chemical plant with an expected lifetime of 20 to 40 years or more, decision makers must choose the best design today that will also remain the best in the future. The novelty of this thesis is that it not only tries to reduce technical uncertainty but aims to reduce the uncertainty produced by time. This is achieved by studying the influences on a chemical process during its lifetime and then using this information to better postulate future scenarios.

In this thesis it was stated that technology, market and environmental regulations are tightly interconnected. The technological development of a

chemical process is ruled by changes in the objective definition. A new market situation led to a price drop of the chemical produced or a new environmental regulation led to changes in the process technology. Having a study of how environment and market influenced the development of a chemical process can help reduce the uncertainty of how they will do so in the future.

In order to evaluate the environmental performance over time, a new methodology to obtain the dynamic life cycle analysis of the production of a chemical product was presented. The objective of the method is to obtain an overall evolution of the environmental performance of the different processes involved. Sources of information for such analyses were obtained from the study of the technological development of the processes involved and the evolution of environmental regulations.

On the other hand, the analysis of the economic performance was performed using standard economic indicators. The influence of time was introduced by studying the evolution of the raw materials, energy carriers, and products over the period of study.

The methodology was applied to the case study of the production of hydrogen cyanide. The results revealed that the environmental performance of this process was highly influenced by the technological development and to a lower extent by the environmental regulations. Thus, it can be concluded that in the case of hydrogen cyanide not only legislation, but also technical progress led to a better environmental performance. This case study shows that investment in technological development may also pay off in terms of being ahead of tightened environmental legislation, with potential cost consequences such as carbon dioxide tax. Of course that the BMA process is a very specific case study, but results can be extrapolated to several

commodities chemical production processes. Major differences to other processes may reside in the fact that hydrogen cyanide is a very toxic material and emissions have always been limited. Emission limits in other processes that have non as toxic products may have change due to environmental regulations.

The study of the influence of the market and environmental regulations was represented as the evolution of the economic and environmental performance of the process. It was observed that most of the motivations that provoked changes in technology were changes in the market situation. Environmental regulations had a lower direct impact but it must also be stated that changes in technology that improved the economic objectives also improved the environmental performance. This relationship that lead to a win-win situation making it difficult to differ between both influences, but on the other hand it can be stated that for this case study. The technological improvement improves both the economic and environmental performance of a process. It seems clear that the better the technology a process has the better positioned it is towards the future. One of the conclusions that can be extracted from this thesis is that investment in process development might look expensive in present times but will pay off in the future.

A chemical process usually is not on the cutting edge of its technological development when it begins production. Chemical companies are ruled by the market situation when there is an urgent need of a certain product. In such a case, time is the constraint, perhaps because other processes inside the company require this product as a raw material or just because the first to make a move will receive a larger market share later. However, certain technological advances are not available at the time production begins, new materials (new ceramics for tubes in the BMA process) or development of

more efficient process equipment (centrifugal compressors in the ammonia production).

If we look back to our process of study of the BMA process, it is very easy to now say (looking at its evolution) that several decisions were not most appropriate. Among others, the reactor configuration and its constraints have led the technological evolution of the whole process. Obviously there was much room for improvement in that reactor but this statement is not an attempt to criticize decisions made by engineers at that time. Who forgot to tell them that hydrogen cyanide would become a commodity chemical quickly dropping in price or that there would be an energy crisis, or that environmental regulations were going to appear sooner or later? The BMA reactor is technologically very complicated and consequently very expensive. But if we learn from this example, next time, besides economic motivations the design should include flexibility and environmental motivations among others. The continuously changing situation and the long lifetime of chemical plants are reasons enough to invest time and resources in developing small and flexible processes that can easily adapt to new regulations and market needs. This fact sometimes forgotten in that past will define the economic and environmental performances of a process in the future.

At this point it seems clear that technology is a major driving force of the environmental and economic performance of a process, but what have been the effects of environmental regulations? The introduction of the clean air act began restricting the amounts of air pollutants released from combustion of energy carriers. Environmental regulations improved the end of pipe technologies that allowed remaining at the established emission limits. Nevertheless, energy savings at the core process have been the major driving force for the reduction of emissions. But looking at the results from Figure 6.7

one can see how two indicators have been chosen, SO_x and GWP. On one hand, SO_x emissions are directly affected by the emission limits established by environmental regulations. On the other hand, GWP are only affected by the limits established for the NO_x emissions. It is clear that SO_x emissions had had experience more reduction than GWP but major reductions have been achieved by improvements of the energy efficiency of the process and not by the effect of regulations. A critical market situation highly influenced the technological improvements of the process and by this the environmental performance of the process as well. It is not surprising to discover that a more economically efficient process improves its environmental performance at the same time. It is time to question whether a reactive mode of legislation as environmental restrictions is more effective than proactive solutions. Facing the current possibility of a CO₂ tax, the question would be which proactive solutions can be formulated? Appearance of environmental regulations in the past provoked the use or improvement of end of pipe technologies. It was stated that improvements in the core process technology had a higher influence on the environmental performance. Promoting the investment in research and development to develop the core technology of the processes would be a way to obtain better environmental "AND" economic performance. This option together with responsible environmental regulations will help merging economic and environmental concerns into a single objective tackling the problem from a proactive point of view.

The effect of environmental regulations was relatively small compared to the effect of the market. These results show that policy makers should reformulate the environmental regulations to be more effective. Results from this thesis show that environmental objectives are not contrary to economic objectives. As stated before, a better integration of these objectives performed

by both sides, stake holders and policy makers, would more effectively and beneficially influence chemical processes.

The effect of technological development on a chemical process opens a new way of retrofitting methodologies. Designers can identify potential improvements by studying the evolution of each part and their influence on the economic and environmental performance. Current retrofit methodologies focus only on the state of the art of the technology. If however information about the evolution of the technology is included, new alternatives can be discovered. As stated in the case study analysis the reaction part is the driving force of the economic and environmental performance, but the closer it is to the thermodynamic minimum the higher the influence other parts of the process will have. It can be concluded that a combined study of the process using available retrofit methodologies and a study of the technological development of the process can more effectively generate more and better retrofit alternatives.

Results presented in chapter 7 show how the reaction part has been improved during the process development. This part has traditionally been the target of efforts to improve the process because of its high influence on the economic and environmental performance of the process. One of the advantages obtained from merging current retrofit methodologies with the study of the process evolution is that one can observe that in improving one part others become more important. In the BMA process separation and purification parts played a minor role in the economic and environmental performances. Once the reaction part approximates the thermodynamic minimum other parts increase their importance, simply because the closer the reaction part is to this minimum the less improvement potential can achieve.

Results from chapter 7 show different alternatives to the different parts of the current BMA process. These alternatives can be combined obtaining better results. For the clarity of the results, however, they were presented separately. It is clear that further analysis should be performed in order to reduce the technical uncertainty and obtain more accurate results. Nevertheless these alternatives were presented as possible future directions of the process.

In summary, the information obtained from this thesis is useful towards understanding how the environmental and economic performances of a process including its precursors developed in the past. This information is used to reduce the technical and time uncertainties of the process. It was combined with retrofit methodologies in order to obtain process alternatives with a better performance today and well positioned towards the future.

CHAPTER 9 - FUTURE RESEARCH

A methodology to improve the economic and environmental performance of a process by developing the concept of time in decision making was presented. Many opportunities for future research arise if one looks closely at the information that this method provides.

In the first place, the methodology should be tested using other case studies in which emissions of the materials produced have a real impact on the performance of the process.

One of the first tasks to be developed is the use of future scenarios. Scenarios can be postulated taking into account changes in the market, such as prices or demand, or changes in environmental regulations, such as a new carbon dioxide tax. These scenarios can contribute to decreasing the temporal uncertainty and help in the decision making process.

The information gathered during this thesis provided a first analysis of the influence of regulations on the performance of chemical processes. This information can be used to improve the policy making procedure. A better analysis of the results will allow improving the regulations in a way that have a strong positive influence over chemical processes.

A third line for future research could be the development of tools to better integrate the information obtained from the study of the evolution of the economic and environmental performance with the use of state of the art retrofit methodologies.

Finally some minor tasks, discarded for the while due to its smaller influence could be carried out. Among others, a better study of raw material production and its emissions, for example including water emissions in the study.

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ACCRONIMS

AF	Accumulation factor
aMDEA	Activated Methyldiethanolamine
AQCR	Air quality control regions
BAT	Best available technology
BMA	Blausäure methanaAmmoniak
BMC	Bare module cost
CAA	Clean air act
COMPR	Compressor model in ASPEN PLUS®
CPI	Consumer price index
GWP	Global warming potential
DLCA	Dynamic life cycle analysis
DEA	Diethanolamine
ELECCTRL	Electrolytes and activity coefficient thermodynamic method
EPA	Environmental protection agency
EIA	Energy information administration

EWC	Energy and waste costs
P	Profit
HEATER	Shortcut heater/cooler model in ASPEN PLUS®
HEATX	Rigorous heat exchanger model in ASPEN PLUS®
HEW	Health, education welfare
HTSC	High temperature shift converter
ICI	Imperial chemical industries
IPCC	International panel on climate change
LC	Life cycle
LCA	Life cycle assessment
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LTSC	Low temperature shift converter
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
MVA	Material value added
NGL	Natural gas liquids
NPV	Net present value
NTRL	Activity coefficient thermodynamic method
PM	Particulate matter
RADFRAC	Rigorous absorption distillation model in ASPEN PLUS®
RGIBBS	Gibbs free energy minimization reactor model in ASPEN PLUS®
RKS	Redlich-Kwong-Soave equation of state
RKS-BM	Redlich-Kwong-Soave equation of state and Boston-Mathias alpha function
RSTOIC	Stoichiometric reactor model In ASPEN PLUS®
RPLUG	Plug flow reactor model in ASPEN PLUS®
RQ	Reaction quality

SEP	Ideal separator model from ASPEN PLUS®
TACK	Total annualized cost per kilogram
TAPK	Total annualized profit per kilogram
TAIK	Total annualized income per kilogram
t.p.d.	Tons per day
TVA	Total value added
VOC	Volatile organic carbon

APPENDIX A - SIMULATION INPUT

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A.1.1 reaction section

The base of the reaction section (described in Figure A.1) is the reactor, simulated with RPLUG model of ASPEN PLUS® and the quenching simulated with the model HEATER. Figure A.1 describes the specifications required to define the reactor. Heat transfer parameters together with size of tubes and pressure drop are required to specify the plug flow reactor. The reaction type used is described in following section.

-Reactor:

Model:	RPLUG
Type:	Reactor with constant coolant temperature
Temperature:	1610 K
Heat transfer:	200 J/sec-sqm-K
N° of tubes:	1600
Length of tubes:	2 m
Diameter of tubes:	15 mm
Pressure at inlet:	1 atm
Reaction type:	LHHW

Figure A.2: RPLUG reactor specifications.

-Quenching

The gases have to be rapidly cooled in order to avoid polymerization. This operation is simulated using a simple HEATER model as shown in Figure A.3.

ID:	H1
Model:	HEATER
Type:	Ideal cooler
Temperature:	363 K
Pressure :	1 atm

Figure A.3: Model specifications required to simulate the quenching of reaction gases.

-Reaction

As described in previous chapters the BMA process is based on the reaction of methane and ammonia under the absence of oxygen. There is also the side reaction consisting in the decomposition of ammonia. The reactions are described by Hasenberg and Schmidt [93]. The reaction modes described in the publication are transformed in order to fit the LHHW parameters required to specify both reactions. Figure A.4 represents the mass balance of the reaction section.

	FEED	1	2
Temperature C	426.9	1300.8	89.9
Pressure bar	1	1	1
Vapor Frac	1	1	1
Mole Flow kmol/hr	126.698	244.72	244.72
Mass Flow kg/hr	2101.425	2101.425	2101.425
Volume Flow cum/hr	7373.881	32025.015	7385.904
Enthalpy MMkcal/hr	-1.243	4.074	1.56
Mass Flow kg/hr			
H2	0	356.877	356.877
CH4	914.666	123.975	123.975
NH3	1186.759	16.156	16.156
HCN	0	1332	1332
N2	0	272.417	272.417
H2O	0	0	0
H2SO4	0	0	0
NAOH	0	0	0

Figure A.4: Mass balance of the reaction section (see Figure A.1).

A.1.2 Separation section

The separation section is formed by the ammonia absorber (ABS1) a HCN stripper (STP1), the ammonium sulfate crystallizer (H4) (see Figure A.1). The system was simulated first using rigorous models and an electrolyte property method in order to calculate the sulfuric solution requirements. Once the amounts of sulfuric acid and water were defined models the absorption and

stripping columns were calculated as ideal separator in order to not complicate overall convergence.

ID:	ABS1
Model:	SEP
Type:	Ideal separator
Split fractions:	
H2	1
CH4	1
NH3	1
HCN	0.98
N2	1
H2O	0.3
H2SO4	0
NAOH	0

Figure A.5: ABS1 simulation parameters.

ID:	STRP1
Model:	SEP
Type:	Ideal separator
Split fractions:	
H2	0
CH4	0
NH3	1
HCN	0
N2	0
H2O	1
H2SO4	1
NAOH	1

Figure A.6: STRP1 simulation parameters.

ID:	H4
Model:	HEATER
Type:	Ideal evaporator
Vapor fraction:	1
Pressure :	1 atm

Figure A.7: Crystallizer simulation parameters.

Figure A.5, Figure A.6, and Figure A.7 represent the parameters used for the simulation of the absorber, stripper and crystallizer.

The crystallizer was simulated using a HEATER model in ASPEN PLUS[®] defining the vapor fraction to 1 in order to achieve a total separation of solid and liquid phase and obtaining this way the required amount of heat. Figure A.8 represents the simulation parameters used for the simulation of H2. Figure A.9 Shows the mass balance obtained for the separation section.

ID:	H2
Model:	HEATER
Type:	Ideal cooler
Temperature:	298 K
Pressure :	1 atm

Figure A.8: Input data for the H2 model.

	2	H2SO4	3	4	5	6	16	SULFAT	20
Temperature C	89.9	18.9	30.1	30.1	15.1	29.5	19.7	15.1	192.4
Pressure bar	1	1	1	1	1	1	1	1	1.013
Vapor Frac	1	0	1	0	1	1	1	0	1
Mole Flow kmol/hr	244.72	25.489	250.279	19.929	10.986	261.265	10	18.944	18.944
Mass Flow kg/hr	2101.425	500	2193.628	407.796	65.371	2259	38.731	381.156	381.156
Volume Flow cum/hr	7385.904	0.49	6311.225	0.431	263.293	6574.916	243.483	0.377	723.705
Enthalpy MMkcal/hr	1.56	-1.804	0.998	-1.285	0.024	1.022	-0.007	-1.318	-1.083
Mass Flow kg/hr									
H2	356.877	0	356.877	0	18.35	375.227	18.35	0	0
CH4	123.975	0	123.975	0	6.375	130.35	6.375	0	0
NH3	16.156	0	0	16.156	0	0	0	16.156	16.156
HCN	1332	0	1305.36	26.64	26.64	1332	0	0	0
N2	272.417	0	272.417	0	14.007	286.424	14.007	0	0
H2O	0	450	135	315	0	135	0	315	315
H2SO4	0	50	0	50	0	0	0	50	50
NAOH	0	0	0	0	0	0	0	0	0

Figure A.9: Mass balance of the separation section(see Figure A1).

A.1.3 Purification section

The purification section is the most complex of the three sections of the BMA process. It consists in the HCN absorption column (ABS2) simulated with the

rigorous model RADFRAC. Two heat exchangers (HX1 and H3) one simulated with the rigorous model HEATX and the other with the shortcut model HEATER. One distillation column (DIST1) simulated with the rigorous model RASDFRAC and finally the NaCN absorber (ABS3) simulated in the first place with RADFRAC and electrolytes thermodynamic package but once mass balances were obtained it was implemented as an ideal separator SEP. Figure A.1 shows the configuration of the separation section.

Figure A.10 and Figure A.11 represent the input data for the ABS2 and HX1 models. One can observe how the number of stages, pressure drop and position of feed streams is defined.

ID:	ABS2
Model:	RADFRAC
Type:	Absorber
N° Stages:	12
Condenser:	none
Reboiler:	none
Convergence:	Standard
Feed streams:	
7	13 above-stage
9	1 on-stage
Product streams:	
10	12 liquid
8	1 vapor
Top stage pressure:	1 atm

Figure A.10: Input data for the ABS2 model.

The heat exchanger model was simulated using a rigorous model but with shortcut calculations. This is due to the fact that dimensions of the heat exchanger are modified by the optimization algorithm described in next sections. One can also observe that a specific heat transfer coefficient has been defined for this heat exchanger.

ID:	HX1
Model:	HEATX
Type:	Heat exchanger
Calculation:	Shortcut
Type:	Symulation
Exchanger area:	160 sqm
Temperature:	298 K
U value:	850 Watt/sqm-K

Figure A.11: Input data for the HX1 model.

Figure A.12 represents the input data for the H3 model, this heat exchanger has been introduced for simulation purposes. It assures that the temperature of stream 19 will always be 15°C adding robustness to the simulation and allowing faster convergence.

ID:	H3
Model:	HEATER
Type:	Ideal cooler
Temperature:	15 °C
Pressure :	1 atm

Figure A.12: input data for the H3 model.

ID:	DIST1
Model:	RADFRAC
Type:	Distillation column
N° Stages:	15
Condenser:	Partial-vapor-liquid
Reboiler:	Kettle
Convergence:	Standard
Feed streams:	
11	6 above-stage
Product streams:	
13	15 liquid
HCN	1 liquid
12	1 vapor
Top stage pressure:	1 atm
Condenser specification:	15°C

Figure A.13: Input data for the DIST1 model.

Figure A.13 represents the input parameters specified for the DIST1 model. Number of stages, type of convergence and feed stream location are specified. Operating specifications are defined by later altered by the internal design specifications. Figure A.14 and Figure A.15 represent the two design specifications defined for the DIST1 model. One is related to the mass purity required for the product stream and the other one to the. The other one on the other hand tries to recover most of the product by defining that only a small amount can exit from the bottom stream.

One can observe how both operating specifications from Figure A.13 are altered by the design specifications. That it is why design specifications are considered as feed back controllers because no matter what the composition of the feed is that the design specifications will alter the operating conditions of the column to achieve the specific goal of the column.

ID:	DIST1
Model:	RADFRAC
Type:	Internal design specification 1
Design specification:	Mass purity
Specification:	0.995
Stream type:	Product
Selected Components:	HCN
Selected feed stream:	HCN
Adjusted Variable:	Reflux ratio
Lower bound:	0.1
Upper bound:	40

Figure A.14: Internal design specifications for the DIST1 model.

Figure A.16 represents the input parameters for the NaCN absorption model. A first analysis was performed using electrolytes and rigorous models to obtain mass balances. These mass balances were used to implement a ideal separator to improve overall convergence of the process.

ID:	DIST1
Model:	RADFRAC
Type:	Internal design specification 2
Design specification:	Mole purity
Specification:	0.001
Stream type:	Product
Selected Components:	HCN
Selected feed stream:	HCN/H2O
Adjusted Variable:	Distillate rate
Lower bound:	20 kmol/hr
Upper bound:	90 kmol/hr

Figure A.15: Internal design specifications for the DIST1 model.

ID:	ABS3
Model:	SEP
Type:	Ideal separator
Split fractions:	
H2	1
CH4	1
NH3	1
HCN	0
N2	1
H2O	0
H2SO4	0
NAOH	0

Figure A.16: Input parameters of ABS3 model.

	7	8	9	10	11	12	13	14	15	16	17	18	19	H2	HCN
Temperature C	24.9	16.3	15	27.9	77.3	15	98.5	16.3	19.7	19.7	98.5	40.5	15	19.7	15
Pressure bar	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Vapor Frac	1	1	0	0	0.009	1	0	1	1	1	0	0	0	1	0
Mole Flow kmol/hr	261.266	211.197	1848.318	1898.387	1898.389	0.065	1851.568	211.262	204.485	10	1836.568	1836.568	1836.568	194.485	46.756
Mass Flow kg/hr	2259.005	958.689	33314.519	34634.84	34634.911	1.257	33373.202	959.946	792.004	38.732	33102.837	33102.837	33102.837	753.272	1260.452
Volume Flow curu/hr	6473.3	5083.017	33.253	36.068	533.51	1.559	36.349	5084.506	4978.875	243.483	36.055	33.877	33.042	4735.391	1.816
Enthalpy MMkcal/hr	1.013	-0.292	-126.256	-124.95	-123.013	0.001	-123.732	-0.291	-0.152	-0.007	-122.729	-124.666	-125.452	-0.145	1.169
Mass Flow kg/hr	375.227	375.188	0	0.04	0.04	0.029	0	375.227	375.227	18.35	0	0	0	356.877	0
H2	130.352	130.328	0	0.023	0.023	0.023	0	130.351	130.351	6.375	0	0	0	123.977	0.001
CH4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	1332	76.364	49.639	1305.28	1305.36	1.169	50.044	77.533	0	0	49.639	49.639	49.639	0	1254.147
HCN	286.426	286.401	0	0.024	0.024	0.024	0	286.425	286.425	14.007	0	0	0	272.418	0
N2	135	70.407	33264.88	33329.472	33329.463	0.002	33323.158	70.409	0	0	33035.199	33035.199	33035.199	0	6.304
H2O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2SO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure A.17: Mass balance of the purification section (see Figure A1)..

Figure A.17 represents the mass balance of the purification section. One can observe the complexity of the section by the number of streams defined.

A.1.4 External design specifications

Figure A.18 represents the first external design specification. It is used to control the recovery of hydrogen cyanide in the absorption column ABS2. For this purpose the amount of fresh water is varied to achieve a 98% mole recovery.

ID:	DS-1
Model:	DESIGNSPEC
Type:	Design specification
Flowsheet variable:	
HCN41	moleflow, stream 7, component HCN
HCN52	moleflow, stream 10, component HCN
Design specification expressions:	
Spec:	HCN52/HCN41
Target:	0.98
Tolerance:	1E-4
Vary:	
Type:	Stream-var
Stream Name:	WATER
Substream:	MIXED
Variable:	Mole flow
Upper bound:	1
Lower bound:	100000

Figure A.18: External design specification.

Figure A.19 represents the second design specification. It is used to assure that the production of hydrogen cyanide is going to be of 10.000 tons per year. For this purpose the overall mole flow of the feed stream is varied to adjust to the production specifications.

ID:	DS-2
Model:	DESIGNSPEC
Type:	Design specification
Flowsheet variable:	
HCNREA	massflow, stream 1, component HCN
Design specification expressions:	
Spec:	HCNREA
Target:	0.37
Tolerance:	1E-4
Vary:	
Type:	Stream-var
Stream Name:	FEED
Substream:	MIXED
Variable:	Mole flow
Upper bound:	0.03
Lower bound:	1

Figure A.19: External design specification

A.1.5 Calculator block

The calculator block is used to perform economic calculations and use them as an objective for the optimization of the process. It is carried out by linking ASPEN PLUS® variables into an EXCEL© sheet. These variables serve as input for the economic calculations and the calculator bloc exports the NPV as an export variable that can be used in an optimization block.

A.1.6 Optimization blocks

Several local block optimization blocks can be defined once the NPV has been defined as the objective function to maximize. Figure A.20 represents the maximization of the net present value by changing the heat exchanger area of the HX1 block.

ID:	O-1
Model:	OPTIMIZATION
Type:	Optimization block
Flowsheet variable:	
NPV	parameter 1
Objective function:	
Maximize:	NPV
Vary:	
Type:	Block-var
Block Name:	HX1
Variable:	Area
Upper bound:	50
Lower bound:	200

Figure A.20: Input data for the optimization block.

A.1.7 Convergence block

In order to accelerate convergence a convergence block has been defined. A Broyden block in which the design specification and the tear stream are converged at the same time is used (see Figure A.21). It can be observed how design specification DSN-1 using stream 11 as a tear stream is defining this convergence block.

ID:	C-1
Model:	CONVERGENCE
Type:	Broyden convergence block
Design specs:	DS1
Tear streams:	11

Figure A.21: Input information for the convergence block

A.2 Ammonia process

This section describes a flowsheet used for the simulation of the ammonia process. The first step in order to simulate the ammonia process is to define the components and the property method. The thermodynamic method used for the simulations is the Redlich-Kwong-Soave equation of state with the Boston-Mattias modifications.

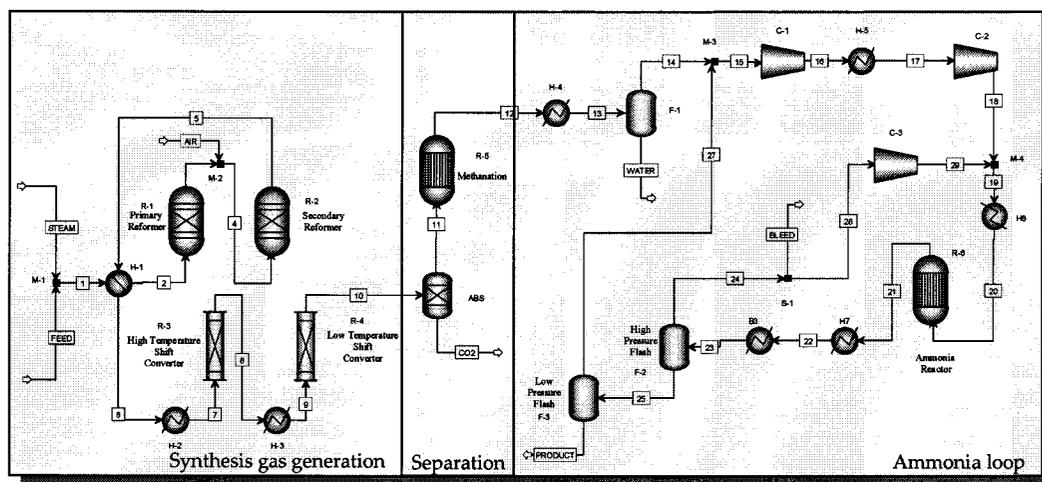


Figure A.22: Ammonia process.

A.2.1 Synthesis gas generation section

The purpose of the synthesis gas generation section as described in Figure A.22 is to generate a stoichiometric mixture of hydrogen and nitrogen to be converted in ammonia in the ammonia loop. Figure A.23, Figure A.24, Figure A.25, Figure A.26, Figure A.27, Figure A.28, and Figure A.29 describe the unit operation parameters used in this section.

ID:	HX1
Model:	HEATX
Type:	Heat exchanger
Calculation:	Shortcut
Type:	Design
Cold stream spec:	600 C

Figure A.23: Input parameters for the HX1 model.

ID:	R1
Model:	RGIBS
Type:	Primary reformer
Temperature:	800 C
Pressure :	35.29 bar

Figure A.24: Input parameter for the primary reformer.

ID:	R2
Model:	RGIBS
Type:	Secondary reformer
Temperature:	996 C
Pressure :	35.29 bar

Figure A.25: Input parameters for the secondary reformer.

ID:	H2
Model:	HEATER
Type:	Ideal heater
Temperature:	350 °C
Pressure :	35.29 bar

Figure A.26: Input parameters for the H2 model.

ID:	R3
Model:	RPLUG
Type:	Constant specified reactor temperature
Temperature:	420 C
Length of tubes:	10 m
Diameter of tubes:	2.5 m
Pressure drop:	0 atm
Reaction type:	POWERLAW

Figure A.27: Input parameters for the primary shift converter.

ID:	H3
Model:	HEATER
Type:	Ideal heater
Temperature:	200 °C
Pressure :	35.29 bar

Figure A.28: Input parameters for the H3 model.

ID:	R4
Model:	RPLUG
Type:	Constant specified reactor temperature
Temperature:	200 C
Length of tubes:	10 m
Diameter of tubes:	2.5 m
Pressure drop:	0 atm
Reaction type:	POWERLAW

Figure A.29: Input parameters for the secondary shift converter.

	1	2	3	4	5	6	7	8	9	10	AIR	FEED	STEAM
Temperature C	228.2	600	800	764.1	996.2	712.1	350	420	200	200	600	33	247.9
Pressure bar	39.22	39.22	35.29	35.29	35.29	35.29	35.29	35.29	35.29	35.29	35.29	39.22	39.22
Vapor Frac	0.949	1	1	1	1	1	1	1	1	1	1	1	1
Mole Flow kmol/hr	5004.443	5004.443	6516.253	8245.583	8823.492	8823.492	8823.492	8823.492	8823.492	8823.492	1729.33	1254.443	3750
Mass Flow kg/hr	87783.203	87783.203	87783.203	137880.26	137880.26	137880.26	137880.26	137880.26	137880.26	137880.26	50097.052	20225.903	67557.3
Volume Flow cum/hr	4581.981	9208.378	16578.726	20301.223	26564.442	20632.578	12998.512	14519.551	9817.955	9817.955	3601.533	771.649	3564.253
Enthalpy MMkcal/hr	-234.172	-212.192	-162.433	-155.166	-154.912	-176.892	-203.255	-205.587	-221.43	-221.43	7.267	-22.743	-211.428
Mole Flow kmol/hr	1.443	1.443	1.286	1350.436	1348.565	1348.565	1348.565	1348.565	1348.565	1348.565	1349.15	1.443	0
N2	0	0	2653.554	2653.554	3365.848	3365.848	3365.848	3365.848	3365.848	4180.616	0	0	0
H2	0	0	0.313	0.313	4.056	4.056	4.056	4.056	4.056	4.056	0	0	0
NH3	0	0	0	17.28	17.28	17.28	17.28	17.28	17.28	17.28	0	0	0
AR	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	1250	1250	493.938	493.938	21.662	21.662	21.662	21.662	21.662	21.662	0	1250	0
H2O	3750	3750	2608.099	2608.099	2834.742	2834.742	2834.742	2019.975	2019.975	2019.974	0	0	3750
CO	0	0	370.222	370.222	815.618	815.618	815.618	0.851	0.851	0.85	0	0	0
CO2	3	3	388.84	388.84	415.72	415.72	415.72	1230.487	1230.487	1230.488	0	3	0
O2	0	0	0	362.9	0	0	0	0	0	0	362.9	0	0

Figure A.30: Mass balance for the synthesis gas generation section (see Figure A.22).

A.2.2 Separation section

The separation section has a dual function, reduce the amount of inert gases introduced in the loop and at the same time eliminate the carbon dioxide which is a poison for the ammonia converter catalyst. Figure A.31 and Figure A.32 describe the input parameters of the unit operations used in this section. Figure A.33 describes the mass balance obtained from this section.

ID:	ABS
Model:	SEP
Type:	Ideal separator
Split fractions:	
N2	0
H2	0
NH3	0
Ar	0
CH4	0
H2O	0.99
CO	0
CO2	1
O2	0

Figure A.31: Input parameters for the ABS model.

ID:	R5
Model:	RSTOIC
Type:	Stoichiometric reactor
Temperature:	330 C
Pressure:	35.29 m
Reaction:	$\text{CO} + 3\text{H}_2 = \text{H}_2\text{O} + \text{CH}_4$

Figure A.32: Input parameters for the methanator.

	10	11	12	CO2
Temperature C	200	200	330	200
Pressure bar	35.29	35.29	35.29	35.29
Vapor Frac	1	1	1	0.739
Mole Flow kmol/hr	8823.492	5593.229	5591.53	3230.263
Mass Flow kg/hr	137880.26	47700.23	47700.23	90180.025
Volume Flow cum/hr	9817.955	6340.519	8056.779	2472.394
Enthalpy MMkcal/hr	-221.43	5.265	10.361	-234.378
Mole Flow kmol/hr				
N2	1348.565	1348.565	1348.565	0
H2	4180.616	4180.616	4178.067	0
NH3	4.056	4.056	4.056	0
AR	17.28	17.28	17.28	0
CH4	21.662	21.662	22.512	0
H2O	2019.974	20.2	21.05	1999.775
CO	0.85	0.85	0	0
CO2	1230.488	0	0	1230.488
O2	0	0	0	0

Figure A.33: Mass balance for the separation section.

A.2.3 Ammonia loop

The ammonia loop consists of the compression section, the ammonia converter, purge and flash sections. Figure A.22, Figure A.34, Figure A.35, Figure A.36, Figure A.37, Figure A.38, Figure A.39, Figure A.40, Figure A.41, Figure A.42, Figure A.43, Figure A.44, and Figure A.45 represent the input parameters for the ammonia loop section. Figure A.46 shows the mass balance obtained from simulation.

ID:	H4
Model:	HEATER
Type:	Ideal heater
Temperature:	299 K
Pressure :	35.29 bar

Figure A.34: Input parameters for the H4 model.

ID:	F1
Model:	FLASH
Type:	Flash drum
Temperature:	298 K
Pressure :	35.29 bar

Figure A.35: Input parameters for the F1 model.

ID:	C1
Model:	COMPR
Type:	Compressor
Model:	Polyprotic using GPSA method
Discharge pressure :	640 psi

Figure A.36: Input parameters for compressor C1.

ID:	H5
Model:	HEATER
Type:	Ideal cooler
Temperature:	332 K
Pressure drop:	0 bar

Figure A.37: Input parameters for the H5 model.

ID:	C2
Model:	COMPR
Type:	Compressor
Model:	Polyprotic using GPSA method
Discharge pressure :	3100 psi

Figure A.38: Input parameters for the compressor C2.

ID:	H6
Model:	HEATER
Type:	Ideal cooler
Temperature:	371 K
Pressure drop:	0 bar

Figure A.39: Input parameters for the H6 model.

ID:	R6
Model:	RGIBS
Type:	Ammonia converter
Heat duty:	0
Pressure :	211 bar

Figure A.40: Input parameters for the ammonia converter.

ID:	H7
Model:	HEATER
Type:	Ideal cooler
Temperature:	60 C
Pressure drop:	211bar

Figure A.41: Input parameters for the H7 model.

ID:	H8
Model:	HEATER
Type:	Ideal cooler
Temperature:	-29 C
Pressure drop:	211bar

Figure A.42: Input parameters for the H8 model.

ID:	F2
Model:	FLASH
Type:	Flash drum
Heat duty:	0
Pressure :	207 bar

Figure A.43: Input parameters for the high pressure flash model.

ID:	F3
Model:	FLASH
Type:	Flash drum
Heat duty:	0
Pressure :	6.9 bar

Figure A.44: Input parameters for the low pressure flash model.

ID:	C3
Model:	COMPR
Type:	Compressor
Model:	Polyprotic using GPSA method
Discharge pressure :	213 bar

Figure A.45: Input parameters for the compressor C3 model.

	12	13	14	15	16	17	18	19	20	21	22	23	24	25	27	28
Temperature C	330	25.9	24.9	24.5	344.6	60	340.5	59	371	548.6	60	-29	-29	-29	-24.2	-29
Pressure bar	35.29	35.29	35.29	6.9	44.126	44.126	213.737	213.737	213.737	211	211	211	207	207	6.9	207
Vapor Frac	1	0.997	1	1	1	1	1	1	1	1	1	0.888	1	0	1	1
Mass Flow kmol/hr	5591.53	591.53	5574.686	5600.853	5600.853	5600.853	47837.192	28339.072	29339.072	21017.186	21017.186	21017.186	18671.532	2345.654	26.167	17737.956
Mass Flow kg/hr	47700.23	47700.23	47396.791	47887.192	47887.192	47837.192	6631.11	3994.331	6316.208	7235.11	3012.558	2117.58	2076.962	74.134	440.401	148689.83
Volume Flow cum/hr	8086.779	4008.31	3994.331	20164.198	6631.11	3603.676	1449.404	3405.817	6316.208	48.499	48.499	-32.32	-57.957	-39.902	77.431	1973.114
Enthalpy MJ/kmol/hr	10.361	-1.822	-0.708	-0.846	11.824	0.655	12.056	-4.65	48.496	48.499	48.499	-32.32	-57.957	-39.902	-0.143	-17.162
Mass Flow kmol/hr	1348.565	1348.565	1348.565	1354.689	1354.689	1354.689	1354.689	4922.132	4922.132	3761.189	3761.189	3761.189	3761.189	6.497	6.124	3566.957
N2	4178.067	4178.067	4178.067	4186.081	4186.081	4186.081	4186.081	17368.305	17368.305	13905.475	13905.475	13905.475	13905.475	8.157	8.014	13202.452
H2	4.056	4.056	4.053	10.199	10.199	10.199	10.199	274.271	274.271	2596.158	2596.158	2596.158	277.957	2318.201	6.146	264.089
NH3	17.28	17.28	17.28	19.524	19.524	19.524	19.524	394.655	394.655	394.655	394.655	394.655	331.722	2.933	2.244	315.136
AR	22.512	22.512	22.512	26.152	26.152	26.152	26.152	415.497	415.497	415.497	415.497	415.497	409.841	5.656	3.639	389.349
CF4	21.05	21.05	4.209	4.209	4.209	4.209	4.209	4.212	4.212	4.212	4.212	4.212	0.003	4.209	0	0.002
H2O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure A.46: Mass balance for the ammonia loop section (see Figure A.22).

APPENDIX B – ECONOMIC INDICATORS

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B.1 Introduction

Economic evaluation methods have been deeply studied since the principal objective of a process is to make a profit out of it [52] ,[66]. Basically all these methods only differ in extend and dept of the evaluation.

As a first approximation to economic evaluation one can obtain the economic potential from the mass and energy balances:

Economic Potential= Revenue – Raw Material Cost –Utility Costs- Waste
treatment

$$EP = \sum F_{prod} P_{prod} - \sum F_{raw\ mat} P_{raw\ mat} - \sum F_{util} P_{util} - \sum F_{waste} P_{waste}$$

In order to obtain more precise results other economic variables (e.g. labor costs, equipment costs) that cannot be directly estimated from the mass and energy balances should be included. This way the economic evaluation will be structured as follows [66]:

- Fixed Costs: Costs related to the direct investment specially capital investment costs which are incurred at the start of the project
- Variable Costs: Raw material, labor, utilities and other costs dependent on operations.

Fixed Costs

As mentioned before fixed costs will be focused on the capital investment that represents the total expenses required at the beginning of the plant life. The capital investment can be divided into the following parts (see Figure B. and Figure B.) [52]:

1. Direct Project Expenses:	
- Equipment cost	C_p
- Piping, insulation, instrumentation, (Materials required for installation)	C_M
- Labor associated to installation	C_L
2. Indirect Project Expenses	
- Freight, insurance and taxes	C_{FIT}
- Construction overhead	C_O
- Contractor engineering expenses	C_E
3. Contingency and Fee:	
- Contingency (unforeseen circumstances)	C_{Cont}
- Contractor fee	C_{Fee}
4. Auxiliary Facilities:	
- Site development (land, grading, etc)	C_{Site}
- Auxiliary Buildings	C_{Aux}
- Offsite and Utilities	C_{Off}

Figure B.1: Costs factors.

Turton defines Bare Module Costs for equipment as the sum of direct and indirect costs and using relationships showed above:

$$C_{BM} = C_p F_{BM} F_M F_P F_{Lang}$$

$$\text{Bare Module Factor: } F_{BM} = (1 + \alpha_L + \alpha_{FIT} + \alpha_O \alpha_L + \alpha_E) (1 + \alpha_M)$$

$$\text{Material Factor: } F_M = 1 \text{ for carbon steel}$$

$$\text{Pressure Factor: } F_L = 1 \text{ for carbon steel}$$

$$\text{Lang Factor: } F_{Lang} = 4.74 \text{ for fluid processing plant}$$

1. Direct Project Expenses:	
- Equipment cost	C_p
- Piping, insulation, instrumentation, (Materials required for installation)	$C_M = \alpha_M C_p$
- Labor associated to installation	$C_L = \alpha_L (C_p + C_M)$
Total Direct	$C_{DE} = C_p + C_M + C_L$
2. Indirect Project Expenses:	
- Freight, insurance and taxes	$C_{FIT} = \alpha_{FIT} (C_p + C_M)$
- Construction overhead	$C_O = \alpha_O C_L$
- Contractor engineering expenses	$C_E = \alpha_E (C_p + C_M)$
Total Indirect	$C_{IDE} = C_{FIT} + C_O + C_E$
Bare Module	$C_{BM} = C_{DE} + C_{IDE}$
3. Contingencies and Fee:	
- Contingency (unforeseen circumstances)	$C_{Cont} = \alpha_{Cont} C_{BM}$
- Contractor fee	$C_{Fee} = \alpha_{Fee} C_{BM}$
Total Module	$C_{TM} = C_{BM} + C_{Cont} + C_{Fee}$
4. Auxiliary Facilities:	
- Site development (land, grading, etc)	C_{Site}
- Auxiliary Buildings	C_{Aux}
- Offsite and Utilities	C_{Off}

Figure B.2: Cost factors.

The Fix Capital Investment (FCI) is the then the sum of all the total nodule cost and the cost of auxiliary facilities.

$$\text{FCI} = \text{Total Module} + \text{Auxiliary Facilities}$$

Variable Costs

These costs are associated with the day-to-day operation of the plant. Many elements may influence the cost of manufacturing chemicals. Turton [52] divides them into three categories (see Figure B. and Figure B.):

1. Direct Manufacturing Costs:	
Raw Materials:	Costs of chemical feed stocks required by the process. Flow rates are obtained from the flow sheet.
Waste Treatment:	Costs of waste treatment to protect environment.
Utilities:	cost of utility streams required by process. Includes: <ul style="list-style-type: none"> - Fuel gas, oil and/or coal - Electric power - Steam - Cooling water - Process water - Boiler feed water - Inert gases - Refrigeration
Operating Labor:	Costs of personnel required for plant operations.
Direct supervisory:	Cost of administrative/engineering and support and personnel.
Maintenance:	Cost of labor and materials associated with equipment maintenance.
Operating Supplies:	Cost of miscellaneous supplies.
Laboratory charges:	Cost of routine and special laboratory tests.
Patent and Royalties:	Cost of using patented or licensed technology
2. Fixed Costs:	
Depreciation:	Cost associated with the physical plant. Legal operating expenses for tax purposes
Local Taxes & Insurance:	Costs associated with property taxes and liability insurance.
Plant Overhead Cost:	Fire protection, medical services, accounting services, etc.
3. General Expenses:	
Administration Costs:	Cost for administration including salaries.
Sales Costs:	Marketing and sales costs.
R&D:	Costs of research activities related to the product.

Figure B.3: Cost of manufacturing chemicals

1. Direct Manufacturing Costs:	
Raw Materials:	C_{RM}
Waste Treatment:	C_{WT}
Utilities:	C_{UT}
Operating Labor:	C_{OL}
Direct supervisory:	$0.18 C_{OL}$
Maintenance:	$0.06 FCI$
Operating Supplies:	$0.009 FCI$
Laboratory charges:	$0.15 C_{OL}$
Patent and Royalties:	$0.03 COM$
2. Fixed Costs:	
Depreciation:	$0.1 FCI$ (approximation)
Local Taxes & Insurance:	$0.032 FCI$
Plant Overhead Cost:	$0.708 C_{OL} + 0.036 FCI$
3. General Expenses:	
Administration Costs:	$0.177 C_{OL} + 0.09 FCI$
Sales Costs:	$0.11 COM$
R&D:	$0.05 COM$
Cost of Manufacturing (COM):	
$COM = 0.304 FCI + 2.73 C_{OL} + 1.23 (C_{UT} + C_{WT} + C_{RM})$	

Figure B.4: Cost of manufacturing.

B.1 Economic analysis

There are other type of expenses that should be included in the evaluation such as start-up costs ($C_{start-up}$) and the Working Capital (WC). Adding these costs one obtains the total fix capital investment:

$$TFCI = FCI + C_{start-up} + WC$$

In order to be able to perform economic analysis, one must study the total lifetime of the plant. Consequently the time value of money should be included in these calculations. For this reason the FCI is multiplied by the Capital Charge Factor (CCF). The simplest model for annuity calculations would be:

$$CCF = \frac{i(1+i)^N}{(1+i)^N - 1}$$

Where N is the plant lifetime and *i* is the year discount rate 25 years and 12% in this case.

In order to obtain a total annualized profit (TAP):

$$TAP = (\text{Revenue} - \text{COM}) - (\text{CCF}) (\text{FCI})$$

One must notice that depreciation is not included in the TAP. There exist other economic evaluation methods

B.1 The hydrogen cyanide case (TAPK and TACK)

In the Hydrogen Cyanide case study it is very difficult to set a price for the product due to the fact that sometimes it is an intermediate product inside the company. For this reasons several economic indicators are going to be considered.

In the first place no revenues from Hydrogen Cyanide are going to be considered and only cost per kilogram of CN⁻ group will be used as economic indicator. Consequently the economic potential equation will be as follows:

Economic Potential= - Raw Material Cost -Utility Costs- Waste treatment

$$EP = -\sum F_{raw\ mat} P_{raw\ mat} - \sum F_{util} P_{util} - \sum F_{waste} P_{waste}$$

The main reason why only the CN⁻ group is studied and not the HCN is because NaCN can be produced and both prices differ; it is also a strategic question how much to produce of one or the other, but this problem is not going to be discussed.

A new indicator will be developed, the total annualized cost per kilogram of product (TACK). If we define the total annual production (TAPr) as the total production of hydrogen cyanide in one operating year, the TACK will be considered as follows:

$$TACK = \frac{COM - CCF \cdot FCI}{TAPr}$$

As a second indicator the total annualized profit (TAP) will be modified in order to obtain the total annualized profit per kilogram of product (TAPK) described as follows:

$$TAPK = \frac{(\text{Revenue} - COM) - CCF \cdot FCI}{TAPr}$$

The Net Present Value (NPV) at the same time can be defined as the cumulative discounted cash position at the end of the project. NPOV is greatly influenced by the level of fixed capital investment and a better criterion for comparison of projects with different investment levels.

The NPV is the addition of all the TAPK for the expected lifetime of the project taking into account the time value of money. The NPV was used for the evaluation of potential improvement with a total discount rate of 12% and a plant life-time of 25 years.

B.4 The hydrogen cyanide case calculations

The following figures represent the economic calculations performed for the evolution of the economic performance of the BMA case study.

AMOUNTS													
Year	Raw Material				W.W.		Utilities				Personel		
	NH3 ton/yr	N.Gas ton/yr	H2SO4 96% ton/yr	NaOH 100% ton/yr	H2O m3/yr	N.Gas ton/yr	Elec. MWh/yr	Cooling Water Tm3/yr	N° tubes	Catal. Life month	Oper. Days/yr	Oper. Labour	Direct Superv.
1957	345	309	120	12	128	662	150	76	104	5	300	4.5	0.25
1959	345	309	120	12	128	662	150	76	104	5	300	4.5	0.25
1960	350	492	191	19	203	1106	239	122	190	5	369	4.5	0.25
1965	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1969	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1970	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1973	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1974	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1975	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1976	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1977	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1978	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1979	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1980	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1982	743	665	258	26	274	1224	322	164	260	12	355	4.5	0.25
1983	1084	971	376	38	400	1469	1207	237	380	12	355	4.5	0.25
1984	2557	2288	886	90	944	2612	2846	565	650	23	357	4.5	0.25
1985	2557	2288	886	90	944	2612	2846	565	650	23	357	4.5	0.25
1987	2557	2288	886	90	944	2612	2846	565	650	23	357	4.5	0.25
1990	2557	2288	886	90	944	2612	2846	565	650	23	357	4.5	0.25
1993	2557	2288	886	90	944	2612	2846	565	650	23	357	4.5	0.25
1994	2721	2435	943	96	1004	2780	3029	602	650	33	360	4.5	0.25
1996	2721	2435	943	96	1004	2780	3029	602	650	33	360	4.5	0.25
1998	2721	2435	943	96	1004	2780	3029	602	650	33	360	4.5	0.25
1999	2721	2435	943	96	1004	2780	3029	602	650	33	360	4.5	0.25

Figure B.5: Amount of inputs.

PRICES												
Year	Raw Material				W.W.		Utilities				Personel	
	NH3 \$/kg	N.Gas \$/Btu E6	H2SO4 96% \$/kg	NaOH 100% \$/kg	H2O \$/ton	N.Gas \$/Btu E6	Elec. \$/ kWh	Cooling Water \$/ m3	N° \$/tube	Catal. Life \$/month	Oper. Labour	Direct Superv.
1957	0.91	0.90	0.005	0.19	53	0.90	0.20	0.64	381	2000	6480	
1959	0.86	1.00	0.005	0.20	53	1.00	0.19	0.61	363	2000	6480	
1960	0.82	1.03	0.005	0.21	53	1.03	0.19	0.58	350	2000	6480	
1965	0.61	1.02	0.006	0.21	53	1.02	0.18	0.50	356	2000	6480	
1969	0.31	0.89	0.007	0.22	53	0.89	0.18	0.41	365	2000	6480	
1970	0.29	0.82	0.008	0.23	53	0.82	0.17	0.38	406	2000	6480	
1973	0.31	0.99	0.008	0.26	53	0.99	0.16	0.35	387	2000	6480	
1974	0.65	1.36	0.008	0.28	53	1.36	0.16	0.36	472	2000	6480	
1975	0.97	2.04	0.008	0.28	53	2.04	0.16	0.36	389	2000	6480	
1976	0.56	2.15	0.010	0.27	53	2.15	0.15	0.29	330	2000	6480	
1977	0.55	1.92	0.010	0.25	53	2.92	0.15	0.29	336	2000	6480	
1978	0.48	3.11	0.011	0.25	53	3.11	0.14	0.27	480	2000	6480	
1979	0.39	3.43	0.013	0.26	53	3.43	0.14	0.23	669	2000	6480	
1980	0.46	4.08	0.014	0.22	53	4.08	0.14	0.20	876	2000	6480	
1982	0.42	5.11	0.018	0.21	53	5.11	0.13	0.16	382	2000	6480	
1983	0.37	5.15	0.019	0.20	53	5.15	0.13	0.16	457	2000	6480	
1984	0.41	5.06	0.019	0.20	53	5.06	0.12	0.15	381	2000	6480	
1985	0.37	4.63	0.020	0.19	53	4.63	0.12	0.15	315	2000	6480	
1987	0.30	4.08	0.018	0.20	53	4.08	0.11	0.16	588	2000	6480	
1990	0.30	3.23	0.019	0.45	53	3.23	0.10	0.15	476	2000	6480	
1993	0.16	3.13	0.016	0.36	53	3.13	0.09	0.12	329	2000	6480	
1994	0.17	2.55	0.030	0.31	53	2.55	0.08	0.11	322	2000	6480	
1996	0.22	3.06	0.028	0.38	53	3.06	0.08	0.11	340	2000	6480	
1998	0.15	2.53	0.039	0.42	53	2.53	0.08	0.11	324	2000	6480	
1999	0.16	2.79	0.039	0.47	53	2.79	0.08	0.11	292	2000	6480	

Figure B.6: Price of inputs.

COSTS															Deprec.		
Year	Raw Material				W.W.		Utilities				Personnel		Maintenance				\$/year
	AMH \$/year	M.Gm. \$/year	H2SO4 36% \$/year	NaOH 100% \$/year	W.W. H2O \$/year		N.Gm. \$/year	Gas \$/year	Cooling Water \$/year	Coal Life \$/year	Oper. \$/year	Direct Superv. \$/year	Minim. \$/year	Oper. Supplies \$/year	Lab. Charges \$/year	R&D Charges \$/year	
1997	313363	19177	540	2308	7	28191	25582	49114	79949	109000	19440	40768	4077	16200	42544	81336	
1998	299662	23999	572	2429	7	31434	28818	46339	75607	109000	19440	40768	4077	16200	41976	81336	
1999	450308	32583	933	3963	11	34132	45338	70644	133146	109000	19440	54164	5416	16200	59462	108327	
1995	455737	47021	1486	5485	15	39313	58201	82651	91351	109000	19440	54164	5416	16200	59973	108327	
1969	230196	96013	1823	5641	15	31369	56654	67370	142289	109000	19440	72917	7292	16200	56886	145835	
1970	211986	94846	1964	5876	15	47684	56389	62537	104175	109000	19440	72917	7292	16200	53591	145835	
1973	229976	114005	2174	6669	15	37316	52723	59086	99928	109000	19440	72917	7292	16200	55339	145835	
1974	485377	42906	2092	7313	15	78996	51502	58708	120961	109000	19440	72917	7292	16200	66721	145835	
1975	717615	64223	2080	7261	15	115245	50280	59915	99701	109000	19440	72917	7292	16200	80283	145835	
1976	414856	67902	2555	7052	15	125017	49058	48057	84517	109000	19440	72917	7292	16200	64269	145835	
1977	406167	91998	2569	6582	15	169375	47836	47901	86114	109000	19440	72917	7292	16200	67240	145835	
1978	353233	97886	2781	6477	15	180221	46615	44155	123025	109000	19440	72917	7292	16200	67038	145835	
1979	290391	108009	3268	6660	15	198559	43393	37373	171560	109000	19440	72917	7292	16200	67404	145835	
1980	343231	128451	3703	5746	15	236496	44171	33162	224597	109000	19440	72917	7292	16200	75296	145835	
1982	309900	153089	4568	5483	15	296587	41728	26980	97829	109000	19440	72917	7292	16200	71917	145835	
1983	401850	236704	6973	7624	21	358231	151747	37030	171261	109000	19440	72917	7292	16200	92890	145835	
1984	1052009	548478	17181	17975	50	626099	346982	84589	126548	109000	19440	102387	10239	16200	172228	204775	
1985	947270	502572	17693	17076	50	573687	336191	82141	104565	109000	19440	167904	16790	16200	175702	335809	
1987	762931	442572	16110	17927	50	505197	314608	50212	198084	109000	19440	167904	16790	16200	163874	335809	
1990	750971	350600	17279	40115	50	400212	282234	84111	158141	109000	19440	167904	16790	16200	151125	335809	
1993	409423	339615	13942	32372	50	387872	249860	58235	109166	109000	19440	167904	16790	16200	127169	335809	
1994	452696	294099	27848	30067	53	335715	254414	65219	75408	109000	19440	167904	16790	16200	123416	335809	
1996	363018	353995	26095	36444	53	403630	254414	67426	79712	109000	19440	167904	16790	16200	136959	335809	
1998	409308	291808	36348	40215	53	333100	251385	64865	75845	109000	19440	167904	16790	16200	121786	335809	
1999	440548	321450	37111	43403	53	366936	248328	68468	68971	109000	19440	167904	16790	16200	126079	335809	

Figure B.7: Cost of inputs.

TOTAL COSTS	PACK	Raw&Util COST	Fixed COSTS	Per.R&D COSTS
883624	1.96	1.13	0.42	0.41
881493	1.94	1.10	0.42	0.41
1248712	1.72	1.09	0.35	0.28
1259441	1.29	0.81	0.26	0.21
1194607	1.22	0.66	0.38	0.20
1125413	1.15	0.59	0.35	0.20
1162123	1.19	0.63	0.38	0.20
1401141	1.43	0.86	0.35	0.21
1685906	1.72	1.14	0.38	0.23
1349649	1.38	0.81	0.35	0.21
1412045	1.44	0.87	0.38	0.22
1407797	1.44	0.87	0.35	0.22
1415482	1.45	0.87	0.38	0.22
1581219	1.61	1.04	0.35	0.22
1501849	1.33	0.96	0.38	0.22
1950682	1.36	0.95	0.24	0.17
3618787	1.87	0.83	0.14	0.09
3689737	1.09	0.76	0.23	0.09
3441356	1.02	0.69	0.23	0.09
3173628	0.94	0.61	0.23	0.09
2670555	0.79	0.47	0.23	0.08
2591736	0.72	0.42	0.22	0.07
2876135	0.80	0.49	0.22	0.08
2557503	0.71	0.41	0.22	0.07
2847529	0.74	0.43	0.22	0.08

Figure B.8: Cost indicators.

Year	PRODUCTION					PRICES			
	Main Products			Energy		Products			Energy
	HCN ton/yr	NaCN ton/yr	Sulfate ton/yr	Steam N. Gas Equiv. Btu E-6	H2 N. Gas Equiv. Btu E-6	HCN \$/kg	NaCN \$/Btu E6	Sulfate \$/kg	N. Gas \$/ Btu E6
1957	455	7	155	3296	11900	2.37	2.20	0.37	0.90
1959	455	7	155	3296	11900	2.05	1.91	0.35	1.00
1960	725	12	247	5746	18950	1.89	1.76	0.34	1.03
1965	979	16	333	5209	25590	1.24	1.16	0.27	1.02
1969	979	16	333	5209	25590	1.04	0.97	0.22	0.89
1970	979	16	333	5209	25590	0.99	0.92	0.20	0.82
1973	979	16	333	5209	25590	0.87	0.81	0.20	0.99
1974	979	16	333	5209	25590	0.83	0.77	0.39	1.36
1975	979	16	333	5209	25590	1.24	1.16	0.54	2.04
1976	979	16	333	5209	25590	1.52	1.41	0.29	2.15
1977	979	16	333	5209	25590	2.09	1.94	0.29	2.92
1978	979	16	333	5209	25590	2.24	2.08	0.29	3.11
1979	979	16	333	5209	25590	1.91	1.77	0.27	3.43
1980	979	16	333	5209	25590	2.05	1.90	0.28	4.08
1982	979	16	333	5209	25590	2.07	1.93	0.27	5.11
1983	1430	23	486	4591	37350	2.18	2.02	0.23	5.15
1984	3370	55	1146	2765	88060	2.08	1.94	0.22	5.06
1985	3370	55	1146	2765	88060	2.21	2.06	0.23	4.63
1987	3370	55	1146	2765	88060	2.03	1.88	0.23	4.08
1990	3370	55	1146	2765	88060	2.13	1.98	0.23	3.23
1993	3370	55	1146	2765	88060	1.86	1.73	0.12	3.13
1994	3587	59	1220	2936	93713	1.78	1.66	0.11	2.55
1996	3587	59	1220	2936	93713	1.63	1.52	0.14	3.06
1998	3587	59	1220	2936	93713	1.49	1.39	0.10	2.53
1999	3587	59	1220	2936	93713	1.59	1.48	0.10	2.79

Figure B.9: Amount and price of outputs.

Year	INCOME				
	Main Products			Energy	
	HCN \$/yr	NaCN \$/yr	Sulfate \$/yr	Steam N. Gas Equiv. \$/yr	H2 N. Gas Equiv. \$/yr
1957	1079569	16386	57690	2963	10700
1959	935189	14195	54431	3304	11932
1960	1374346	20860	82902	5934	19570
1965	1217840	18485	89432	5325	26161
1969	1018007	15452	71669	4612	22657
1970	973455	14776	66401	4281	21032
1973	851275	12921	64970	5146	25280
1974	814093	12357	130856	7092	34842
1975	1218605	18497	179681	10616	52153
1976	1489162	22603	95625	11224	55140
1977	2043440	31016	97828	15206	74705
1978	2191257	33260	97524	16180	79489
1979	1869213	28372	89839	17853	87709
1980	2004517	30425	92731	21232	104310
1982	2032110	30844	89871	26627	130814
1983	3113844	47263	113265	23625	192217
1984	7022398	106589	257261	13983	445395
1985	7463710	113288	259809	12812	408117
1987	6829793	103666	263391	11283	359394
1990	7175308	108910	262629	8938	284708
1993	6283178	95369	133047	8658	273787
1994	6397294	97101	132004	7482	238825
1996	5856295	88889	176360	8996	287139
1998	5361521	81380	118704	7424	236965
1999	5700231	86521	125013	8178	261036

Figure B.10: Total income.