LIFE CYCLE ASSESSMENT IN DESIGNING GREENER SEMICONDUCTOR

A THESIS

SUBMITTED TO THE DEPARTMENT OF CHEMICAL AND ENVIRONMENTAL ENGINEERING

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

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ABSTRACT

The semiconductor industry has established an excellent environmental, safety and health (ESH) performance record, but it is important for the industry to continue to be proactive in these areas. Technological shifts have recently been made to realize increased environmental performance objectives; one of them is the shift from PFC (C_2F_6) to NF_3 in chamber cleaning.

While ESH conscious design considerations have been integrated into the design of individual products and manufacturing processes, life-cycle assessment (LCA) has not been implemented to reduce the overall environmental impacts in this industry. By using LCA, we can achieve cooperative approaches to protecting the global environment; staying committed to scientifically-based, positive environmental policies.

In this project we use an LCA approach to select among manufacturing strategies for chamber cleaning. We simulate and develop NF_3 and C_2F_6 production and abatement strategies while evaluating the NF_3 and C_2F_6 chamber cleaning cycle. Using LCA to evaluate the trade-off decision opportunities between NF_3 and C_2F_6 involves collecting and creating a chamber cleaning information data base before assessing and interpreting the data base. From this work, we want to reveal tradeoffs in the semiconductor manufacturing process that may be improved upon in future ESH decisions. This will lead to a better vision of where improvements should be focused for other technology shifts in this industry.

A significant improvement in the evaluation of green chemical products can be approached by the complementary use of the methodologies of LCA and risk assessment, which will be discussed. By collecting information for a uniform database in

semiconductor manufacturing for the most environmentally impacting chemicals, the industry will be able to carry out the LCA approach better and make more informed ESH decisions. This will require collaboration from many constituencies from academia, industry, and government in order to be successful.

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Thank my parents for their unconditional support. Thanks to Dr. Paul Blowers and Dr. Farhang Shadman for their trust and direction.

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CHAPTER 1: INTRODUCTION

1.1 THESIS STATEMENT

This thesis is intended to develop systematic procedures and approaches in evaluating chemical processes which incorporate green design concepts, and to evaluate potential environmental and economic impacts in a whole life cycle for a product. In this work, we try to combine traditional chemical engineering process design with Life Cycle Assessment, modeling the design process while evaluating the environmental impacts.

The research has examined a general problem approach with a object-oriented practical case. The tradeoffs among conflicting objectives have been evaluated, and the incorporation of Life Cycle Assessment into decision making is discussed. The procedures demonstrated in this project should be applicable in many other multi-criteria design projects.

The case that has been studied extensively using Life Cycle Assessment (LCA) in this project for selecting among manufacturing strategies for improved ESH (environment, safety and health) impact is semiconductor manufacturing chamber cleaning with the use of either NF_3 or C_2F_6. The expected results from an explicit incorporation of environmental objectives in chemical process design are trying to reveal:

- That using LCA can reveal better trade-off decision opportunities.
- That all units are involved in the 'whole picture' and have been investigated, so we can improve from 'sub-optimisation'.
- That LCA will look globally at ESH impacts like ozone depletion, resource depletion, toxicity, etc. Externalities like transportation, upstream manufacturing activities, and downstream usage all become important.
- That anticipation and avoidance of future regulations could impact a process

since new regulations are typically introduced years after knowledge regarding environmental hazards first becomes available.

1.2 STRUCTURE OF THESIS

Chapter 2 presents issues involving environmentally conscious design; discusses the interrelationship of environmental issues with chemical process design; introduces LCA design approaches which can be integrated into the chemical process design.

Chapter 3 discusses life cycle assessment in detail, including the historical background, including the origin of LCA, main uses of LCA, components of LCA, processes of LCA, pros and cons of LCA.

Chapter 4 breaks down the LCA methodology into details, explains major categories that are been used to evaluate environmental impacts; discusses the scientific background of each category, including historical and current situations of the categories, originations of the categories and how they are measured and calculated.

Chapter 5 develops the process-by-product input-output life cycle assessment methodology. Life-cycle assessment tools are needed in the context of environmental evaluation of chemical processes in order to take into account the impacts generated by the upstream processes that provide the inputs used by a design. The process of chamber cleaning using NF_3 and C_2F_6 has been compared on a fair basis, using LCA to demonstrate the method and its possible usage in other processes.

Chapter 6 contains recommendation for future work and conclusions from this LCA study.

1.3 SUMMARY OF CONTRIBUTIONS

The major purpose of the study is to incorporate ESH performance into the consideration of designing a process to create a win-win situation for economic and environmental performance. This means we have accomplished the objectives in the following list:

- Explicit use of Life Cycle Assessment as a means to evaluate pros and cons of certain processes regarding environmental impacts.
- Incorporating uncertainties in life-cycle impact assessment study.
- Refinement of existing models used to assess some of the categories that have been used to indicate impacts on the environment.
- Development of an environmental knowledge management tool to organize LCA data
- Demonstration of the application of the LCA method developed in this project through well documented case studies.
- Establishment of user-friendly features for future studies carried out using the same methodology.

1.4 READING REFERENCES

I hope that this document will be valuable to chemical process designers who might not be experts on decision analysis or environmental science. In the process of writing this thesis, I have taken pains to make it more vivid and straightforward to be more effective when it reaches a wider audience. The following reading list attempts to compensate for any shortcomings in attaining this goal:

Coulson, J. M. and J. F. Richardson (1999). Coulson & Richardson's chemical engineering. Oxford ; Boston, Butterworth-Heinemann.

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CHAPTER 2: ENVIRONMENTALLY CONSCIOUS DESIGN

2.1 THE STATE OF THE ENVIRONMENT

Thirty years ago after the first world energy crisis, almost everybody became conscious that energy sources were not unlimited. A period followed in which the majority of energy analysts believed that fossil fuels would be exhausted within a very short period, even less than 20 years [1]. Some industry experts recently predicted that the world's oil supply will reach its maximum production and midpoint of depletion sometime around the year 2010[2]. Analysts such as Dr. C. J. Cambell, predict that we are not far from the coming global energy crisis**.** And various measures of US energy security indicate that the US might be heading for another energy crisis[1]. Many of the warning signs that existed before the energy crises of 1973 and 1979 exist today and they show that the current situation could be even worse because US dependence on petroleum imports has grown steadily for over a decade, and has been at record levels for several years. Petroleum inventories are low and the ability of either Strategic Petroleum Reserves (SPR) or commercial petroleum stocks to cope with an interruption in imports matches the historic lows preceding the 1973 and 1979 energy crises.

Although many specialists in the area of petroleum resources and the environment may be intimately aware of the crisis we may face in the near future, the general public and even most practicing engineers are unaware. One method of attempting to improve processes for their environmental footprint, including their use of fossil fuels is green design, or Environmentally Conscious Design. This is one way of improving the environmental performance of current practices while still meeting all design specifications. Another way of stating this is that sustainable designs will allow us to meet today's goals and needs without compromising those of the future. With all that said, the concept of

Environmentally Conscious Design is accepted by most regulators, engineers, and those in the general public who acknowledge that these activities affect the environment.

2.1.1 ENVIRONMENTAL PROBLEMS

After long and deep discussions in several international meetings[3], there were three main interrelated atmospheric pollution problems that were identified and can be used as a focus for discussion of environmentally based design: global warming, urban industrial pollution, and the acidification of the environment.

All three of the above problems are related to the use of conventional sources to produce energy, and that unfortunately, threaten the survival of life on Earth [4-6]. The greenhouse effect, induced in the atmosphere primarily by the increase of carbon dioxide coming from the burning of fossil fuels raises the atmospheric temperature and consequently produces a sea level rise, as well as a drastic climatic change which affects agricultural production [7-34]. At the same time, air pollution that is killing forests and lakes, and the rising occurrence of ground acidification both compromise the overall sustainable balance of the ecosystem.

2.1.2 TYPICAL SOLUTIONS FOR ENVIRONMENTAL PROBLEMS

Our global home needs to be preserved and we as engineers are in the best position to affect sustainable manufacturing processes. One could think about solving the pollution problem from energy sources as a starting point. The energy solution cannot be based on non-renewable resources because this will only be a viable approach when non-renewable sources are still available. When those run out, we will have to seek other sources for energy. The first and obvious approach to the solution for the pollution problem created by the production of energy from fossil fuels is to consume less energy. This approach to reduce energy usage implies improving the efficiency of the processes that use energy and so-called energy conservation, which actually means to diminish undesired energy losses. Unfortunately, most consumers will not accept this second method. One only needs to look as far as California during the energy crisis of 2002 to see that consumers were unwilling to change their usage habits without drastic measures by the state to institute rolling blackouts.

A second step that could be done is to reduce energy problems is the development of all environmentally sound and ecologically viable alternative sources of energy and material resources, but only if the are economically viable and do not involve other externalities that would negatively impact their long term usage [35]. This involves a life cycle level of viewing the process or product in a “global view” that exhausts the possibilities of the externalities.

Environmentally Conscious Design is heavily implemented in this particular area of energy usage. To promote energy efficiency and environmentally sensitive energy generation, the Environmental Protect Agency (EPA) is using renewable energy technologies to supplement or replace a large portion of their energy requirements in many facilities[36].

2.1.3 RENEWABLE ENERGY

Renewable energy is derived from the sun, wind, water, or the Earth's core. It also can be derived from biomass—or plant matter—which is grown, harvested, and transferred into energy by one of a number of processes. Renewable technologies are designed to capture and store this energy. They include:

- Photovoltaic solar panels—convert sunlight directly into electricity.
- Wind turbines—capture wind to turn rotors, which turns a generator and creates electricity.

- Transpired solar collectors—sunlight is used to preheat air for heating purposes.
- Solar hot water heaters—use the sun to heat water for domestic applications.
- Small-scale hydroelectric power plants—flow water over turbines, which turn a generator and create electricity.
- Fuel cells—combine hydrogen and oxygen to produce electricity and heat.
- Ground-source heat pumps—transfer heat to the ground in summer and extract heat from the ground in winter.
- Green power—electricity generated from renewable sources such as wind, geothermal, biomass, and landfill gas.

Another example of where ecologically oriented design is important is in the depletion of the atmospheric ozone layer caused by gases released during the production of insulation foams and the use of refrigerant fluids, as well as by the liberation of aerosols. The disappearance of the ozone layer could have terrible effects on human and livestock health [37-46] and on some life forms at the base of the sea food chain[47]. The discovery of a hole in the ozone layer above the Antarctic suggests the possibility of a faster depletion rate than previously suspected. Again, Environmentally Conscious Design would identify the environmental challenges to be solved and then work within the economic and technological feasibility constraints to identify, develop, and use new techniques that are sustainable in the long term.

We can raise many examples like this that prove how important Environmentally Conscious Design is as a necessity to secure our future. Solving the current problems we all face is also challenged by the exponential expansion of the population growth—a reality in developing countries[48, 49].

Hence a tremendous effort will have to be made to provide more energy and materials to Third World countries that aspire to the consumerist lifestyle of the First World countries. This is another subject in which scientists should be involved in order to contribute to new solutions, new materials, and new manufacturing techniques that can avoid the mistakes made in the past. It should be noted that these problems we are dealing with here are all interrelated.

2.1.4 THE STATE OF ENVIRONMENTALLY CONSCIOUS DESIGN

Environmentally Conscious Design is a multidisciplinary subject. It involves engineers and designers, as well as science specialists, like chemists and physicists. It also involves economists, business managers, sociologists, etc. Engineers and scientists are involved in designing processes, which also requires many chemists and physicists for some specific information. Economists and business personnel can view from an economic account aspect, reinforcing the evaluation of the design in a cost perspective. Taking one component of LCA evaluations, climate perturbation, involves a lot of information and multiple technological concerns, as shown in figure 1.

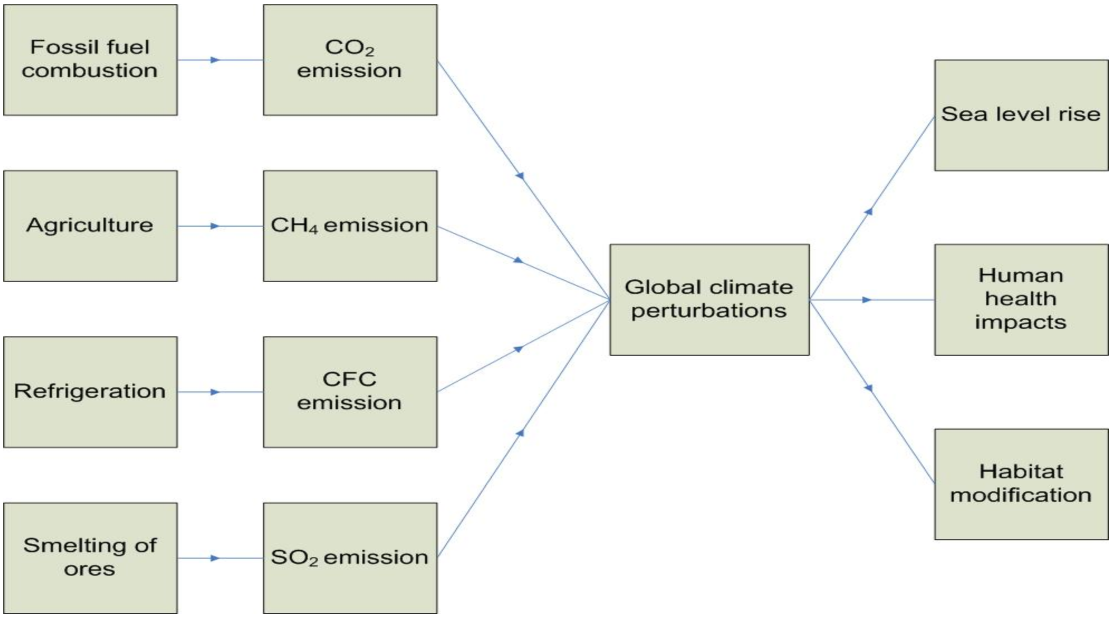

Figure 1 Climate perturbation, example of a single environmental concern related to multiple technological activities

On the other hand, by comparison, only a few percent of scientists, physicists, and engineers devote their research to environmental science and green design. Knowledge is required of classical fields like thermodynamics, fluid dynamics and heat transfer, and reactor design—from the theoretical and latest experimental viewpoints—as well as advanced subjects like progress in material science, and the use of complex mathematics to deal with computational models. Scientists in the area of benign design have to work intensively because, besides the problems of lack of information to apply the conscious design approach, some of the technology is not fully developed. Of course, it is possible to design alternative processes with today's knowledge, but sometimes it is not possible to quantify their behaviors precisely to find the best ways to improve performance [50].

Decision making for improving a process involves tradeoffs at almost every step. At present, much of the needed information for making informed decisions in a global context with many criteria is scattered throughout the literature. One of my goals is to identify the issues, information sources and approaches to process design that have the potential to lead to improvements in both economic performance and environmental quality so that future engineers may benefit from this general approach.

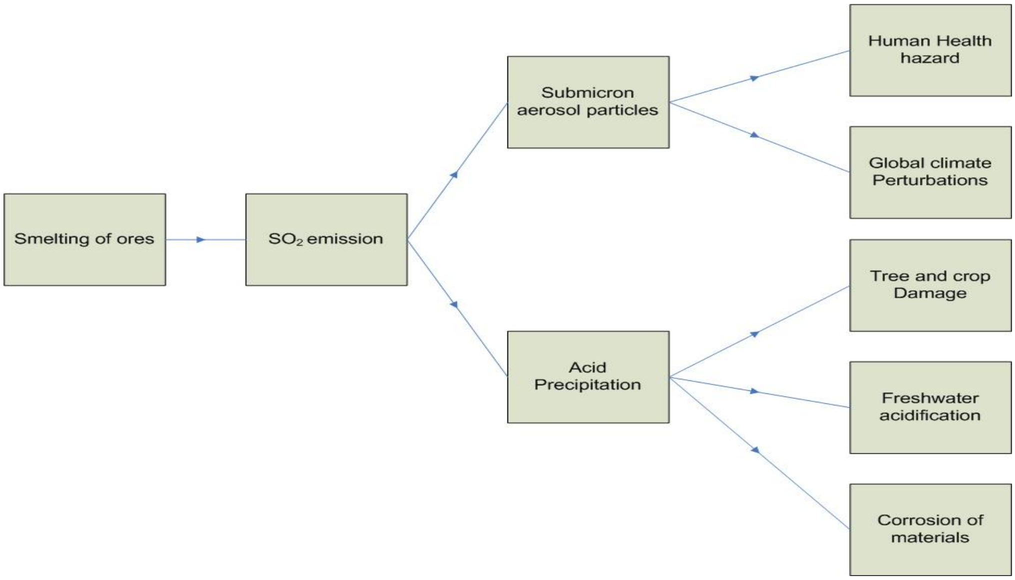

Figure 2 Example of multiple environmental impacts related to a single technological activity

In the area of chemical manufacturing and chemical uses, companies (including the semiconductor industry) face many challenges that mainly include economic competition, complying with regulatory demands for more benign products, and the technical constraints of production processes. As shown in figure 2, there are many environmental problems generated by every chemical process, such as smelting ores. Due to the recent spotlight on many products, one of the growing aspects on how society perceives the chemical industry is to focus on how companies are dealing with environmental issues [51, 52]. Product manufacturing often involves producing undesirable environmental, health, and safety impacts that are called externalities [53]. Images of dangerous pollution, reinforced by data on the generation of hazardous pollutants, have continued to drive public perception, which in turn has put pressure on governments and regulatory agencies to tighten environmental regulations. Many manufacturers feel the pressure to use recycled materials whenever possible[54]. Sometimes manufacturers are even required to take care of their products at the end of their useful lives, as is common in the European Union (EU). For instance, in Germany, car manufacturers are required to dispose of the cars after the consumers complete their use of the cars[55]. This has created a need to design products that are friendly towards the environment, while being easy to disassemble and recycle so that companies do not incur heavy costs at the end of the consumer life cycle. Thus, manufacturers are no longer just concerned with the production of their products, but also have to consider the effects of their manufacturing and the end-of-use environmental impacts in order to have long term profitability and growth. Industry has taken action by developing programs (such as Responsible Care) that establish goals for environmental health, safety, and product stewardship. More than 4,000 companies or facilities around the world have embraced the ISO 14001 environmental management system standard. The standard requires senior management to adopt an environmental policy document that demonstrates commitment to compliance with national laws and regulations, continual improvement in design and pollution prevention. While the goals are certainly appropriate, the real problem and opportunity is how to translate them into action.

For long term profitability and growth, manufacturing organizations adopt Environmentally Conscious Manufacturing and design for reducing existing and potential harmful environmental effects from within manufacturing. In Figure 3 we see very clearly the interaction of government policy and corporate actions. This shows a clear need for environmentally conscious design concepts to be developed to interact with these different aspects.

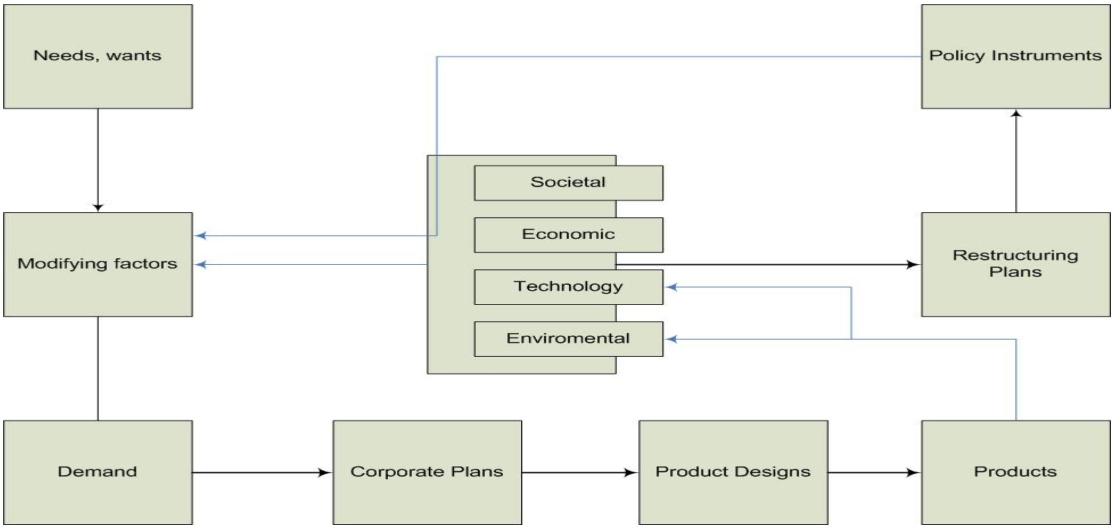

Figure 3 Interactions between industrial activities and societal systems. Planning stages necessary to connect forcing functions and responses

In this process, we, as chemical and environmental engineers need to recognize that the sellable products produced by the manufacturing firms are not the only outputs from a manufacturing firm. The other outputs are waste materials, scrap, wastewater, chemicals and other quantifiable materials and energies that are produced or used during the manufacturing steps. These secondary outputs have to be minimized or eliminated since they have an adverse effect on the total economic output of a firm and on the environment. For any manufacturer, pursuing high profit is always the number one priority and this can be accomplished by pairing Environmentally Conscious Design with normal economic practices in an environ-economic win-win situation.

For example, in the early 1990s, an orange juice manufacturer in Victoria, Australian had a waste problem with orange peels. The Original Juice Company squeezed up to 90,000 tons of fresh citrus fruit each year, leaving lot of peel left over after making the juice. They looked for uses for the peels, but were confronted by the lack of suitable markets.

In a dry form, the peel could be sold as a high protein stock feed, but to achieve the necessary degree of dryness, it needed pressing. This generated up to 4 million liters a month of effluent – liquid waste high in citrus oil and sugars. Discharged into a nearby waterway, the waste created environmental problems. Of particular concern was biochemical oxygen demand. But with some creative thinking, the orange-peel problem was turned into an asset. The company realized that citrus oil and sugar were potentially marketable products. By investing in equipment worth just over $1 million, they now save about $450,000 each year in waste disposal costs and earn $250,000 a year in citrus oil and molasses sales. The company profit has increased, and the pollution load on the environment has decreased [56].

A more general example would be to reuse a raw material, which is one major way of generating high profit that can be achieved while reducing overall manufacturing costs. Hence waste minimization should be considered as an effective way to bring about high profit in modern day plants. There are enormous challenges, however, that can be seen in this waste minimization field. Even just using material economy as a measure of waste generation, there are wide variations across the chemical industry and semiconductor industries, and obviously there are many opportunities for improvement in the way we manufacture products. New environmentally driven technologies, such as green chemistry, LCA, and environmentally conscious design applied concept to manufacturing, will result in a revolution of new manufacture processes after integration.

Typically the most common way to reduce pollutant emissions has been to add control technologies to bring the process into compliance with regulatory discharge standards. However, a consequence of this approach has been the allocation of large amounts of capital to the installation and operation of environmental control equipment to prevent pollution. As of 1999, 4% of US sales were spent in installation of pollution control measures to meet regulations. These efforts are made up of three parts: pollution control capital expenditures, pollution control operating costs, and hazardous waste site remediation. The total cost is approximately $15 billion/yr [57].

We can see here that there is a clear benefit to improve both the economic and environmental performance of manufacturing processes. There unfortunately is very little operational guidance about how to accomplish both improvements simultaneously. Many of the books currently used in teaching chemical process design contain little or no mention of environmental issues. The process of decision making involving tradeoffs, or the larger context of the design process itself [57-64] are often the only topics covered in design books. At present, much of the needed process data and metrics information is scattered throughout the rapidly developing literature on green design. The focus of the rest of this chapter is to identify the issues, information sources and approaches to process design that have the potential to lead to improvements in both economic performance and environmental quality.

2.2 DESIGN PROCESS

Chemical engineering product design is a complex activity. It involves accepting as input an abstract description of the desires of an organization to deliver a detailed description of a concrete product, process or system that will satisfy those desires. The activity is well characterized as a decision process, involving many decision-makers and multiple levels of detail. As shown in figure 4, the design process is composed of many discrete steps. Design starts with problem framing; however, its critical importance in determining the outcome of the design process is often overlooked. Design problems are rarely fully specified. Along the path from receiving a problem statement to delivering a completed design, design teams make decisions about concept definition, scope of analysis, design objectives, constraints, evaluation criteria, and stopping rules. Often framing decisions are made implicitly by following available precedent. In a recent paper[65], it was recognized that the role of problem framing is distinguishing between performance models (those used in the analysis stage of the cycle), and valuation models (those used for alternative evaluation).

Once a design problem has been properly specified, the next step is the generation of design options. There are many different methods for generating chemical process design options, including the application of existing design concepts and the generation of new ones from first principles. Since the time available to complete a design project is often very limited, it is unavoidable that there is a tradeoff between the number of options that are explored and the level of detail with which they can be analyzed[66].

After options have been generated, the next step is the analysis of alternatives. In this step, engineering analysis (most often starting with mass and energy balances) is applied to each alternative to make predictions about the expected performance of the system. The result of this step might be a list of the inputs and outputs of the process, including the flow rates, composition, pressure, temperature and physical state of all material streams in the process, as well as the energy consumption rate from various sources. Other useful information concerns the stocks of materials in the process, as well as other information related to the sizing of equipment units [67].

The analysis step of alternatives will result in a large number of information elements for each alternative generated. In the evaluation step, this information is summarized into indicators of performance that can be used to assess whether the requirements specified during the objective formulation step have been met, and the extent to which the design objectives have been advanced. These indicators typically include economic indicators, such as the capital investment required and the operating cost, but should also include indicators of safety and environmental performance[68]. The evaluation step ends with a ranking of alternatives according to their overall level of attractiveness.

The process of design is iterative. Before returning to the beginning of the design cycle, a designer must examine the results obtained at the evaluation stage to identify opportunities for improvement. This can be done at the sensitivity analysis stage. If the design team concludes that there are no significant remaining opportunities for improvement, then the design work stops and implementation phases are begun. Otherwise, an additional iteration on the design cycle is undertaken. Iterations might involve generating additional alternatives, or modifying the framing of the problem (for example, by deciding to carry out more detailed analyses on certain parts of the process). There is a strong interaction between alternative generation, analysis, and evaluation, as depicted in by the inner feedback loop connecting these three activities.

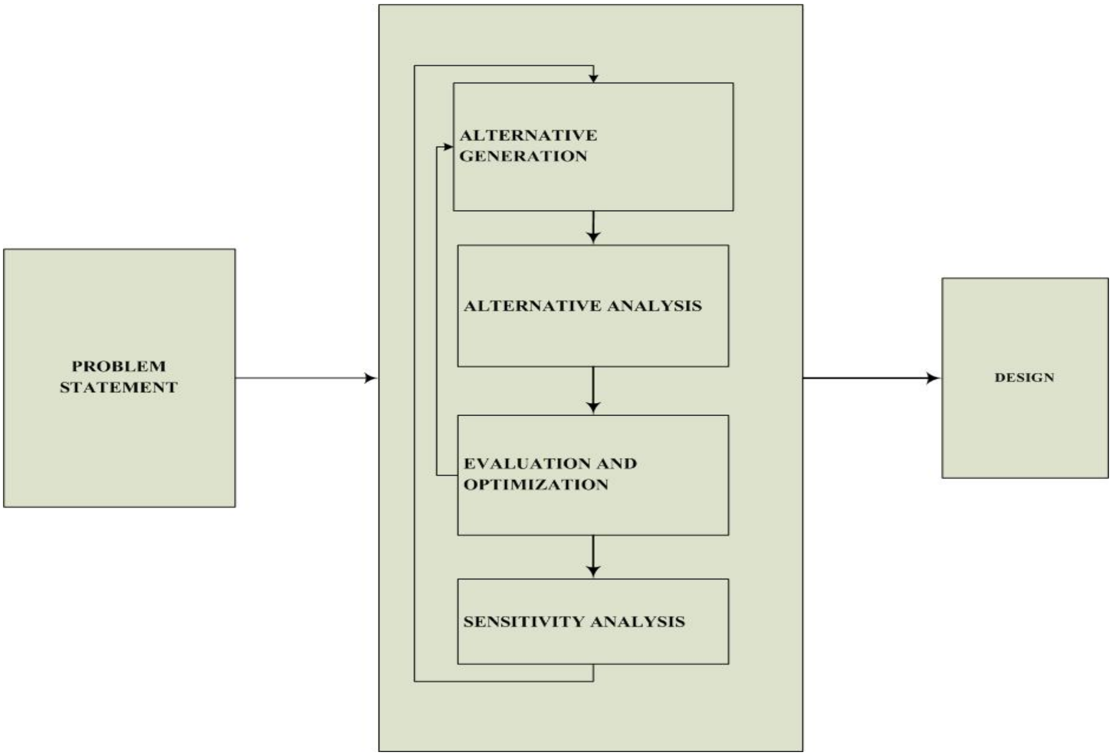

Figure 4 Interactions between industrial activities and societal systems. Planning stages necessary to connect forcing functions and responses

Initially, chemical process design was limited to the design of the core reaction and separation processes involved in making a product. This is historically true because the environment was not an issue at that time. In response to the 1970s energy crisis as mentioned above, the domain of chemical process design was increased to include the interaction of the core process with utility systems. Methods for heat and power integration were developed and applied to industrial problems, and today most chemical process design books include at least one chapter on heat integration or heat exchange network design. More recently, as the cost of complying with environmental regulations has increased, chemical process designers have become aware of the need to take waste generation into account in their work.

2.2.1 INCORPORATE ENVIRONMENTAL ISSUE IN DESIGN

There are four emerging trends in the evolution of problem framing with respect to the consideration of environmental impacts:

1) *Inclusion of the waste treatment infrastructure in the analysis boundaries.* It is estimated that a large percent of the capital for new processes is devoted to handling wastes. As a result, industry is incorporating waste handling in the scope of process synthesis activities and making efforts to design processes that can use existing waste processing infrastructures to avoid the need for investing in new treatment facilities.

2) *Materials integration*. The success of energy integration techniques in reducing operating and capital costs raised the question of whether similar savings can be achieved through materials integration. It has been suggested that process design should include efforts to identify potential matches between wastes (material sources) and raw material requirements (material sinks) across processes and plants within a company. Some groups of scientists [69-71] are developing materials integration techniques as a cost-effective way of reducing pollutant emissions.

3) *Life cycle analysis*. Life-cycle assessment (LCA) (also referred to as life-cycle analysis sometimes) is a framework for considering the environmental impacts associated with every stage in the life cycle of a product, from raw materials production to final disposal. The consequences of ignoring impacts over the entire life-cycle can be damaging. Academia has recently applied life-cycle thinking to chemical process synthesis problems [72-75], and there is growing interest in its use industry, particularly in Europe. LCA represents a new way of thinking about manufacturing that focuses on the most efficient and productive use of raw

materials and natural resources that minimizes waste while avoiding adverse impacts on workers and the natural environment. In its most advanced application, a product's entire life cycle is considered, from design, raw material and natural resource usage, to the product's end use and disposal or reuse of raw materials. LCA strives to minimize both the use and generation of hazardous materials, minimize energy consumption, and facilitate opportunities to reduce the environmental burdens by creating new production designs and techniques

4) *Shift in emphasis from effluent concentrations to environmental impacts*. Most environmental regulations are written in terms of effluent concentration standards. Some scientists pointed out that regulation in terms of concentrations does not give a real account of the actual emissions [76]. Furthermore, design problems stated as “minimizing costs subject to not exceeding allowable concentration limits” can result in solutions where dilution of waste streams is used to meet the standard without changing the amount of pollutants released to the environment. Limiting effluent concentrations is only a means to achieve the end objective of improving environmental quality. A couple of scientists have recently coupled environmental receptor models to the mass exchange network synthesis problem in order to pose the environmental constraint as an environmental quality standard, instead of as an effluent concentration standard [77].

2.2.2 GOAL OF ENVIRONMENTALLY CONSCIOUS DESIGN

The design of chemical processes with lower environmental impacts starts with an understanding of the sources of emissions and waste in chemical processes. In a chemical process, raw materials are processed into desired products. Byproducts might be generated, either as a result of the desired reaction stoichiometry, or as the consequence of undesired secondary reactions. Unwanted byproducts might also be generated in the separation system. Purge streams are necessary to prevent the accumulation of trace components in recycle streams, unless these components can exit the process in the product or byproduct streams. Other materials introduced to the process include reaction agents (e.g. catalysts, solvents, diluents, heat carriers) and separation agents (e.g. solvents, adsorbents), which contribute to waste generation since they degrade with time and may exit the process with the purge or byproduct streams. Leaks (known in the literature as "fugitive emissions") might occur anywhere in the system. In addition, emissions are produced in the systems that provide utilities to the process.

The goal of environmentally conscious alternative generation is to produce designs that:

- have high economic potential,
- have high conversion of raw materials into desired products,
- use energy efficiently, and
- avoid the release of hazardous substances to the environment.

2.2.3 CONSCIOUS DESIGNS AND ALTERNATIVE EVALUATION

The key to the discovery of designs that meet the above criteria is process integration (energy integration, materials integration, and processing task integration). Pollution from a chemical process can be viewed as the consequence of using the environment as a sink for unwanted byproducts and un-recovered materials. Using nonrenewable resources as a source of raw materials for a process also raises issues of sustainability. Framing of the problem influences the range of alternatives that may be considered through the decisions made during concept definition. A narrow concept definition might fix prematurely the process chemistry, or limit the type of unit operations considered (e.g. it might restrict the design team to use conventional, well-proven technologies).

To form design alternatives, we can rely on documented pollution prevention solutions. Ideas for reducing waste generation in chemical processes have been published in professional journals[78-95]. These ideas range from general questions intended to elicit ideas to very specific process and equipment changes. Government agencies also compile and publish ideas for preventing pollution in specific industry sectors from time to time[88, 96-100]. We can further generate design alternatives by case study process models. The process model is modified to incorporate the proposed changes, and simulations are carried out to check whether the desired performance improvements are realized in the model. We can also use structured hierarchical design approaches. Some scientists applied the hierarchical process to the problem of identifying potential pollution problems and identifying process alternatives that can be used to eliminate these problems[73, 101]. Other scientists have also used a form of mathematical programming to synthesize optimum processes through a reducible superstructure to find the best combination of process units that achieve the design task[102, 103].

There are a large number of published mathematical programming formulations of the problem of synthesizing recycle/reuse networks for waste reduction [104-106]. A common feature in these formulations is the use of cost minimization as the objective function in the optimization[107]. The solution of a mixed integer linear programming transshipment problem to design a network with the minimum number of units that meets the minimum operating cost targets is generated. Objective functions include only the cost-side of the profit equation. As the value of recovered materials is not included, opportunities to improve the economic performance of these networks by increasing material recovery beyond targets specified in the framing of the optimization problem might be overlooked.

One trend for this kind of research is the involvement of artificial intelligence and knowledge-based expert systems[69, 108, 109].

Computer-assisted systems for the rapid generation of alternative synthesis paths to a desired chemical are available (e.g. SYNGEN, LHASA). Their use to support pollution prevention initiatives has been explored by government agencies and as teaching aides[110].

The function of the analysis step of design is to generate the information elements needed to evaluate the merit of a design. A challenge for designers interested in incorporating environmental considerations into their work is that many of the information elements needed to evaluate the environmental impact of a proposed design alternative are not normally generated in the analysis stage when economic performance is the only design objective. In addition, environmental concentrations of released pollutants might be necessary for a proper evaluation of the potential environmental impact of a design. In this case, the material balances used to evaluate the process need to be expanded to include the fate and transport of environmentally sensitive species.

It has been noted that commercial process simulators are still very deficient in predicting chemical species concentrations in dilute process effluent or waste streams [111, 112]. Unit operation models for innovative separation technologies (e.g. membrane separations) and waste treatment equipment are not included in commercial process simulators, and are therefore usually not included in conceptual process designs. It is noted that a challenge in the development of these models is that they often involve the handling of types of materials that are not well characterized.

How do we evaluate design alternatives from an environmental perspective? How do we balance environmental objectives with other design objectives? A quantitative evaluation of process flow sheets involves summarizing the information generated during the analysis stage of design into a few metrics that can be used to optimize and rank design alternatives. It allows a design team to summarize into a single number information regarding production and consumption of materials and utilities, as well as design specifications for equipment[113]. The additional information needed are unit prices for materials and utilities, correlations that relate equipment design specifications to their installed cost, and the discount rate used by the firm to make tradeoffs between capital spent in the present and future cash flows.

The most common approach to incorporate environmental considerations in chemical process design has been to treat them as constraints: upper limits are set for pollutant flows or concentrations in waste streams (based on regulatory requirements), and designs that satisfy these constraints are evaluated in terms of economic indicators, such as annualized profit, payback period, total annualized cost, or operating cost[91, 114-116].

The main problem with incorporating environmental considerations as constraints on the flow or concentration of chemical species in particular waste streams is that the proposed solutions might not address the underlying environmental concern. Instead of treating environmental considerations as constraints, designers can choose to treat them as an objective to be balanced against other objectives in the design.

This requires establishing environmental performance measures. It has been noted that the lack of metrics to support objective environmental assessments is one of the main barriers to developing effective pollution prevention and design for the environment approaches.

The various issues involved in environmentally conscious design potentially include:

- Economic aspects of environmental conscious design
- End-of-life recovery
- Environmentally benign packaging
- Integrated disassembly line
- Life cycle assessment of environmentally conscious design
- Logistic aspects of environmentally conscious design
- Product reuse
- Recycling process planning
- Remanufacturing process planning
- Design for disassembly
- Design for environment
- Design for recycling
- Design for remanufacturing
- Disassembly process planning
- Disassembly scheduling
- Disposition and waste management

2.3 LIFE CYCLE ASSESSMENT DESIGN APPROACH

Within the last two years, Life-Cycle Assessment (LCA) has received much attention from a research standpoint, which we will cover in a more detailed discussion in the following chapter. LCA is probably the most commonly accepted method for analyzing the environmental impacts of products. It is a method for assessing systematically the environmental impacts of a product through all of its life-cycle stages: from extraction and processing of raw materials, to manufacturing, transportation, distribution, maintenance, reuse and recycling, and the final disposal methods that product designers can themselves apply[117-137].

Normally, life cycle design evaluates four process design criteria for a product [1]:

- Material selection,
- Manufacturing processes,
- Consumer utilization, and
- Material recovery analysis.

*Material Selection**:*** This covers the environmental impact of materials choices and quantitatively determines the life-cycle assessment and environmental burden. It is concerned with the selection of materials to satisfy cost, performance, and quality with respect to the minimization of hazardous wastes over the product life cycle. The possibility of using both recyclable and virgin items should be considered. Another possibility is of open and closed-loop recycling that is, reintroducing the materials at the end of the life cycle into the same product stream as raw materials, or into a new product stream, respectively.

Manufacturing Process Analysis: This is concerned with reducing energy consumption while minimizing waste within different processes. This can be done by monitoring the inputs and outputs of the processes.

Consumer Use Analysis: During this analysis, deleterious environmental impacts during usage of the product are taken into consideration.

Material Recovery Analysis: This takes into consideration the possibility of designing for recycling, remanufacturing and reuse of components or subassemblies. Incorporating various design aspects for ease of disassembly may help in liberating components more easily at the end of the life cycle.

Environmentally Conscious Design in Product Design: Incorporating environmentally conscious design issues during the product design stage can result in future savings of energy and resources. The usual approach taken is as follows. The environmental experts build life-cycle models, and designers separately build appropriate product models. Then an interface is decided between the designers and the environmental experts. Using this interface, information is exchanged and a model is developed which satisfies both the designer's requirements and the environmental experts' requirements. The various topics that are discussed by the environmental experts during the design stage are recyclability, ease of disassembly, ease of disposal, reuse, and effects on the environment.

2.4 CONCLUSIONS

Environmental issues are emerging as one of the major driving forces for change in the chemical industry. There are clearly many needs, and perhaps one of the most overriding opportunities is for a change in attitudes. A view of product and process design that sees preserving the environment as an objective and not just as a constraint on operations can lead to the discovery of design alternatives with improved environmental and economic performances. An adoption of Environmentally Conscious Design ideas in academic curricula is perhaps the most significant milestone for moving the practice of chemical process design in this direction.

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CHAPTER 3: LIFE CYCLE ASSESSMENT METHODOLOGY

3.1 GENERAL INTRODUCTION

Life cycle assessment (LCA) is an organized set of procedures for compiling and examining the inputs and outputs of materials along with energy and the associated environmental impacts directly attributable to the functioning of a product or service system throughout its life cycle (ISO standards) [1-3]. It is a technique for assessing the potential environmental aspects associated with a product (or service) by compiling an inventory of relevant inputs and outputs, evaluating the potential environmental impacts associated with those inputs and outputs, and interpreting the results of the inventory and impact phases in relation to the objectives of the study.

In recent years, as stated in the last chapter, significant attention and emphasis has been given to cleaner and greener technologies in processes and product manufacturing [4-9]. This is recognized as a key element in pollution prevention and the development of environmentally conscious design. Life cycle assessment (LCA) is a systematic approach that enables achievement of cleaner and greener products and process concepts in industry [10]. In recent times, considerable progress has been made in the use of LCA for product evaluation and selection. However, its use in greener process design and decision-making has not been explored extensively in much of the industry.

3.1.1 HISTORICAL BACKGROUND

The initial studies to look at the life cycle aspects of products and materials date from the late sixties and early seventies and focused on issues such as energy efficiency, the consumption of raw materials and, to some point, waste disposal. In 1969, for example, the Coca Cola Company funded a study to compare resource consumption and environmental releases associated with beverage containers. Meanwhile, in Europe, a similar inventory approach was being developed, later known as the ‘Ecobalance’ [11, 12]. In 1972, in the UK, Ian Boustead calculated the total energy used in the production of various types of beverage containers, including glass, plastic, steel, and aluminum. Over the next few years, Boustead consolidated his methodology to make it applicable to a variety of materials, and in 1979, published the *Handbook of Industrial Energy Analysis* [13].

The energy analyses that were popular in the 1960s and early 1970s were preliminary LCA attempts to understand the environmental impacts of products and processes. The early 1990s brought about new corporate and government philosophies of waste minimization and pollution prevention along with a renewed interest and demand for LCA approaches. In 1991, SETAC (The Society of Environmental Toxicology and Chemistry) published the first guidelines for conducting an LCA. More recently, LCA criteria are beginning to find their way into environmental labeling schemes such as Germany's Blue Angel designation and the ISO 14000 environmental management standards (www.iso.ch) [1]. Simplified LCAs even pop up in popular magazines; for example, *Consumer Reports* occasionally comments on the environmental impacts of different product packaging types and chemicals.

An LCA can show the major environmental problems of a material, product, or process [14]. The act of doing the assessment also builds awareness about environmental impacts and focuses improvement efforts appropriately. This has led companies such as AT&T and Volvo to develop internal LCA tools for their product lines [15], and government agencies such as the EPA to provide generic guidelines for conducting LCAs [16]. In fact, many proponents and users of

LCA information suggest that the main role of LCAs should be to guide internal decision making rather than as a consumer marketing or information tool [17-19].

3.1.2 INCORPORATION IN DESIGN PROCESSES

The incorporation of environmental issues as a design objective is limited in practice by the availability of environmental impact indicators appropriate for making quantitative tradeoffs [20, 21]. In contrast, designers have easy access to managerial cost accounting data that provide them with unit costs for the raw materials, utilities, and waste treatment services that might be part of their design. The availability of these unit costs allows designers to compare the economic performance of alternative designs and to optimize their performance by resolving tradeoffs in the direction that maximizes profitability [22]. If unit environmental indicators for raw materials, utilities, waste treatment services, and environmental releases were available, designers could also compare alternative designs and resolve tradeoffs in the direction that minimizes potential environmental impacts [23]. A combination of economic and environmental objectives could then be used to identify superior design alternatives [24]. Life cycle assessment methods provide systematic procedures for generating unit environmental impact indicators in a transparent manner [25, 26]. In addition to providing indicator values, the procedure provides data that allow the user to interpret the results and to identify the factors that drive the indicator values [27-29]. The method can be easily implemented on a spreadsheet. The resulting spreadsheet models can be rapidly updated when new information becomes available.

As we saw in the last chapter, process design and decision-making are challenging activities that involve trade-offs of conflicting objectives, namely costs, technical feasibility and environmental impacts [16, 30]. These conflicting objectives can be analyzed at the early design and decision-making stage by considering the full life cycle of a process or a product. A cleaner and greener process is the one that is cost optimal, technically feasible, and environmentally benign [31, 32]. To obtain these results, LCA requires various tools and techniques in a systematic methodology so that the result is reproducible. This study has combined the traditional LCA approach with multi-criteria decision-making methods. This methodology is simple and applicable at the early design stage and is more robust against uncertainty in the data [27, 33, 34]. Application of the methodology has been demonstrated in the thesis through a chamber cleaning gas production, usage, and disposal case study.

3.1.3 THEORETICAL ADVANTAGE OF LCA INCORPORATED DESIGN

LCA has proven to overcome many of the problems faced in the conventional design approaches [35, 36]. Most important of all, it establishes a link between the environmental impacts, operation, and economics of a process; it offers an expanded environmental perspective, considering impacts from resource extraction to the end product use and disposal [37, 38]. The LCA relates these effects to the mass and energy flows into, out of, and within a process. According to the ISO 14040 series standards, the LCA should assess the potential environmental issues and aspects associated with a product or service by compiling an inventory of relevant inputs and outputs [1, 2]; evaluating the potential environmental impacts associated with those inputs and outputs; and interpreting the results of the inventory and impact phases in relation to the objectives of the study. Considering these, the LCA has an ability to focus both process feasibility and environmental concerns along with other attributes. The present work focuses on the comparison of process selection and design methodology considering assessment and minimization of risks/impacts of process systems by embedding the LCA principles within a formal process design and decision-making framework. It has implications to process synthesis as it includes environmental objectives together with technological and economic concerns at the design stage to determine cost efficient solutions. It is believed that employing the LCA within a process design and decision-making system will yield an optimal design and a best management alternative. This thesis presents a detailed description of a revised methodology for cleaner and greener process design.

According to ISO 14041, “A product system is a collection of unit processes connected by flows of intermediate products which perform one or more defined functions. The essential property of a product system is characterized by its function, and cannot be defined solely in terms of the final products”. The terms “economic process” or “economic activity” have been used as synonyms alongside 'unit process' to refer to any kind of process producing an economically valuable material, component or product, or providing an economically valuable service such as transport or waste management [39]. Economic or unit processes are the smallest portions of a product system for which data are collected during execution of an LCA. They are linked to one another by flows of intermediate products and/or waste for treatment, to other product systems by product flows, and to the environment by elementary flows (ISO 14040, 1997E), i.e. inputs from and outputs to the environment.

LCA takes as its starting point the function fulfilled by a product system. In principle, it encompasses all the environmental impacts of resource use, land use, and emissions associated with all the processes required by this product system to fulfill this function - from resource extraction, through materials production and processing and use of the product during fulfillment of its function, to waste processing of the discarded product [40, 41].

LCA as defined in most cases deals only with the *environmental* impacts of a product (system), thus ignoring financial, political, social, and other factors. This does not, of course, imply that these other aspects are less relevant for the overall evaluation of a product [42, 43].

In 1994, ISO established a technical committee charged with standardizing a number of environmental management tools, including LCA. Various international standards have been published by ISO on the topic of LCA. These ISO guides are important in providing an international reference with respect to principles, framework and terminology for conducting and reporting LCA studies. In order to implement the LCA methodology, some additions to the ISO Standards have been necessary. On some points, it was also necessary to deviate from these standards, but only when the rationale for doing so was particularly significant.

3.2 THE PURPOSE OF LCA

Although we agree that the purpose elaborated here is to be viewed as an ideal that will never be fully achieved, we see it as guiding LCA in a certain direction.

The purpose of LCA is to compile and evaluate the environmental consequences of different options for fulfilling a certain function [44].

We restrict LCA to environmental consequences. Nonetheless, the exact defining of this may still be subject to debate. For an example, inclusion of resource depletion may be controversial, as some see this as an economic problem only. However, we exclude economic consequences, such as cost effects or unemployment, as well as social consequences, such as violation of human rights, and many other types of consequences from our study. We do so not because they are unimportant, but because we wish to have a more focused analyses on the environment. As real life decisions are ultimately made on the broader basis, it is important that LCA remain comparable to allied types of analysis in other fields as far as is reasonably possible. Another thing to be noted is that ‘purpose’ relates to the fulfillment of a function. Functions are services that are embodied in material objects, often referred to as goods or products. Certain functions involve material products that are intimately related to the potential function they fulfill. In this thesis, the project we have conducted is to fulfill the "cleaning chamber" function. This is where either of two chemicals can be used to remove contamination from a semiconductor processing vacuum chamber. If NF_3 and C_2F_6 are not bonded with this function fulfilling, we can not simply compare the two on the impacts to the environment, which will be a trivial practice which does not yield any benefit. In another word, two products or processes that do not serve the same function do not have comparability and meaning using LCA. Another more understood example for vast involvement of 2^{nd} order and 3^{rd} order product, 'beer' is virtually congruent with the function 'having the pleasure of drinking a beer'. However, it embodies only part of that potential function, because other products (like a glass) may also be required. Beer is produced using ingredients (water, barley, etc.) as well as ancillary goods (electricity, etc.) and also requires capital goods (breweries, etc.). 'Second-order products' are also produced, and require a third-order level of products. A comparative analysis of the environmental consequences of different methods of beer production should naturally include relevant environmental impacts for at least several orders of these 'upstream' products and production operations. The same applies to the 'downstream' side, which in the example of beer would cover using of the glass and cleaning the glass, as well as the operation of the entire waste water treatment system, its construction and its demolition. As in the NF_3 vs. C_2F_6 project comparison, the same case applies. We have to discuss what happens to the byproducts that are produced while manufacturing the two chemicals so we can address the implications of the 2nd and 3rd order products involved in cleaning the chamber.

Focusing on a function leads to a comprehensive analysis of the entire life cycle of the function in a “global view”. Observe the phraseology ‘life cycle of the function’ rather than ‘life cycle of the product’, to signify the fact that the pivot of the analysis is the function, not the material product that is associated with it. We also see how naturally the concept of a ‘product system’, consisting of the several life cycle stages, enters the arena. This will be elaborated further in the subsequent chapters on goal and scope definition and Inventory analysis.

3.3 THEORETICAL FOUNDATIONS OF LCA

The foundational issue is one that will inevitably be raised whenever there is disagreement among parties: between industry and the environmental movement, for example, between individual industrial sectors and companies, or between consumer organizations and the government. While noted earlier, LCA must be focused on unambiguous and transparent reporting of data, assumptions, and methods. However, it is now clear that this does not suffice [45]. Some differences in data may be caused by differences in the scope, geographical boundaries, and so on, of the LCA under review. There are also differences that may be argued to originate from differences in attitude. The use of quantitative safety factors for toxic mechanisms that are poorly understood provides another instance where diverging frames of the various parties may lead to disagreement on the findings of an LCA [46-49]. At the same time, though, it also points a way to possibly validating the results of an LCA. Bringing cases to a hypothetical decision point then leads us to consider a series of crucial questions. The first is: does LCA speak the truth? Or does an LCA only provide a certain measure of the truth? How can we ensure that assertions made by or with an LCA have certain truth content? The purposes of LCA, the questions posed in an LCA, the methodological means of achieving answers to these questions, the principles that underlie the modeling of the economy-environment interaction are all logically related and deserve coherent treatment.

3.4 THE METHODOLOGY OF LCA

The terms ‘method’ and ‘methodology’ are often used to indicate what essentially the method is. A method is a structured way to achieve a certain goal: to measure the toxicity of a compound, for example, or to construct a bridge. A method consists of rules, recipes, formulas, descriptions, and so on.

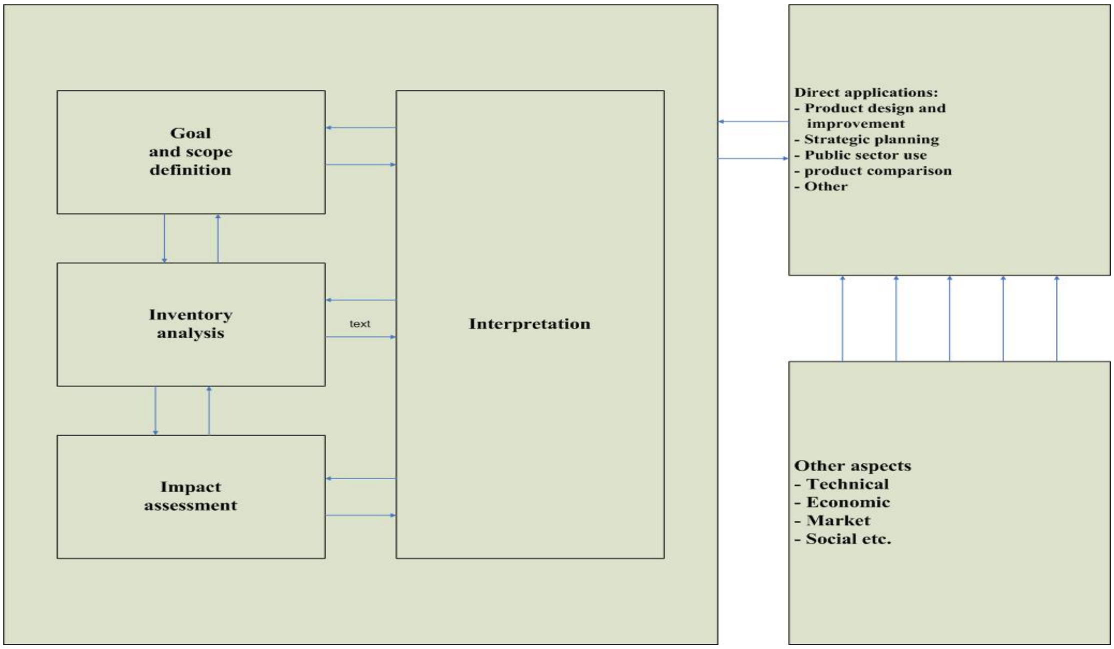

Figure 1 *Life cycle assessment framework - phases of an LCA (ISO, 1997a).*

The LCA methodology has four components: goal and scope definition, life cycle inventory (LCI), impact assessment, and improvement assessment. A full life cycle assessment includes each of the four components [50-52] as discussed below and shown in figure 1.

At its most basic, an LCA consists of four broad steps:

1. Goal and scope definition of LCA defines the purpose of the study, the expected product of the study, the boundary conditions, and the assumptions [53]. This stage has always been a part of LCI (Life Cycle Inventory) and LCA studies because the process of setting boundaries and of defining the specific LCA being studied is an essential first step for any LCI or LCA study. Increased interest in LCA over the past 5 years has been a catalyst for practitioners to more clearly address this stage [54].

2. *Life cycle inventory is a set of data and material and energy flow calculations that quantifies the inputs and outputs of a product life cycle.* Values sought during this stage of LCA are quantities derived using material and energy balances. Other data are more subjective and depend on assumptions that have been made during the assessment.

Tracking material flows over all of the stages of a life cycle is required for a comprehensive life-cycle inventory as shown in Figure 2. This includes the acquisition of raw materials from the earth, the acquisition of energy resources form the earth, processing of raw materials into usable components, manufacturing products and intermediates, transportation of materials to each process step, manufacture of the product being studied, distribution of the product, use of the product, and final disposition (which may include recycling, reuse, incineration, or landfill). [50, 53]

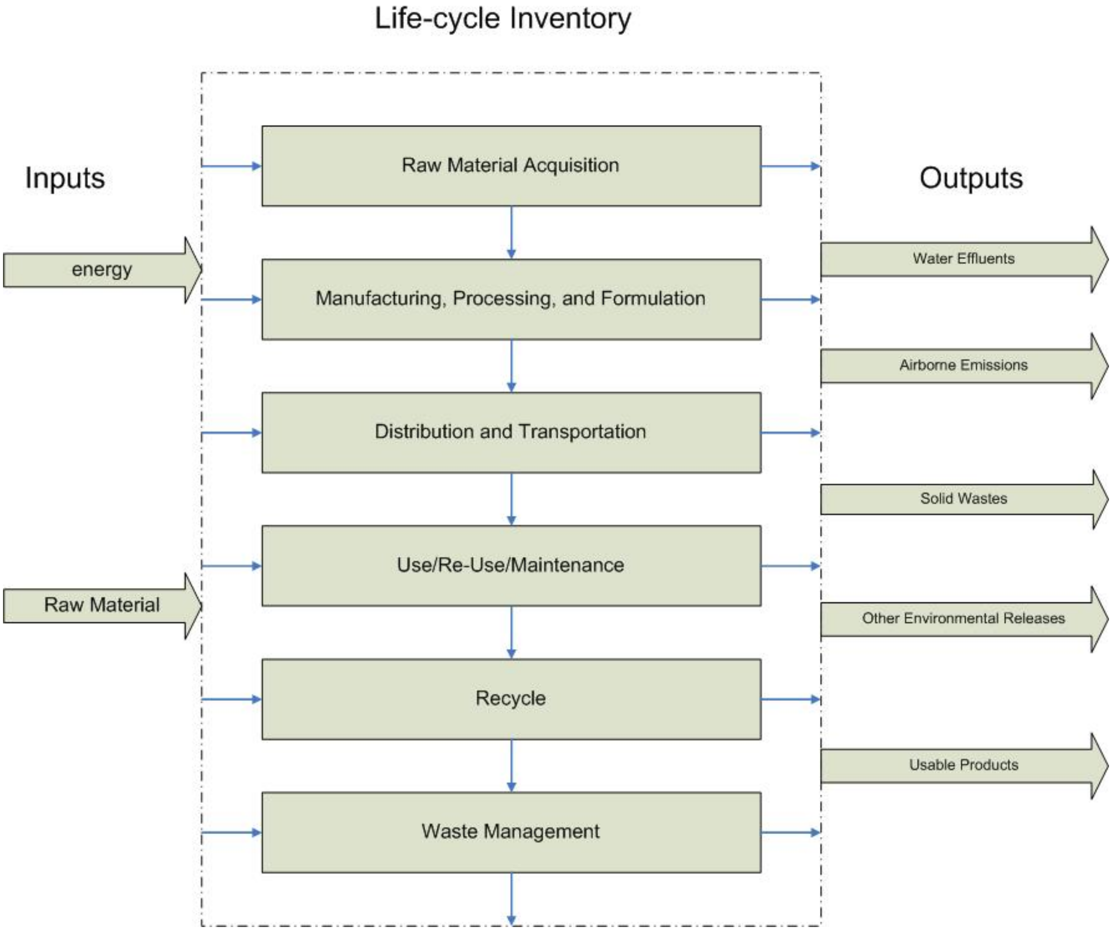

Figure 2 Life cycle inventories account for material use, energy, wastes, emissions, and by products over all of the stages of a product's life cycle.

3. Impact assessment

Life cycle inventories do not by themselves characterize the environmental performance of a product, process or service. Overall quantities of a wastes and emissions, and raw material and energy requirements must be considered in conjunction with the potency of their effects on the environment. Once the inputs and outputs of a system have been quantified by the LCI, impact assessment (IA), the third stage of LCA, can be performed. It consists of three stages: classification, characterization, the valuation [53].

For developing the global scale characterization of the environmental performance of a product, process, or service requires that data acquired in the life cycle inventory stage be converted into estimates of environmental impact [13].

The methodology for impact assessment is still in the developmental stage [48, 55-57]. The few life cycle assessment that have been performed in recent years have generated much interest in the scientific community. Conceptual guidelines for IA have been published by SETAC, EPA, and the Canadian Standard Association [51, 58]. It should be noted that there is still no impact assessment methodology that is widely accepted.

4. LCA improvement analysis

This stage involves interpreting the results of the impact assessment in order to suggest improvements. When LCA is conducted to compare products, this step may consist of recommending the most environmentally desirable product. This is called an improvement analysis. The desire to reduce burdens on the environment by altering a product or process is often the driver for a given study. Another driver for LCA studies has been the desire to benchmark a product against competitive products or to prove that one product is environmentally preferable to another [6, 59]. Our focus on the NF_3 vs. C_2F_6 falls into the second category.

Interpretation is performed in interaction with the three other phases of the life cycle assessment, as we can see clearly in Figure 1. If the results of the inventory analysis or the impact assessment are found not to fulfill the requirements defined in the goal and scoping phase, the inventory analysis must be improved by e.g. revising the system boundaries, further data collection, etc., followed by an improved impact assessment. This iterative process must be repeated until the requirements in the goal and scoping phase are fulfilled as can be described by the subsequent steps [60]:

1. Identify the significant environmental issues.
2. Evaluate the methodology and results for completeness, sensitivity and consistency.
3. Check that conclusions are consistent with the requirements of the goal and scope of the study, including, in particular, data quality requirements, predefined assumptions and values, and application oriented requirements.
4. If so, report as final conclusions. If not, return to step 1 or 2.

This section is also referred to as life cycle interpretation.

3.5 THE KEY FEATURES AND LIMITATIONS OF LCA

Some major key-features of the LCA methodology are summarized (ISO 1996):

- LCA studies should systematically and adequately address the environmental aspects of product systems, from raw material acquisition to final disposal.
- The depth of detail and time frame of an LCA study may vary to a large extent, depending on the definition of goal and scope.
- The scope, assumptions, description of data quality, methodologies and output of LCA studies should be transparent. LCA studies should discuss and document the data sources, and be clearly and appropriately communicated.
- Provisions should be made, depending on the intended application of the LCA study, to respect confidential and proprietary matters.
- LCA methodology should be amenable to the inclusion of new scientific findings and improvements in state-of-the art technology.
- Specific requirements are applied to LCA studies which are used to make comparative assertions that are disclosed to the public.

- There is no scientific basis for reducing LCA results to a single overall score or number, since trade-offs and complexities exist for the systems analyzed at different stages of their life cycles.
- There is no single method for conducting LCA studies. Organizations should have flexibility to implement LCA practically as established in this International Standard, based upon the specific application and the requirements of the user" (ISO 14040).

On the other hand, there are important *limitations* of LCA that need to be mentioned in advance.

- The most important limitation is that any LCA will necessarily involve assumptions and subjective valuation procedures. These assumptions must be fully communicated. As the results might differ substantially according to the assumptions made, great caution should be used in making environmental claims (i.e. in the comparison of products for the public) based on LCA.
- A second big problem is the availability and quality of data. Very clearly, the issue of the quality of data, of how to find missing data and/or correct unreliable data, still requires much methodological and scientific work. One possible path seems to be a collaborative attitude within sectors and countries and the creation of public databases.

- It should be clearly understood that LCA is only one of several environmental management tools and might not always be the most appropriate one in all situations. Decisions for action in a company typically involve other factors such as risks, benefits, costs, which include technical, economic, and social aspects, which are *not* addressed by LCA.

3.6 THE USES OF LCA STUDIES

LCA is designed as a decision-making tool for designers, regulatory agencies, and business organizations. It is used to evaluate the environmental impacts of products and process and also identifies a section within a product or process's life cycle where the greatest reduction in resource requirements and emissions can be achieved [61, 62].

According to a survey of organizations actively involved in life-cycle studies, the most important goal of life-cycle studies is to minimize the magnitude of pollution [60, 63]. Other goals include conserving non-renewable resources, including energy; ensuring that every effort is being made to conserve ecological systems; developing alternatives to maximize the recycling and reuse of materials; and applying the most appropriate pollution prevention or abatement techniques. As discussed in this section, life-cycle studies have been applied in many ways such as developing, improving, and comparing products [64, 65].

3.6.1 PRODUCT COMPARISON

The most widely used function of life-cycle studies is for the purpose of comparing products or services. From literature research, we can find many of this type of comparison study [66-69]. Also, this kind of study has received a great deal of attention. These studies are often sponsored by organizations that have a high interest in the results of the studies, most often for decision making purposes. And because of the open-ended nature of life-cycle studies, there is always room for criticism of the assumptions that were made regarding the data that were gathered, and the uncertainty that occurred in the course of the study. Life-cycle studies have generated a great deal of controversy and debate. They have also created skepticism over the value of life-cycle studies. This has diverted attention away from some of the less controversial applications, such as studies conducted in order to improve products [60].

3.6.2 STRATEGIC PLANNING

One of the important functions life-cycle studies is to provide guidance in long-term strategic planning concerning trends in product design and materials [70, 71]. By their nature, life-cycle studies include environmental impacts whose costs are external to business (e.g., acid rain formation) as well as internal (e.g., the cost of waste generation). Assessing these external costs is a key to strategic environmental planning, as regulations tend to internalize what are currently external costs of doing business.

3.6.3 PUBLIC SECTOR USES

Life-cycle studies are also heavily used in the public sector [72]. Policymakers report that the most important uses of life-cycle studies are

1) Helping to develop long-term policies regarding overall material use, improving resource conservation, and reduction of the environmental impacts and risks posed by materials and processes throughout the product life cycle,

2) Evaluating resource effects associated with source reduction and alternative waste management techniques, and

3) Providing information to the public about the resource characteristics of products or materials [63].

Some of the most visible applications of life-cycle studies are environmental or ecolabeling initiatives [73]. Besides environmental labeling programs, public sector uses of life-cycle studies in making decisions and developing regulations

[16]. For example, the US (EPA) used life-cycle information when making a decision about regulation of industrial laundries whose effluents were a problem because of the oily shop rags they laundered. The concern was that tighter regulations may have made the costs of industrial laundering so expensive that a shift from cloth shop rags to disposable shop rags would occur. Would this be a benefit to the environment? Life-cycle concepts provided some insights [74].

3.6.4 PRODUCT DESIGN AND IMPROVEMENT

Manufacturers also state that the most important uses of life-cycle studies are

- To identify processes, ingredients, and systems that are major contributors to environmental impacts [75-78], and
- To compare different options within a particular process with the objective of minimizing environmental impacts.

Manufacturers have more potential for influencing the environmental impacts of products than any other "owners" of life-cycle stages. This is because they can exert some influence over the environmental characteristics of the supplies they use because manufacturing processes account for a large portion of the wastes generated in the United States. Also the manufacturers determine to some extent the use and disposal impacts of the products they make.

3.6.5 CHOOSING SUPPLIERS

Manufacturers have potential to influence the environmental characteristics of the supplier companies. For example, using a life-cycle approach, Scott Paper Company found that the issues of major concern were not in the life-cycle stages directly controlled by the company, but rather by the supplier chain [51].

After making this discovery, Scott required pulp suppliers to provide LCA information about their processes such as emissions, energy uses, manufacturing processes, and forestry practices. Following an impact assessment method, they found that there was considerable variation in performance among suppliers. As a result of this excise, Scott changed about 10% of its pulp supply base. Scott publicized their efforts and its products were seen as environmentally preferable by consumers and environmental advocacy groups.

3.6.6 IMPROVING EXISTING PRODUCTS

One of the most common uses of life-cycle assessments is to identify critical areas in which the environmental performance of a product can be improved [79-82].

One life-cycle study was conducted for the purpose of product improvement in a nitric gas plant. After conducting LCA on a nitric gas plant, the whole system was examined; the improvement opportunities have been identified. The study showed that if the system pressure increase, emission and hazardous incidents were greatly decreased. In the life-cycle study for product improvement of clothing, it was shown that the means of transportation used in delivering a garment to a customer can have a profound impact on the garment's life-cycle energy requirements [83]. This study showed that in the case where next-day shipping is used, transportation and distribution energy requirements can be 28% of manufacturing life-cycle energy requirements. However, transportation and distribution of products generally contribute negligibly to the energy requirements of a product and are frequently neglected in life-cycle studies. Prior to this study, the garment manufacturer was unaware that their choice of delivery mode could contribute significantly to the energy required over the life cycle of their products.

In yet another life-cycle study conducted for product improvement, the components of a computer workstation were assessed to reveal which parts were responsible for the majority of raw material usage, wastes, emissions, and energy consumption [84]. The components studied included semiconductors, semiconductor packaging, printed wiring boards and computer assemblies, and display monitors. One of the findings of the study was that the majority of energy usage over a workstation's life cycle occurs during the use phase of the display monitor. Therefore, to reduce the overall energy usage of a computer workstation, efforts are best directed at reducing the energy consumed by the monitor. On the other hand, semiconductor manufacturing was found to dominate hazardous waste generation and was also found to be a significant source of raw material usage. This is in spite of the fact that by weight, semiconductors are a very small portion of a workstation.

3.6.7 USING LIFE-CYCLE CONCEPTS IN EARLY PRODUCT DESIGN PHASE

Increasingly, environmental aspects are included with a core group of design criteria among the traditionally dominant design boundaries: performance, cost, cultural requirements, and legal requirements. Life-cycle studies can be used to assess environmental performance [16, 23, 34, 85-87]. As we have stated in earlier chapters, optimizing environmental performance from the beginning of the design process has the possibility of the largest gains, but it is a moving target as markets, technologies, and scientific understanding of impacts change, especially in the case of the semiconductor industry. This is the main concern in this thesis. However, as stated earlier, roughly 80% of the environmental costs of a product are determined at the design phase, and modifications made to the product at later stages may have only modest effects [60]. Thus, it is in the early design phase that life-cycle studies for improving the environmental performance of a product are most useful. So, LCA is useful in evaluation of product design options.

Motorola has developed a matrix for simple streamlined LCA that is intended in part to specifically address early design stages [10, 88]. There are five life-cycle parts and three impact assessment categories in the matrix. Motorola intends to use this matrix in three phases: the initial design concept phase, the detailed drawings phase, and the final product specifications phase. In the initial design phase, the matrix elements can be filled out by asking a series of yes and no questions. An overall score is computed by adding the yes answers, and changes in that score show progress in the product's environmental characteristics. This example is typical of emerging trends in product design.

Impact		Part Sourcing	Manufacturing	Transportation	Use	End of Life
Sustain-ability	Resource Use					
	Energy Use					
Human Health						
Eco Heath						

Table 1 sample of Motorola Life-Cycle Matrix

3.7 PROCESS DESIGN

For a designer, it has been a serious question on how to accommodate various constraints such as economic, technologic and environmental ones to the design and operation of cleaner and greener processes. Earlier design approaches were economics- centered and based on cost-benefit analysis. These approaches attempt to trade off environmental and economic assets with an aim to maximize differences between socioeconomic benefits of an activity against the financial and environmental liabilities [10]. Such practices ultimately seek to attach a monetary value to the environment and are therefore fraught with difficulty.

Industrial process changes should be given strategic thought because they are generally in place for decades and retrofits tend to be expensive and difficult. As stated in the last chapter, while the life-cycle stages of a process are different from those of a product, the types of inputs and outputs and impact categories are the same. Generally, process choices (including choices of feed materials for the process) are likely to have more impact over the life cycle of the process than production of the equipment itself.

Jacobs Engineering has also developed a life-cycle matrix tool that has been applied to processes (as opposed to products) [88]. This tool identifies five inventory categories and seven environmental impact categories at two spatial scales (shop level and global). A base case process is determined and elements in the matrix are assigned +1, 0, or -1, depending on whether the alternative is an improvement, equivalent, or worse than the base case. Not all life-cycle stages are explicitly identified in this scheme, but it is still usefull.

3.8 CONCLUSION

LCA is useful in guiding a wide range of decisions—from design choices to policy frameworks. LCA allows the user to take a "bird's eye" look at the situation rather than focusing narrowly on a narrow range of issues. LCA is useful for assessing the impact of human activities. These impacts can only be fully understood by assessing them over a life cycle, from raw material acquisition to manufacture, use, and final disposal. The main contribution of LCA to engineering, design, and policy analysis is the systems perspective it provides. LCA can highlight priority areas for improvement and, if used correctly, can provide an objective means of comparing the environmental impacts of products, processes, services, and policies. Even for simple products, comprehensive life-cycle studies require a great deal of time and effort. Also, no matter how much care is taken in preparing a study, the results obtained have uncertainty.

Environmental concerns that are identified early in product or process development can be most effectively and economically resolved and life-cycle studies can be used as tools to aid in decision-making. Life-cycle assessments of products can be valuable from a variety of perspectives. They can help to identify areas for environmental improvement that, at times, can be surprising. They can also help identify processes, components, ingredients, and systems that are major contributors to environmental impacts, and they can be used to compare options for minimizing environmental impacts.

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CHAPTER 4: LIFE CYCLE ASSESSMENT PROCEDURES

4.1 GOAL DEFINITION AND SCOPE DEFINITION

The goal and scope definition are the phases where the initial choices which determine the working plan of the entire LCA are made. The goal of the study is formulated in terms of the exact question, target audience and intended application. The scope of the study is defined in terms of temporal, geographical and technological coverage, and the level of sophistication of the study in relation to its goal. Finally, the products (or product/service) that are the object of the analysis are described in terms of function, functional unit and reference flows.

4.1.1 GOAL DEFINITION

The first phase of LCA is goal definition, which is trying to fix the objective of the study. This includes determining the use to which the environmental analysis will be put and at the same time assessing what it can and cannot be used for.

A major part of the method depends on the objective, which if not properly defined can lead to incorrect conclusions. In this section of LCA, some questions have to be answered:

- For what will the results of the LCA be used
- What decision can be made on the basis of the LCA
- What is the extent and nature of these decisions? (this can be estimated)

Usage of LCA

- Generate environmental info on the product’s life cycle.
- Identify improvement potentials
- Compare alternative solutions at the concept level
- Compare alternative solutions at the level of details

So goal definition consists of clarifying what the LCA can and cannot be used for, which includes the decisions which it must support and the environmental consequences to which these decisions can lead.

4.1.2 SCOPE DEFINITION

The objective of this practice is to identify and to define the object of the LCA while limiting it to include that which is significant for the goal of LCA:

- Defining the object of study, including defining the functional unit
- Selecting one or more reference products or reference systems to represent the object of the study
- Designating the environmental assessment parameters which are important for the goal of the LCA
- Identifying the environmentally significant processes in the product system, connected with goal definition of LCA

4.2 INVENTORY ANALYSIS

We have selected the process and products at this point of LCA. Their product systems have been established, and the scopes of these are defined. The following phase is inventory analysis. This is the phase in which the product system (service system) is defined. The defining includes: setting the system boundaries (between economy and environment, with other product systems), designing the flow diagrams with unit processes, collecting the data for each of these processes, allocating steps for multifunctional processes, and completing the final calculations. Its main result is in an inventory table listing the quantified inputs from and outputs to the environment associated with the functional unit, in terms of kilograms of carbon dioxide, mgs of phenol, kilograms of iron ore, cubic meters of natural gas, etc.

4.3 EVALUATION OF ENVIRONMENTAL IMPACT

It is very hard to quantify the environmental impacts while making them comparable among different processes. As my mentor said “how do you quantify the loss of a beautiful mountain scene destroyed by our actions?” These kinds of nontangibles are very hard to quantify even under the best of circumstances. However, being able to quantify these issues and others is very important because they are encountered in every study using LCA because we have to attempt to quantify the total environmental impact of a process. At this stage of an LCA, these issues are mostly under-developed because we do not have a good model to calculate the impact indices for some measures. It is especially true that overall toxicity effects of individual chemicals or mixtures of chemicals[1, 2] are not well understood. Much modeling work in these areas has to be done before a more accurate LCA study can be done.

In the first part of this chapter, we introduced the first two steps of the LCA process. In this part, we will introduce the other steps for a full LCA. These new areas will be the environmental impact and the LCA improvement part of LCA. Impact assessment is a tool for relating the outcome of an inventory analysis to environmental themes. Usually the inventory process generates a long list of substances, which is difficult to be interpreted on an impact basis, especially when comparing two products or methods, which is the case in this thesis. Environmental impacts caused by different products are of a different nature and these impacts cannot be directly compared easily, which will complicate the interpretation of any full LCA report. In the impact assessment, the inventory is translated into the potential contributions to various impacts within the main groups: environment, resources, and the working environment. This leads to a strong reduction in the size of the body of data, especially for emissions to the environment. At the same time, there is a weighting of the individual environmental interchanges according to the level of their potential impact[3].

The full LCA assessment also helps to focus work on any subsequent qualification of the data of the inventory. It shows which of the interchanges have the largest potential impacts and it should thus be performed with the highest possible degree of precision and certainty. The impact assessment thus qualifies the inventory as a basis for decisions in comparisons between products, and it can also be used to focus the further collection of data to areas where uncertainties exist[4].

The LCA method's impact assessment phase is subject to the same general requirements with respect to transparency, reproducibility and scientific foundations as the other phases in the LCA. However, it is in the nature of the concept that an assessment can never be totally objective because of the issues described earlier in this chapter about the inability to have an absolute measure for some environmental effects.

4.3.1 EVALUATION OF ENVIRONMENTAL IMPACT

The impact assessment progresses through three steps:

1. Calculation of potential contributions to various categories of impact.

In the first step of an LCA impact assessment, the types of environmental impacts which attribute to the interchange are assessed. For each individual emission to the environment, a calculation is then made of the magnitude of the contributions to various impact categories. The main categories are: Abiotic depletion (ADP); Energy depletion (EDP); Global warming (GWP); Human toxicity (HT); Ecotoxicity (ECA/ECT); Acidification (AP); Nitrification (NP); Ozone depletion (ODP); Photochemical oxidant creation potential (POCP).

These contributions are called the emission's environmental impact potentials. The procedure for calculation of environmental impact potentials is introduced in the following part of this chapter.

2. Comparison of impact potentials and resource consumptions with a common reference to show which are large and which small.

In many cases, the process or material alternative that will have the least impact cannot be determined on the basis of the summarized resource consumption or the potential impacts on the working environment or the calculated environmental impact potentials.

One alternative will often have the least impact in some areas, while another alternative will have the least impact in others. In such situations, it is important to be able to assess which of the potential impacts and resource consumptions are large and which are small and to weight them in such a way that an aggregate environmental impact can be determined. This assessment can be difficult to perform on the basis of the figures alone. Potential impacts and resource consumptions are therefore compared with a common reference[5-7]. For an example, we use CO_2 as an equivalency to evaluate different chemicals. More examples will be showen when we go through the major categories in LCA.

3. Weighting of the normalized impact potentials and resource consumptions to determine which impacts are most significant overall.

Before the normalized impact potentials or resource consumptions can be made to be compared directly, account must be taken of the seriousness of each individual impact in relation to the others. Scientific, political and normative considerations are involved in this step, expressed in a weighting factor for each of the impact categories and resource consumptions[8, 9].

The normalization and weighting elements are interdependent of the LCA method and are therefore presented together in the total result.

For the environmental impact categories, the quantitative assessment of "ecotoxicity" and "human toxicity" involves a considerable amount of work[1, 10, 11]. A qualitative assessment method for these impact categories has therefore also been developed as a part of the LCA method by others, based on the information presented in the chemicals' hazard classification and labeling [7].

4.3.2 ENVIRONMENTAL IMPACT CATEGORIES

Description of most common environmental impact categories:

Classification and characterization are a calculation process in which each impact parameter of the inventory is converted to a contribution to environmental impact. Generally, the following environmental themes are considered:

Abiotic depletion potential (ADP) - abiotic depletion concerns the extraction of nonrenewable raw materials such as ores.

Energy depletion potential (EDP) - energy depletion concerns the extraction of nonrenewable energy carriers.

Global warming potential (GWP) - an increasing amount of CO_2 in the earth's atmosphere leads to more absorption of radiative energy, and consequently, to an increase in temperatures on Earth. This is referred to as global warming. CO_2, N_2O, CH_4, and aerosols all contribute to global warming.

Human toxicity (HT) - exposure of humans to toxic substances causes health problems. Exposure can take place through air, water, or soil, especially via the food chain.

Ecotoxicity (ECA/ECT) - exposure of flora and fauna to toxic substances cause health problems in them. Ecotoxicity is defined for water (aquatic ecotoxicity) and soil (terrestrial ecotoxicity)

Acidification potential (AP) - acid deposition onto soil and into water may lead, depending on the local situation, to changes in the degree of acidity. This affects flora and fauna mostly in negative ways.

Nitrification potential (NP) - addition of nutrients to water or soil will increase the production of biomass. This in turn leads to reduction in the oxygen concentration, which affects higher organisms like fish, can lead to undesirable shifts in the number of species in an ecosystem, and thus to a threat to biodiversity. Main elements in this section are nitrogen containing substances, phosphates, and organic materials.

Ozone depletion (ODP) - depletion of the ozone layer leads to an increase in the amount of UV light reaching the earth’s surface. This may lead to human diseases and may influence ecosystems in a negative way.

Photochemical oxidant creation potential (POCP) - Reaction of NO_x with volatile organic substances leads, under influence of UV light, to photochemical oxidant creation, which causes smog.

We have discussed in previous chapters the status of the environment, including a review of the various environmental impacts known today. Each category of environmental impact is calculated separately before being weighted and aggregated. However, criteria are established to determine whether a substance contributes to a certain environmental impact category before it will be included. An equivalency factor expresses the potential environmental impact for a substance as the quantity of a reference substance which will make the same contribution to the environmental impact as one gram of the substance. For each environmental impact category, the reference substance is chosen as a typical or important contributor. For instance, CO_2 is used in the case of green house gases is because it is the biggest contributor of the green house effect[12-15].

For non-global impact categories, it can be relevant to consider use of site factors in the calculation of potential impacts. Inclusion of site factors will qualify the calculated impact potentials for that local region. The use of site factors is, however, not yet generally implemented in the LCA method[16-18].

4.4 QUANTIFYING ENVIRONMENTAL IMPACT

There are thousands of different substances which can contribute to the impacts considered under "ecotoxicity" and "human toxicity". Equivalency factors have, however, only been calculated for a few hundred substances due to the difficulty of data collection, especially for human impacts. Many users of the LCA method will not possess the necessary chemical or eco-toxicological backgrounds in order to calculate equivalency factors for these two categories themselves. The work must then be given to an external consultant with the requisite expertise before the full LCA is complete. Another approach is to do approximations and estimations of those approximations on the overall results so that uncertainties in data can be handled[4, 19].

4.4.1 GLOBAL WARMING POTENTIAL

Determine which substances contribute to global warming

For a substance to be regarded as contributing to global warming, it must be a gas at normal atmospheric temperatures and:

- be able to absorb infrared radiation and be stable in the atmosphere with a residence time of years to centuries, or,
- be of fossil origin and converted to CO_2 on degradation in the atmosphere.

There are various models proposed in the past literature to rank chemicals with respect to the various substances involved. Agarwal and Narain[20, 21] base their proposed method on the natural removal mechanisms which exist for some of the greenhouse gases (CO_2 and CH_4). On the other hand, Smith[22]proposed a calculation of a Natural Debt Index for each country. The index would reflect the country's total contribution to an environmental impact exceeding nature's carrying capacity. Hammond, *et al.*[23] propose omitting all historical considerations and instead focused on the observed rate of increase for each individual greenhouse gas. The rate increase would be allocated among countries according to current emissions.

The Intergovernmental Panel on Climate Change (IPCC) [24-26] has developed an equivalency factor system which can weight the various substances according to their efficiencies as greenhouse gases. GWP, global warming potential, is a characterization factor that defines to characterization of potential contribution from a given substance which is in use for a time horizon of 100 years (standard). CO_2 is used as a reference material, so all the emissions which are characterized by this method are expressed as equivalent emissions of the CO_2. The LCA method's criteria for which substances contribute to global warming generally follow the IPCC's recommendation of excluding indirect contributions to the greenhouse effect. The indirect effects are difficult to model, and the IPCC is therefore refraining, for the time being, from quantifying indirect contributions with the exception of contributions from methane gas[27].

Calculate the global warming potential

One can calculate the global warming potential by multiplying the magnitude of the emissions with the equivalency factor: EP(gw) = Q • GWPi (gw).

$$GWP_i = \frac{contribution\ to\ global\ warming\ \ from\ gas\ i\ over\ T\ \ years}{contribution\ to\ global\ warming\ \ from\ CO_2\ over\ T\ \ years} = \frac{\int_0^T a_i(t) \bullet c_i(t)dt}{\int_0^T a_{co_2}(t) \bullet c_{co_2}(t)dt}$$

a_i (W/m^2pmol) is the gas's specific IR absorption coefficient, its instantaneous radiative forcing, assuming that the composition of the atmosphere remains the same

c,(t) (pmol) is the time-dependent residual concentration of gas ‘i’ deriving from the pulse-emission in question in 1986,

$a_{co_2}(t)$ and $c_{co_2}(t)$ are the magnitudes of the corresponding emission of CO_2. Examples of results are shown in Table 1 below.

Gas	**Atmospheric Lifetime**	**100-year GWP**	**20-year GWP**	**500-year GWP**
Carbon dioxide (CO_2)	50-200	1	1	1
Methane (CH_4)	123	21	56	6.5
Nitrous oxide (N_2O)	120	310	280	170
HFC-23	264	11,700	9,100	9,800
HFC-125	32.6	2,800	4,600	920
HFC-134a	14.6	1,300	3,400	420

HFC-143a	48.3	3,800	5,000	1,400
HFC-152a	1.5	140	460	42
HFC-227ea	36.5	2,900	4,300	950
HFC-236fa	209	6,300	5,100	4,700
HFC-4310mee	17.1	1,300	3,000	400
CF_4	50,000	6,500	4,400	10,000
C_2F_6	10,000	9,200	6,200	14,000
C_4F_{10}	2,600	7,000	4,800	10,100
C_6F_{14}	3,200	7,400	5,000	10,700
SF_6	3,200	23,900	16,300	34,900

Table 1 Global Warming Potentials (GWP) and Atmospheric Lifetimes (Years) Used in the Inventory Source: IPCC (1996)

Indirect contributions to GWP are hard to calculate because the IPCC does not include indirect contributions from gases other than methane. The LCA method, nevertheless, offers the option of including that part of the indirect contribution from volatile organic compounds (VOCs) and carbon monoxide (CO) attributable to their predictable conversion to CO_2. This applies only if the gases originate from fossil resources[7, 27].

As is clear from Table 1, the choice of the time scale, t, plays a large role in the magnitude of the equivalency factor. For those gases with atmospheric lives significantly shorter than that of the reference gas CO_2, the equivalency factor decreases with an increase in t. The opposite is the case for those gases with significantly longer lives than CO_2. In accordance with general LCA practice, one uses a time scale of 100 years, but equivalency factors for 20 and 500 years are also given in the table in order to show the significance of t and to provide an option of alternative choices on this method.

GWP values allow policy makers to compare the impacts of emissions from different gases. According to the IPCC, GWPs typically have an uncertainty of roughly 35 percent [28], though some GWPs have larger uncertainties than others, especially those in which lifetimes have not yet been ascertained. In the following work, we have chosen to use the 100 year time horizon which is consistent GWPs from the IPCC Second Assessment Report (SAR)[29, 30].

4.4.2 STRATOSPHERIC OZONE DEPLETION

Stratospheric ozone is broken down as a consequence of man-made emissions of halocarbons, i.e. CFCs, HCFCs, halons and other long-lived gases containing chlorine and bromine. This can have dangerous consequences in the form of increased frequency of skin cancer in humans and damage to the plants which form the basis of all ecosystems. The stratospheric depletion of ozone is an impact which affects the environment on a global scale.

Determine which substances contribute to ozone depletion

For a substance to be considered as contributing to stratospheric ozone depletion, it must:

1. be a gas at normal atmospheric temperatures,
2. contain chlorine or bromine,
3. be stable with a lifetime in the atmosphere of several years to centuries, to allow for its transportation up into the stratosphere.

The most important groups of ozone-depleting halocarbons are the CFCs, the HCFCs, the halons and methyl bromide. In contrast to these, the HFCs are a group of halocarbons which contain neither chlorine nor bromine but only fluorine, and which are therefore not regarded as contributors to stratospheric depletion of ozone.

CFCs and HCFCs are used mainly as foaming agents in foam plastic, as refrigerants, and as solvents. Halons are used as fire-extinguishing agents in fire-fighting equipment. Methyl bromide is used in the disinfection of buildings and of soil in market gardens.

The production of halocarbons is regulated under the Montreal Protocol by the United Nation. Under this protocol, production of CFCs and halons ceased in the industrialized world on 1 January 1996. Consumption of methyl bromide was frozen in 1995, and consumption of HCFCs is to be decreased gradually. The deadlines for phasing out have been brought forward in a number of countries. CFCs and halons can, however, continue to be produced in Third World countries until 2010 (UNEP, 1993), and they will therefore also occur in future inventories of product systems.

Calculate the ozone depletion potential

First, one chooses the time scale for which the ozone depletion potential is to be calculated. Unless specific reasons indicate otherwise, one selects a infinite time scale. After finding the substance's equivalency factor for the chosen time scale, calculate the ozone depletion potential by multiplying the magnitude of the emission by the equivalency factor:

$$EP(od) = Q \bullet EF(od).$$

Together with UNEP (United Nations Environment Programme) and a number of other organizations, the World Meteorological Organization (WMO) organizes the “Global Ozone Research and Monitoring Project”, a research network of experts in atmospheric chemistry. The network reviews international developments in scientific knowledge of stratospheric ozone depletion and every few years issues status reports summarizing the latest findings [31]. The status reports present the Ozone Depletion Potentials (ODPs), which for individual gases express the ozone depletion potential as an equivalent emission of a reference substance CFC11 ($CFC1_3$). These ODP values are used as equivalency factors in the calculation of the ozone depletion potential. The equivalency factor is thus defined as:

$$ODP_i = \frac{\text{contribution to stratospheric ozone depletion from gas } i}{\text{contribution to stratospheric ozone depletion from } CFC11}$$

For the most short-lived of the gases, especially the HCFCs, this will result in some markedly larger equivalency factors.

In accordance with general LCA practice, however, recommend use, for equivalency factors of ODP values representing the gases' full contributions, but the in most references also gives equivalency factors for 5, 20 and 100 years for some of the gases.

4.4.3 PHOTOCHEMICAL OZONE FORMATION

When solvents and other volatile organic compounds are released to the atmosphere, they are often degraded within a few days [32]. The reaction involved is an oxidation, which occurs under the influence of light from the sun. In the presence of oxides of nitrogen (NO_X), ozone can be formed. The oxides of nitrogen are not consumed during ozone formation, but have a catalyst-like function. This process is termed photochemical ozone formation[33, 34].

The volatile organic compounds are broken down especially in the troposphere, the lowest region of the atmosphere, to which they are emitted[33, 34]. The most significant man-made sources of VOCs are road transport with its emission of unburned gasoline and diesel fuel and the use of organic solvents, e.g. in paints [35, 36].

Ozone attacks organic compounds in plants and animals or materials exposed to air. This leads to an increased frequency of problems of the respiratory tract in humans during periods of photochemical smog in cities. For agriculture, it causes a reduction in yield which for Denmark is conservatively estimated to be about 10% of total production [7].

Determine which substances contribute to photochemical ozone formation

Photochemical ozone formation is an impact which affects the environment on both local and regional scales. The substance is consider as a contributor to photochemical ozone formation if Check whether the substance is an organic compound with a boiling point below 250°C and

1) contains hydrogen or
2) contains double bonds between carbon atoms

Consider carbon monoxide CO as a further contributor to photochemical ozone formation. The presence of oxides of nitrogen can be equally important a man-made factor in photochemical ozone formation as emission of VOCs. Despite this, a contribution from oxides of nitrogen to photochemical ozone formation cannot be calculated because the equivalency factor system used for calculation of ozone formation potentials does not facilitate calculation of an equivalency factor for NO_x.

The significance of NO_X for ozone formation is, however, reflected in the fact that two sets of equivalency factors are used: one for emissions of VOCs occurring in areas with a low background concentration of NO_X and one for emissions occurring in areas with a high background concentration of NO_X.

Calculate the photochemical ozone formation potential

Calculate the photochemical ozone formation potential by multiplying the magnitude of the emission by the equivalency factor found: EP(po) = Q • EF(po).

In the same way as the GWP values for global warming and the ODP values for stratospheric ozone depletion, the POCP values express the ozone formation potential as an equivalent emission of a chosen reference substance. For photochemical ozone formation the reference substance is the gas ethylene (C_2H_4).

$$POCP_i = \frac{contribution\ to\ ozone\ \ formation\ \ from\ gas\ i}{contribution\ to\ ozone\ \ formation\ \ from\ C_2H_4}$$

There is no international panel of experts for the environmental impact of photochemical ozone formation such as there are for other global environmental impacts.

The POCP values are calculated with the aid of atmospheric chemical models and a series of assumptions must be made on climatic conditions and the magnitude of the simultaneous emissions of a number of other VOCs and of NO_X. The assumptions underlying the POCP values in appendix correspond to typical situations in areas with low and high background concentrations of NO_X. The assumptions are discussed in the references presenting these POCP values [37, 38].

A time scale must also be chosen for ozone formation in model calculations of POCP values. A POCP value for a short time scale of 24 hours describes the photochemical ozone formation immediately surrounding the place of emission corresponding to potential contribution to episodes of photochemical smog. For a longer time scale, such as a week, most of the VOCs will be broken down and the POCP value provides a better expression of the total ozone formation potential. POCP values have been calculated only for the individual VOCs of greatest significance for total photochemical ozone formation. But these are not necessarily the compounds of greatest significance for the ozone formation potential in an LCA. For example, styrene will give a significant contribution to the ozone formation potential in the LCA of the polymer polystyrene, but none of the references gives a POCP value for styrene. It can therefore be an advantage to be able to make an estimation of missing POCP values. Hauschild & Wenzel describe various methods of estimating POCP values[7].

Emissions of VOCs will often figure in the inventory for a product system, without an indication of which individual compounds they are composed of. The composition can vary greatly for different sources, but if the source of the VOC emission is known (e.g. “exhaust from gas-engine cars”), it may be possible in to find an average POCP value which is representative for the VOC mixture. The average POCP values are calculated as a weighted average for the VOC mixture which is characteristic of the type of source[39, 40].

Weighted average POCP values can be calculated for other types of sources if the average composition of the source's VOC emission is known. For example, a weighted POCP for the aggregated VOC “source” “polystyrene production from oil to final polystyrene polymers” is calculated in Hauschild & Wenzel [7, 41].

4.4.4 ACIDIFICATION

When acids and compounds that are convertible to acids are emitted to the atmosphere and deposited in water and soil, this may eventually result in a decrease in pH, which causes an increase in acidity. This has consequences in the form of a widespread decline of coniferous forests in many places in Europe and the USA and increased fish mortality in mountain lakes in Scandinavia and central Europe. Corrosion damage to metals and disintegration of surface coatings and mineral building materials are also caused by acidification on exposure to wind and weather[42].

Combustion processes in electricity and heating production are the most significant man-made sources of acidification. The contribution to acidification is greatest when the fuels contain sulphur. Acidification is an impact which mainly affects the environment on a regional scale.

Determine which substances contribute to acidification

1. For a substance to be considered a contributor to acidification, it must cause introduction of or release of hydrogen ions in the environment, and
2. The anions which accompany the hydrogen ions must be leached or washed out from the system.

The addition of hydrogen ions occurs either when the substance itself is an acid or is converted to an acid, or when hydrogen ions are released as the substance is converted in the environment.

The number of substances which should be considered contributors to acidification is not large, and in practice the list of equivalency factors is calculated which can be used to decide whether a substance contributes to acidification.

Note that emission of organic acids is not regarded as a contribution to acidification

Calculate the acidification potential

1. Find the substance's equivalency factor
2. Calculate the acidification potential by multiplying magnitude of the emission by the equivalency factor found: EP (ac) = Q • EF (ac).

There is no internationally accepted system of equivalency factors for acidifying substances. In contrast to the global environmental impacts and photochemical ozone formation, it has therefore been necessary to develop equivalency factors for acidification.

Calculation of the equivalency factor for a substance is based on the number of hydrogen ions which can theoretically be released from the substance directly or after any conversions in the environment.

Whether or not the acidification potential is realized depends on the accompanying anion release from the ecosystem which receives the emission. For some substances, the proportion of anions released can vary from ecosystem to ecosystem. To reflect this, Hauschild & Wenzel [7] propose a site factor, the value of which can vary between 0 and 1.

As for the potentials for the other types of environmental impacts, the acidification potential is expressed as an equivalent quantity of a reference substance. Sulphur dioxide (SO_2) is used as the reference substance for acidification. Should the inventory include compounds causing acidification, it is easy to calculate equivalency factors for them. The method is given in Hauschild & Wenzel [7].

4.4.5 ECOTOXICITY

Chemicals emitted as a consequence of human activities contribute to ecotoxicity if they affect the function and structure of the ecosystems by exerting toxic effects on the organisms[15, 43, 44]. If the concentrations of environmentally hazardous substances caused by the emission are high enough, the toxic effects can occur as soon as the substances are released[10, 45]. This form of toxic effect is called **acute ecotoxicity.** It often results in the death of organisms exposed[46, 47].

Toxic effects which are not acutely lethal and which first appear after repeated or long-term exposure to the substance are called **chronic ecotoxicity.** Chronic ecotoxicity is often caused by substances which have a low degradability in the environment and which can therefore remain for a long time after their emission (persistent substances)[10]. Some substances also have a tendency to accumulate in living organisms so that tissues and organs can be exposed to concentrations of the substance which are far higher than the concentrations in the surrounding environment. The chronic ecotoxicity of a compound is thus determined by its toxicity, its biodegradability and its ability to accumulate in living organisms[48]. The result of a chronic ecotoxic impact can, for example, be reduced reproductive capacity, which means that the species' chances of survival in the long term are reduced.

Ecotoxicity is an impact which predominantly affects the environment on local and regional scales. It can be a global impact for some toxic substances of very low biodegradability with a strong tendency to accumulate in living organisms[43].

For a substance to be classified as ecotoxic, it must be toxic to organisms in a manner which affects the functioning and structure of the ecosystems in which the organisms live. Toxicity is a relative concept[49, 50]. To be classified as ecotoxic, properties like persistence and bioaccumulation ability are considered along with direct toxicity. Ecotoxicity is determined empirically in ecotoxicity tests, EC50 value for acute ecotoxicity or NOEC value for chronic ecotoxicity; persistence is determined empirically or estimated on the basis of octanol-water partitioning coefficient, P_{ow}[7, 41, 51].

The calculation of the equivalency factors is based on considerations of the substance’s potential fate in the environmental and effects on the ecosystems exposed to it. Potential contributions to ecotoxicity are considered for the following emissions in a product system, in water, in soil, in wasted water treatment plants[7, 41].

$$EP_i = EF_i \times Q_i$$

EF_i is the equivalency factor for ecotoxicity from substance i in compartment C

Total understanding of ecotoxicity has not been reached yet at the present stage. The quantifying methods that are used in research are normally based on empirical methods. This is an area that needs much improvement, which can lead us to less uncertainty involved with any LCA study[1, 52].

4.4.6 HUMAN TOXICITY

In contrast to the other impact categories, human toxicity includes many different impact mechanisms, such as damage to DNA, induction of allergy or inhibition of specific enzymes[53, 54].

It is still in a development stage; because the mechanism of action is not known for many substances[11]. The different mechanisms which underlie toxicity are therefore treated here as if there were one primary impact mechanism. The list of substances from the product system classified as contributing to human toxicity is more comprehensive and less uniform than the corresponding list for the other environmental impact categories[55].

Ways to become exposed to impacts of pollutants in the environmental include: inhalation, ingestion of polluted groundwater, surface water or soil.[56]. Indirect exposure also occurs via: ingestion of primary producers which are exposed to pollution, ingestion of consumers or their products [57].

Key properties to evaluate:

1. Toxicity (empirically determined)
2. Persistence (empirically determined in biodegradability tests)
3. Bioaccumulation potential (empirically determined or estimated)

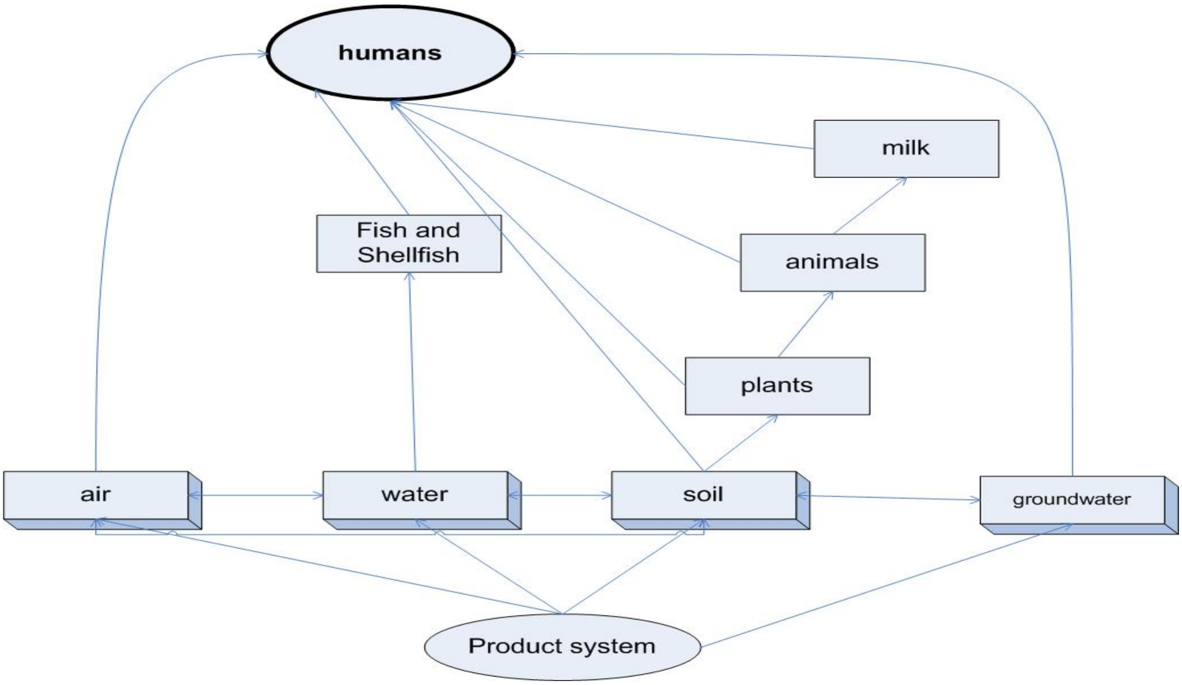

Figure 1 the exposure routes under consideration for humans in the environment. 7 exposure routes are outlined.

To calculate the equivalency factor for human toxicity form substance i in compartment C:

$$EP(htc)_i = EF(htc)_i \times Q_i$$

$EF(htc)_i$ is the equivalency factor for toxicity from substance i in compartment C.

The expression for the equivalency factor is constructed as shown in figure 2 [15, 43, 44].

Transfer Biodegradability

Intake

$$EF(htc)_i = \boxed{I_c \times T_{c,i} \times BIO_i}$$

Effect

Figure 2 composition of human toxicity: intake, biodegradability, transfer.

4.4.7 RESOURCE DEPLETION

The procedure of assessing resource consumption enables a ranking of consumptions of the various types of resources which occur in a product system. SETAC has a working group to develop the method[13].

In order to make an inventory of consumptions of various types of resources, it is necessary to follow the consumption of all materials and fuels back to extraction of primary resources form nature, including the earth crust, the sea, the forest, etc. All consumptions of primary resources in the product system must in principle be inventoried. This principle is inherent from the LCA itself [15, 43].

The first step in the method is therefore to express all intakes in the product system as primary intakes, which is as pure resources.

4.4.8 WORKING ENVIRONMENT

A range of relevant exposures was selected for each of the selected impact categories:

1. Chemical: exposure to carcinogens, exposure to neurotoxins, and exposure to allergens
2. Noise: exposure to noise which causes hearing impairment
3. Work accidents: mainly includes bodily damage
4. Odor: the odor of chemicals sometimes causing harsh working environment, sometimes causing health problems for workers.
5. Monotonous work: effects on the musculoskeletal apparatus.

An exposure threshold is defined for each of the listed major category: for chemical exposure is 10% of the working environment limit value or skin contact. For noise is 80 dB (A), and for monotonous repetitive work it is repetition of the same movement more than twice per minute[9, 15, 43, 44]. The odor threshold value of a substance is defined as the concentration of that substance under defined standard conditions at which 50% of a representative sample of the population can just detect the difference between a sample of air mixed with that substance and a sample of clean air[9, 15, 43, 44].

The environmental impacts are classified as global, regional and local. Impacts on working environment are highly local.

4.5 LIFE CYCLE IMPROVEMENT ANALYSIS

In a LCA study, the goal and scope definition provides the initial plan of the study. The inventory analysis supplies the data on relevant processes and interventions on which the assessment is to be based. In the impact assessment phase, the interventions are translated into potential environmental impacts. The final phase of LCA is interpretation, often called life cycle improvement analysis[3, 58-61].

Life cycle improvement analysis is akin to the use of continuous improvement strategies. The goal in environmentally conscious manufacturing should be to achieve zero pollution. This can be achieved if the entire system processes are continuously improved on [19, 54, 62]. From raw material acquisition through manufacturing and processing to distribution and transportation, then, recycling, reuse, maintenance and waste management, each stage involves creation of waste, energy consumption, and material usage [63].

A life cycle improvement strategy is needed to identify areas where improvements can be achieved such as a product design that has less demand for material requirements, i.e. reduction in the size of automobiles, replacement of 8 cylinder engines with fewer; enhanced consumer usage of products by reuse, or creating alternative uses for products, cutting down consumption of fossil fuels, participating in recycling programs, and so on. This will require the tracking and monitoring of the product through its life cycle to detect areas which have improvement opportunities [64]. Life cycle improvement analysis has led to many changes in design thus, the design for environment[65].

ISO 14043 defines interpretation as "a systematic procedure to identify, qualify, check, and evaluate information form the result of LCI and /or LCIA of product system, and present them in order to meet the requirements of the application as described in the goal and scope of the study [15, 43, 44]. Furthermore, life cycle interpretation includes communication to give credibility to the results of other LCA phases in a form that is both comprehensible and useful to the decision maker"[53, 65]. This is the place to reflect on the results of the previous phases of the LCA and on the choices that have been made during the process of generating these results.

It was only recently that the interpretation phase was introduced by ISO, and it is a topic scarcely referred to in previous LCA literature [16, 43, 66].

Normally, interpretation follows these steps.

Consistency Check and Completeness Check

This part is to determine whether the assumptions, methods, models and data are consistent with the goal and scope of the LCA study, in terms of both the chain embodied in individual product life cycles and among the products compared[67].

Incomplete or erroneous data is often generated in the course of an LCA study. The methodology used in the various phases of the LCA, must be checked results, and conclusions of the analysis in relation to the goal and scope of the study. The assumptions or methodological choices that are incompatible with the goal and scope of the LCA, missing or erroneous emissions, economical inflows and outflows or product characteristics could also be reevaluated. So it is very necessary to check the completeness of the LCA. One way is to have peer review, another is comparing to similar studies[68].

Contribution Analysis

The aim of contribution analysis is to establish the contribution to the overall LCA result of various identifiable elements and parameters. Normally, we should have data for individual processes, systems of processes, production stages, packaging, and emission calculations [7, 43].

The best results we get from the contribution check is to answer the question of "which intervention, economic flow or process can we best change in order to reduce the climate change score of the production system". This type of improvement question can be answered if the linkages among the different processes are covered right up to the highest order. Also, contribution analysis can serve as a focus for the sensitivity analysis.

Perturbation Analysis

In a perturbation analysis, the effects of small changes in the parameters that describe the system are studied on the overall results of an LCA. [7] The effects of these small changes are calculated simultaneously for all the flows of a system, i.e. economic flows and environmental interventions. The analysis may be performed at different levels of aggregation: inventory table, indicator results, normalized indicator results or weighting results. All the factors used to calculate the aggregated result are included in the perturbation analysis[6, 69].

The result of the perturbation analysis is normally a list of processes or flows with associated multiplication factors in decreasing order of significance for a specific type of result (e.g. CO_2 emission, indicator result for climate change, etc.). Although the mathematics can be quite complicated, the perturbation analysis is relatively easy to implement if a matrix type of calculation method is used [70]. Besides its use in improvement analysis, it can help to focus the sensitivity analysis on those variables and (modeling) choices of greatest influence on the results of the study. In this respect, it can significantly reduce the effort required for gathering uncertainty data, because it identifies which data items are crucial for uncertainty analysis [3]. In interpreting the results of the perturbation analysis due caution should again be exercised.

Sensitivity and Uncertainty Analysis

If LCA is to be usefully employed as a decision-making tool, the robustness of the results must be clear.

A basic distinction must be made between accuracy and precision. Data may be precise but inaccurate, for instance when use is made of a high-precision clock which has not been adjusted to local time. Data may also be accurate but imprecise [71-73].

The result of a calculation is sensitive to several sources of uncertainty. We mention uncertainties in the data, for instance when there are several different measurements or estimates of an emission, and uncertainties in the model, for instance due to essentially arbitrary decisions relating to system boundaries, allocation, and so on. Data uncertainty may arise because data are in themselves variable, or the data may be the outcome of a stochastic process[74]. The former is referred to as variability, the latter leads to sampling error. In addition, data may be measured incorrectly; we can then distinguish random errors from systematic errors. In general, random errors lead to inaccurate data, and systematic errors to imprecise data[71, 72].

Model uncertainty leads to doubts regarding the validity of a result, data uncertainty to doubts on its reliability. Even when results are highly imprecise or inaccurate, they may still be robust. For instance, if product X remains preferable to product Y even when the absolute difference varies wildly under sensitivity analyses, the ranking of these two products is said to be robust[4].

An Example of Improvement Analysis

In this particular project, because CVD tools may not be capacity limited at all times [75], the clean recipe that achieves the fastest clean time may not be the optimum. If a comparable clean time to the baseline in-situ clean could be achieved with lower NF_3 flow, the total clean gas cost could be reduced since NF_3 is a relatively expensive gas.

An evaluation of lower NF_3 flows showed the lowest achievable NF_3. A flow rate with recipe of 500 sccm NF_3 and 1000 sccm argon was used with a 30% overetch. The resulting clean time with the lower flow NF_3 was still 25% faster than the baseline C_2F_6 clean. So an NF_3 flow of 500 sccm can result in a viable clean process. The improvement in that practice is we have lower gas recipe, and we have lowered the gas usage, the cost, and still maintain the function of the process.

4.6 CONCLUSION

Most criticisms of LCA techniques are not so much from analyses that were not correctly carried out, but from LCA results that were misused.

One cannot use LCA in a consistent and sound manner unless one recognizes both its practical and theoretical limitations. Also, as a technique, LCA helps in decision making, but does not replace it. The fact that LCA always come up with mixed or complex results should not cast a shadow over the usefulness of these results. They reflect a complex situation.

Impact assessment is still in a developing stage. Even after 25 years of development, it is hampered by a lack of data of sufficient quality and a lack of scientifically accepted methodologies. However, significant progress is being made. We can look forward to resolution of some issues in the near future while some parts of impact assessment will remain subjective for many years.

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Chapter 5: CHAMBER CLEANING CASE STUDY

5.1 GENERAL INTRODUCTION

Before we get into a detailed description of the CVD chamber cleaning process, let's look at some numbers that will put some perspective on where the semiconductor industry stands in the sense of environmentally conscious design.

- Economically, there is a 30 to 1: cost ratio to treat and use city water to ultra-pure quality
- Currently, there are 6.7 million: gallons of water used per day by a large semiconductor manufacturing facility for the next generation of semiconductors
- 60,000: city population that can be served by the amount of water used by this next generation facility
- 2: number of new natural gas fired power plants needed to supply the projected annual energy requirements of the Northwest's semiconductor industry for the next decade
- 30: number of days a typical household could be run from the energy needed to manufacture 1 semiconductor chip
- 50: percent of total energy used for HVAC in a semiconductor manufacturing facility
- 7500: number of houses that use the equivalent amount of power needed for a typical semiconductor fabrication plant; $1,000,000: typical monthly electric bill for a large fab [1]

From the data above, we can see that the semiconductor industry still has a large potential for reducing the impacts from production to make it a more benign process in the future. On the other hand, the U.S. semiconductor industry ranks in the top 5% of safest U.S. industries, with a rate of only 2.2 reportable injuries and illnesses per 100 employees [2]. This outstanding safety record is due in part to SIA's (Semiconductor Industry Association) long and close involvement with environment, safety and health (ESH) issues. The U.S. semiconductor industry also leads the way in developing alternatives to hazardous chemicals and in reducing pollutant emissions while sharing information about best practices with companies from other nations. Figure 1 is an ESH subway picture that shows the group of organizations that are working together to improve the semiconductor industry [3].

In the past several years, the semiconductor industry has been presented with various options for cleaning of plasma enhanced chemical vapor deposition (PECVD) tool chambers. In this thesis, we assess the relative merits of two recent chamber-cleaning processes. These processes will be compared on the overall cleaning performance (process throughput, efficiency of clean), the economic performance (gas usage, costs), and the environmental performance (perfluorocarbon (PFC) emissions). Direct comparisons between chemistries will be made whenever relevant process factors are held constant.

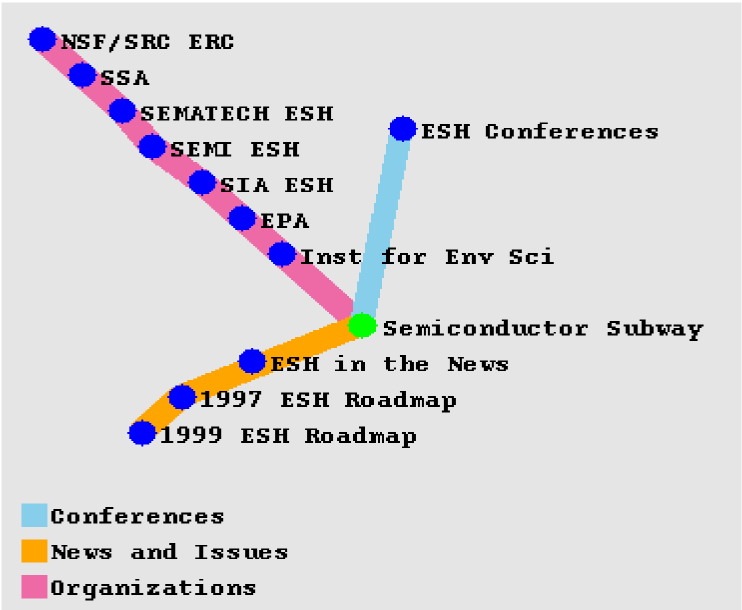

Figure 1 The *ESH Subway provides links to information and news about semiconductor manufacturing and the environment.*

In the change from 200-mm to 300-mm production lines, the manufacturers aim at cost reduction. At the same time, increased wafer size and reduced critical dimensions demand higher process stability and often new processes for increasing throughput.

5.2 FLUORINATED PROCESSES IN THE SEMICONDUCTOR INDUSTRY

There are many cleaning technologies that have been developed for various applications. Some have been regulated because of environmental problems which were identified overtime, as shown in figure 2.

The use of fluorinated process gases for plasma-based thin film processing applications has been one of the enabling technologies helping to drive the phenomenal growth in semiconductor manufacturing which has led in turn to the development of the huge electronics industry in the world today. Fluorine containing gases have enabled increasing levels of process automation during wafer manufacturing as new dry processing technology has replaced wet-chemistry processes which were labor intensive and fraught with health and safety concerns. As new generations of chip designs incorporating greater complexity and smaller dimensions are designed and manufactured, these process benefits have become even more pronounced. Additionally, the development of increasingly higher purity process gases has allowed large improvements in chip yields, also resulting in the growth of the industry[4, 5].

5.2.1 CHAMBER CLEANING

Modern plasma enhanced chemical vapor deposition (PECVD) tools are used for the deposition of a variety of thin film materials on silicon wafer substrates. As shown in figure 3, a typical wafer may undergo several dozen deposition steps during its transformation from bare silicon into a functioning computer chip. Types of films that are deposited include both metals and dielectrics, such as: silicon dioxide (SiO_2), silicon nitride (Si_2N_3), various doped oxides, silicon oxynitride, and tungsten[5-8]. During the deposition process, specific chemical vapor precursors, e.g. silane, tetraethylorthosilane (TEOS), WF_6, etc. are delivered to the CVD chamber where the gas is dissociated, resulting in deposition of a thin film of the desired material. Unreacted material, as well as gaseous by-products are then pumped out of the chamber.

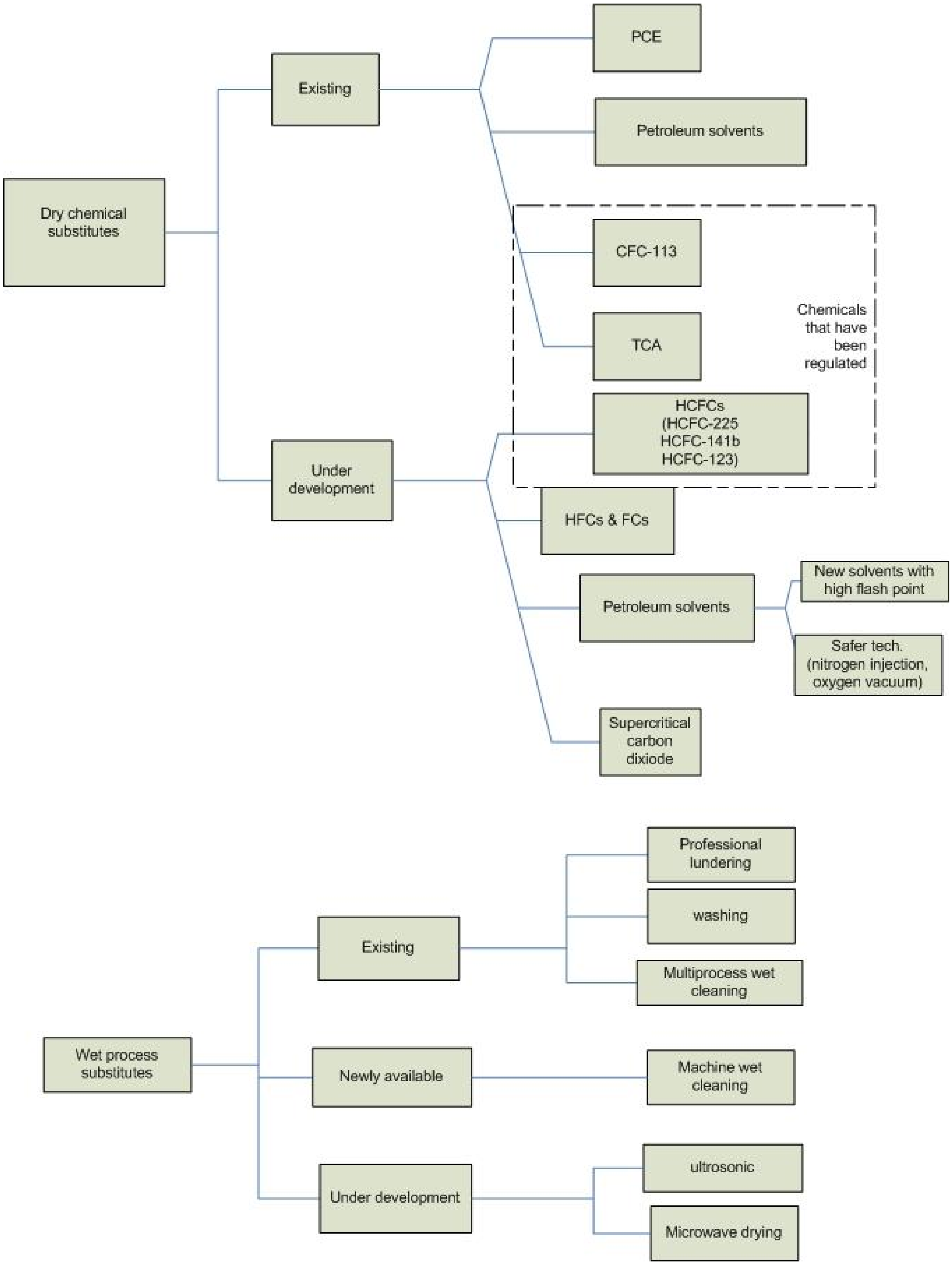

Figure 2 *cleaning technologies and alternatives*

While this technology is excellent for forming thin films on the wafer substrate, film material is also deposited on other internal surfaces of the chamber. Over

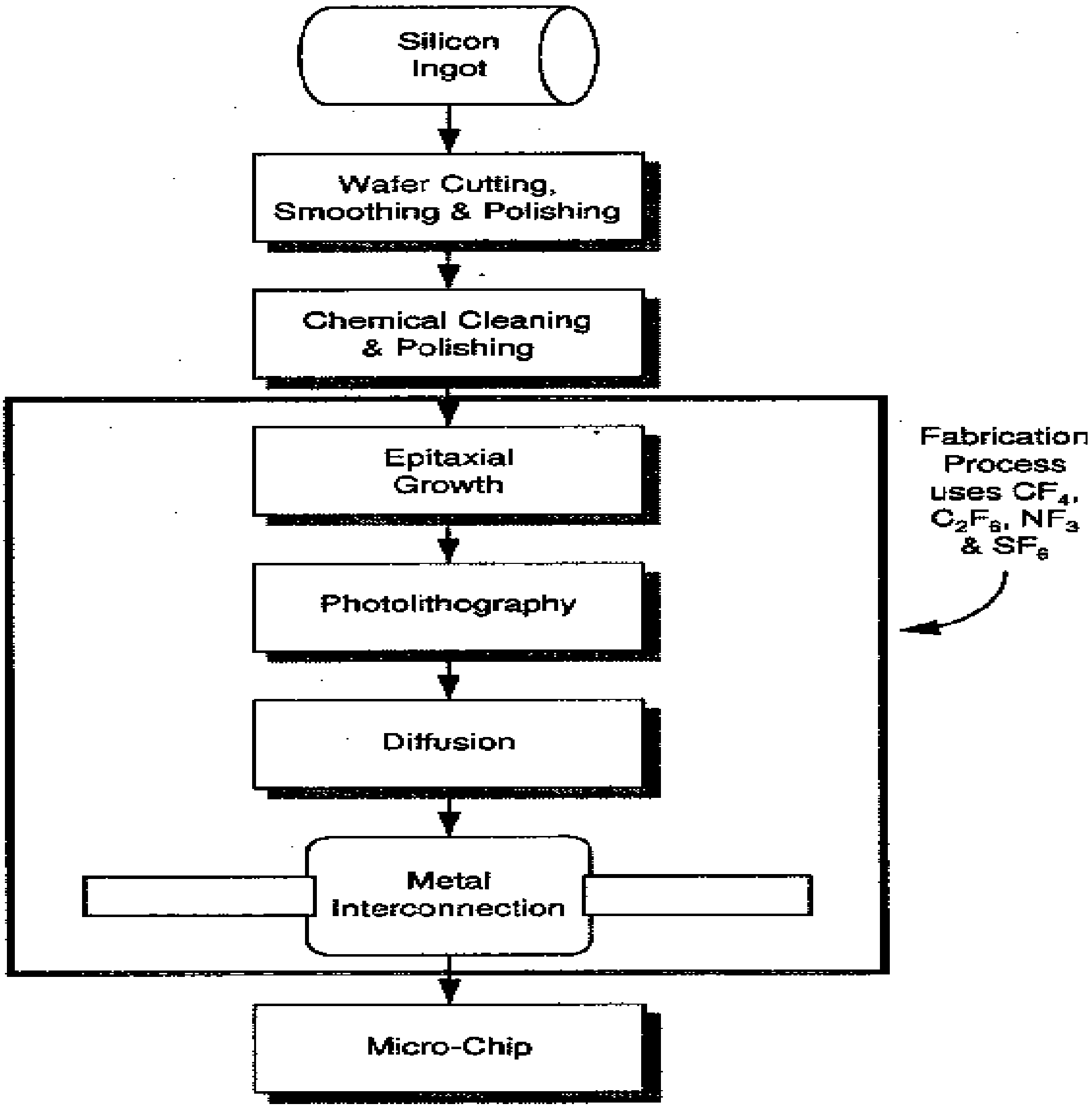

Figure 3 *semiconductor manufacturing steps*

time if this material were not removed, it would build up and eventually these depositions on the chamber wall would cause particle generation in the chamber, and thus influence the quality of the films formed by CVD and reduce reproducibility of the CVD process. This is so called "flake off", resulting in particulate contamination of subsequently processed wafers. This type of contamination would be disastrous to product yields.

The chamber cleaning step is, therefore, indispensable to create reliable processes. Amorphous silicon (a-Si) and polycrystalline silicon (poly-Si) films are generally synthesized by CVD and PECVD (plasma-enhanced chemical vapor deposition). Historically, many of these chamber cleans required taking the chamber offline, cooling it down, opening it for a manual cleaning, reassembling it, and reconditioning it prior to returning it to operation. The down time, as well as the labor costs and safety concerns associated with these manual ''wet'' cleans made this maintenance step a major problem for integrated circuit manufacturers.

The development of ''dry'' clean technologies based on the *in situ* generation of reactive cleaning species has made a tremendous impact on reducing the downtime and labor, as well as eliminating many of the chemical handling and safety concerns [9]. In PECVD chamber cleaning for many processes, a fluorinated gas is allowed to flow into the chamber where it is dissociated by a high-energy plasma. The reactive fluorine species (predominantly F radicals) are then free to scavenge silicon residues from the chamber walls and other internal surfaces. A variety of fluorinated gases have been proposed and/or evaluated for use in these types of processes. Gas choice is often a trade off in finding a fluorinated precursor molecule to deliver the reactive fluorine functionality efficiently and cost effectively into the manufacturing process while maintaining the proper balance of safety and health requirements needed for large scale manufacturing operations.

5.2.2 PFC CHAMBER CLEANING ENVORNMENTAL PROBLEMS

Among semiconductor fabrication processes, the plasma-chamber cleaning process during chemical vapor deposition (CVD) is known to emit the largest quantities of PFC (Perfluorinated Carbons) gases. Also, more severe environmental statutes often apply to the new production lines being built. On top of that, there is the world-wide goal of PFC emission reductions as agreed to by industrial members. Therefore, it is necessary to develop various methods to drastically reduce the emission of PFC gases using the development of optimization, replacement gases, recovery/capture/ recycle, and reuse or abatement [10].

Generally SF_6, CF_4/O_2, $CF_4/O_2/Ar$ and $C_2F_6/O_2/Ar$ plasmas are used in the conventional chamber cleaning processes[11]. In these chamber cleaning processes, F atoms generated from the dissociation of SF_6 and CF_4 gases play an important role for etching reactions of Si and W. SF_6 and perfluoro-carbon (PFC) gases, however, cause a serious environmental problem, namely global warming. The global warming potentials of these gases are estimated to be thousands of times as high as that of CO_2 gas because of their long life times in the atmosphere as shown in Table 1. Therefore, the restriction on SF_6 and PFC gases has been intensively discussed, and the use and production of SF_6 and PFC gases in industries may be prohibited in the near future.

Table 1 t (life time) AND GWP_{100} for PFC gases

PFC	t (years)	GWP_{100}
CF_4	50000	6500
C_2F_6	10000	9200
C_3F_8	2600	7000
SF_6	3200	23900
NF_3	740	8000

To prevent further increases in global warming, members of the semiconductor industry have decided to reduce the emission of PFCs responsible for global warming by 10% before 2010[12-16]. A number of members of the Semiconductor Industry Association (SIA) voluntarily agreed to measure and evaluate options for reducing PFC emissions (mostly generated from plasma-aided processes) from their manufacturing operations in a joint agreement-Memorandum of Understanding(MOU) with the United States Environmental Protection Agency (EPA) in 1996[17]. The WSC (World Semiconductor Council) subsequently announced further agreements on an international basis to reduce absolute emissions of global warming gases in 1999[18]. In 2001, the MOU was renewed with wider participation and more specific emission reduction goals. Industry efforts resulting from these agreements have included: process optimization; abatement, capture and recycle programs; and the adoption of alternative plasma chemistries[19].

Usually the utilization of etch gas in these processes is less than 50%; the remaining gas has to be destroyed and removed by a waste gas abatement system. Generally, for CVD and etch processes, waste gas abatement is necessary for three reasons:

- Environmental concerns and legal restrictions on emissions,
- Safety within the fabrication area,
- And, to prevent corrosion or clogging of exhaust lines and thus to guarantee process stability.

5.2.3 NF_3 AS A ALTERNATIVE FOR CHAMBER CLEANING

The use of NF_3 as an etch gas for chamber cleaning processes is reported to give promising results. Gas consumption is lower since the utilization of NF_3 is very high (85-99%) [10, 20]. At the same time, NF_3 has a much lower atmospheric lifetime (740 years) than standard etch gases like CF_4 and C_2F_6 (estimated atmospheric lifetimes of 50000 and 10000 years, respectively). When comparing the global warming potentials, often a 100 year integrated time horizon is used (as discussed in the earlier chapters), so that the full advantage of NF_3 is not shown by the present accounting methods.

The change from C_2F_6 to NF_3 chamber cleaning has several environmental advantages: (a) near zero emissions of PFCs due to the high conversion rates of NF_3 in the process and abatement; and (b) lower energy consumption in abatement (therefore less CO_2 emissions during the life cycle [20]. The major disadvantage is the toxicity and higher reactivity of NF_3, but this will not be a significant problem in semiconductor manufacturing because etching of the chamber wall is at a very slow rate. For the economic costs, an overall reduction is expected from: (a) lowering the operating cost for abatement and, (b) reduced costs for process gases if NF_3 prices drop. So far, these two kinds of assumptions and conclusions have never been quantified so we cannot say which one is a better process just by these trends. These is the questions we will try to answer.

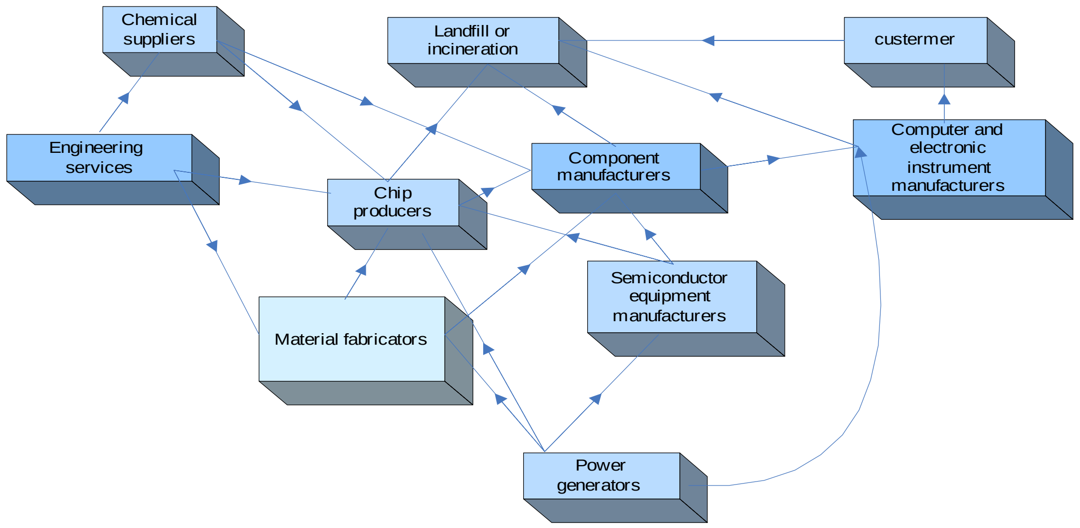

Figure 4 *Industrial ecology relationships in the semiconductor industry*

As we can see here in Figure 4, this is a problem that can be solved with LCA, which not only qualifies the pros and cons of each chemical, but also evaluates the impacts from every stage of the chemicals, such as the use and abatement phases.

5.2.4 COMPLICATION OF THE LCA IN THIS CASE STUDY

LCA is very information demanding in order to quantify all aspects of a process. You must collect all the information for each stage of the process. These include the manufacturing stage, processing stage, abatement stage, and depending on the boundary conditions, the transportation of the product, and use phases. All of these factors need to come together in order to complete an LCA.

Take NF_3 as an example in this case and in Figure 4. We can see we need the information for many material production and material extraction steps. Most important of all, we cannot get the information on this kind of process data from published sources. In most cases, they are proprietary data that are not easily extracted from currently available databases or publications. The information needed include the material inputs and outputs of the process and the economic data that is involved in the process,.

How can proprietary information be used? Information is difficult to share because of competitive advantages. Is it possible to create a "black box" approach to aggregate data (UT Austin Cluster Tool approach) for this particular problem?

We have another choice for performing an LCA, which is to use slightly outdated 'data' from recently discarded processes to provide snap shots of environmental impacts from similar manufacturing processes. However, this suffers from the fact that all of the data will be outdated and for processes that are no longer currently in use. Another alternative is to estimate data for the LCA through two methods to avoid proprietary information sharing. The two viable ways of gathering information here are: using patents to build representative LCA data which will have many uncertainties and estimations, or using a semiconductor industry standard – a "standard wafer" like information furnished by Philips. We have chosen the former method.

5.3 GOAL AND SCOPE DEFINITION

The first phase of LCA is goal definition, which is trying to fix the objective of the study. This includes determining the use to which the environmental analysis will be put and at the same time assessing what it can and cannot be used for.

5.3.1 GOAL DEFINITION

- For what will the results of the LCA be used?

For the purpose of evaluating two technologies; LCA compares which one has a higher impact over the environment as a whole. One of the technologies has been substituted by the other one in industry. NF_3 substituted C_2F_6 in most of the fabs as a CVD chamber cleaning tool is our example. As engineers, we always have doubts when we shift to new technologies, and we have incorporated this LCA study to verify if the industry has made the right decision for the environment at this time.

- What decision can be made on the basis of the LCA?

The decision making involved here is minimal, we try to model the process to see if we have made the right decision for the environment. If it is shown that NF_3 actually brings a higher negative impact on environment, and after peer review that the outcome can be verified, then the industry will have to consider a new alternative or think of other ways of reduce the impacts.

Moreover, some improvement opportunities can be revealed by conducting individual LCA evaluations. Since NF_3 is the focus here, we hope LCA can make the improvement opportunities more transparent to decision makers.

- What is the extent and nature of these decisions?

In terms of an LCA study, this is a comparison study, just like many paper diaper and cloth diaper studies that has been conducted [21]. However, this study is based more on an engineering approach than most of the earlier studies.

5.3.2 USAGE OF THE LCA

- Generate environmental information on chamber cleaning chemical life cycles.
- Identify improvement potentials for both cleaning chemicals
- Compare alternative solutions at the conceptual level

- Compare alternative solutions at the level of details

So goal definition consists of clarifying what the LCA can and can not be used for, which includes the decisions which it must support and the environmental consequences to which these decisions can lead.

5.3.3 SCOPE DEFINITION

The objective of this practice is to identify and to define the object of the LCA and to limit it to include that which is significant for the goal of LCA:

- Defining the object of study, including defining the functional unit:

  The object of this study is a specific activity that is necessarily carried out in all the semiconductor manufacturing fabs, CVD chamber cleaning, and the importance of this cleaning has already been mentioned.

  The functional unit in this study is the cleaning of the chamber. Two chemicals recipes have to fulfill this service, which also means that both of them are compared on an equal level.

- Selecting one or more reference products or reference systems to represent the object of the study
- Designating the environmental assessment parameters which are important for the goal of the LCA

  In this study, we are dealing with production and use of hazardous gases. After identifing the character of the gases, we can see the environmental assessment parameters which are important here are:

  - Ozone depletion potential
  - Human toxicity (cancer/non cancer)
  - Global warming
  - Photochemical smog

- Acidification

- Identifying the environmentally significant process in the product system, connect with the goal definition of LCA

  The suspected significant process includes the energy generation of making both chemicals, the emissions that are generated while making the chemicals, and usage of the chemicals.

- The boundary condition of the study was not initially defined, the reason of that is because we do not know how much data is available. Most of the cost and process data is propitiatory information, which is difficult to get. For the fairness of the comparison, chamber cleaning and immediate production has been considered within the boundary for this case study. While removing from consideration the upstream processes.

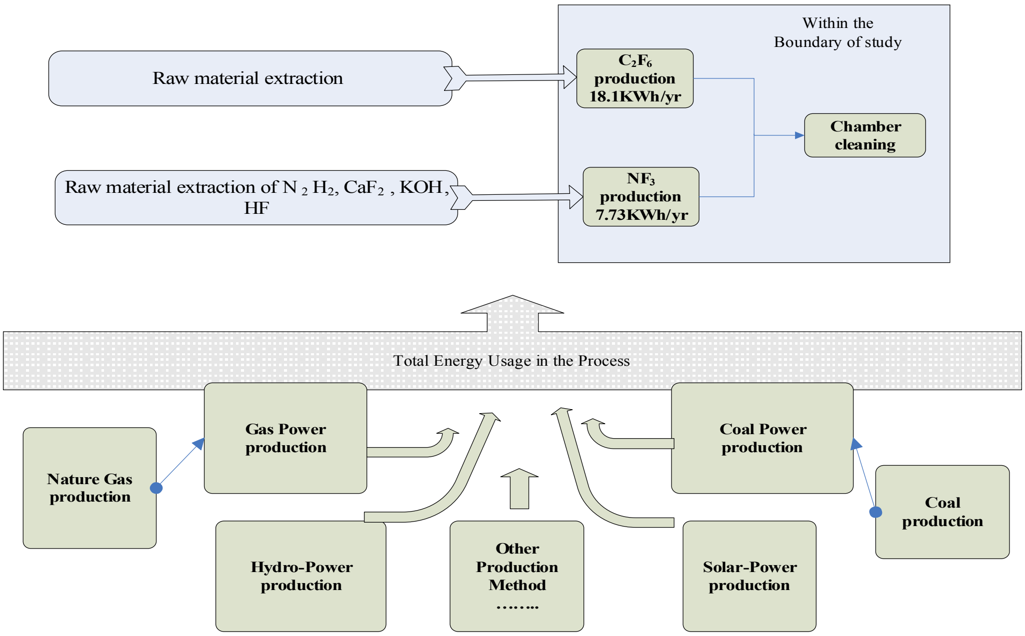

Figure 5 *boundary condition of this study*

We can conduct a study in multi-boundaries and this may affect the final results. For example, we can study only the condition and use of the cleaning tools, which is a boundary that excludes making of the chemicals and the precursors. Or, we can have a boundary which is only the abatement strategies of both chemicals. With each study with different boundaries, we can have a more focused view to identify where the improvement opportunities are or where the most crucial process is from an environmental standpoint.

5.4 INVENTORY ANALYSIS

In this work, we have decided to build the process information from published data and patent information. It then inherently leads to some uncertainty through the estimation of some data. In most cases, the data extracted from a patent is not very precise and may create a gap between reality and the research outcome. In all cases, we have sought feedback from industrial partners to verify that our estimates are reasonable compared to real processes.

We have selected the process and products at this point of LCA. Their product systems have been established, and the scopes are defined. From the various literatures we have gathered and studied, some assumptions are made. Of course the uncertainty issue appears every time you have made an assumption, but in this study, uncertainties are unavoidable.

5.4.1 MAJOR ASSUMPTIONS

1) Etch rates: this differentiates the rate of both chemicals need to satisfy the function of cleaning.
2) Cleaning time is not an issue here, which we keep in a reasonable range. This means that even if one of the chemicals can shorten the clean time, it will not have an impact on this study. This is assumed because we have identified that in most fabs, cleaning downtime is not a real issue. (One of the improvements this study offers is that after we have identified this phenomenon, we suggest that dilute NF_3 can lower the environment impact on NF_3 chamber cleaning, still maintain a reasonable time and quality of chamber clean) [22].

3) The fabrication facility produces 20,000 wafers a year.
4) Destruction rate: NF_3 is 99%, C_2F_6 is 50% in usage.
5) Energy sources are from the same kind of source regardless of the cleaning system. This means we can just calculate the impact on the environment (energy side of story) by comparing the difference in energy usage.
6) Both processes clean in one cycle, which means there is no yield loss for both processes, also meaning that the two can clean the chamber to the same quality.

5.4.2 MODEL THE EMISSION DATA FROM THE NF_3 CHAMBER CLEANING PROCESS

In the NF_3 chamber cleaning process:

$$
\begin{aligned}
&2NF_3 + plasma \rightarrow N_2 + 6F^- \quad destruction\ rate \geq 99\% \\
&6F^- \rightarrow 3F_2 \geq 99\% \\
&4F^- + Si \rightarrow SiF_4 \leq 1\%
\end{aligned}
$$

Abatement process:

$$
\begin{aligned}
&H_2 + F_2 \rightarrow 2HF + Heat \\
&HF + water \rightarrow HF_{(aq)}
\end{aligned}
$$

Notice that much fluorine has been generated and then has to be abated; it is a very important feature of NF_3 chamber cleaning. PFC has been destructed, but at the same time has a lot of fluorine get involved in the process.

Also, in studying the NF_3 process, we have noticed that the argon flow rate and chamber pressure don't have a significant effect on chamber cleaning time. One of the biggest advantages is that the cleaning time is short. However dilute NF_3 will work until 350 sccm.

In this study, overetch of 20% is sufficient, proven that at this condition, the chamber is cleaned. From that table 2, we can see a normal recipe for NF_3 cleaning is as following:

Table 2 sample of recipe for NF_3 cleaning

NF_3 flow rate (sccm)	cleaning time (s)
1500	52
700	99
1400	77

To evaluate the two processes on a fair basis this means that both of the chemicals fulfill equal functionality: cleaning the chamber. A flowrate relationship has been established for C_2F_6 and NF_3:

Table 3 comparison NF_3 and C_2F_6 chamber cleaning inputs

recipe			average cleaning time (s)
NF_3/argon	NF_3 1400 sccm	Argon 2000 sccm	80
C_2F_6 optimized	C_2F_6 900 sccm	O_2 900 sccm	220

The chamber cleaning emission data is shown in the following table[23-25], with units in scc, standard cubic centimeter.

Table 4 emission data for NF_3 process and C_2F_6 process

Emission	amount
NF_3 flow rate (sccm)	1400
influent NF_3 (scc)	1860
clean time (s)	80
NF_3 (scc)	5
CF_4 (scc)	2
SiF_4 (scc)	398
F_2 (scc)	2333
HF(scc)	50
COF_2 (scc)	21
F balance	1.14

Emission	amount
C_2F_6 flow rate (sccm)	900
O_2 (sccm)	900
influent C_2F_6 (scc)	3300
clean time (s)	220
C_2F_6 (scc)	924
CF_4 (scc)	1570
SiF_4 (scc)	818.23
CO (scc)	759.2
CO_2 (scc)	2421.7

From this information we can figure out the flowrate needed for chamber cleaning, thus linking us to the production input and outputs in the manufacturing process.

5.4.3 MANUFACTURING PROCESS

NF_3 manufacturing process

This process involves the production of nitrogen trifluoride and the purification of this product to 99.5%. The process involves two reactions. The first reaction (1) produces nitrogen trifluoride. The second reaction (2) separates the undesirable product HF from the first reaction by reacting it with potassium hydroxide.

$$NH_4FHF + 3F_2 \rightarrow NF_3 \; + \; 5HF$$

(ammonium acid fluoride + fluorine $\rightarrow$ nitrogen trifluoride + hydrogen fluoride

$$KOH + HF \rightarrow KF \; + \; H_2O$$

(potassium hydroxide + hydrogen fluoride $\rightarrow$ potassium fluoride + water)

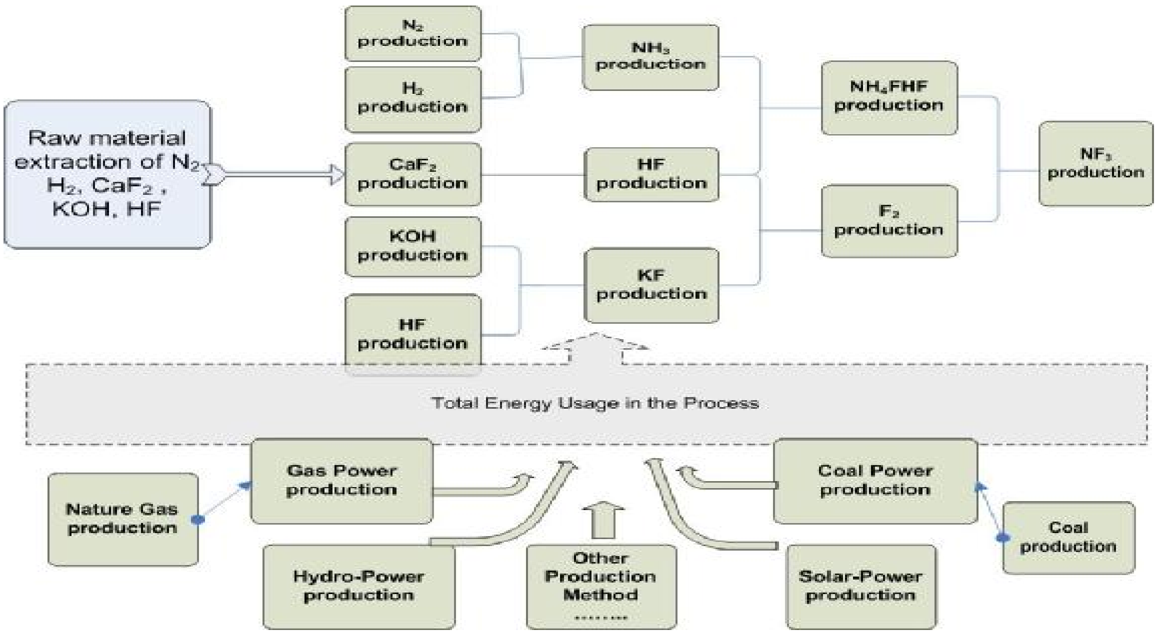

Figure 6 *upstream of the NF_3 production*

After this reaction, the product gases leave the reactor and enter a mist eliminator. This unit is used to remove unreacted liquid ammonium acid fluoride. The liquid ammonium acid fluoride returns to the reactor. The effluent gas from the mist eliminator enters the recovery system. The first recovery unit is a simple trap that condenses HF and it is followed by a scrubber. In the scrubber, potassium hydroxide reacts with residual hydrogen fluoride to produce KF salt that is purged from the system. Next, the gases flow through a cold trap that condenses a considerable amount of the water vapor produced in the scrubber. The partially dried gas stream enters alternate molecular sieve dryers that remove all traces of water. The next separation step is a condensing heat exchanger. Here the temperature is reduced to an extremely low value near liquid nitrogen temperatures. At these temperatures, virtually all of the NF_3 condenses and is separated from the residual gaseous N_2 and the trace F_2. The residual nitrogen is vented and the liquid nitrogen fluoride product is sent to a distillation column where it is separated from the trace amount of CF_4. The final product leaving the distillation column is 99.5% pure electronics grade NF_3 [26]. A flowsheet is shown in the appendix.

Input

Chemical	Amount (kg / hr)
Fluorine	2630.39
Ammonium Acid Fluoride	814.74
Potassium Hydroxide	1250.00
Nitrogen	8,166.422
Carbon Tetrafluoride	14.548
Water	95,393.724

Product

Chemical	Amount (kg / hr)
Nitrogen Trifluoride	1000.0

Process Emissions

Chemical	Amount (kg / hr)
Fluorine	1002.055
Hydrogen Fluoride	1000.357
Potassium Hydroxide	48.027
Potassium Fluoride	1244.824
Nitrogen	8166.422
Carbon Tetrafluoride	14.548
Water	95,779.392
Mass Balance Difference	14.191

Potassium hydroxide is a required input and is manufactured by the electrolysis of potassium chloride brine in electrolytical cells. The brine feed is filtered to remove insoluble materials, and then is pre-heated to 60 C and passed to an equalizer tank.

From the equalizer tank, the brine is fed to the cell. Hydrogen and chlorine are withdrawn from the cell. The rest of the reaction mixture contains KOH, water, and unreacted potassium chloride. This reaction mixture is then concentrated to 50% of KOH in an evaporator. Most of the KCl crystallizes during concentration by evaporation, and it is sent back to the cell.

After evaporation, the liquor is cooled and then passed to a crystallizer, where the potassium hydroxide precipitates. The liquor is then filtered, the filtrate is discarded as water waste, and the cake is dried to yield the final product.

C_2F_6 manufacturing process

We can build a process according to the patents we have found on this subject [27].

This process involves the production of perfluoroethane and the purification of this product to 99.5%. The process involves several reactions.

$$C_2Cl_2F_4 + HF \rightarrow C_2ClF_5 + HCl \qquad \textbf{(1)}$$

Disproportionation of $C_2Cl_2F_4$

$$2CClF_2 - CClF_2 \xrightarrow{disprop} CCl_2F - CClF_2 + CClF_2 - CF_3$$
$$2CCl_2F - CF_3 \xrightarrow{disprop} CCl_3 - CF_3 + CClF_2 - CF_3$$
$$\rightarrow FCCl_2 - CClF_2 + CClF_2 - CF_3$$
$$CCl_2F \xrightarrow{isomerization} CCl_3 - CF_3$$
$$CCl_3 - CF_3 + HF \rightarrow FCCl_2 - CF_3 + HCl$$
$$CCl_2F - CClF_2 \rightarrow CClF_2 - CF_3 + HCl$$
$$CClF_2 - CF_3 + HF \rightarrow CF_3 - CF_3 + HCl$$

The production of C_2F_6 by catalytic fluorination of CFC114 is a multi-unit process involving many separation steps. The procedure can be simplified into two main categories: creation of C_2F_6 and side products, and separation of C_2F_6 from these side products. The process begins by contacting HF and CFC114 in a reactor. This is accomplished by finely dispersing HF gas and CFC114 into the bottom of a reactor. Upon mixing these components, a series of reactions will occur:

$$2CClF_2 - CClF_2 \xrightarrow{disprop} CCl_2F - CClF_2 + CClF_2 - CF_3$$
$$2CCl_2F - CF_3 \xrightarrow{disprop} CCl_3 - CF_3 + CClF_2 - CF_3$$
$$\rightarrow FCCl_2 - CClF_2 + CClF_2 - CF_3$$
$$CCl_2F \xrightarrow{isomerization} CCl_3 - CF_3$$
$$CCl_3 - CF_3 + HF \rightarrow FCCl_2 - CF_3 + HCl$$
$$CCl_2F - CClF_2 \rightarrow CClF_2 - CF_3 + HCl$$
$$CClF_2 - CF_3 + HF \rightarrow CF_3 - CF_3 + HCl$$

After these reactions, the product gases leave the reactor and enter a washer. This unit is used to remove some of the HF and HCl. The rest of the products include organic C_2F_6 CFC113, CFC114, and CFC115. Inorganic HF and HCl returns to the reactor. The effluent gas from the cold trap enters the recovery system. In this recovery system, azeotropic distillation with HCl is used in a column for purifying a feed stream containing the stated chemical stream. Anhydrous HCl has been added to draw an azeotropic component with the desired purification product CFC116. The first recovery unit is a distillation column. The hexafluoroethane product leaves in the column distillate steam as an azeotropic or azeotrope-like composition with HCl; the remaining HCl and CFCs exits in the column bottoms. The PFC116 and azeotroped HCl are then cooled to a temperature around -50^{o}C and the two layers are separated in a decanter. The PFC116 layer is then sent to a second distillation column for removing the remaining HCL as an overhead azeotrope; the recovered HCl may be then recycled to the first distillation column. The PFC116 from the bottoms of the second distillation column is then given some further purification steps before using. The final product leaving the distillation column is 99.5% pure electronics grade C_2F_6. a simplified flowsheet is shown as in figure 7, and a more detailed flowsheet is shown in appendix. From the past 2 sections, one can see the complexities building even just the first precursor step for upstream LCA. This is why studies will use mostly a “gate-to-gate” approach.

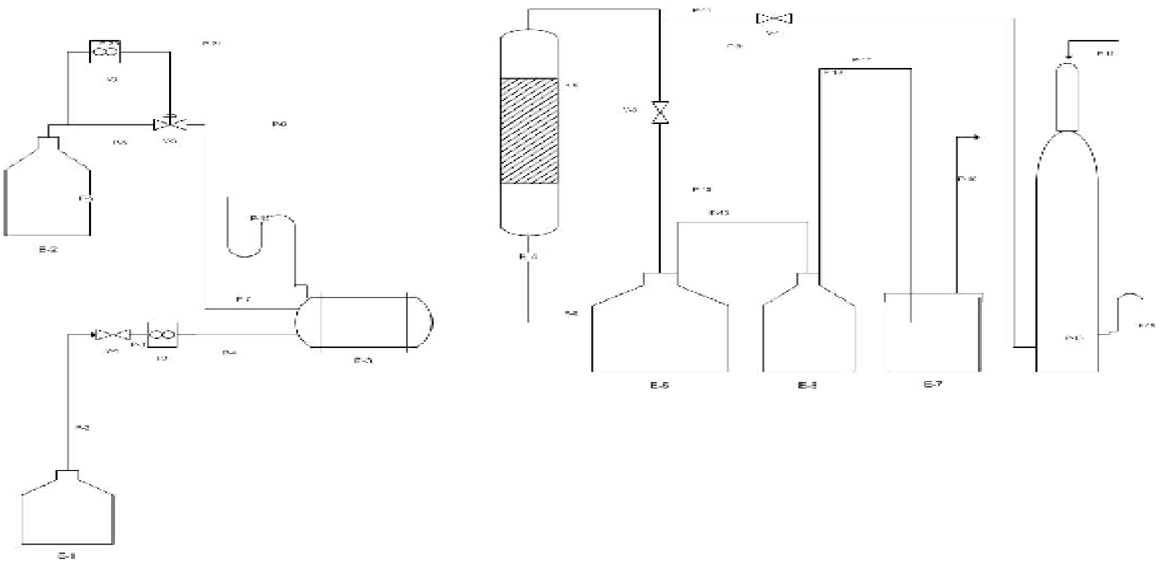

Figure 7 *manufacturing process for C_2F_6*

Inputs

Chemical	Amount (kg / hr)	Comments
$C_2Cl_2F_4$	1002.06	
HF	1724.39	
HCl	1250.00	Azeotropic add

Product

Chemical	Amount (kg / hr)	Comments
C_2F_6	1000.0	99.95% pure

Process Emissions

Chemical	Amount (kg / hr)
Hydrogen Fluoride	29.59
$C_2Cl_3F_3$	174.748
$C_2Cl_2F_4$	2035.49
C_2ClF_5	7967.85
Nitrogen	3200.68
HCl	3752.92

5.4.4 USE PHASE

The use of nitrogen trifluoride (NF_3) in the presence of argon has been examined for oxide etching in inductively coupled, high density plasma etch tool [28]. In the use phase, we can compare the process usage and emissions. Because NF_3 is ionized more efficiently to atomic fluorine than C_2F_6, and because the recombination of atomic F is reduced due to the chamber lid design, clean times can be reduced significantly, increasing wafer throughput. Clean time reductions of 25–30% for a resistively-heated chamber and up to 65% over the optimized C_2F_6 clean with 20% over-etch for a chamber have been reported.[29]

5.5 LIFE CYCLE INTEPRETATION

As in this part of the life cycle, we use a metric called million metric tons of carbon equivalent (MMTCE) in an attempt to quantify the relative impacts a process will have from an emission standpoint. This quantity is calculated as following:

$$MMTCE = \frac{\sum_i Q_i \times (12/44) \times GWP_{100i}}{10^9}$$

Where, Q_i is the total PFC amount emitted. And GWP100i is the global warming potential of that PFC as calculated over a 100 year time horizon.

$$kgCE = \sum_{i=1}^{n} Q_i \times \frac{12}{44} \times GWP_{100i}$$

From the data for each process, we can calculate the emission impact on the environment in various categories. ODP (ozone depletion potential) is not evaluated, because no halocarbon is emitted here, it will only be evaluated in the C_2F_6 case.

Other categories have been carefully evaluated:

- Ozone depletion potential
- Human toxicity (cancer/non cancer)
- Photochemical smog
- Acidification
- Depletion of abiotic resources

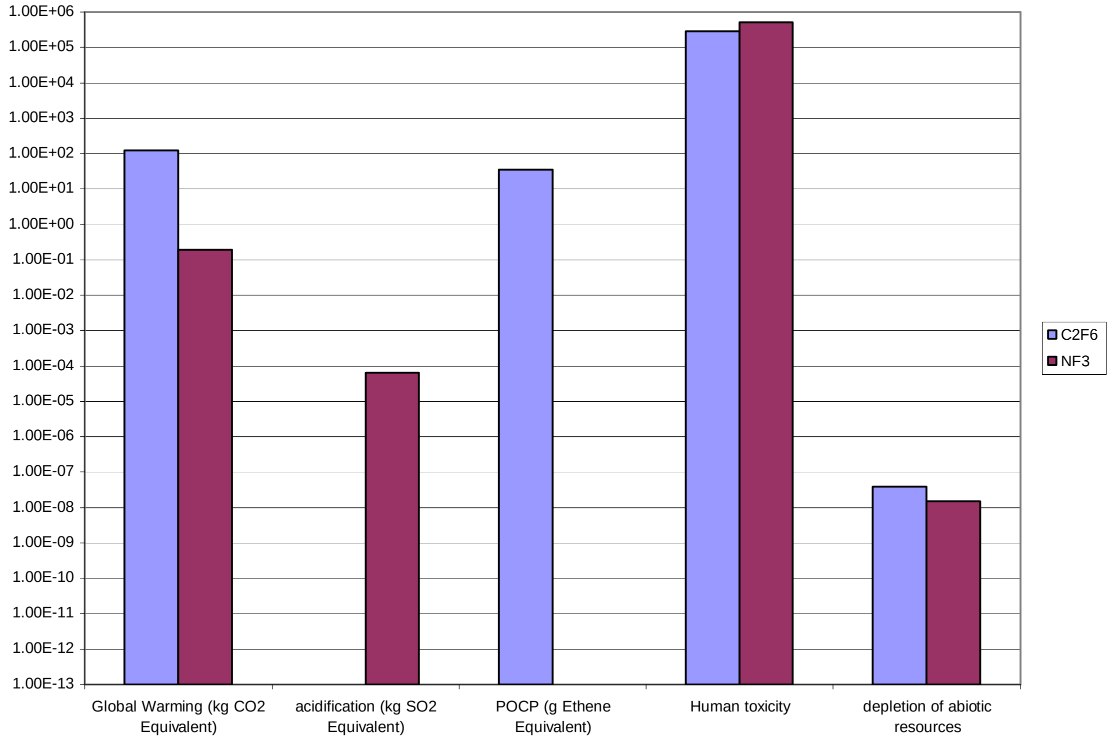

Figure 8 *Environmental impacts for the two chamber cleaning cases*

As we can see here, C_2F_6 is eventually worse in almost every category. That means we have made a correct shift for the new technology.

5.6 LIFE CYCLE IMPROVEMENT

After close study of the NF_3 and C_2F_6 chamber cleaning processes, we have identified some opportunities to improve both processes.

1) For the NF_3 process, we can lower the NF_3 flow rate which will decrease the density of the emissions and lower emission. Although the cleaning time will be increased in this case, according to literature and reports, the chamber is not always fully capacitated and saved the time by using higher density flow is not going to generate economic benefit.
2) We can adapt some new technologies in the process, which includes use gas circulation, which will have an improved usage for C_2F_6 process.

According to a study that has been done at Motorola, an evaluation of lower NF_3 flow was conducted to determine the lowest achievable NF_3. A recipe has been found in a very low concentration to fulfill the function of cleaning chambers. [30] Also, there are some other gases that can be viewed as alternative designs for NF_3 or C_2F_6. For example, in a Novellus Concept One 200 dielectric PECVD tool, we can calculate the data as shown in the following table, which reveal that C_3F_8 can be a good chemical to turn to as an alternative for chamber cleaning application.

Table 5

method	Cleaning time(s)	MMTCE ($\times 10^9$)
C_2F_6	370	58
C_3F_8	380	50
NF_3+C_2F_6	290	54.2

5.7 CoO AND ENERGY STUDY

Cost-of-Ownership (CoO) models have met wide acceptance in the semiconductor world for helping decide which process and which tool is best suited for a particular task. In the compound semiconductor world, there are many different techniques and processes. In addition to device types, as the production volumes increase, dominant techniques tend to emerge, and this helps simplify some of the decision making.

Cost of ownership considerations:

- Design costs
- Purchase price
- Installation costs
- Operation costs
- Calibration costs
- Reagents and other consumables
- Spares cost and availability
- Power requirement

- Training costs
- Depreciation and replacement costs

CoO Study for this particular case has included:

- Capital cost: equipment, installation of equipment, water circulation system.
- Operation cost: maintenance cost, required abatement cost, consumable equipment and gas cost
- Cleaning consumables cost: NF_3 and C_2F_6 cost (unit price: C_2F_6 \$25/lb; NF_3 \$110/lb

C_2F_6Process + TPU Abatement	**Remote NF_3 Retrofit**
TPU Unit Cost = \$30,000	Remote Plasma Unit Cost = \$59,900 (1 Chamber)
Installation=\$30,000	Installation=\$3,360 (Labor Only Amortized Over
Methane Installation = \$30,000	Facilitization Not Included
Water Recirculation Unit Cost =	Requires: NF_3 and Argon Plumbed to System
Consumables = \$4,500/yr	AC Power From System Controller
Maintenance = \$2,000/yr	Preventive Maintenance Kit = \$11,000/yr
Methane = \$2,400/yr	NF_3 Process: 50 lbs NF_3/yr @ \$110/lb
Standard Process: 100 lbs C2F6/yr @	TCU Unit Cost = \$85,000

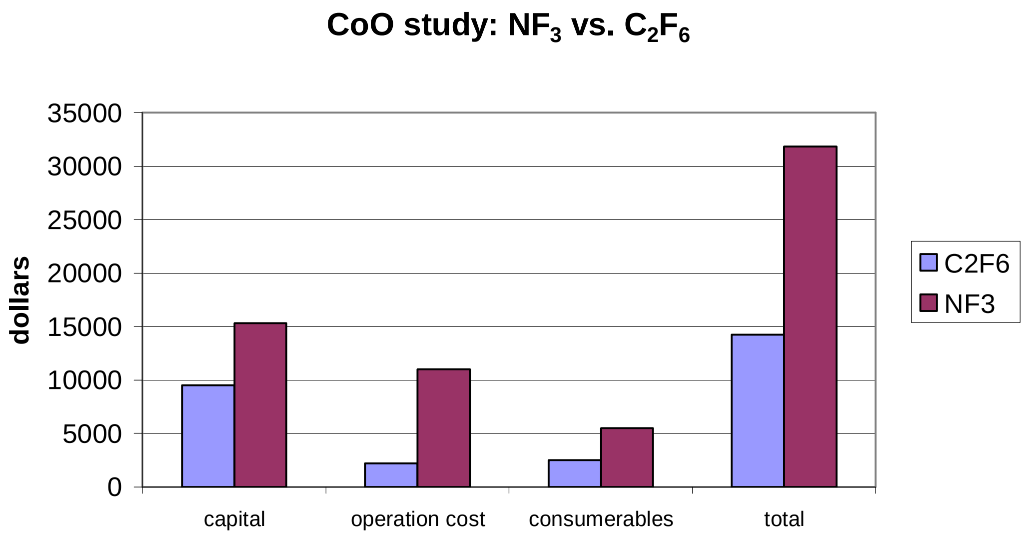

Figure 9 *COO study of NF_3 and C_2F_6 in the chamber cleaning case*

This means that the final cost per wafer for the C_2F_6 process is \$0.71/wafer, and for the NF_3 process is \$1.592/wafer. The higher CoO for the NF_3 has been broken down into categories, and the two cleans had significant price differences for equipment cost, and installation, consumerables.

The energy usage for both systems in the clean stage only, uses 5880 KWh/year [10]. A standard process use 100 lbs C_2F_6/yr, or 50 lbs NF_3/yr. Linked to the energy usage for production of both chemicals, we can see that the NF_3 process production energy usage is 164.83 KWh/yr, while C_2F_6 production system need 18.1 KWh/yr.

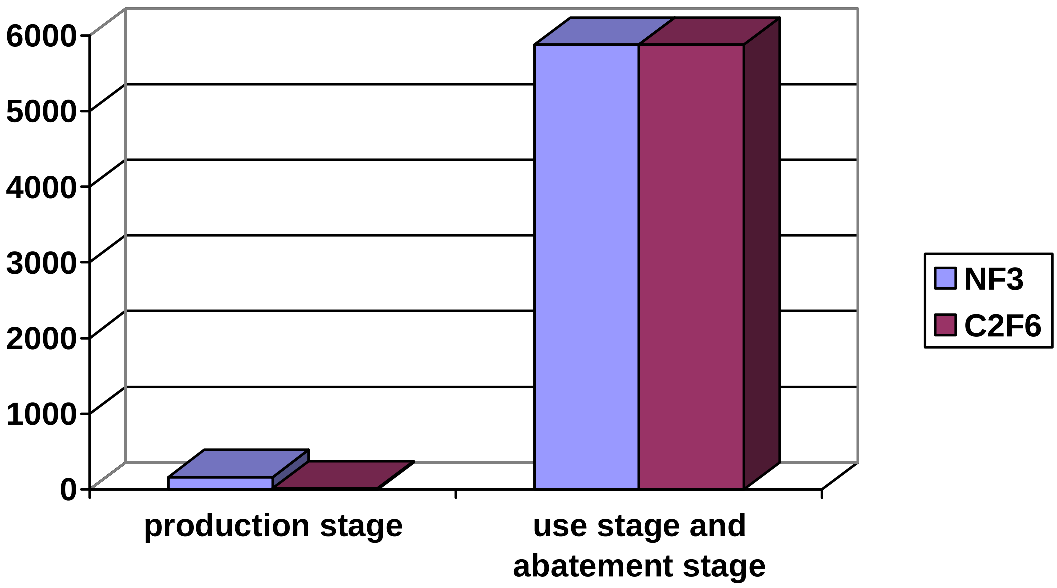

Figure 10 *Energy analysis for the chamber cleaning study*

From the comparison of LCA study and CoO study, we see that they do not agree with each other. If we make a decision according to the cost of ownership study like we used to do, it is going to be a choice that is based on partial evaluation of the systems. If we choose C_2F_6 as solution here, it is going to actually bring larger impacts on the environment.

On the other hand, we should not only make a decision based on the LCA study. It is very helpful in making the decision, but it can not replace decision-making itself. With the incorporation of the CoO study and life cycle study, the decision-maker can obtain a better view of the circumstances.

5.8 CONCLUSIONS

Remote plasma clean technology represents a new approach to PFC emissions reduction in that NF_3 is substituted for C_2F_6, producing considerably less amounts of the CF_4 greenhouse gas. Advantages in throughput and uniformity are also attributed to the remote plasma clean. However, the associated increase in F_2 emissions using NF_3 requires special consideration. Given the resultant expected increase in fluoride ion load, a thorough evaluation of a site's discharge limits, existing handling/treatment infrastructure and capacity, and air pollution control strategy should be completed before initiating NF_3-based chamber cleans.

CVD tools at most times are not capacity limited [31]. So, the fastest cleaning time achieved in this study might not be the optimum from environmental standpoint. If a reasonable cleaning time could be achieved with lower NF_3 flow, the total cleaning, economic and environment cost can be reduced.

NF_3 performs better in each category of the LCA study, which means that the industry has shifted to a better technology. Due to the lack of information on extraction of raw materials and a huge amount of needed information, this study has been within the "gate to gate" level.

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Chapter 6 RECOMMENDATIONS FOR FUTURE WORK

Through out this thesis, we systematically discussed life cycle assessment methodology and applications. We also discussed the integration of life cycle assessment with design for the environment. There are many opportunities to enable us to incorporate process design with environmental considerations as part of the design objectives rather than taking them as constraints. There is still much room for improvement in our research to implement this goal.

We have focused on using the environmental conscious concept as a decision concept, where it is possible to develop tools that facilitate the generation of green designs that are likely to have lower environmental impact. Also with help of LCA, this designs can be evaluated to prove how “green” they really are. We should always:

- Try to evaluate alternative reaction pathways and catalysts that may result in smaller environmental impacts with improved economics
- Try to quantify non-conventional processes that result in smaller impacts than conventional processes while showing improved economics,
- Develop methods that shorten the time span of LCA studies, especially on the identification of process improvement opportunities,
- Further research on how to handle uncertainties in the inventory stage of LCA study.

In this project we have relied on process simulation and existing literature for the generation of input-output process information. However, some information needed to assess environmental performance is not always available. We have to make this assumption part of the study more robust:

- Incorporate experiments to obtain some of the data
- Improve predictions of reaction rates and undesired byproducts, possibly using ab initio method
- Improve prediction of fugitive emissions and emissions from operations steps
- Include more detailed waste-treatment unit operations in process simulators

The following is a list of ideas for integrating models (e.g. process flow sheet models) with environmental valuation models:

- Incorporate ESH software, such as to Aspen plus, so that important environmental information for chemicals is displayed when a new chemical is added to a model.
- Compile databases with typical chemical processes that include mass and energy balances for widely used chemical and raw materials in the chemical industry to facilitate the characterization and evaluation of upstream processes.
- Further conceptual research on the valuation part of the LCA study. To complete LCA studies, make it more robust and increase its reliability as this part is crucial part, while been the most underdeveloped part.

Also, more case studies are needed for use in chemical engineering education, as this thesis hopefully will be used.

Chapter 7 CONCLUSIONS

- Environmental issues are emerging as one of the major driving forces for change in the chemical industry. A view of product and process design that sees the environment as an objective and not just as a constraint on operations can lead to the discovery of design alternatives with improved environmental and economic performance.
- Life cycle assessment is a systematic tool that quantifies the environmental impacts of products and services, which can lead to big advantages in the decision making process, possibly leading to win-win situation on both economic and environmental aspects.
- Application of the life cycle assessment tools should used to design future regulations on the processes. This should be done more rapidly since knowledge about potential environmental impacts is typically available years before the relevant regulations come along. The tools can also be used to educate customers and companies who do not share the same values regarding the environment.
- Proper environmental assessment of products and processes requires a life cycle perspective. Unfortunately, most life-cycle emission inventories today do not allow users to trace specific emissions back to the first process that originated them. In addition, the data are difficult to maintain as new information becomes available.
- Environmental concerns that are identified early in product or process development can be most effectively and economically resolved and life-cycle studies can be used as tools to aid in decision-making. Life-cycle assessments of products can be valuable from a variety of perspectives.
- LCA helps in decision making, but does not replace it. The fact that LCA always come up with mixed or complex results should not cast a shadow over the usefulness of these results. They reflect complex situations.
- NF_3 performs better in each category of the LCA study, which means that the industry has shifted to a better technology. However, COO study indicated that

NF_3 is costing more to implement, so decision should be based on the social, environmental and economical research findings.

APPENDIX A EQUIVALENCY FACTORS

Table 1 net GWP values for indirect contributions from the indirect greenhouse gases over time periods of 20, 100 and 500 years

Substance	Formula	Indirect effect via:	GWP(indirect), $kgCO_2$/kg substance		
			20 years	100 years	500 years
Methane	CH_4	Tropospheric ozone	24	8	3
Methane	CH_4	Carbon dioxide	3	3	3
Methane	CH_4	Stratospheric water	10	4	1
Carbon	CO	Tropospheric	5	1	0
Carbon	CO	Carbon dioxide	2	2	2
Nitrogen	NO_X	Tropospheric	150	40	14
NMHC	various	Tropospheric	28	8	3
NMHC	various	Carbon dioxide	3	3	3

Table 2 Equivalency factors for acidifying substances, n is the number of H ions released in recipient as a result of conversion

Formula	Conversion	M_W g/mol	n	EF(fs) kg SO2/ kg stof
SO_2	$SO_2+H_2O – H_2SO_3$ - $2H^+ + SO_3^{2-}$	64.06	2	1
SO_3	$SO_3+H_2O – H_2SO_4$ - $2H^+ + SO_4^{2-}$	80.06	2	80
NO_2	NO_2+ '/$_2H_2O+^1/_4O_2$ - $2H^+$-NO_3H^-	46.01	1	0.7
NOx	NO_2+ '/$_2H_2O+^1/_4O_2$ - $2H^+$-NO_3H^-	46.01	1	0.7
NO	NO+ '/$_2H_2O+O_3$ - H^+-$NO_3^-+^3/_4O_2$	30.01	1	1.07
HC1	HCI –$H^+ + Cl^-$	36.46	1	0.88
HNO_3	HNO3 -$H^+ + NO_3^-$	63.01	1	0.51
H_2SO_4	H2S04 - $2H^+ + SO_4^{2-}$	98.07	2	65
H_3PO_4	H_3PO_4 - $3H^+ + PO_4^{3-}$	98	3	0.98
HF	HF - $H^+ + F^-$	2001	]	1.6
H_2S	$H_2S + ^3/_2O$- H_2O - $2H^+ + SO_3^{2-}$	34.03	2	1.88
NH_3	NH_3+2O_2, - $H^+ + NO_3^- + H_2O$	17.03	1	1.88

Table 3 Total ODP values and atmospheric lifetimes for the most important man-made halocarbons ODP

Substance	Formula	Atmospheric lifetime, years	Total ODP gCFCll/g subsance
CFCs			
CFC 11	$CFCl_3$	50±5	1
CFC 12	CF_2C1_2	102	0.82
CFC 113	$CFC1_2CF_2C1$	85	90
CFC 114	CF_2OCF_2Cl	300	O.S5
CFC115	CF_2ClCF_3	1700	0.4
Tetrachloromet	CC14	42	1.2
HCFCs			
HCFC22	CF_2HCl,	13.3	0.04
HCFC123	CF_3CHCl_2	1 4	0.014
HCFC124	CF_3CHFC1	59	3
HCFC141b	CH_3CFC1_2	9.4	0.1
HCFC142b	CH_3CF_2C1	19.5	0.05
HCFC225ca	$CF_3CF_2CHC1_2$	2.5	0.02
$HCFC_{22}5cb$	CF_2C1CF_2CHFCI	6.6	0.02
1,1,1-tnchloroethane	CH_3CC1_3	5.4±0 4	0.12
Methyl chloride	CH_3C1		0.02
Brominated substances			
Halon 1301	CF_3Br	65	12
Halon 1211	CF_2ClBr	20	51
Halon 1202	CF_2Br_2		-1.25
Halon 2402	CK_2BrCF_2Br	25	~7
HBFC 1201	CF_2HBr		~ 1.4
HBFC2401	CF_3CHFBr		-0.25
HBFC 23 1 1	$CF_3CHClBr$		-0.14
Methyl bromide	CH_3Br	3.3	0.64

Table 4 POCP values for individual substances and functional groups of substances for use as characterization factors in calculation of impact potentials.

Substance	POCP (low No.)	POCP (high No,)	Substance	POCP (low NO,)	POCP (hij-h NO,)
	g C_2H_4/g gas	g C_2H_4/g gas		g C_2H_4/g gas	g C_2H_4/g gas
Alkanes	04±0.1	0.4±0.1	1,2,4-Trimethyl-Benzene	0.3	1.2
Methane	0.007	0.007	1,2,5-Trimethyl-Beazene	0.3	1.1
Ethane	0.1	0.1	O-Ethyltoluene	0.4	0.7
Propane	0.5	0.4	M-Ethyltoluene	0.4	0.8
N -Butane	0.5	4	P- Ethyltoluene	0.4	0.7
I-Butane	0.4	0.3	N-Propylbenzene	0.5	0.5
N-Pentane	0.3	0.4	Isopropylbenzene	0.5	0.6
I-Pentane	0.3	0.3	Aldehydes	0 3±0.2	0.5±0 4
N-Hexane	0.5	0.4	Formaldehyde	0.3	0.4
2 -Methylpentane	0.5	0.5	Acetaldehyde	0.2	0.5
3 -Methylpentane	0.4	0.4	Ppropionaldehyde	0.2	0.6
2.2-Dimethylbutane	0.3	0.3	Butyraldehyde	0.2	0.6
2.3-Dimethylbutane	0.4	0.4	Lsobutyraldehyde	0.3	0.6
N-Heptane	0.5	0.5	Valeraldehyde	0.3	0.7
2-Methylhexane	0.5	0.5	Acrolein	0.8	0.8
3-Methylhexane	0.5	0.5	Benzaldehyde	-	-0.3
N-Octane	0.5	0.5	Ketones	0.2±0. 1	0.4±0.2
2-Methylheptane	0.5	0.5	Acetone	0.1	0.2
N-Nonane	0.4	0.5	Methyl Ethyl Ketone	0.2	0.4
Z-Methyloctane	0.5	0.5	Methyl I-Butyl Ketone	0.3	0.6
N-Decane	0.4	0.5	Alcohols	0.2±0.02	0 3±0. 1
2-Methylnonane	4	0.4	Methanol	0.2	0 1
N-Undecane	0.4	0.4	Ethanol	*0.2*	0.3
N-Dodecane	3	0.4	Isopropanol	0.2	0.2
Nethylcyclohexane	0.5	06	Butanol	0.2	0.4
Alkenes	0.5±0.2	0.9±0.1	Isobutanol	3	0.3
Ethylene	1	1	Butan-2-Diol	0.3	0.3
Propylene	0.6	1	Ethers	0.4±0 1	0.4±0.2
L-Butene	0.5	1	Dimethyl Ether	3	03'
2-butene (trans)	0 1	1	Propylene glycol methyl ether	0.5	0.5

i-pentene	0.4	1.1	Esters	0.2±0.1	02±0.1
2-pentene (trans)	0.4	0.9	Methyl acetate	0.1	0.03
2-methylbut-1-ene	2	0.8	ethyl acetate	1	2
2-methylbut-2-ene	0_5	0.8	Isopropylacetate	0.2	0.2
3-methylbut-l-ene	0.5	0.9	n-bulyl acetate	0.3	0.3
Isobutene	0_6	0.6	Isobutyl acetate	4	0.3
Isoprene	6	08	Propylene glycol methvl ether acetate	2	0.1
Alkynes	0.4	0.2	chloroalkanes	0.01 ±0.01	0.004±0.004
Acetylene	4	0.2	Methylene chloride	2	0.01
aromatics	0.4±0.1	0.8±0.3	Chloroform	0.004	0.003
Benzene	0.4	0.2	Metthyl chloroform	2	0001
Toluene	0.5	0.6	Chloroalkenes	0.2±0.3	03±04
o-xylene	0.2	0.7	Trichloroethylene	0.1	o.r
m-xylene	0.5	1	Tetrachloroethylene	1	0.01
p-xylene	0.5	0.9	Allyl chloride	0.5	0.7
Ethylbenzene	0.5	6	Inorganic		
1,2,3-trimethyl -benzene	0.3	1.2	Carbon monoxide	4	0.03

Table 5 physical properties of PFCS used in the semiconductor manufacturing process

Property	Units	CF_4	C_2F_6	C_3F_8	c-C_4F_8
CAS number	-	75-73-0	76-16-4	79-19-7	115-25-3
Molecular weight	g/mol	88.01	138.01	188.03	200.03
Boiling point at 1 atm	°C	-128	-78.2	-36.7	-6.0
Freezing point	°C	-186.8	-100.7	-183	-40.2
Critical temperature	°C	-45.6	L9.7	71.9	115.2
Critical Pressure	MPa	3.74	2.99	2.68	2.32
Critical Volume	l/g	1.59×10^{-3}	1.64×10^{-3}'	1.59x10^{-3}	1.624×10^{-3}
Critical compressibility factor	—	0.227	0.274	0.279	0.279
Liquid molar volume at boiling point	l/mol	0.054773	0.086369	0.117173	0.123887

Acentric factor	—	0.1855	0.2452	0.3264	0.3557
Dipole moment	C m	0.0	0.0	-	0.0
van der Waals volume	l/mol	0.02733	0.04266	0.05799	0.06132
van der Waals area	m^2/mol	4.6×10^5	6.9×10^5	9.2×10^5	9.2×10^5
Refractive index	—	1.151 (-73"C)	1.206 (-73°C)	-	1.217 (25°C)
Viscosity of gas (25 ^{0}C, 1atm)	cp	0.017	0.0144	0.01454	0.01168
Thermal conductivity of gas (25 ^{0}C, 1atm)	J/s cm ^{o}C	1.80×10^{-4}	1.62×10^{-4}	1.38×10^{-4}	-
Solubility in water	mole/l	1.70×10^{-4}	-	-	
Solubility parameter at boiling point	$(J/m^3)^{1/2}$	1.3834×10^{-4}	1.2956×10^4	1.2303×10^4	1.3018×10
Heat of vaporization at boiling point	kJ/kg	135.9	117.0	104.8	116.1

APPENDIX B: DEFINITION AND ISO STANDARD

Environmental Life Cycle Assessment: see Life-Cycle Assessment

Functional Unit: The quantity of product that is used to base calculations of material and energy flows across a system.

Life Cycle: Consecutive and interlinked stages of a product system, from raw material acquisition, through manufacturing, use and final disposal.

Life Cycle Assessment (LCA): Compilation and evaluation of the inputs and outputs and the potential environmental impacts of a product or process system throughout its life cycle.

Life Cycle Impact Assessment (LCIA): A phase of LCA aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts of the product or process system.

Life Cycle Inventor Inventory y (LCI): A phase of LCA involving the accounting of inputs and outputs across a given product or process life cycle.

Life Cycle System: The boundaries of the interconnected activities associated with a product or process including all mass and energy inputs and outputs. A system is defined by the function of a product, process, or activity being evaluated.

Life Cycle Thinking: Using the life-cycle concept to evaluate environmental issues in a holistic system-wide perspective.

Screening LCA: An application of LCA used primarily to determine whether additional study is needed and where that study should focus.

Streamlined LCA: Identification of elements of an LCA that can be omitted or where surrogate or generic data can be used without significantly affecting the accuracy of the results.

ISO 14000 STANDARDS ON LCA

In September 1996, ISO, the International Organization for Standardization based in Switzerland, initiated the ISO 14000 series of environmental management system standards. These are a series of standards that deal with the components of an effective environmental management system along with guidelines for auditing; ecolabeling, environmental performance evaluation, and LCA.

ISO 14000 Series of Environmental Standards (as of September 1999)

ISO 14001 Environmental Management Systems—Specifications with Guidance for Use

ISO 14004 Environmental Management Systems—General Guidelines, Principles, Systems, and Supporting Techniques

ISO 14010 C Guidelines for Environmental Auditing—General Principles on Environmental Auditing

ISO 14011 Guidelines for Environmental Auditing—Audit Procedures— Auditing of Environmental Management Systems

ISO 14012 Guidelines for Environmental Auditing—Qualification Criteria for Environmental Auditors Life Cycle Assessment—Principles and Guidelines, Standards in draft or committee discussion

ISO 14015 Environmental Aspects of Sites and Entities

ISO 14020 Environmental Labels and Declarations—General Principles

ISO 14021 Environmental Labels and Declarations—Environmental Labeling—Declared Environmental Claims—Terms and Definitions

ISO 14024 Environmental Labels and Declarations—Environmental Labeling Type I—Guiding Principles and Procedures

ISO 14025 Environmental Labels and Declarations—Environmental Labeling Type III—Guiding Principles and Procedures

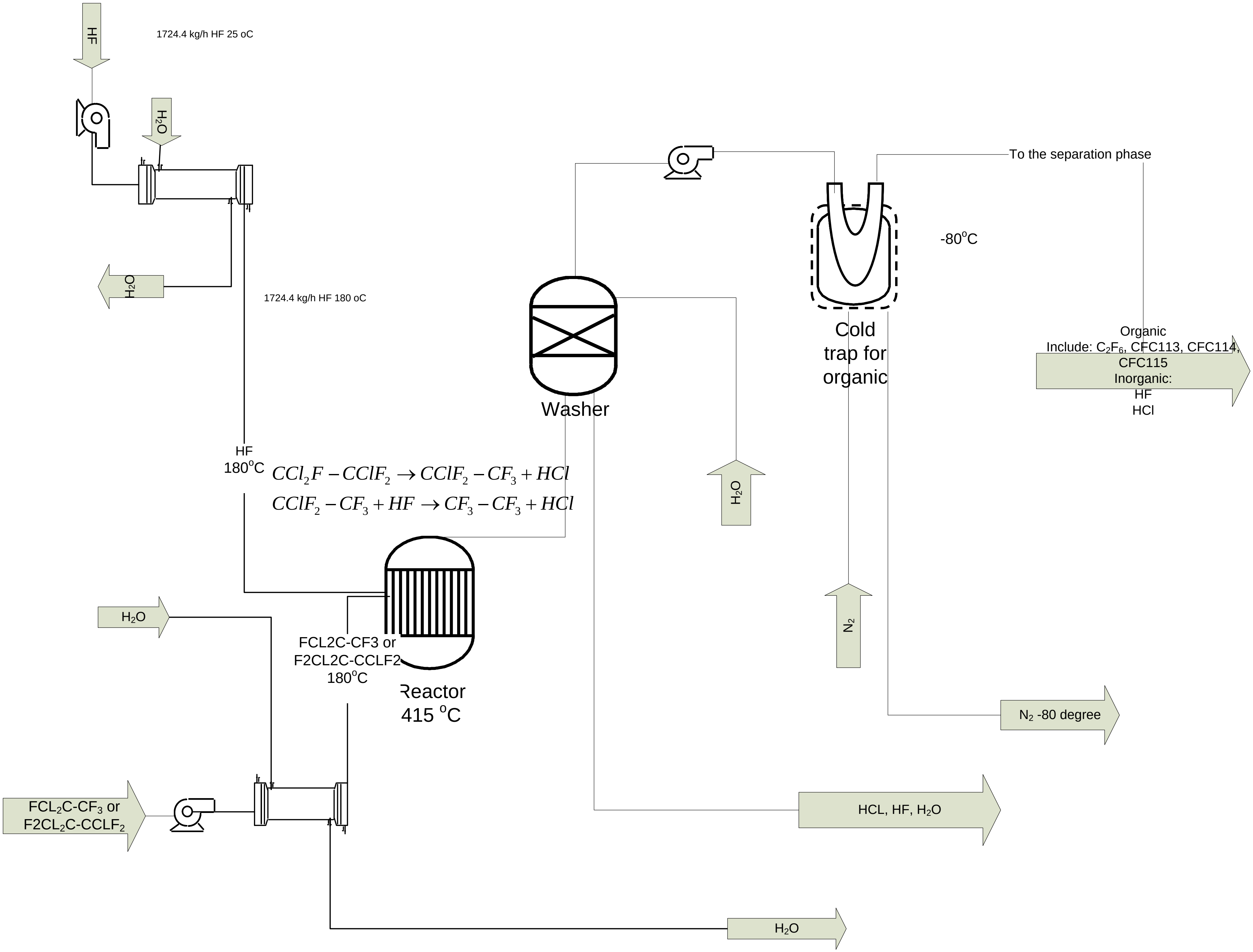
ISO 14031 Environmental Performance Evaluations

ISO 14032 Environmental Performance Evaluation—Case Studies in the Use of ISO 14031

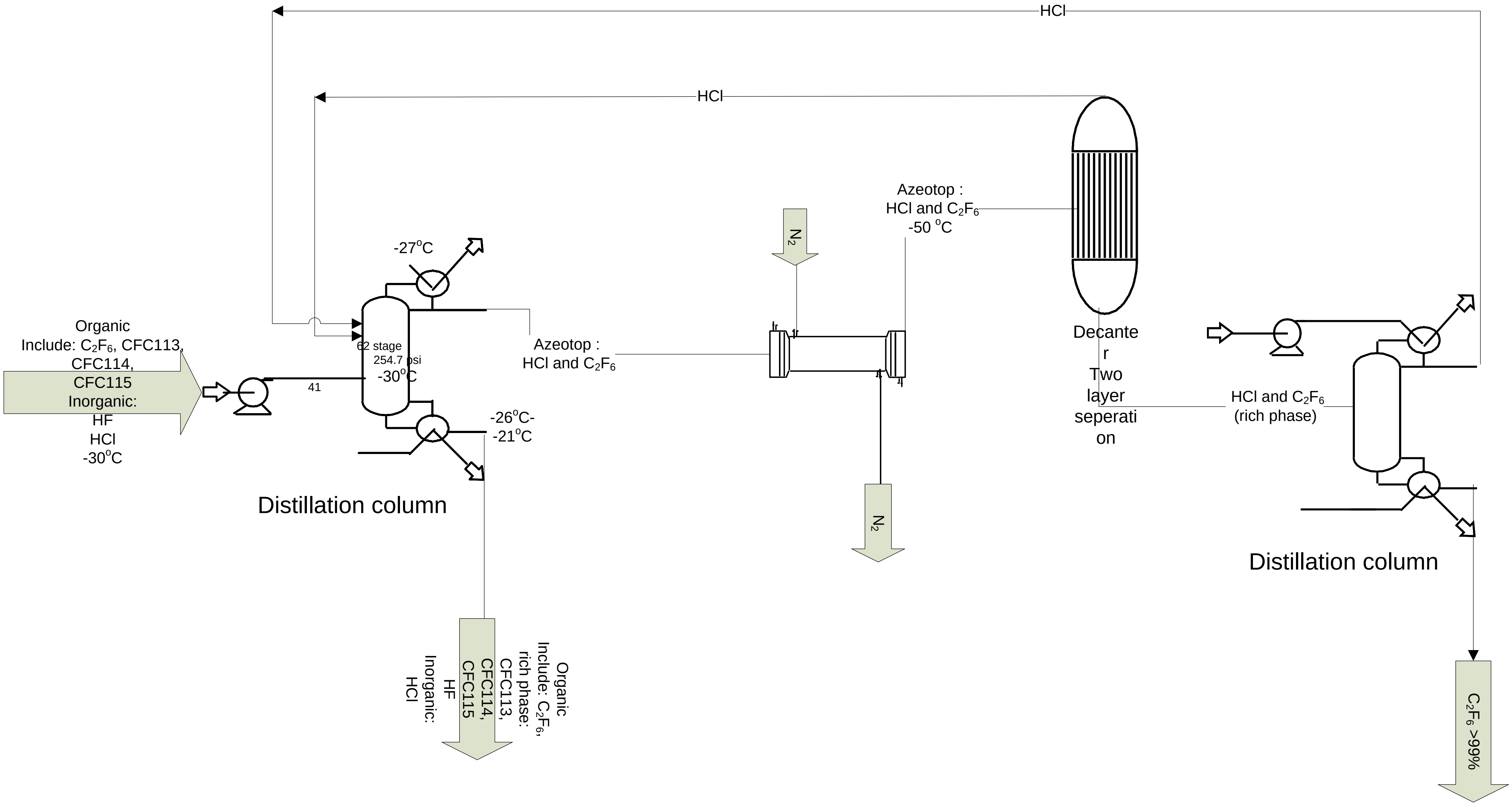
ISO 14041 Life Cycle Assessment—Goal and Scope Definition and Inventory Analysis

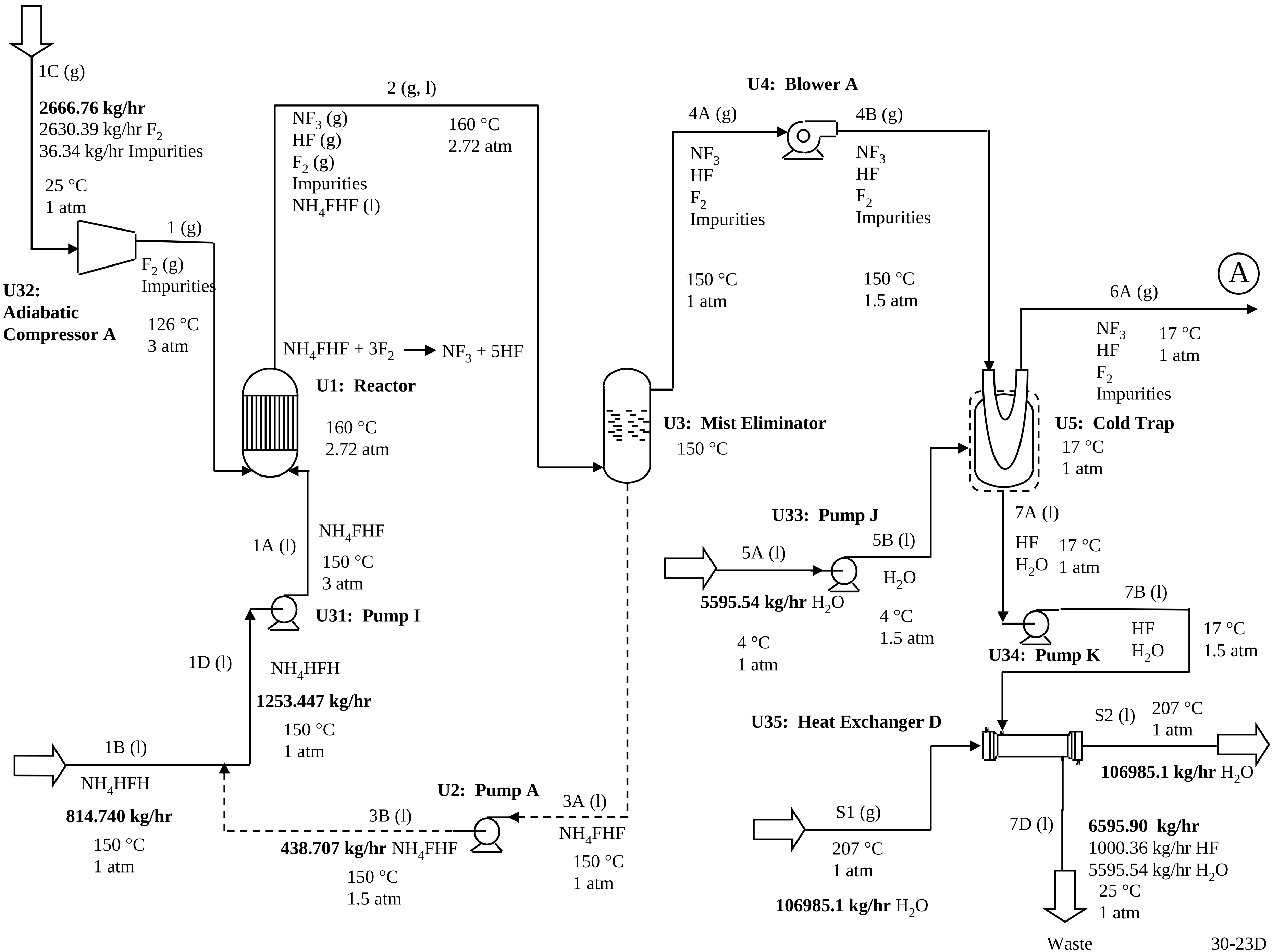
ISO 14042 Life Cycle Assessment-Impact Assessment ISO 14043 Life Cycle Assessment-Interpretation

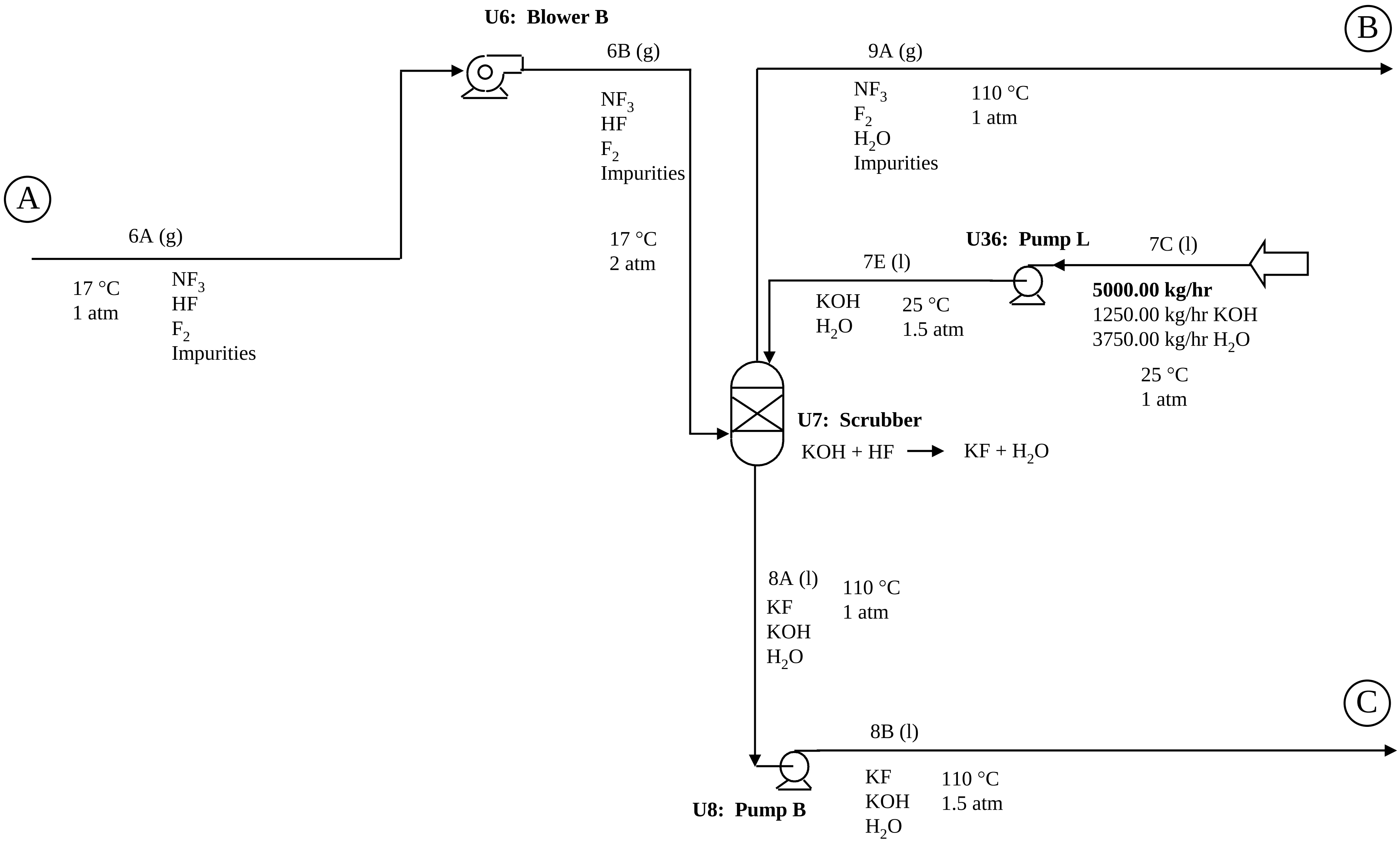
APPENDIX C FLOWSHEET FOR MANUFACTURING NF_3 AND C_2F_6

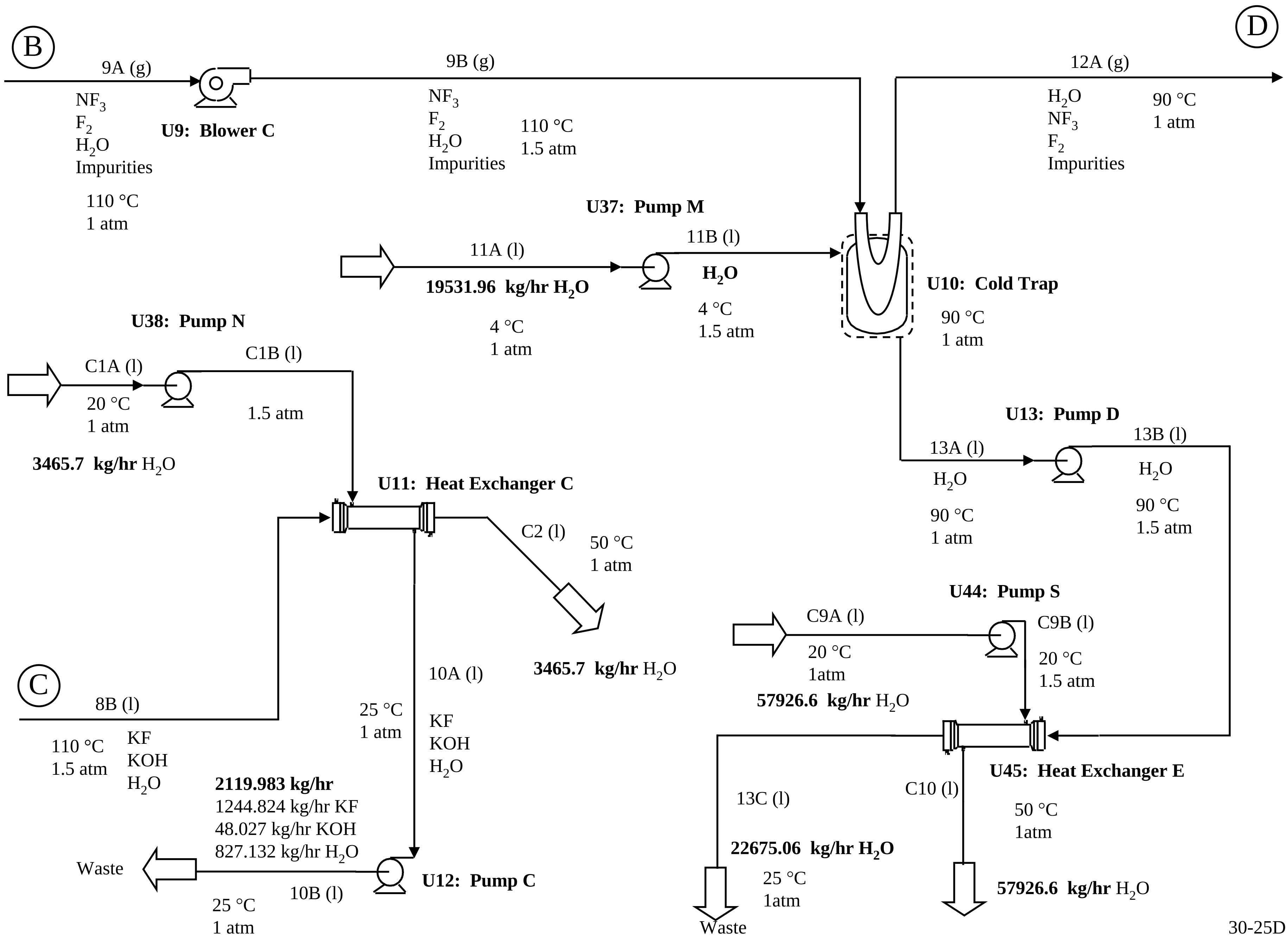


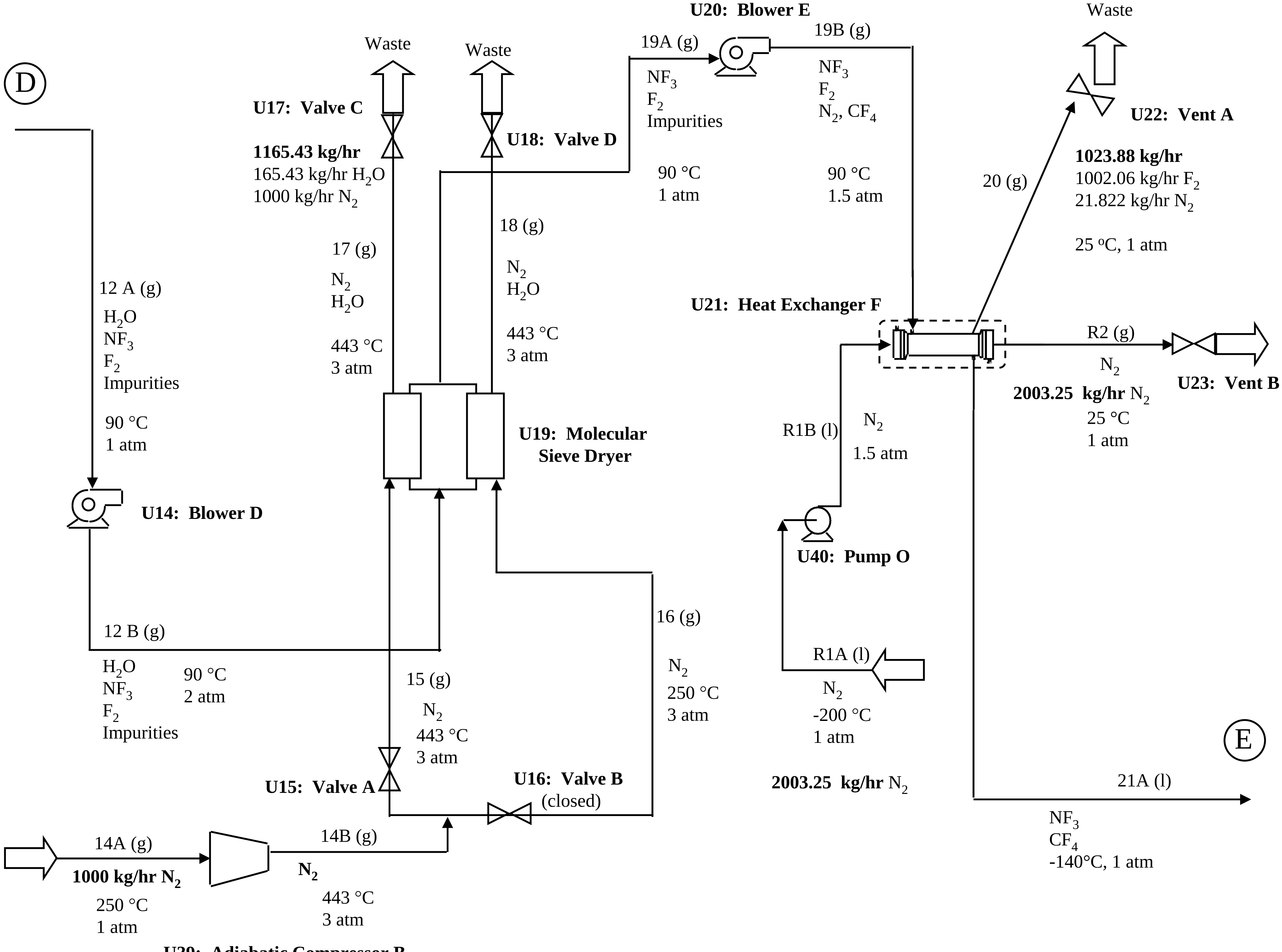
HF
1724.4 kg/h HF 25 oC
H2O
H2O
1724.4 kg/h HF 180 oC
HF
180oC
CCl2F − CClF2 → CClF2 − CF3 + HCl
CClF2 − CF3 + HF → CF3 − CF3 + HCl
H2O
FCL2C-CF3 or
F2CL2C-CCLF2
180oC
Reactor
415 oC
FCL2C-CF3 or
F2CL2C-CCLF2
H2O
Washer
H2O
To the separation phase
-80oC
Cold
trap for
organic
Organic
Include: C2F6, CFC113, CFC114,
CFC115
Inorganic:
HF
HCl
N2
N2 -80 degree
HCL, HF, H2O
H2O

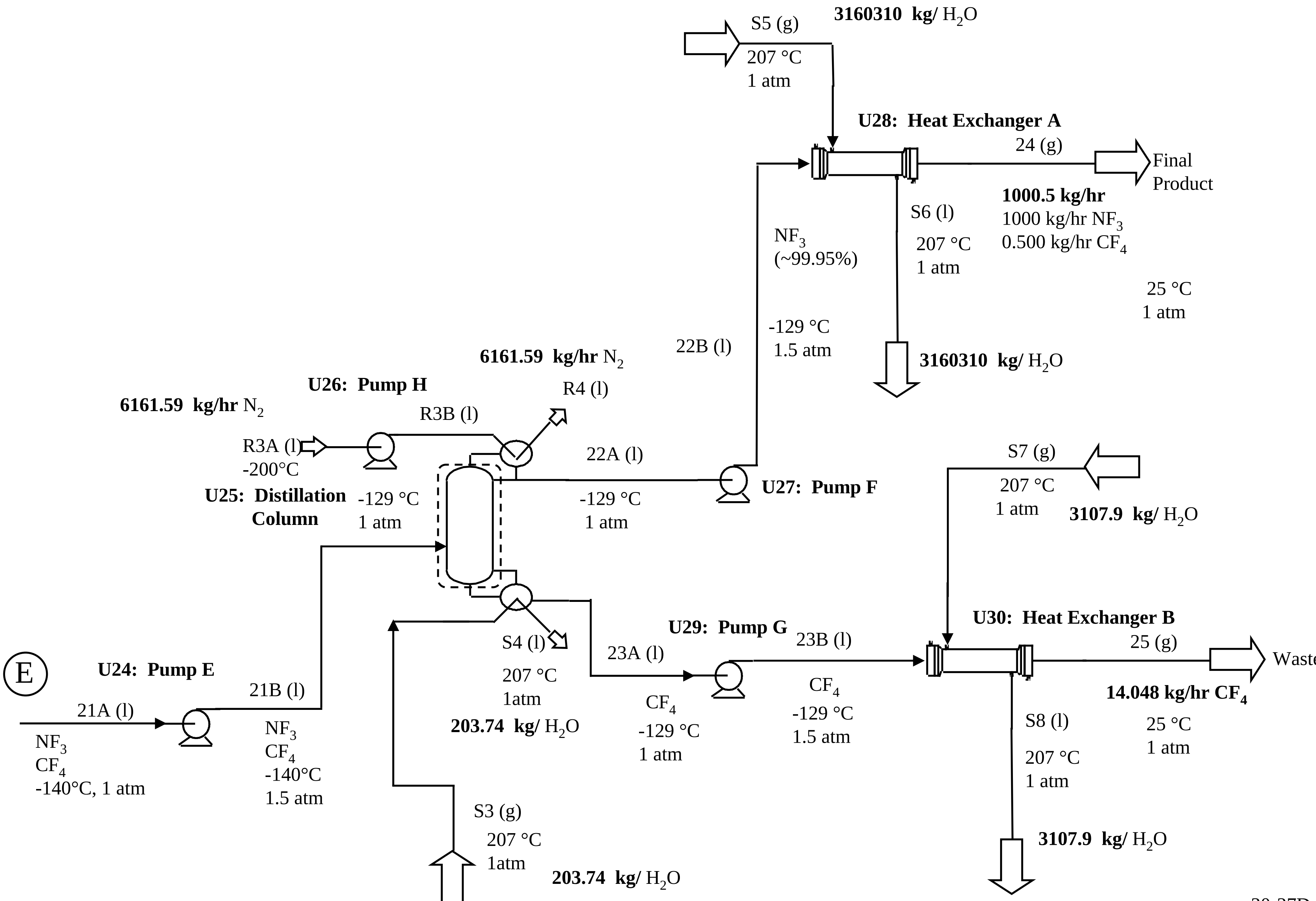

HCl
HCl
Azeotop :
HCl and C_2F_6
-50 °C
N_2
-27°C
Organic
Include: C_2F_6, CFC113, CFC114, CFC115
Inorganic:
HF
HCl
-30°C
41
62 stage
254.7 psi
-30°C
Azeotop :
HCl and C_2F_6
-26°C-
-21°C
Distillation column
N_2
Decanter
Two layer seperation
HCl and C_2F_6
(rich phase)
Distillation column
Organic
Include: C_2F_6, rich phase: CFC113, CFC114, CFC115
Inorganic:
HF
HCl
C_2F_6 >99%


1C (g)
2666.76 kg/hr
2630.39 kg/hr F2
36.34 kg/hr Impurities
25 °C
1 atm
U32: Adiabatic Compressor A
1 (g)
F2 (g)
Impurities
126 °C
3 atm
2 (g, l)
NF3 (g)
HF (g)
F2 (g)
Impurities
NH4FHF (l)
160 °C
2.72 atm
NH4FHF + 3F2 → NF3 + 5HF
U1: Reactor
160 °C
2.72 atm
1A (l)
NH4FHF
150 °C
3 atm
U31: Pump I
1D (l)
NH4HFH
1253.447 kg/hr
150 °C
1 atm
1B (l)
NH4HFH
814.740 kg/hr
150 °C
1 atm
U2: Pump A
3B (l)
438.707 kg/hr NH4FHF
150 °C
1.5 atm
3A (l)
NH4FHF
150 °C
1 atm
U3: Mist Eliminator
150 °C
U4: Blower A
4A (g)
NF3
HF
F2
Impurities
150 °C
1 atm
4B (g)
NF3
HF
F2
Impurities
150 °C
1.5 atm
A
6A (g)
NF3
HF
F2
Impurities
17 °C
1 atm
U5: Cold Trap
17 °C
1 atm
U33: Pump J
5A (l)
5595.54 kg/hr H2O
4 °C
1 atm
5B (l)
H2O
4 °C
1.5 atm
7A (l)
HF
H2O
17 °C
1 atm
7B (l)
HF
H2O
17 °C
1.5 atm
U34: Pump K
U35: Heat Exchanger D
S2 (l)
207 °C
1 atm
106985.1 kg/hr H2O
S1 (g)
207 °C
1 atm
106985.1 kg/hr H2O
7D (l)
6595.90 kg/hr
1000.36 kg/hr HF
5595.54 kg/hr H2O
25 °C
1 atm
Waste
30-23D


U6: Blower B
6B (g)
NF3
HF
F2
Impurities
17 °C
2 atm
9A (g)
NF3
F2
H2O
Impurities
110 °C
1 atm
B
A
6A (g)
17 °C
1 atm
NF3
HF
F2
Impurities
U36: Pump L
7C (l)
7E (l)
KOH
H2O
25 °C
1.5 atm
5000.00 kg/hr
1250.00 kg/hr KOH
3750.00 kg/hr H2O
25 °C
1 atm
U7: Scrubber
KOH + HF → KF + H2O
8A (l)
KF
KOH
H2O
110 °C
1 atm
C
8B (l)
KF
KOH
H2O
110 °C
1.5 atm
U8: Pump B


B
9A (g)
NF3
F2
H2O
Impurities
110 °C
1 atm
U9: Blower C
9B (g)
NF3
F2
H2O
Impurities
110 °C
1.5 atm
D
12A (g)
H2O
NF3
F2
Impurities
90 °C
1 atm
U37: Pump M
11A (l)
19531.96 kg/hr H2O
4 °C
1 atm
11B (l)
H2O
4 °C
1.5 atm
U10: Cold Trap
90 °C
1 atm
U38: Pump N
C1A (l)
20 °C
1 atm
3465.7 kg/hr H2O
C1B (l)
1.5 atm
U11: Heat Exchanger C
C2 (l)
50 °C
1 atm
3465.7 kg/hr H2O
U13: Pump D
13A (l)
H2O
90 °C
1 atm
13B (l)
H2O
90 °C
1.5 atm
U44: Pump S
C9A (l)
20 °C
1atm
57926.6 kg/hr H2O
C9B (l)
20 °C
1.5 atm
C
8B (l)
110 °C
1.5 atm
KF
KOH
H2O
2119.983 kg/hr
1244.824 kg/hr KF
48.027 kg/hr KOH
827.132 kg/hr H2O
25 °C
1 atm
10A (l)
KF
KOH
H2O
Waste
10B (l)
25 °C
1 atm
U12: Pump C
U45: Heat Exchanger E
13C (l)
22675.06 kg/hr H2O
25 °C
1atm
Waste
C10 (l)
50 °C
1atm
57926.6 kg/hr H2O
30-25D


D
U17: Valve C
Waste
1165.43 kg/hr
165.43 kg/hr H_2O
1000 kg/hr N_2
U18: Valve D
Waste
U20: Blower E
19A (g)
NF_3
F_2
Impurities
90 °C
1 atm
19B (g)
NF_3
F_2
N_2, CF_4
90 °C
1.5 atm
Waste
U22: Vent A
20 (g)
1023.88 kg/hr
1002.06 kg/hr F_2
21.822 kg/hr N_2
25 °C, 1 atm
12 A (g)
H_2O
NF_3
F_2
Impurities
90 °C
1 atm
17 (g)
N_2
H_2O
443 °C
3 atm
18 (g)
N_2
H_2O
443 °C
3 atm
U19: Molecular Sieve Dryer
U21: Heat Exchanger F
R2 (g)
N_2
2003.25 kg/hr N_2
25 °C
1 atm
U23: Vent B
R1B (l)
N_2
1.5 atm
U14: Blower D
U40: Pump O
12 B (g)
H_2O
NF_3
F_2
Impurities
90 °C
2 atm
15 (g)
N_2
443 °C
3 atm
16 (g)
N_2
250 °C
3 atm
R1A (l)
N_2
-200 °C
1 atm
2003.25 kg/hr N_2
E
U15: Valve A
U16: Valve B
(closed)
21A (l)
NF_3
CF_4
-140°C, 1 atm
14A (g)
1000 kg/hr N_2
250 °C
1 atm
14B (g)
N_2
443 °C
3 atm
U39: Adiabatic Compressor B


S5 (g)
3160310 kg/ H2O
207 °C
1 atm
U28: Heat Exchanger A
24 (g)
Final Product
1000.5 kg/hr
1000 kg/hr NF3
0.500 kg/hr CF4
25 °C
1 atm
S6 (l)
207 °C
1 atm
NF3
(~99.95%)
-129 °C
1.5 atm
22B (l)
3160310 kg/ H2O
6161.59 kg/hr N2
R4 (l)
U26: Pump H
R3B (l)
6161.59 kg/hr N2
R3A (l)
-200°C
22A (l)
U27: Pump F
U25: Distillation Column
-129 °C
1 atm
-129 °C
1 atm
S7 (g)
207 °C
1 atm
3107.9 kg/ H2O
U30: Heat Exchanger B
U29: Pump G
23B (l)
25 (g)
Waste
S4 (l)
23A (l)
207 °C
1atm
203.74 kg/ H2O
E
U24: Pump E
21B (l)
21A (l)
NF3
CF4
-140°C, 1 atm
NF3
CF4
-140°C
1.5 atm
CF4
-129 °C
1 atm
CF4
-129 °C
1.5 atm
14.048 kg/hr CF4
25 °C
1 atm
S8 (l)
207 °C
1 atm
S3 (g)
207 °C
1atm
203.74 kg/ H2O
3107.9 kg/ H2O

30-27D