SOCIAL, ECONOMIC AND ENVIRONMENTAL METRICS FOR THE SUSTAINABLE OPTIMIZATION OF CHEMICAL AND PETROLEUM PROCESSES

By

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2005

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
December, 2010

SOCIAL, ECONOMIC AND ENVIRONMENTAL METRICS FOR THE OPTIMIZATION OF CHEMICAL AND PETROLEUM PROCESSES

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DEDICATION

This dissertation is dedicated to my lovely parents Mr. and Mrs. Olasupo Shadiya for constantly supporting me throughout the beginning of my studies and believing in me.

Also to my brother and sister, Akinola Shadiya and Feyisola Shadiya for always lifting up my spirits and inspiring me.

Lastly this thesis would not have been completed without the constant motivation, prayers and encouragement from my cherished friend and fiancé, Tolulope Oluwadairo.

ACKNOWLEDGMENTS

First and foremost, I will like to thank God for seeing me through the years I worked on this degree. I express deepest gratitude to my advisor Dr. Karen High for all her mentorship, advice and the financial support she provided while working on my doctorate degree. I would like to thank my committee members Dr. A.J Johannes, Dr. Rob Whiteley and Dr. DeeAnn Sanders for their guidance while completing this research. I would like to thank the Yarborough Distinguished Graduate Fellowship and the Department of Chemical Engineering for the Funding I received towards completing this degree. Lastly, I would like to thank Modupe Oluwadiya, Obianuju Udezue, Subuola Sofolahan, and Kanyinsola Keleko for their support and taking time to read and edit different aspects of my dissertation. Your efforts are greatly appreciated.

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CHAPTER I

INTRODUCTION

The world we live in today is not the same as it was in the 20th Century. Pollution, a threatened ecosystem, limited resources, global climate change, industrial health risks are some of the issues facing us in the 21st century. Most of these issues, and the associated concerns, are caused by man's desire for industrialization. To avoid the extinction of mankind and to maintain a sustainable planet, some of these issues must be addressed as we progress in the new century.

The awareness of the need to protect the environment did not occur overnight. Several 20th century scientists have promoted the need for protecting our planet. In 1949, Aldo Leopold published a book titled "A Sand Country Almanac" to express the importance of conservation and environmental responsibility (Leopold, 1949). Another prominent environmentalist, Rachael Carson, known for spearheading the environmental movement in the United States, published a book titled "Silent Spring" (Carson, 1962). Carson addressed the contamination of pesticides and insecticides in the environment which affected wildlife and potentially humans. Through her efforts, dichlorodiphenyltrichloroethane (DDT) was banned from the United States because of the adverse effect it had on the birds and the environment.

As the world became aware of the ecological issues, several groups such as "Greenpeace" (1969) and "Friends of the Earth" (1971) were established to ensure environmental protection. Regulatory bodies such as the United States Environmental Protection Agency (1970), United Kingdom Environmental Agency (1898) and the Australian Department of Sustainability, Environment, Water, Population and Communities (2010) have been established by the governments of these countries to ensure protection of land, air and water resources. Also, world summits such as United Nations Conference on the Human Environment (1972) and United Nations World Commission on Environment and Development (1983) were created to discuss uprising environmental issues affecting the global community. Despite the long history of environmental awareness and governmental regulations, our planet is still threatened, and something must be done about it.

As we approached the 21st century, it became clear that environmental concerns were not the only issues affecting the global community; a new term called "sustainability" was coined. Sustainability can be defined as "economic well being linked to health of the environment and the success of the world citizens" (Schwarz et al., 2002). Another definition of sustainability according to the report of the 1987 World Commission on Environment and Development, Our Common Future, sustainability is defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland, 1987).

Per current level of understanding, sustainability covers the following elements: economic benefit, resource efficiency, environmental protection and social development (Darton, 2003). As shown in the Venn diagram (Figure 1.1), it can be concluded that a process that is designed for only economic and environmental concerns is classified as viable; a process that is designed for only environmental and social concerns is classified as bearable and a process that is designed for economic and social concerns is equitable. Thus, a sustainable process is one that covers all the three dimensions.

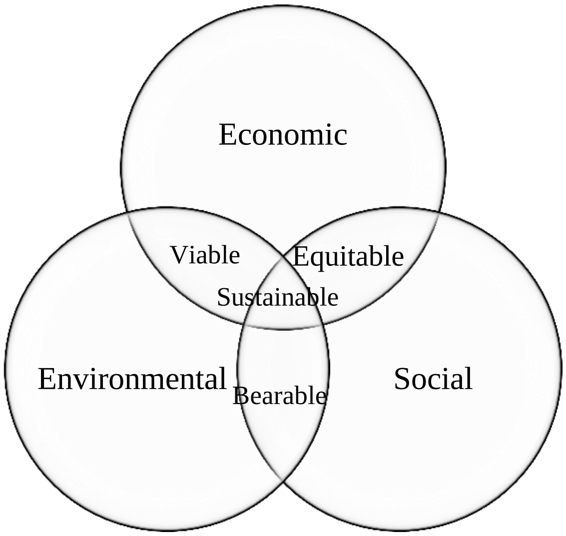


Figure 1.1:Dimensions of Sustainability (Adams, 2006)

There has been an increased awareness towards sustainability development in the last few years. Major key players including industry, academia, the United States Government and the United Nations are all concerned with the sustainability challenge. Per United Nations Environmental Programme's GEO-2002, some of the concerns driving the need for sustainability development are as follows (Azapagic et al., 2004):

- 2 billion ha of soil (15%) of the earth land, is categorized as being degraded.
- Around half of the world's water supply systems such as rivers can be classified as depleted and polluted.
- 24% of mammal and 12% of bird species are threatened worldwide.

- The ozone layer is depleting steadily as a result of chlorofluorocarbon emissions.
- There is an increase concentration of CO_2 (25% higher than 150 years ago)
- Around 80 countries, which account for 40% of humanity, have limited access to safe drinking water.
- About 2.8 million people live on only $2 a day or less income.
- Increased death rate of around 11 million people due to poor nutrition, sanitation, and health education.

As stated by the International Council of Chemical Associations (ICCA) representing the global chemical industry in the summit, the chemical industry has laid a solid platform for moving towards becoming a sustainable sector. However, some issues still have to be resolved properly. One of them is “continuing to evaluate alternative products and manufacturing processes, and substituting more sustainable products where appropriate” (ICCA, 2002).

The petroleum industry is an important sector of the world economy, supplying up to 90% of the energy needs of the world because of high dependence on oil and other petroleum products. As petroleum is a non-renewable resource, finding ways to conserve this resource, including optimizing product refining processes is vital for sustainability for the next few decades to come. For several years, environmental agencies have struggled to regulate the environmental impacts resulting from oil exploration & production and petroleum refining. This proved to be very difficult for the oil and gas refining sector. Determining ways to incorporate sustainability into petroleum refining processes will be important in addressing the challenges surrounding conservation of world petroleum resources in the long term.

The launching of a new product in industry involves a series of step by step events. These include chemical discovery, product development, process development and full scale production. In this work, the concentration is on the process development stage (Sugiyama, 2007). In process development stage, a sequence of events must be carried out. These are market research, product specification, early stages and later stages of process design as well as product registration. The focus of this research is on the early stages of process design as shown in Figure 1.2.

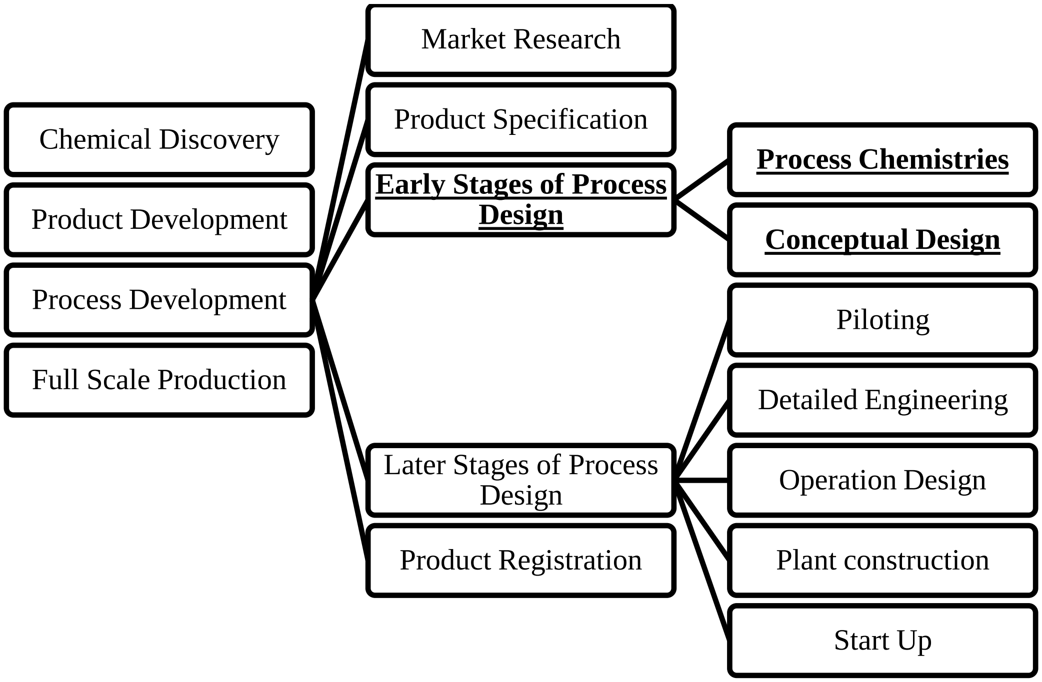


Figure 1.2: Step by Steps Events used in Launching a New Product

The burning question engineers must resolve is "how can sustainability be incorporated into early stages of process design?" The answer to this question is not as easy as it seems. Process design has always had difficulties as engineers deal with lots of details, while at the same time taking into consideration profits, regulations and even community relationships. Early process design was carried out by hand until computer-aid design (CAD) tools appeared. Today, small single-functional programs have been replaced by professional design suites consisting of synergistically integrated software. This software, featuring scientific models and massive databases, has significantly facilitated the engineer's ability to accurately mimic the system's physical condition and carry out sophisticated designs. Yet when engineers are confronted with sustainability, it is not clear which tools they should use. This leads to one of the most critical driving forces of this study: process designers need a well-defined methodology and effective and efficient computer-aided tools to handle sustainability issues.

Although researchers have put forth efforts towards quantifying some sustainability concerns, there are several limitations in existing methods. One of the important drawbacks is that existing methods could be complicated, time consuming and not address the three dimensions of sustainability. Also, process design for sustainability involves complicated decision making scenarios because of several concerns as shown in Table 1.1. This makes it difficult to determine benefit tradeoffs using current methods.

Thus, the main objective of this work is to introduce a methodology for designing sustainable chemical and petroleum processes during early stages of design. This methodology incorporates the three dimensions of sustainability into an optimization framework. This approach ensures that the most sustainable process is designed while taking into account profitability, environmental impacts and health and safety issues. This project seeks to examine processes that use non-renewable resources, identify ways to conserve these resources and develop a methodology for optimizing processes for sustainability. This project addresses the following green chemistry principles: "Prevention-It is better to prevent waste than to treat or clean up waste after it has been created and Design for Energy Efficiency-energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized (Anastas and Warner, 2000).

Table 1.1: Sustainability Concerns (de Haes et al., 1999; Fiksel et al., 1999; IChemE Metrics, 2002; Azapagic et al., 2004)

Economic concerns	Environmental concerns	Social concerns
Micro-Economic	Energy Use	Health and Safety
Capital Costs	Water Use	Illness & Disease Reduction*
Operating Costs	Water Discharge	Accident & Injury Reduction*
Profitability	Solid Waste	Peace of Mind*
Decommissioning Costs	Abiotic Reserve Depletion	Quality of Life*
Macro-Economic Costs	Global Warming	Complaints*
Value- added	Ozone Depletion	Employment opportunities*
Taxes paid on investment (e.g. pollution prevention, health and safety, decommissioning and ethical investments	Acidification Eutrophication Eco-toxicity	External stakeholders* Community benefits* Work force capability* Public reporting* Organizational learning
Environmental Liability		Remuneration* Management attention to HR*

*Not addressed in this research

The proposed framework explores the possibility of using the sequential process simulator, ASPEN PLUS (version 22) to simulate processes and calculate mass and energy balances. As part of the methodology, an Excel based tool titled the "SUSTAINABILITY EVALUATOR" has been developed for this research to address the three dimensions of sustainability. The "SUSTAINABILITY EVALUATOR" is used with ASPEN PLUS and the methodology to optimize chemical processes while addressing sustainability concerns.

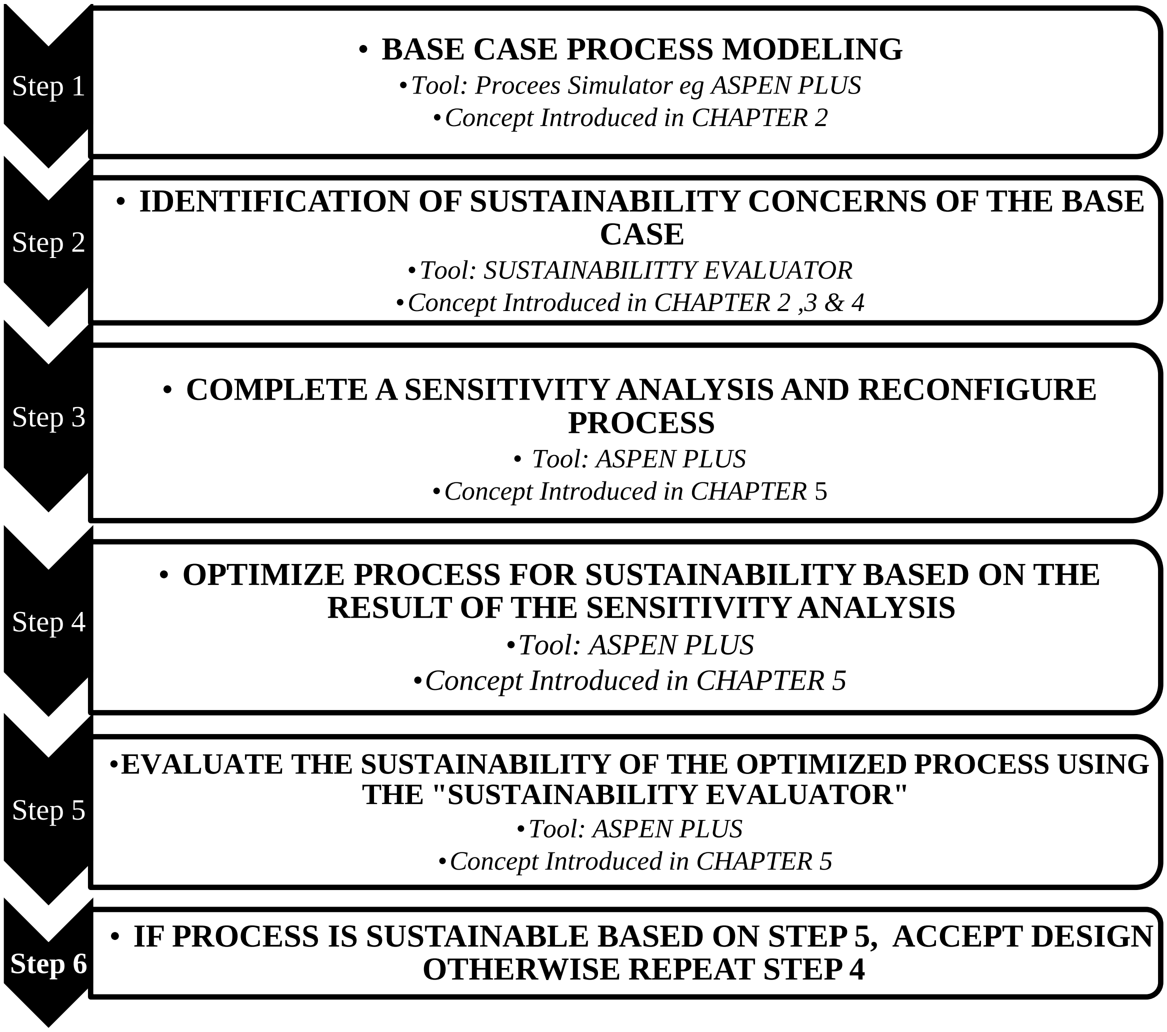
To get a better understanding of the framework of this dissertation, several topics as shown in Table 1.2 are presented in the next few chapters. This dissertation was written for several audiences. The concepts introduced in Chapter 2 presents information for an audience without a process design background. In this chapter, process issues that need to be tackled when designing or modifying processes are presented. Chapter 3 provides information for an audience without an environmental or health or safety background. This chapter discusses economic, environmental and health and safety concerns as well as tools available for addressing these issues. Because several tools are available to handle certain aspects of sustainability, this chapter reviews some of these tools and presents applicability and drawbacks of existing tools used in the evaluation of process economics, environmental and health and safety concerns.

Table 1.2: Summary of Following Chapters

Chapter	Content
2	Process Design Synthesis. Tools available for designing chemical processes. Features of process simulators and classification of process simulators. Issues engineers are faced with during early stages of process design. Discussion of optimization and chemical process design.
3	Tools and databases available for economic, environmental and health and safety evaluations. The applications of the tools and the databases and the limitations of each proposed tool.
4	Introduction to sustainability metrics and indicators. The applications of sustainability metrics and introduction to the different categories of metrics.
5	Introduction to the proposed methodology. Detailed description of the features of the SUSTAINABILITY EVALUATOR. Detailed description of how the tool works and its applications.
6	Results: Demonstration of the methodology and the tool using the following processes: methyl chloride, dimethyl ether, acrylonitrile and allyl chloride.
7	Conclusions and Recommendations

In Chapter 4, sustainability metrics and indicators that address economic, environmental and social concerns are introduced, and the limitations and contributions of each work are presented. Chapter 5 introduces the proposed framework. The methodology combines already established approaches, concepts and tools discussed in the previous four chapters into a novel systematic technique that addressed sustainability concerns in chemical process design as shown in Figure 1.3. Lastly in Chapter 6, the applicability of the proposed methodology and tool are demonstrated on the following four industrial processes that have been simulated on ASPEN PLUS (version 22):

- Dimethyl Ether
- Acrylonitrile
- Allyl Chloride
- Methyl Chloride



Step 1
- **BASE CASE PROCESS MODELING**
  - *Tool: Procees Simulator eg ASPEN PLUS*
  - *Concept Introduced in CHAPTER 2*

Step 2
- **IDENTIFICATION OF SUSTAINABILITY CONCERNS OF THE BASE CASE**
  - *Tool: SUSTAINABILITTY EVALUATOR*
  - *Concept Introduced in CHAPTER 2 ,3 & 4*

Step 3
- **COMPLETE A SENSITIVITY ANALYSIS AND RECONFIGURE PROCESS**
  - *Tool: ASPEN PLUS*
  - *Concept Introduced in CHAPTER* 5

Step 4
- **OPTIMIZE PROCESS FOR SUSTAINABILITY BASED ON THE RESULT OF THE SENSITIVITY ANALYSIS**
  - *Tool: ASPEN PLUS*
  - *Concept Introduced in CHAPTER 5*

Step 5
- **EVALUATE THE SUSTAINABILITY OF THE OPTIMIZED PROCESS USING THE "SUSTAINABILITY EVALUATOR"**
  - *Tool: ASPEN PLUS*
  - *Concept Introduced in CHAPTER 5*

Step 6
- **IF PROCESS IS SUSTAINABLE BASED ON STEP 5, ACCEPT DESIGN OTHERWISE REPEAT STEP 4**

Figure 1.3: Proposed Methodology for Addressing Sustainability Concerns During Early Stages of Design

This research will contribute to sustainability development in chemical processes as benefits such as reduced pollution, resource usage minimization and more economic products will be thoroughly explored. The application of this research extends well beyond the sustainability considerations to more extensive designer's concerns such as safety, operability and controllability.

CHAPTER II

PROCESS DESIGN FRAMEWORK

The purpose of this chapter is to provide a background for process design concepts. What tools are available for designing chemical processes? Also, what issues are engineers faced with when designing or modifying existing chemical processes? How are these issues addressed?

2.1 PROCESS DESIGN SYNTHESIS

Process design is an area of engineering which consists of designing new products, new manufacturing processes and a more efficient process configuration (retrofits), and or exploring new technology. The design process could be very complicated, as it is necessary to account for several constraints. Also, process design is quite unique; there is never a single solution towards attaining a specific goal. As an example, consider a process engineer that is tasked with creating a new manufacturing process for dimethyl ether production (500,000 metric tons per year). The engineer is already aware that dimethyl ether can be synthesized by the dehydration of methanol as shown in Equation 2.1.

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O \tag{2.1}$$

The first step is to develop a base case process flowsheet. Process flowsheet synthesis is one of the important goals of chemical process design (Diwekar et al., 1992). The best approach to solving this problem is to use the Douglas five step hierarchical approach for process synthesis (Taal et al., 2003). This hierarchical approach consists of the following steps (Turton et al., 2009):

- Select the process type - batch versus continuous
- Design the input - output structure of the process
- Define recycle structure
- Design the separation scheme
- Design energy recovery system

The following sections show the implementation of the Douglas hierarchical approach on the dimethyl ether process.

2.1.1 Select the Process Type – Batch vs. Continuous

According to Biegler, Grossman and Westerberg (1997), there are several factors that influence whether a production process should be batch or continuous. One of these factors is time. If there is an urgent demand for the product, and there is a competitive market advantage, then a batch process could be selected. Another factor is quantity of product. If the quantity of product needed is low such that a small amount is required a few times a year, then a batch process could be selected. Another factor is limited information. If the information required to design the process is limited, then the batch process is the favorable option. Finally if the product is not profitable, then a batch process is usually selected. For the dimethyl ether production process, reasons above are not valid for this process, so a continuous process is selected.

2.1.2 Design the input-output structure

The input-output structure of a process is developed based on the reactions taking place to create the product. When products are formed, there is never 100 percent conversion of raw materials. Thus, separators will be needed to separate the un-reacted raw material from the product. Figure 2.1 shows the input-output structure for this process.

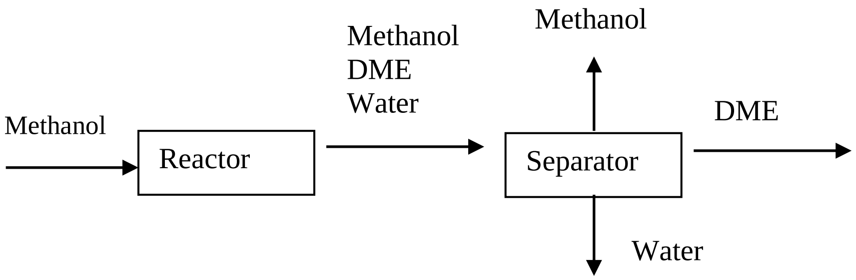


Figure 2.1: Input-Output Structure for Dimethyl Ether Production

2.1.3 Define Recycle Structure

At this step, the recycle structure for the process is defined. Many processes have un-reacted raw materials and by-products, and thus it is important to recycle the un-reacted raw material for economic reasons. In the dimethyl ether example, there is some un-reacted methanol which is recycled and sent back to the reactor, as shown in Figure 2.2.

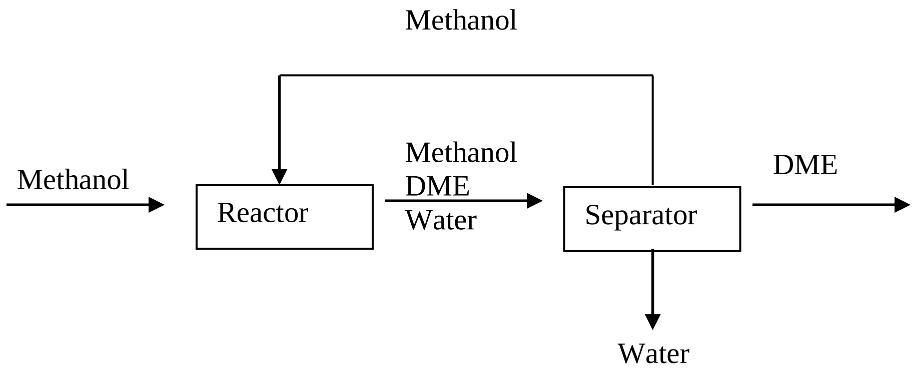


Figure 2.2: Recycle Structure for Dimethyl Ether Production

2.1.4 Define Separation Scheme

This step involves the design and placements of separation units. Designers might be faced with some of the following questions:

- What components should be separated first?
- Should purge streams be considered?
- What type of separation method should be considered?

The key thing is that the designer must determine the order of the separation columns and their operating conditions. For the dimethyl ether process, the separation scheme sequence is shown in Figure 2.3. Dimethyl ether is separated first because it has a lower boiling point compared to methanol and water.

2.1.5 Define Energy Recovery System

For any manufacturing process, energy usage for utilities and day to day operation is one of the most expensive aspects. Therefore, investigating ways to conserve, integrate and optimize the energy consumption is vital for economic reasons. This aspect of the process flowsheet development could be complicated as there are several alternative solutions the designer could generate in solving this problem. Such solutions will be discussed in later sections of this dissertation. Once a process flowsheet has been developed, the next stage of process design is to calculate the mass and energy balances for the process of interest. The next section discusses the tools available for achieving this objective.

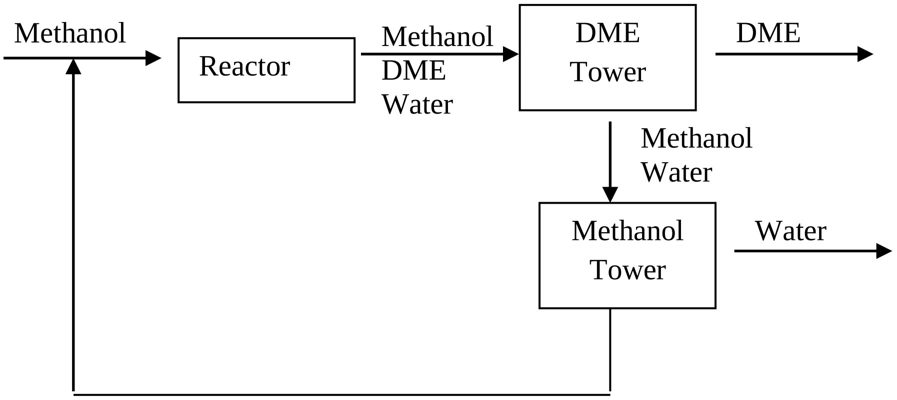


Figure 2.3: Recycle Structure for Dimethyl Ether Production

2.2 TOOLS AVAILABLE FOR DESIGNING CHEMICAL PROCESSES

When a designer was faced with devising a new chemical process, six decades ago, it took months or even years to design the process flowsheet for a particular process (Motard et al., 1975). This was due to the complicated mass and energy balance calculations that were needed to be hand-calculated for the process. It was not until the late 50's that a new tool called the chemical process simulator was developed to solve this problem (Motard et al., 1975).

Chemical process simulators are software tools developed to mimic the behavior of an actual process plant. Chemical process simulators are best known for designing, optimizing, testing and integrating new or retrofit processes (Casavant and Côté, 2004). Process simulators combine mathematical, thermodynamic and process unit modeling to solve mass and energy balance for a processing unit (Motard et al., 1975). The process simulator can be used to locate process malfunctions and predict process performance (Seider et al., 2008). If the material stream is entered, the process simulator is able to predict the process conditions for the waste, product sand by product streams. The process simulator is also able to calculate information for equipment sizing and subsequently process economics.

It is clear that the advancement of chemical process simulators has been a tremendous accomplishment in the chemical engineering profession, because material and energy balances can now be calculated in a matter of days or hours. Today, most chemical process simulators offer a graphical user interface where users can see the objects being selected for the simulation and later run it. Over the years, several process simulators such as CHEMCAD, ASPEN, HYSYS, FLOWTRAN and BATCH PLUS have been developed for the chemical industry. The proceeding sections discuss the features and the classifications of process simulators.

2.2.1 Features of a Process Simulator

Process simulators have the same generic structure and have six main features (Turton et al., 2009). The first feature, the component database, is where the constants that are needed for calculating thermodynamic models are located. Another feature is the thermodynamic model solver, which contains thermodynamic models that can predict phase behavior. Additionally, the flowsheet builder is a graphic user interface, where the designer is able to keep track of selected process equipment and flow streams. The unit operation block solver is the fourth feature that has computational blocks for mass and energy balance calculations and other design calculations. The data output generator is the section where the results of the simulation run are provided. Lastly the flowsheet solver shows the sequence of how the calculations in the simulation were completed and how well it converged.

2.2.2 Classifications of Chemical Process Simulators

The following are the three basic types of solution algorithm chemical process simulator (Turton et al., 2009):

- Sequential Modular Chemical Process Simulator
- Equation Solving Chemical Process Simulator
- Simultaneous Modular Chemical Process Simulator

2.2.2.1 Sequential Modular Chemical Process Simulator

A sequential modular chemical simulator is unique in that the equations characterizing process equipment are grouped and solved sequentially, starting from the first to the last. In this approach, the output from one piece of equipment becomes the input for the next, thus, this simulator requires detailed degree of freedom analysis before it converges. One key assumption held by this type of simulator is that “variables and the process stream variables associated with streams entering the flow sheet are completely defined and are not treated as unknowns (Stephenson and Shewchuk, 1986).

The advantages of the sequential modular simulator are that it is straightforward, easy to visualize, very robust, even when complex process flow diagrams are simulated, and it is able to reach rigorous convergence (Sloan, 2006; Baudet et al., 2008). Another advantage of this simulator is that it is able to complete initialization when considering optimization problems. Due to the key assumptions held by this type of simulator, a setback with this type of simulator is that it only runs in the forward direction, thus limiting its application in complex design and optimization problems. Another limitation to this type of simulation is that it does not perform at optimum standards when there are several recycle streams (Britt et al., 1997). Popular examples of this type of simulator include CHEMCAD, ASPEN PLUS, PROII and HYSYS.

ASPEN PLUS, a FORTRAN coded simulator, has been selected for simulating chemical processes in this research. ASPEN PLUS was developed by Evans at Massachusetts Institute of Technology (Kotoupas et al., 2007). It can be linked with other tools for external analysis. As this software is readily available at Oklahoma State University, it has been selected for this research.

2.2.2.2 Equation Solving Chemical Process Simulator

In the equation modular simulator, all non-linear equations representing the process are solved simultaneously using matrix techniques. In this approach, because all unknowns are solved simultaneously, inputs can be changed anytime (Sloan, 2006). This category of simulator also requires a detailed degree of freedom, so that relevant equations are determined. Although this approach is computationally efficient, a lot of time is required to set-up all equations representing the process (Turton et al., 2009). Therefore, because variables are not specified, the equation solving simulator is an excellent option for a complex optimization problem. Examples of this simulator include: ASCEND, FLOWSIM, MASSBAL, QUASILIN and SPEEDUP.

2.2.2.3 Simultaneous Modular Chemical Process Simulator

The simultaneous modular chemical process simulator combines the equation solving and sequential modular approaches. In this approach all simulation modules are solved simultaneously by a single routine. Thus, good initial guesses need to be provided to ensure simulation accuracy (Kulikov et al., 2005). This approach is able to address the limitations of the other types of simulators. Several researchers (Mahalec, Kluzik and Evans (1979), Patterson and Rozsa (1980), Fagley and Carnahan (1983), Byrne and Bogle (2000) have done extensive work on developing simultaneous modular simulators. In essence, an optimization algorithm is incorporated with the sequential modular simulator to allow the software to become a simultaneous modular simulator.

Once a process has been simulated, an engineer must still investigate ways to improve performance. The next section discusses some of the concerns engineers must consider when designing chemical processes and provides applications of optimization to chemical process design.

2.3 PROCESS DESIGN ISSUES AND OPTIMIZATION

This section covers the issues designers are faced with when designing chemical processes. Optimization applications are introduced as well as how they are used to tackle sustainability issues.

2.3.1 Process Design Issues

Every designer must ensure that any newly proposed project is making a profit. Economics has been the number one driving force for building any process, thus trying to ensure that the process is running optimally can really ensure optimum returns. Chemical process improvement is one important way of ensuring this. Chemical process improvement involves evaluating the process flowsheet and ensuring that the process is operating at optimum conditions in order to meet economic goals. This involves completing studies that involve varying different types of equipment, varying operating conditions and varying process configurations.

Some of the questions a designer might ponder upon during the process improvement stage include:

- Should one consider a batch reactor, plug flow reactor or continuous stirred tank reactor for the reactions taking place in a process?
- Should one operate a distillation column or the reactor at 400^{o}F or at 600^{o}F?
- Should separation columns of a process be placed before the first reactor or after the second reactor?

Until recently, it was the job of a process designer to ensure that all process conditions were optimized to meet economic goals only. With the advancement of strict regulations enforced by governmental regulatory bodies such as the United States Environmental Protection Agency (EPA), it became necessary to design processes that met both environmental standards and economic goals. For a long time, most environmental considerations for any process were considered as an afterthought i.e.

considered at later stages of design even as late as the operation stage. In essence, waste was generated and treated from air, water, and land sources. One problem with this type of plan is that it is very unlikely that there will be significant environmental protection (Chen and Shonnard, 2004). With rising concerns about limited resources, wastes must be minimized, processed back to new resources, eliminated or even prevented. Industrial activities that have caused drastic consequences leading to air, water and soil pollution must be prevented. One thing to keep in mind is that environmental regulation fines are high, the ability to directly reduce unnecessary resource consumption and waste treatment is directly related to financial benefits (da Silva and Amaral, 2009).

Safety is another aspect an engineer must consider when creating a new process. Most chemical processing plants deal with hazardous chemicals and are operated at high temperatures and pressures. Thus, the health and wellbeing of employees and neighboring inhabitants could potentially be compromised if safety considerations are not incorporated into design. Exposure to chemicals, fire and explosion are the major safety concerns in industry because such events lead to drastic health hazards. Exposure to chemicals in industry could be by ingesting contaminated food and water sources, breathing in chemicals during leaks and adsorption through the skin by accidental spills. Drastic health hazards from industrial tragedy are a social issue of concern because they can result in shortened life expectancy and even instant death. For example, the Bhopal industrial catastrophe, which occurred in 1984, involved the release of methyl isocyanate gas and other toxins at a Union Carbide plant is one of the largest disasters in the history of the chemical industry. Over 10,500 people died from this incident, and over 50,000 people suffered from various illnesses such as visual impairment, respiratory problems and other chronic illness (Wright, 2007).

It is evident that industry still has a long way to go in terms of reducing workplace fatalities. In 2008, exposure to harmful substances or environment and fire and explosion accounts for about 12% of deaths in the private industry (United States Bureau of Labor Statistics, 2008). Although workplace fatalities has reduced over the years, as shown in Figure 2.4, the numbers are still at an alarming high and must be reduced at all costs. Therefore, it is important for designers to also incorporate safety into chemical process design.

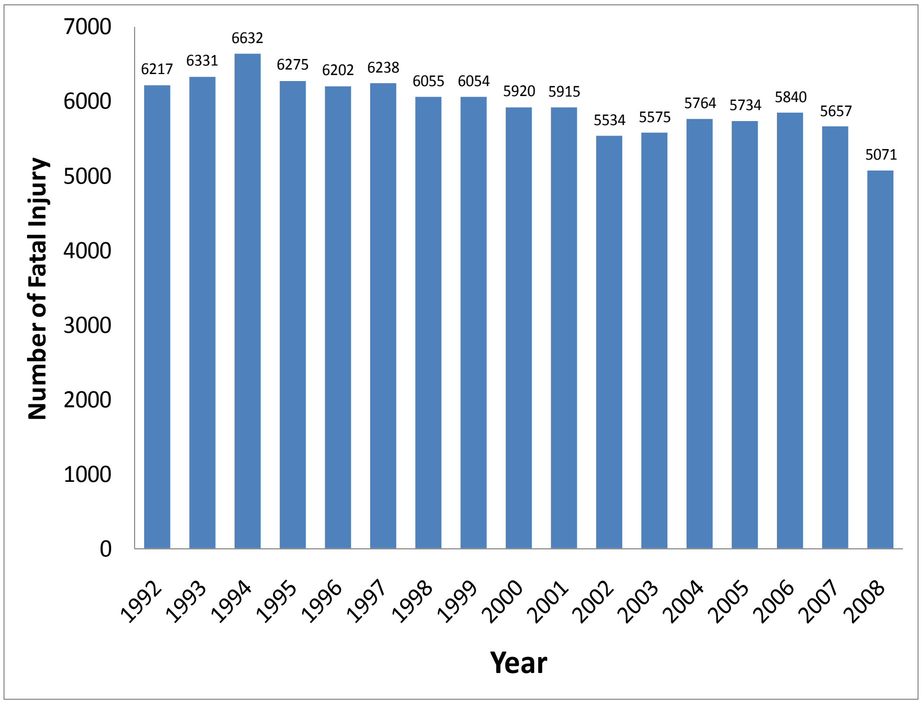


Figure 2.4: Work Place Fatalities from 1992- 2008 (U.S Bureau of Labor Statistics, 2008)

An approach that has been used to incorporate economic, environmental and health and safety concerns into chemical process design is optimization. Optimization provides several opportunities to prevent safety losses, reduce environmental impact while maximizing economics. This could be via reducing energy costs and wastes, while operating at safer operating conditions. These objectives can be conflicting and must be handled using an appropriate technique. The next section provides an overview of the various optimization methodologies that have been incorporated into chemical process design.

2.3.2 Optimization

One approach researchers have implemented to accomplish the task of designing processes for conflicting objectives is optimization. When economics was the major goal, most chemical engineering optimization problems were formulated as a single objective. Several researchers have applied single objective optimization to chemical engineering (Storti et al., 1993; Storti et al., 1995; Dunnebier and Klatt, 1999; Karlsson et al., 1999; Wu et al., 1999). As discussed earlier, other concerns such as environmental impact and social concerns must be accounted for by using a technique called multiobjective optimization. Multiobjective optimization is an approach that involves the simultaneous optimization of several competing objectives while finding an optimum solution over a feasible set of decisions.

2.3.2.1 Classification of Optimization Problems

Handling sustainability concerns in chemical process design is a multiobjective optimization problem because a wide range of concerns, as shown in Table 1.1, must be addressed. Designing and incorporating all the concerns tends to be difficult because of competing goals. Therefore, formulating the problem into a multiobjective framework in which economic, environmental and social objectives are formulated is the ideal way to tackle sustainability issues in process design. Several researchers have presented methods for formulating multiobjective optimization problems.

Multiobjective optimization problems can be classified into two major categories, generating methods and preference based methods, as shown in Figure 2.6 (Miettinen, 1999; Diwekar, 2003; Rangaiah, 2008). Generating method can be defined as an optimization technique where one or more solutions are created without the assistance of a decision-maker. The preference based optimization approach needs the assistance of the decision maker to input preferences before the optimization problem can be solved.

2.3.2.1.1 Generating Methods

No Preference methods, a posterior methods implementing scalerization techniques, and a posterior methods using pareto optimization techniques are the three categories of generating methods. In the No Preference approach, objectives are not prioritized and preferences articulation by the decision-maker are not required (Marler and Arora, 2004; Rangaiah, 2008). Examples of this method include global criterion methods and neutral compromise solution. For more information about this approach, the article by Marler and Arora (2004) can be consulted. One application of Preference method was in the work by Krokida and Kiranoudis (2000) who applied this approach in the minimization of product color and unit cost for a fluidized bed reactor.

A posterior methods implementing scalerization technique is one approach that has been used to address multiobjective optimization. This involves combining multiple objectives into a single scalar objective by using weight factors. Scalarization can be classified into weighing and epsilon-constraint methods (Rangaiah, 2008). According to Kim and de Weck (2004), the traditional way to tackle the solutions to vector optimization problems is to use the weighted-sums method which solves "the optimal solution is solved one by one by systematically changing the weights among the objective functions." The method however gives poor results near the convex region. Kim and de Weck (2004) proposed the adaptive weighted-sums which give optimum solutions near the non- convex solution area. This new proposed method focused on "unexplored regions by changing the weights adaptively rather than by using a priori weight selections and by specifying additional inequality constraints (Kim and de Weck, 2004).

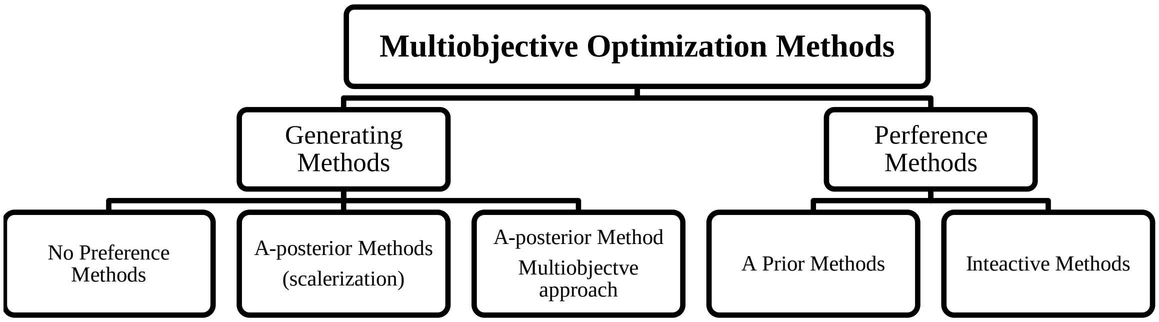


Figure 2.5: Classification of Multiobjective Optimization Methods (Rangaiah, 2008)

Epsilon constrained method was first introduced by Haimes, Ladson and Wismer (1971) but other researchers such as Chankong and Haimes (1983), Ehrgott and Ruzika, (2008) and Berube, Gendreau and Potvin (2009) have also studied this approach. This method involves a process where one objective is minimized and the other objectives are converted to inequality constraints (Ehrgott and Ruzika, 2008). One group of researchers who has used the epsilon constrained approach is Hugo et al. (2004), who maximized net present value, minimized environmental impact and carcinogenic plant emissions for the supply chain of the vinyl chloride monomer and ethylene glycol. Also Hoffmann, Hungerbuhler and McRae (2001; 2004) maximized economic benefit and minimized environmental impact using the epsilon constraint approach for the hydrogen cyanide production process. One limitation of the epsilon method is that it is inefficient and vulnerable to infeasible formulations (Oh et al., 2009).

Although scalarization simplifies the optimization problem, it has several limitations. Scalarization can result in the loss of some optimum solutions because weighting factors are assigned randomly (Haimes, 1977; Chankong and Haimes, 1983; Bhaskar et al., 2000; Zhou et al., 2000). To address this limitation, multiobjective optimization problems are solved using a vector function approach where each objective is treated independently as exemplified by a posterior methods using Pareto optimization techniques (Marler and Arora, 2004). In this approach, many Pareto optimum solutions are presented and the decision-maker selects the optimum solution based on his/her preference. The limitation of this approach is that it could be a waste of computational time since the decision maker only selects one solution. Two examples of this approach are non-dominated sorting genetic algorithm and multiobjective simulated annealing.

Non-dominated sorting genetic which mimics the process of natural selection and genetics involves an evolutionary approach where multiple objectives are reduced to fitness functions using a non-dominated sorting technique (Bhaskar et al., 2000). Information about this approach can be consulted from papers by Srinivas and Kalyanmoy (1994), Kalyanmoy, Samir et al.(2000) and Al Jadaan, Rajamani and Rao, (2008). This approach is better than traditional optimization methods because objective functions are used directly. This approach has been applied to a semibatch reactive crystallization process in which the weight mean size is maximized and the coefficient of variation is minimized in order to find the optimum feed addition profile (Sarkar et al., 2007). Multiobjective simulated annealing is a process where the search method for solving the optimization problem is an imitation of the cooling of molten metal. This approach follows the Boltzmann probability distribution function and is a useful method for finding optimum solutions for cooling procedures (Bhaskar et al., 2000).

2.3.2.1.2 Preference Based Methods

Preference based methods can be classified as A Prior Methods and Interactive Methods. A Prior Methods is an approach that requires the decision maker to specify preferences in advance before solving the optimization problem. This approach is advantageous because it is efficient since one Pareto optimum solution will be provided based on the decision-makers preference. Critics of this approach believe that this approach can be difficult to utilize if the decision maker has no knowledge of the optimum values for the problem (Rangaiah, 2008). Two examples of this approach are lexicographic method and goal programming.

Lexicographic method is an approach where objective functions are arranged according to importance and solved in sequence. The limitation of this method is that it does not satisfy the Kuhn–Tucker optimality conditions[1] (Karush, 1939; Marler and Arora, 2004). Meadowcroft, Stephanopoulos and Brosilow (1992) used the lexicographic optimization technique to find an optimum solution for a modular multivariable controller that was implemented on a heavy oil fractionator. Goal programming is

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[1] For more information on the Kuhn–Tucker optimality conditions, the thesis by (Karush, 1939) can be consulted.

defined as a process where a solution is generated by minimizing the deviation of the weighted average of the objective function by using goals set by the decision-maker. Although this approach allows multiple objectives, limitations of this approach are that it locates inferior solutions and it is difficult to homogenize values. Goal programming has been implemented in waste management for process plants (Chakraborty and Linninger, 2002a; Chakraborty and Linninger, 2002b). In this research, costs and environmental impact are minimized simultaneously for solvent recovery in benzene, ethylene dichloride and toluene mixture.

Interactive Methods require continuous interface with the decision maker. This approach eases the complexity of problems with several objectives since only a few Pareto optimal solutions are presented due to the decision-maker specifying preferences. Therefore this method requires time and high cognitive load from the decision maker and hence might not be realistic approach. Interactive methods have been applied to the optimization of a paper mill recovery system where mass flow rate of steam, heat exchanger area and cooling/heating needs are minimized (Hakanen et al., 2006). Also this method was used to minimize solvent consumption, and maximize product purity and recovery in a simulated moving bed process (Hakanen et al., 2007).

2.3.2.2 Optimization Techniques used in Addressing Sustainability Concerns

The application of optimization towards handling several aspects of sustainability concerns is discussed in this section. Dantus (1999) focused on developing a methodology for the design of more economical and environmental friendly processes using an uncertainty approach. In this work, a thorough environmental analysis was completed which involved classifying waste streams, assessing environmental impacts, developing process models, establishing and implementing pollution prevention techniques (Dantus and High, 1996). To address the uncertainty involved in addressing conflicting economic and environmental concern, multiple objective programming was implemented (Dantus and High, 1999). The capability to reduce pollution generated in a chemical process was achieved. Also, an economic based model for waste minimization and energy reduction in the chemical industry was developed (Dantus and High, 1996). Furthermore, design controllability and operating issues while integrating environmental impact and profitability was analyzed (Gollapalli et al., 1999; Gollapalli et al., 2000).

Venkataraman (1996) focused on "Process Enhancement through Waste Minimization." In this work, acrylonitrile process was studied and a general methodology for implementing multiobjective optimization in the process design was developed. Venkataraman's approach involved three steps: process modeling and analysis, identification and selection of process alternatives and incorporation of multiobjective optimization (Venkataraman, 1996; Shadiya et al., 2010).

Jin (2005) contributed to the area of sustainability research by implementing Multicriteria Decision Analysis (MCDA) into engineering design. The MCDA is a process that is useful in handling conflicting concerns of economic, environmental and social concerns. In this work, he thoroughly explored the sustainability concept and developed a 4-step metric classification system that can be employed in identifying environmental metrics that assist decision makers in classifying ecologically friendly processes (Jin and High, 2004a). In addition, a generic evolutionary algorithm for searching for the global optimal sustainability solution over a set of different process alternatives was proposed. With this algorithm, engineers are able to select the most sustainable alternative from a range of different alternatives.

Singh and Lou (2006) implemented the hierarchal optimization methodology to select the most optimum sustainable process that minimizes material and energy consumption and reduces or eliminates waste disposal in an industrial ecosystem. This method can handle intricate scenarios one level at a time by using the results of a previous level, making the process easier to unravel. The process of hierarchy must be done in an appropriate fashion to avoid complicating important issues. When designing for sustainability, the ultimate solution is not a unique one, rather there are several alternative solutions and the designer must select the optimum.

For example, a certain alternative for a process may be the most economical, but not necessarily meet environmental, health and safety standards. Another alternative may be environmentally efficient, but not economically and socially acceptable. Thus an optimum approach to tackle complex design scenarios is to implement the hierarchical Pareto multi-objective optimization technique. Hierarchical Pareto multi-objective evolutionary optimization technique has the ability to give results in multiple solutions as compared to the traditional multi-objective optimization methods that are converted to a single objective optimization method and give results in a one point solution (Zitzler and Thiele, 1998). With the hierarchical Pareto multi-objective optimization technique, designers developing industrial processes are able to meet the key objective, which is economic benefit while having the flexibility to modify their processes for environmental and social concerns.

In the research of Singh and Lou (2006), an economic index to be maximized and an environmental index to be minimized were proposed. Hierarchal optimization methodology with uncertainty consideration was further demonstrated on an ammonia production process, where profit was maximized and environmental impact was minimized (Sun and Lou, 2008). A Monte Carlo analysis optimization framework was developed to determine the optimum configuration of plants in a chemical complex system using economic, energy, environmental and sustainable costs as constraints while handling uncertainties (Sengupta et al., 2008).

Gonzalo and Grossmann (2009) proposed a methodology that involves a bi-criteria stochastic mixed-integer nonlinear program (MINLP) optimization technique. This methodology addresses sustainability issues in chemical supply chain by optimizing them for maximum net present value and minimum environmental impact. Environmental impact for the chemical supply chain was assessed by using a life cycle assessment tool, Eco-indicator 99 (Gonzalo and Grossmann, 2009). In this approach, net present value was maximized while environmental impacts were all converted to constraints using the epsilon approach. Also, uncertainty has also been addressed in the inventory used for the life cycle assessment of the chemical supply chain.

A systematic methodology that incorporates economic and environmental metrics as well as social qualitative indicators was proposed to design processes for sustainability (Othman et al., 2010). To address economic concerns, calculation of net present value and discounted cash flow was the suggested approach. The waste reduction algorithm approach was implemented to address environmental concerns, and qualitative safety indicators were used to tackle social concerns. For each suggested metric or indicator, weights were assigned based on relative importance of the issue at hand. A four step methodology was proposed by these researchers which included simulation of process, inventory analysis of process, sustainability assessment and decision making based on the results of the sustainability assessment.

2.4 SUMMARY

This chapter presented the issues engineers face when developing a new process as well as the tools available to address these concerns. The chapter also discusses the concerns that must be addressed during process design, and optimization techniques that could be used to address these issues. There are several tools available for mimicking complexes processes, but in this research, ASPEN PLUS, a FORTRAN coded simulator, has been selected for simulating chemical processes. This sequential chemical process simulator has been chosen because it is readily available at Oklahoma State University. In addition to providing the results of mass and energy balances; it could be used to attain the following: complete steady and dynamic mode calculations, size equipment and provide economic analysis results, perform sensitivity analysis and optimization. It can also be linked with other tools for external analysis. ASPEN PLUS will be used to simulate and optimize chemical processes that will be retrofitted for sustainability constraints as discussed in later chapters.

CHAPTER III

ECONOMIC, ENVIRONMENTAL AND HEALTH AND SAFETY EVALUATION TOOLS

3.1 INTRODUCTION

This section provides a brief discussion of the economic, environmental, health and safety assessment tools that are currently used for evaluating the impact of chemical processes on the environment and society. The features and applicability of the tools are presented in this section.

3.2 ECONOMIC EVALUATION TOOLS

Determining the economics of a chemical process is essential because it is illogical to embark on a project that does not assure profit. Therefore, it is necessary to evaluate the manufacturing costs and product revenue of any process to determine viability. The cost of manufacturing is determined by capital, labor, utility and raw material costs. Depending on the information available, the economic analysis can be determined by using methods such as payback period, rate of return on investment and net present value.

Payback period, as shown in Equation 3.1, is defined as the time frame a project must achieve break even, i.e. pay back all expense embarked on the project. Rate of return (ROI) on investment is the ratio of the net income to the capital investment, as shown in Equation 3.2. Net Present Value (NPV) for a project is a sum of all the positive cash flows subtracted from the initial investment over a time period at a particular interest rate. In the past, economic analysis of processing plants was done by hand; this could become cumbersome for process plants with several pieces of equipment, sometimes leading to inaccurate results. Capital cost is the bulk of the estimation that is required for economic assessment. Capital cost estimates can be classified according to level of accuracy as described in Table 3.1.

$$\text{Pay Back Period} = \frac{\text{Cost of Investment}}{\text{Cash flow per period}} \tag{3.1}$$

$$\text{ROI} = \frac{\text{Net Income}}{\text{Cost of Investment}} \tag{3.2}$$

Table 3.1: Capital Costs Accuracy Levels (Taal et al., 2003)

Type of Estimate	Basis	Accuracy
Order of magnitude (ratio estimate)	Previous similar cost information	±40 %
Study (factored estimate)	Knowledge of flowsheet and major equipment	±25%
Preliminary (initial budget, scope	Sufficient data for budget preparation	±12%
Definitive (project control)	Detailed data, but not complete drawings	±6%
Detailed (firm, contractors)	Complete drawings and specifications	±3%

Accurate estimation of the profitability of a process is very vital for project feasibility studies and assessments. Thus the next section discusses the following reliable tools for profit estimation: Capital Cost Estimator (CAPCOST), Aspen Process Economic

Analyzer, HYSYS Spreadsheet, Profitability Analysis and The Design Option Ranking Tool.

3.2.1 Capital Cost Estimator (CAPCOST)

CAPCOST was developed by Turton et al (2009), and approaches proposed by Guthrie (1974) and Ulrich (1984) have been implemented into the tool. CAPCOST is a Microsoft Excel / Visual Basic computer program that can be used for estimating the capital and operating costs for a chemical process. One advantage of CAPCOST is that it is able to evaluate economics while incorporating uncertainties in cost parameters using an inbuilt Monte Carlo Simulation. CAPCOST has served as a useful capital cost estimator for researchers, professors and students (Abedi, 2007; Ferrandona et al., 2008; Holt et al., 2009; Kumar et al., 2010).

3.2.2 Profitability Analysis Spreadsheet

The Profitability Analysis Spreadsheet was developed by Holger (2002), a graduate student at the University of Pennsylvania. This software is a Microsoft Excel / Visual Basic computer program that can evaluate the economics of a chemical process. The types of analysis that can be completed include rate of return on investment, net present value and investors' rate of return. The spreadsheet is unique in that it is able to complete a sensitivity analysis on variable costs. The profitability analysis software has also been used by researchers, professors and students (Murthy et al., 2006; Abuschinow et al., 2009).

3.2.3 HYSYS Spreadsheet

The HYSYS Spreadsheet is an inbuilt tool available in the HYSYS process simulator. This tool has many modeling applications such as optimization, simple calculations such as pressure drop calculations and economic calculations (Prasad, 2009). In this tool, users can input equations for sizing and capital costs evaluations into the spreadsheet. The HYSYS spreadsheet is advantageous because it is linked to the HYSYS simulator, and hence results of the economic calculations are updated automatically when flowsheet variables are changed. This option has not been widely used in assessing economics, probably due to the cumbersome nature of inputting economic equations, however one researcher used this tool to assess the economics of four biodiesel production processes (West et al., 2008).

3.2.4 Aspen Process Economic Analyzer

The Aspen Process Economic Analyze, formally known as the Aspen Icarus Process Evaluator, is an economic assessment tool developed by Aspen Tech (Dunn et al., 1999). The software is a sophisticated tool that is able to collect process data from process simulators such as ASPEN PLUS, CHEMCAD, HYSYS, HYSIM, DESIGN II, WinGEMS and PROII (Taal et al., 2003). This economic analyzer is able to use process data to accomplish the following: size process equipment, provide results of capital, installation and operating costs as well as analyze project planning schedule.

The tool is able to estimate profitability analysis for various process options. As this software has an expert system analysis, most of the inputs are obtained from imported data from a process simulator. The software maps selected equipment, sizes it and provides the capital and operating costs. The Aspen Icarus Economic Analyzer is a widely accepted assessment tool that has been used by industry and academia (Adams and Seider, 2005; Smejkal et al., 2005; Cornelissen et al., 2006; Giorgio et al., 2006; Ordorica-Garcia et al., 2006; Ringer et al., 2006; Fan and Lynd, 2007; Persson et al., 2007; Al Jadaan et al., 2008).

3.2.5 Design Option Ranking Tool (DORT)

The Design Option Ranking Tool (DORT) was developed by a researcher at Michigan Technological University for the economic evaluation of chemical processes (Toth, 1995). This tool is unique in that it is able to incorporate stochastic and multi-criteria decision analysis (Toth, 1995). The tool is able to calculate equipment costs, operating costs, income and other expenses as well as perform a full economic analysis by providing economic results such as payback period, net present value, and fixed capital investment. The DORT software was used by a few researchers at Michigan Technological University (Toth and Barna, 1996; Chen and Shonnard, 2004). For example, the DORT software has been integrated into the Simultaneous Comparison of Environmental and Non-Environmental Process Criteria (SCENE) as an assessment tool. to evaluate the profitability of a process (Chen and Shonnard, 2004)

3.2.6 Summary of Economic Assessment Tools

Five different economic assessment tools were presented in this section. All assessment tools can evaluate capital costs, with the exception of the Profitability Analysis Spreadsheet. Although the profitability analysis spreadsheet can evaluate project economics, in order to use the tool, the engineer will need to calculate capital costs by hand or incorporate one of the other capital cost estimating software such as CAPCOST or Aspen Process Economic Analyzer. CAPCOST is advantageous in that it has an inbuilt Monte Carlo simulator to evaluate fluctuation in costs as economic parameters vary with different conditions. It is also able to determine the net present value for a chemical process when economic parameters are specified. However, one limitation of the software is that it cannot be linked to a process simulator, so whenever there are changes in process conditions, the user will manually have to update the input parameters in the software.

The limitation of the HYSYS spreadsheet is that even though it can estimate capital costs, all equations for capital costs have to be inputted manually into the tool. This could be very cumbersome and time consuming. However, the pros to using the software is that once the equations have been incorporated, the tool will automatically estimate capital cost with any change in process conditions because it is linked to the process simulator HYSYS. Another disadvantage of using the HYSYS spreadsheet is that it does not evaluate full blown economic analysis such as net present value.

The DORT Tool and Aspen Process Economic Analyzer are advantageous because they can link to process simulators and import mass and energy balance data for capital cost estimation making it very convenient for the process engineer. These software tool are also able to complete full blown economic analysis involves estimating net present value and discounted flash flow. However, one limitation of the DORT software and Aspen Process Economic Analyzer is that, unlike CAPCOST, they do not have a Monte Carlo simulator to handle uncertainties in economic parameters.

Because the ASPEN process simulator will be used for simulating processes in this research, the Aspen Process Economic Analyzer has been selected as the tool for the economic assessments.

3.3 ENVIRONMENTAL EVALUATION TOOLS

In this section, environmental concerns relating to industrial activity are introduced and the tools available for addressing these impacts are discussed.

3.3.1 Environmental Concerns

Environmental issues have been a major topic of discussion since the early 1960’s. Activities leading to a more comfortable lifestyle have led to pollution of air, water and land. Air pollutants such as particulate matter, lead, sulfur dioxide, carbon monoxide and nitrogen oxide are prone to causing respiratory diseases such as asthma, bronchitis and emphysema, and even mortality in infants and aging adults (Hersh, 2005). Pollution of water threatens and affects access to clean portable water and affects the health of aquatic organisms.

To protect human life and the environment, the Clean Air Act and Clean Water Act were established by the United States Congress. Although amended in 1990, the Clean Air Act, established in 1970, includes standards set and regulated by the EPA to ensure the reduction of certain harmful air pollutants (United States Environmental Protection Agency, 1990). This act certifies that industrial facilities, car manufacturers and refineries are designing products or processes that meet regulated standards. The Clean Air Act ensures pollutants are emitted at a regulated standard. In 1977, the Clean

Water Act, was established to guarantee water quality standards are met by eliminating the release of toxic materials into water sources (United States Environmental Protection Agency, 1977).

Industrial processes have contributed to the pollution problem. As shown in the onion diagram (Figure 3.1) proposed by Smith and Linnhoff (1988), in the chemical industry, pollution arises from process equipment and utilities. There is never a 100 percent conversion of raw materials into products. By-products and intermediates are formed, raw materials and not completely converted to products and utilities are not used efficiently, which all contribute to waste generation. Even when separators are in place, some products and raw material might not be recovered completely and hence, contribute to waste generation.

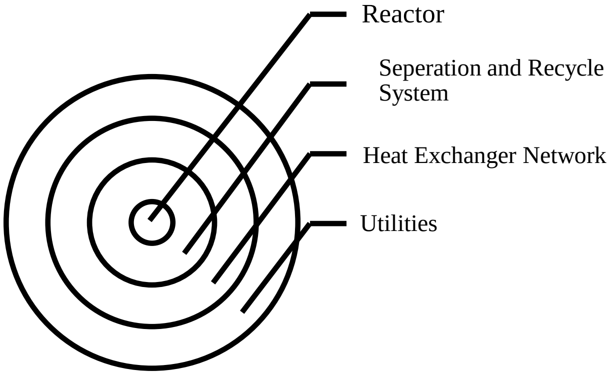


Figure 3.1 :Onion Diagram Showing Wastes from the Chemical Processing Industry (Smith and Linnhoff, 1988)

If pollution issues are not handled appropriately, it could lead to expensive fines and even law suits. Hence, pollution prevention and mitigation strategies have become an integral aspect of the design process. Several methodologies exist for handling pollution issues. These include end of the pipe design and source reduction tools, commonly referred to as process integration technology (Dunn and Bush, 2001).

End of pipe treatment involves using methodologies that separate and treat waste and polluted steams. This treatment effort began as early as the early 70's, and there are so many researchers who have introduced approaches that have benefited the process industry. Notable approaches include mass exchange network (Miguel and Vasilios, 1992), heat induced separation network (El-Halwagi et al., 1995), energy induced separation network (Dunn et al., 1999) and membrane separation network where pollutants are removed from waste streams by using separation equipment (El-Halwagi, 1992). These ends of the pipe treatment options can cost millions of dollars, and source reduction technologies appears to be promising in terms of economic and environmental reasons because waste production and environmental emission are minimized.

Source reduction technology can include introducing new reaction pathways that create the product in an environmentally friendly way, using more benign reactants and solvents, implementing heat integration techniques to reduce energy usage and emissions, recycling waste water and un-used reactants, converting pollutants into useful products and implementing heat and energy induced waste minimization methodologies. Even after, implementing these process integration technologies, it is still important to ensure environmental regulations are being met and economic liability is kept at a minimum. This can be accomplished by conducting ecological impact analysis by using environmental assessments tools.

Environmental impact assessments accomplish the following: allow the identification of waste reduction opportunities, reduce waste treatment costs, allow resource conservation due to unused material recycling and ensures regulatory requirements are met, reduce health risks as well as reduce ecological damage. Several environmental concerns are discussed in literature and in this dissertation. The next section introduces the following: global warming, acidification, eutrophication, photochemical smog formation, abiotic reserve depletion and ozone depletion.

3.3.1.1 Global Warming

Global warming, defined as the change in weather over a long period of time, is caused by increased emissions of greenhouse gases. Although other greenhouse gasses exist, carbon dioxide (CO_2) is the major contributor to global warming. CO_2 is emitted from various sectors such as the residential, commercial, industrial, transportation and electricity generation as shown in Figure 3.2. As shown in the graph, in 2008, the transportation sector accounted for 33%, industrial sector accounted for 27%, the commercial sector accounted for 19% and the residential sector accounted for 23% of the CO_2 emissions. CO_2 in the atmosphere has increased by 35% since 1850 (United States Environmental Protection Agency, 2006).

CO_2 emissions has caused tremendous environmental and health concerns. There has been an increased awareness towards global climate change in the last few years. Major key players including industry, academia, the United States Government and the United Nations are all concerned with global climate change. The effect of global climate change have been noticed around the world with rapid rising temperatures leading to the melting of ice in the arctic region, heavier rainfall leading to floods in certain regions of the world, increased hurricane frequency, droughts, decreased biodiversity and threats to human health due to rapid spread of diseases from warmer temperatures (Gardiner, 2004). Health issues linked to global warming include deaths due to disastrous weather conditions and spread of infectious disease as a result of warmer temperature.

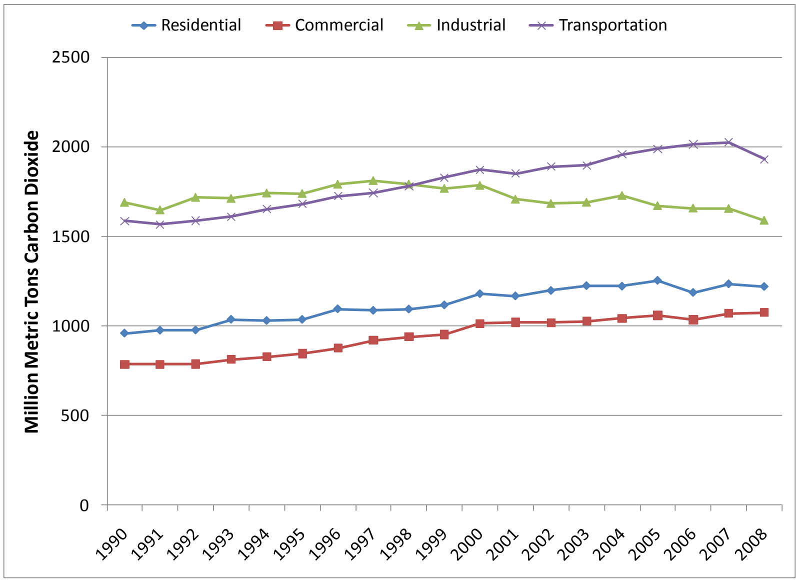


Figure 3.2: Carbon Dioxide Emissions by Sector (United States Information Administration, 2009)

As a result of the environmental and health concerns related to global warming, it has become necessary to determine ways to reduce greenhouse gas emissions. On the personal level, individuals can reduce their footprint by reducing energy consumption, using energy saving bulbs, replacing filters in air conditioners, using energy efficient appliances and reducing fossil fuel consumptions by carpooling, using fuel efficient cars and using public transportation. On the industrial level, companies can determine ways to reduce greenhouse gas emissions by designing processes that minimize wastes and emissions. On the academic level, research can be done to improve carbon capture techniques as well as development of more efficient energy and fuel appliances. On the governmental level, incentive based policies such as implementing a carbon tax i.e. taxing companies who emit certain levels of CO_2 and carbon trade and cap, a process were companies are allowed to trade and buy emission limits from each other are also ways to reduce CO_2 emissions.

3.3.1.2 Acidification

Acidification is linked to the anthropogenic emissions of gases such as sulfur oxide and nitrogen oxide. Acidification of the environment is a problem in industrialized countries (Rodhe, 1989). Fossil fuel consumption, agricultural activities, electric generation and other industrial activities can result in the deposition of acidic causing chemicals that reduce alkalinity and increase acidity of the environment including land and water to pH levels below 5 (Doney et al., 2007). Acidic chemicals such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3) can be deposited dry or wet. Wet deposition commonly known as acid rain, fog or mist, is damaging to the ecosystem, resulting in stunted plant growth, building material decay, poor health of organisms and even decreased biodiversity (United States Environmental Protection Agency, 2008a). Ocean acidification is a major issue to aquatic organisms and depending on the pH level, it affects different organisms as shown in Figure 3.3. Some of the health problems of acidification in humans include respiratory issues, lung and cardiovascular disease.

Acidification of the environment can be curbed by using pollution control devices such as on smoke stacks and exhaust pipes. Scrubbers can be used to eliminate sulfur oxide emissions from power plant stacks. Natural gas can also be used instead of coal for running power plants because it contains fewer pollutants. To reduce pollution from exhaust pipes, efficient working catalytic converters should continue to be used in cars. Using alternative energy such as nuclear, wind, batteries and fuel cell is one other vital way to reduce emissions of acidic causing chemicals.

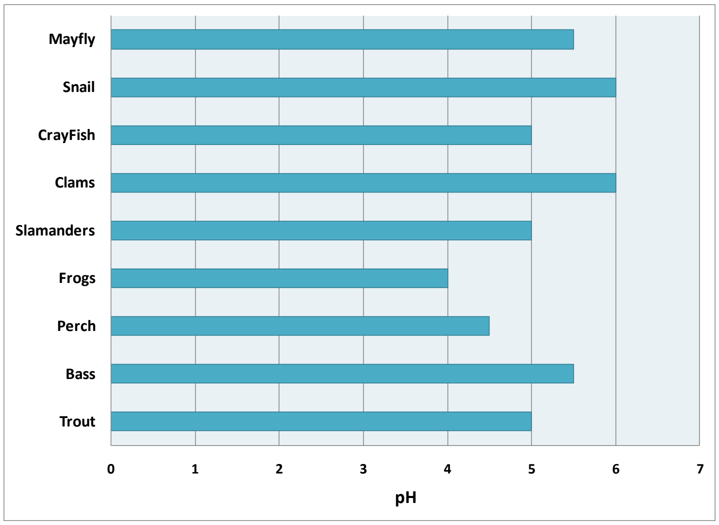


Figure 3.3: Aquatic Organisms Affected by Acidification According to Different pH Levels (United States Environmental Protection Agency, 2008b)

3.3.1.3 Eutrophication

Eutrophication is defined as the deposition of unwanted nutrients namely nitrates and phosphates, in the ecosystem especially in aquatic environments. Sources of unwanted nutrients include: agricultural and husbandry activities such as fertilizer usage; industrial activity due to emission of nitrates and phosphates; sewage from towns and soil erosions. The eutrophication cycle shown in Figure 3.4, illustrates that the outcome of increase in unwanted nutrients in aquatic environments leads to rapid unnatural growth of phytoplankton that will compete for nutrients with submerged aquatic vegetation.

In favorable turbid conditions, phytoplankton growth can be as rapid as doubling every 24 hours (Wright, 2007). Once nutrients become scare, survival becomes difficult and the end result is accumulation of dead phytoplankton which leads to bacteria growth. Bacteria growth leads to depletion of oxygen which affects the health of larger aquatic organisms sometimes leading to suffocation and death. Contaminated water sources due to increase activity as a result of increased microbe organism become unpleasant to humans because water quality becomes poor and even toxic, limiting the access to clean portable water. Turbid and cloggy water conditions, also halts life events such as swimming, boating and fishing.

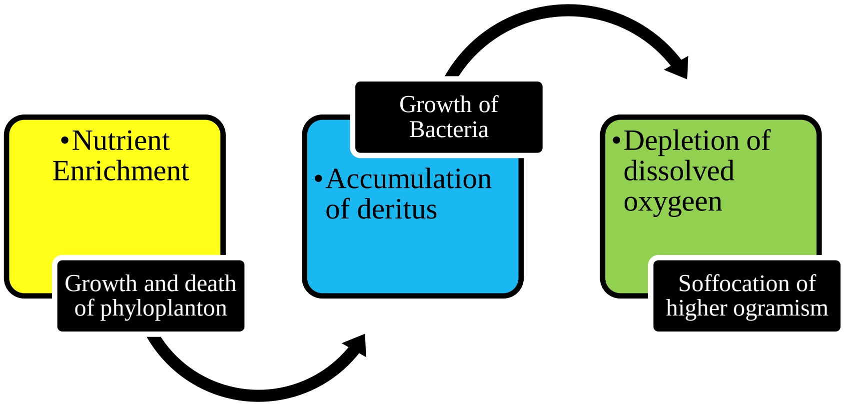
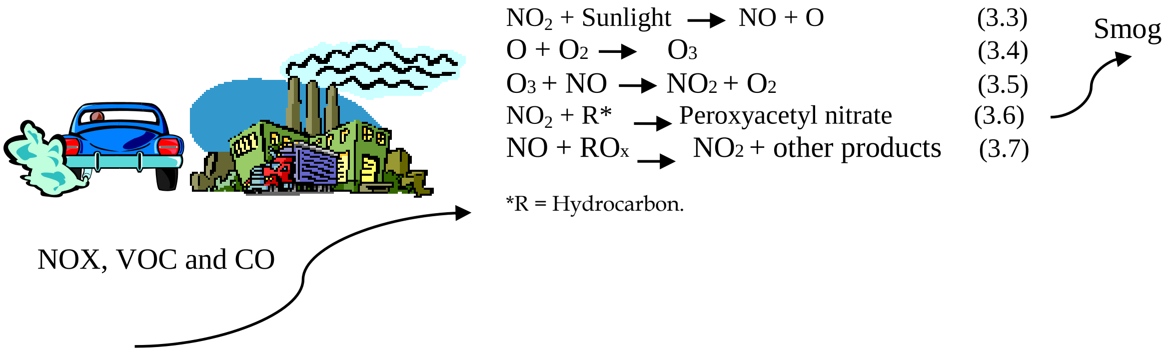


Figure 3.4: Eutrophication Cycle

To protect the environment and human life, it is important to reduce eutrophication. This can be accomplished by reducing industrial emission of pollutants into water sources, improving waste water treatment methodologies, banning the use of phosphorus containing detergents, reducing the use of fertilizers, proper handling of manure and soil conservation practices in order to reduce erosion (Conley et al., 2009). Also treatment options include applying herbicides to lakes and ponds, implementing artificial aeration to avoid oxygen depletion, harvesting aquatic weeds to prevent phytoplankton growth and drawing down dammed lakes to kill aquatic plants.

3.3.1.4 Photochemical Smog Formation

Photochemical smog formation, as shown in Figure 3.5, is a process that occurs when pollutants such as nitrogen oxide and volatile organic carbon react with sunlight to form a haze like appearance in the atmosphere. Sources of nitrogen oxide include emissions from industrial plants; coal fired power plants, exhaust pipes of vehicles. Sources of volatile organic carbon emissions include gasoline, paints, solvents, pesticides, and biogenic sources. At certain weather conditions i.e. when advection and radiation inversion occur, photochemical smog formation is more favorable.



$$NO_2 + \text{Sunlight} \rightarrow NO + O \tag{3.3}$$

$$O + O_2 \rightarrow O_3 \tag{3.4}$$

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{3.5}$$

$$NO_2 + R^* \rightarrow \text{Peroxyacetyl nitrate} \tag{3.6}$$

$$NO + RO_x \rightarrow NO_2 + \text{other products} \tag{3.7}$$

*R = Hydrocarbon.

Figure 3.5: Photochemical Smog Formation (Wright, 2007)

As shown in Figure 3.5, the byproducts of photochemical smog (nitrogen oxides, ozone and peroxyacetyl nitrate) curb photosynthesis and hence reduce plant growth. Health effects associated with photochemical fog formation include respiratory and cardiovascular issues, eye irritation, coughing, wheezing and increased cancer risk (United States Environmental Protection Agency, 2004). To reduce photochemical smog, efficient catalytic converters and lower combustion temperature should be used because it reduces the formation of nitrogen. Alternative fossil fuels such as liquefied petroleum and compressed natural gas reduce the emission of volatile organic compounds compared to coal and petrol.

3.3.1.5 Abiotic Reserve Depletion

This is defined as the depletion of natural resources. Natural resources can be classified as renewable and non-renewable. Renewable resources can be replenished in a short amount of time and these include, water, animals, insects, reptiles, plants, trees, water, grass, solar and wind energy. Fossil fuels, oil, coal; copper, diamonds, natural gas, iron ore, minerals, gold, silver, platinum and rocks are examples of non-renewable resources i.e. resources that take millions of years to regenerate if used up. Environmentalists are most concerned with non-renewable resource depletion. This type of depletion is caused by different reasons such as overpopulation, inefficient use of resources, mining activities and industrialization.

To ensure we have resources for future generations, it is important we use our reserves in a sustainable manner where we are building and improving upon technology. This could include using alternative energy to reduce the burden of fossil fuels, replanting trees, eliminating wastes and reducing our energy footprint by using sustainable options for our day to day activity.

3.3.1.6 Ozone Depletion

Ozone depletion is a process where the ozone found in the atmosphere is gradually diminished. Chlorofluorocarbons (CFCs) are the major chemicals that cause ozone depletion. CFCs are found in refrigerants used in air conditioners and heat pumps. They are also found in plastic foam production, electronic industry for computer parts and pressurizing agents in aerosol cans (Wright, 2007). The breakdown of ozone is depicted in the Equations 3.8-3.10 below. CFC reacts with sunlight and breaks down into chlorine and a smaller CFC molecule. Chlorine reacts with ozone to form oxygen molecule and chlorine oxide. This is the reaction that depletes the ozone layer. A third reaction takes place where two molecules of chlorine oxide combine to form chlorine and more oxygen.

$$CFCL_3 + UV \rightarrow Cl + CFCl_2 \tag{3.8}$$
$$Cl + O_3 \rightarrow ClO + O_2 \tag{3.9}$$
$$ClO + ClO \rightarrow 2Cl + O_2 \tag{3.10}$$

Table 3.2: Ozone Depletion Causing Chemicals Phase Out Dates (Site, 1997)

Chemicals	Phase out date	
	Developed Country	Developing Country
Halons	1994	2010
CFCs, chloroform	1996	2010
Carbon tetrachloride	1996	2015
Methyl bromide – • Freeze • Phase-out	1995 2010	2002
HCFCs – • 90% cut • Phase out	2016 2030	2040

The depletion of the ozone layer is an issue of concern because it protects us from harmful ultraviolet rays. Ultraviolet rays damage proteins and DNA molecules of all organisms and could lead to complications such as sun burn and skin cancer in humans, poor development in aquatic organisms such as fish, shrimp, crab, amphibians and other animals, as well as stunted growth in plants. It is therefore important to reduce ozone depletion by phasing out ozone depleting substances as shown in Table 3.3. Table 3.3 shows fazing schedule for certain ozone depleting chemicals for developed and developing countries. Regulating emitted ozone causing chemicals and ensuring that refrigerants and extinguishers are recycled appropriately are some of the other ways to reduce ozone depletion.

3.3.2 Environment Impact Assessment Tools

The previous section presents a range of environmental concerns that are caused by manmade activities. The key question is how exactly can scientists evaluate the environmental impact processes and products? So much research has been done to addresses these environmental issues. Pioneers in the process industry have considered pinch analysis (Ferrandona et al., 2008; Seay and Eden, 2008), waste minimization optimization approach (Dantus and High, 1999) and environmental impact assessment tools to tackle these concerns. It is clear that in order to address environment concerns; all feasible mitigation options must be considered. However it is important to have tools that can be used to evaluate substantial process improvements. Several environmental impact assessment tools exist and the features and applications of the following assessment tool are discussed below: Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), Waste Reduction Algorithm (WAR), Environmental Fate and Risk Assessment Tool (EFRAT) and Minimizing Environmental Impact (MEI).

3.3.2.1 Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts

The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI) was developed in 2002 by the Environmental Protection Agency to assess environmental concerns, human health and resource depletion associated with using the product of interest. This software is one of the many Life Cycle Assessment (LCA) tool available. LCA can be defined as an incorporated study of the environmental impact of a product, process or service from cradle to grave by completing the following (United States Environmental Protection Agency, 2007):

- Keeping track of the material, energy, wastes and toxic emission from the product or process.
- Accessing the environmental burdens.
- Interpreting the results of the assessment to ensure that a more environmentally sustainable option is considered.

The TRACI software serves as a decision making tool where options can be compared and the product with the least environmental impact can be considered. The tool was developed for product evaluation during the design stage (Bare et al., 2002). In TRACI, the user has the ability of selecting any of the following type of LCA (Umited States Environmental Protection Agency Office of Research and Development, 2002):

- Cradle to Grave: Defined as a LCA approach that includes all stages from raw material acquisition to product disposal.
- Cradle to entry gate: Type of assessment that looks at upstream supplier and transportation before reaching the manufacturing facility.
- Entry gate to exit gate: An assessment of the environmental impact when the product is at the manufacturing facility.
- Exit gate to grave: Evaluation of the environmental impact when it leaves manufacturing facility to final product disposal.

The TRACI software can be divided into four major categories: inventory of stressors, impact categories, characterization and overall effect. An example of how TRACI software works is better illustrated in Figure 3.6.

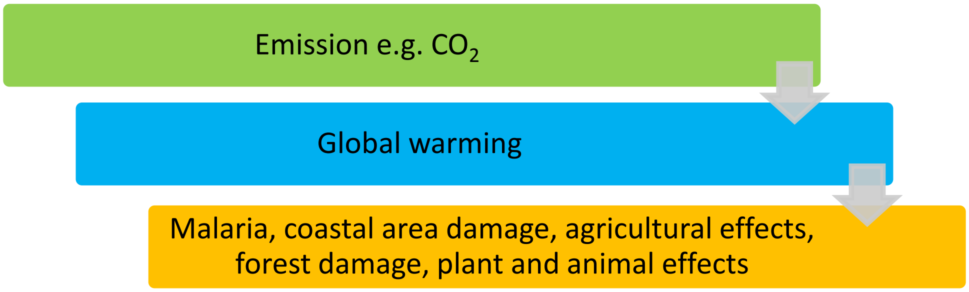


Figure 3.6: Example of How TRACI Provides Overall Effect

TRACI has been used be several researchers (Wu et al., 1999; Kim and Dale, 2005; Morris, 2005; Bare et al., 2006; Güereca et al., 2007; Singh et al., 2007; Thorneloe et al., 2007; Kim and Dale, 2008; Morris and Bagby, 2008; Zhou and Schoenung, 2009). It has been incorporated into the Environmental Knowledge and Assessment Tool (EKAT), a screening tool for environmental and health impacts (Boguski et al., 2007). Although TRACI has been used by researchers it is has some limitations. One limitation is that it only addresses 12 environmental impact categories, thus it is not extensive software. Also TRACI can only be used as a screening tool because risk estimates are not provided in this tool (Bare, 2002). Lastly uncertainty and variability assessments cannot be completed on TRACI (Bare, 2002).

3.3.2.2 Waste Reduction Algorithm

The Environmental Protection Agency (EPA) developed the Waste Reduction Algorithm (WAR), a publicly available screening tool to evaluate the potential environment impact of chemicals found in industrial processes (Chen and Shonnard, 2004; Seay and Eden, 2008). The WAR uses an index based approach to characterize potential pollution reductions using report files from a process simulator such as ASPEN PLUS or CHEMCAD. The tool measures the environmental impact of emission of mass and energy for any simulated process (Cabezas et al., 1999). In the WAR, nine impact categories exist and these include acidification, greenhouse enhancement, ozone depletion, and photochemical oxidant formation, three human toxicity effects from air, water, and soil, and ecotoxicity effects on aquatic and terrestrial environments.

The WAR algorithm has been used my many researchers to evaluate the environmental impact of several processes (Mallick et al., 1996; Young and Cabezas, 1999; Cardona et al., 2004; Eliceche et al., 2007; Li et al., 2007; Carvalho et al., 2008; Quintero et al., 2008; Monteiro et al., 2009). Although the WAR algorithm has been widely used, Fermeglia, Longo and Toma (2007) suggest that the WAR algorithm is limited because it only has toxicology data for 1700 chemicals and some chemicals might not be covered in the software. Also, the WAR algorithm is not a full LCA and it only focuses on the manufacturing step while incorporating the impact of energy consumption when producing a product.

3.3.2.3 Environmental Fate and Risk Assessment Tool Software

The Environmental Fate and Risk Assessment Tool (EFRAT) was developed by Shonnard and Hiew (2000) is a “gate to gate” assessment. The tool is able to evaluate the environmental impact of a manufacturing process by performing three major calculations air emission estimation, environmental fate and transport, and relative risk assessment.

In order to complete these calculations, process simulator data such as number and sizes of equipment, chemicals present in manufacturing process, annual throughput in each piece of equipment, utility type and consumption and production rate are supplied to the EFRAT software. With this information, an overall environment index can be calculated for a process. The results of the EFRAT tool can be used for decision making, i.e. designers can select process option with a lower environmental index.

The limitation of the EFRAT software is that it is a partial LCA since it is a gate to gate assessment. Despite the limitations, EFRAT has been used by several researchers for environmental assessments of several manufacturing processes and also for developing other environmental tools (Chen et al., 2001a; Chen et al., 2001b; Chen et al., 2002; Chen and Shonnard, 2004; Kemppainen and Shonnard, 2005).

3.3.2.4 The Environmental Knowledge and Assessment Tool (EKAT)

Collaborative efforts of the National Environmental Evaluation and the Remediation Consortium resulted in the Environmental Knowledge and Assessment Tool (Boguski et al., 2007). This web-based tool available at www.ekat-tool.com is able to provide assessment resources for environmental, health and safety risks associated with material and systems used in creating products. The tool is able to provide emissions estimates from manufacturing process and equipment; highlight environmental, health and safety compliance issues from chemicals, toxic chemical air concentrations, conduct environmental impact assessment using indexes found in TRACI. The tool also has links to other external databases such as toxicology and hazardous chemicals. Because this a fairly new tool it has not been used by many researchers. One researcher incorporated the screening tool found in the EKAT tool into another tool called the online emergency preparation and green engineering (EPGE) tool in order to identify green solvents (Whiteley et al., 2009).

3.3.2.5 The Methodology for Environmental Impact Minimization (MEIM)

The Methodology for Environmental Impact Minimization (MEIM) was developed by Pistikopoulos, Stefanis and Livingston (1994) to reduce environmental impacts in batch and continuous chemical processes. The tool has an embedded LCA with an optimization framework that accounts for economic concerns as well (Stefanis and Pistikopoulos, 1997). The issues addressed by the software include the environmental risks associated with process wastes, leaks and fugitive emissions. Several researchers have used this tool to evaluate environmental impact (Stefanis et al., 1995; Stefanis et al., 1996; Stefanis et al., 1997).

3.3.2.6 Environmental Optimization Expert System (ENVOP Expert)

The ENVOP Expert system, an automatic tool developed by Halim and Srinivasan (2002) for qualitative waste minimization assessment. This tool provides a systematic procedure for identifying ways to reduce emissions, solid waste generation and utility wastes so that non experts in the area of waste minimization are able to complete the assessment. The tool is able to classify process steams such as raw materials, solvents, cooling, heating agents, and products as valuable, material impurities and waste byproducts as worthless. The tool is able to use imported mass and energy balance data from the HYSYS Process simulator to complete the waste minimization assessment (Halim and Srinivasan, 2002; Halim and Srinivasan, 2006).

3.3.2.7 Summary of Environmental Impact Assessment Tools

Six environmental impact assessment tools were identified. Table 3.3 summarizes the key features and differences between the environmental impact assessments tools discussed earlier. The ENVOP Expert system is not compared in Table 3.3, because it is quite different from the other tools. Unlike the other tools, it used for deducing waste minimization strategies and not for environmental impact assessment. The ENVOP Expert system can be linked to data from a process simulator to determine an appropriate waste minimization strategy.

Table 3.3: Summary of Environmental Impact Assessment Tools

Tools	Process Simulator Linkage	Type of Environmental Impact Assessment	Air Emission Modeling
TRACI	No	Four Options: cradle to grave, cradle to entry gate, entry gate to exit gate, or exit gate to grave	No
EFRAT	Yes	Entry gate to exit gate	Yes
WAR	Yes	Entry gate to exit gate	No
MEIM	No	Cradle to grave	No
EKAT	No	Cradle to grave	Yes

As for the other five environmental impact assessment tools, the WAR and EFRAT are advantageous because they have the ability to get input from a process simulator used in completing the the environmental impact assessment. One pro of TRACI, MEIM and EKAT is that it takes into account the entire life cycle stages for environmental impact. One advantage of EFRAT and EKAT is that they all have the capability of conducting air emission modeling. In all, these tools could be quite complicated and might not be appropriate for early stages of process design. Therefore an appropriate tool is developed and introduced in section 5 to address environmental concerns during process design.

3.4 SAFETY AND HEALTH EVALUATION TOOLS

In this section, safety and health issues relating to industrial activity are introduced and the tools available for addressing these impacts are discussed.

3.4.1 Health and Safety Concerns

This year, we approach the 26th anniversary of the Bhopal tragedy, the largest industrial accident to date. This catastrophe, caused by the release of methyl isocyanate gas from a Union Carbide plant, led to 10,500 deaths, long term environmental issues and liabilities (Wright, 2007). Months after the incident, management in Union Carbide probably completed a safety review, investigating what could have been done differently to avoid the tragedy. The era of waiting for an incident to occur and then implementing other preventive measures is long gone and is no longer acceptable to society. For example, after the Fixborough, England cyclohexane release that killed 28 and injured 99 people due to the collapse of a pipe leading to the escape of 35 tons of cyclohexane, it was determined that calculations were not completed to determine if the pipes could withstand the strain (Flynn and Theodore, 2002).

The key issue is that these incidents could have been prevented. Some notables approaches to preventing safety incident include using less hazardous materials, using devices such as safety valves, emergency shutdown procedures and ensuring operating procedures are incident and injury free. Every new and existing manufacturing facility must now complete a health and safety assessment to predict and prevent an unsafe catastrophe from occurring. Incidents in chemical processing facilities include the following: mechanical crushings, dropped objects, corrosive burns, acute poisoning due to toxic chemical exposure, asphyxiation, fire and explosion. Whenever there is a catastrophic event, the cost is drastic. Companies could lose millions of dollars from an unexpected shut down; millions of dollars in fines imposed by the government will have to be paid back for the damage inflicted on the environments and millions of dollars might have to be paid to employees to compensate them for chronic health effects and even incapacitation.

One cannot over emphasize the importance of completing safety risk assessments during the early stages of process design as it has the potential of preventing dreadful incidents. Companies are now required to conduct safety analysis that addresses the following concerns: hazard that can occur, probability of the hazard to occur and impact of the hazard (Arendt and Lorenzo, 2000). The assessment must also consider the risks of long and short term exposure to chemical substances to employees and the public living in close proximity to the chemical facility. The subsequent sections discuss the different types of chemical processing plant accidents and tools available for predicting health and safety risks.

3.4.1.1 Chemical Processing Plant Accidents

A safe chemical processing plant is characterized by the situation where little to no disastrous accidents occurs. Chemical processing plant accidents are unexpected events that can result in financial and personal loss. In processing plants, accidents can occur as results of the following:

- Equipment Failure: Abnormal conditions such as equipment leaks, irregular temperature and pressure ranges, equipment spills and operational failures such as vacuum problems, blocked out let valve, cooling water failure can lead to an incident.

- Human Errors: Incorrect calculations and assumptions when designing process equipment can lead to accidents. Improper use of process equipment, not grounding electrical systems and thermal hazards.

When any or the combination of the events mentioned above occurs, several of the following incidents can occur at the right conditions: fires, explosion and toxic emissions and hazardous spills.

3.4.1.2 Fires

Fires occur when oxygen reacts with a fuel at the proper temperature in the presence of heat and mixing. The potential for a substance to cause fire is determined by its flammability limit, flash point temperature, burning velocity, ignition energy and auto ignition temperature (Flynn and Theodore, 2002). For most fires to occur there must be an ignition source. Figure 3.7 shows the typical ignition sources for industrial fires, according to a study completed by Factory Mutual Engineering Corporation (Flynn and Theodore, 2002). As shown in the figure, electrical accidents is the major ignition source accounting for 23% of industrial fires while chemical action, lightening, static electricity are the least ignition sources causing 1% of industrial fire.

According to the National Fire Protection Association, fire can be classified into four classes (Firenze, 1979):

- Class A Fires: These are fires that result from the burning of solid materials e.g. wood, paper, cloth, trash etc. This type of fire can be extinguished by water which reduces the ignition temperature.
- Class B Fires: These are fires that occur as a result of a vapor-air mixture over flammable liquid e.g. gasoline, diesel etc. This type of fire can be stopped by using CO_2, foam, and halogenated hydrocarbon fire extinguishers.

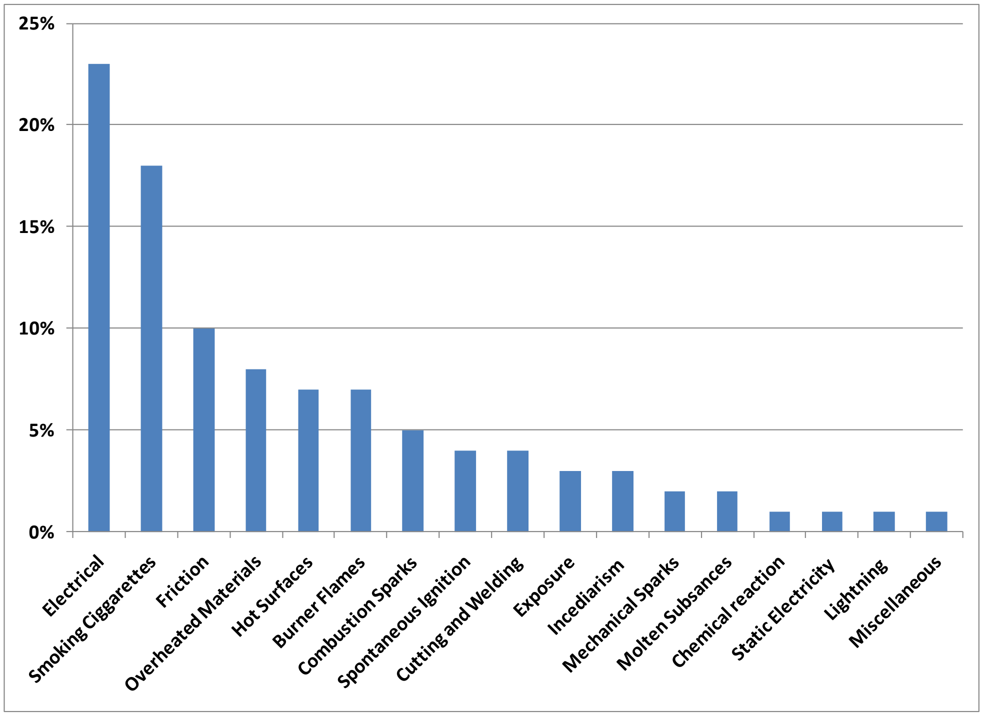


Figure 3.7: Ignition Sources of Industrial Fires (Flynn and Theodore, 2002)

- Class C Fires: These are fires that result from electrical equipment failure and can be stopped by using dry chemicals, carbon dioxide, compressed gas and vaporizing liquid.
- Class D Fires: These are fires that occur in combustible metals e.g. magnesium and aluminum etc. This type of fire can be quenched by using graphite based extinguishers.

To prevent industrial fires, spills should be cleaned up immediately, leaks should be sealed off as soon as possible and equipment that tends to overheat should be insulated with appropriate materials. Also unnecessary inventory of hazardous material should be disposed accordingly and not stored on site. Once the fire occurs, it is important to identify the class of fire in order to quench it with the correct material.

3.4.1.3 Explosions

Explosions occur when there is a rapid release of energy in a constricted volume, which results in extremely high temperature and gas release. Accidental explosion include condensed phase, combustion, pressure vessel and vapor cloud explosions (Flynn and Theodore, 2002). The tendency for a substance to cause an explosion is determined by its explosion limit. The explosion limit is the range of concentration that explosion can occur. The range is bounded by the upper explosion limit (UEL) and the lower explosion limit (LEL). Plant explosions are mainly caused by equipment failures, or incorrect operational procedure. For example when two incompatible chemicals are reacted, an explosion can occur. Vessel rupturing due to pressure build up in a gaseous exothermic reactor can lead to an explosion. Inappropriate vessel material for certain toxic substance at extreme high temperatures can also lead to an explosion. Explosions can often be prevented by ensuring sound engineering practice is implemented when designing process equipment.

3.4.1.4 Toxic Exposure

Exposure of chemicals to humans can be accidental or planned. Accidental chemical exposure can cause significant threats to human life sometimes leading to death.

Planned exposure of chemicals is usually controlled by an exposure limit. Some chemicals are not toxic at certain concentration. The toxicity of most chemicals is evaluated by its toxic limit value. There are three different toxic level limits that are used in industry:

- Toxic Limit Value- Time Weighted Average: The toxic limit value- time weighted average also known as the permissible exposure limit, is defined as the average concentration of toxic chemical that a person can be exposed to in an 8 hour period.
- Toxic Limit Value- Short Term Exposure Limit: According to the American Conference of Governmental Industrial Hygienists, the toxic limit value- short term exposure limit is the concentration of toxic chemical that a person can be exposed to in a short time period without having adverse health effects.
- Toxic Limit Value-Concentration: This is defined as the maximum concentration of a toxic chemical that a person can be exposed to at any point in time.

3.4.1.5 Hazardous Spill

Hazardous chemicals which may exist in the three different states of matter are ignitable, reactive, corrosive, radioactive and infectious. Hazardous spills include the following: chlorinated oils, flammable wastes, synthetic organics, toxic metals, explosives, reactive metals, salts, acids and wastes. Uncontrolled hazardous chemical spills pose serious threats to human life, natural water, land environment and the ecosystem. An example of one of the most significant hazardous spill is the Exxon 1989 Valdez Oil Spill. The ExxonMobil 1989 Valdez Oil spill involved the accidental release of 250,000 barrels of crude oil into the Prince William Sound, Alaska ocean basin. Some of the negative impacts of this incident include the death of 375,000 sea birds, marine animals and habitat loss (Harwell and Gentile, 2006).

Most recently, in April 2010, the largest marine oil spill occurred when one of BP's offshore facilities exploded in the Gulf of Mexico as a result of a failed emergency blow out preventer. The effect of this incident has been devastating, leading to 11 death and 17 injuries (Brown, 2010; Welch and Joyne, 2010). Also for several months, more than 80,000 barrels of oil per day was gushing into the gulf, resulting in serious damage to marine life, wildlife, fishing and tourism (Mcquaid, 2010). It is evident that toxic spills have a tremendous impact on the ecological environment. It is therefore important to prevent, contain and clean these spills up by using sound sustainable engineering practice.

3.4.2 Health Risk Assessment

Health risk assessment measure the probability for a particular chemical at the correct dose to cause an adverse effect on human health. There are four steps that are conducted in a health risk assessments and these include hazard identification, dose-response toxicity assessment, exposure assessment and risk characterization. In hazard identification, information such as chemical identity, identification of equipment that produces, transport or stores the particular hazardous chemical(s), plant design, amount of chemical produced or available and the health investigation of whether exposure to a particular chemical(s) will increase the likelihood for adverse health effect such as cancer, birth effects etc. to occur is completed in this step (Flynn and Theodore, 2002).

There are many published methods for hazard identification and these include toxicology, epidemiology, molecular and structural analysis, material safety and data sheet, fate of chemical assessments and carcinogenic or non-carcinogenic health hazard assessments.

In the dose response toxicity assessment step, the quantitative assessment of chemical(s) toxicity as a function of human exposure is completed in this step. The Environmental Protection Agency Integrated Risk Information System is an excellent source for information on health risk regulatory data. In this database of 540 chemicals, oral reference doses[2], and inhalation reference concentrations[3] for non –carcinogen risk effects and oral slope factors[4] and oral[5] and inhalation[6] unit risks for carcinogenic effects are available (United States Environmental Protection Agency). This information can be used to conduct a quantitative and qualitative risk assessment.

In the exposure assessment step, an evaluation is conducted to determine who will be exposed to a particular toxic chemical and for how long. In exposure assessments, the following must be addressed:

- Probability of exposure: This is an evaluation of the likelihood that a population will be exposed to a particular toxic chemical.
- Magnitude of exposure: This is a measure of the dose of chemical a population is exposed to and the frequency in which the exposure occurs.
- Route of exposure: This determines if a population is in contact with a toxic chemical via inhalation, ingestion and skin absorption.

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[2] The maximum acceptable oral dose of a toxic chemical
[3] The maximum acceptable dose of a toxic chemical that can be inhaled
[4] Upper bound value used in calculating cancer risks
[5] Upper bound value used in calculating life time cancer risks from oral exposure
[6] Upper bound value used in calculating life time cancer risks from inhalation exposure

- Population Exposed: The people who are exposed to a particular toxic substance.

The health risk characterization step involves the estimation of the perceived health and ecosystem risks from a chemical exposure. Non-cancer risks for one substance can be measured by a hazard quotient which is calculated by Equation 3.11.

$$NCHQ = E/ RFD \tag{3.11}$$

Where

E = Exposure level
RFD = Reference dose
NCHQ= Non-cancer hazard dose

The non-cancer risks for several substances can be evaluated by calculating a hazard index as shown in Equation 3.12:

$$HI = E_1/RFD_1 + E_I/RFD_2 \ldots\ldots E_I/RFD_I \tag{3.12}$$

Hazard Index = Exposure

Low and high cancer risk as shown in Equation 3.13 and 3.14 respectively, are a measure of the probability that if one is exposed to a carcinogen, that person will be diagnosed with cancer. To evaluate the cancer risk for a mixture of substances, the risk is evaluated individually and then summed up.

$$\text{Cancer Risk} = (CD1) * (SF) \tag{3.13}$$

Where

CDI = Chronic daily intake averaged over 70 years
SF = Slope factor (mg/kg/day)

$$\text{Cancer Risk} = 1 - \exp(-CD1 * SF) \tag{3.14}$$

There are 5 risks levels that are used to qualitatively identify adverse health effects in hazard characterization and they are listed below (Flynn and Theodore, 2002):

- Risk Level 1: No adverse health effect
- Risk Level 2: Low probability of causing adverse effect
- Risk Level 3: There is possibly that chemical is a health hazard
- Risk Level 4: There is a possibility that chemical will cause adverse health hazards
- Risk Level 5: Chemical will cause adverse health hazard.

Risk assessment on an annual or life time basis can also be expressed quantitatively as shown in Table 3.4. In this table, assessments that have a level 1 characterization are worse in terms of health impact compared to level 7.

Table 3.4: Quantitative Risk Level (Flynn and Theodore, 2002)

Risk Level	Risk Range
1	1 in 1 – 1 in 9
2	1 in 10 – 1 in 99
3	1 in 100 – 1 in 999
4	1 in 1000 – 1 in 9999
5	1 in 10000 – 1 in 99999
6	1 in 100000 – 1 in 999999
7	1 in 1000000 – 1 in 9999999

3.4.3 Health and Safety Screening Tools

Several decades ago, risks were managed in the chemical industry by adding layer of protection between the hazard, people and environment leading to the reduction in the probability of the accident and or the magnitude of the impact. To determine the correct and adequate layer of protection that must be incorporated into design, health and safety risk assessment must be completed. One approach that has been used to assess the safety and health risk in a process is to complete a Hazard and Operability (HAZOP) Study.

A HAZOP analysis is a procedure that is completed for existing and new facilities and it involves identifying all the hazards and operability issues in a chemical process. In the HAZOP study, the safety impact of all the different equipment found in a process, specifically looking at the potential hazards when the process deviates from design conditions is evaluated (Dunjó et al., 2010). In order to complete a HAZOP analysis, detailed engineering design must be completed and process and instrumentation diagrams must be readily available. Although HAZOP analysis has been extensively used in the chemical process industry, it has some limitations. It is time consuming, as only one accident scenario can be looked at a time. It cannot be used during conceptual stages of design, as detailed process and instrumentation diagrams must be completed, requiring knowledge and expertise in order to complete the assessment accurately.

Other simpler tools and approaches that can be used at earlier stages of design that are less time consuming and more straight forward have been developed. This section focuses on screening tools for evaluating various aspects of process health and safety. The following are the tools discussed: Dow Fire and Explosion Index, Dow Exposure Index, Mond Fire, Explosion and Toxicity Index, Simulation of Chemical Industrial Accidents Software Package, Mortality Index, Hazard Identification and Ranking, IFAL Index, MAXCRED, Safety Weighted Hazard Index and Inherent Safety Index.

3.4.3.1 Dow Fire and Explosion Index

The Dow Fire and Explosion Index was developed to quantify the potential damage from fire and explosion hazards in chemical processing plants that handle 1000Ib or more of flammable, combustive and reactive toxic chemicals (Kavitha, 2003). The index is applicable at the design stage when equipment have been configured and sized.

The Dow Fire and Explosion index involves a step by step analysis as depicted in the flow chart shown in Figure 3.8.

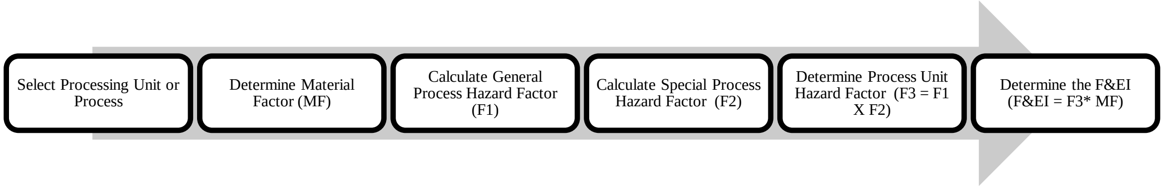

Figure 3.8: Dow Fire and Explosion Index Calculation Steps

The Dow Fire and Explosion Index have been used by many researchers to incorporate safety into chemical process design. It has been implemented into an optimization framework where technical, economic and safety considerations are being met for process design at the conceptual stage (Suardin et al., 2007). A modified version of this index which involves including credit for loss control measures has been demonstrated on an ammonia synthesis reactor (Gupta et al., 2003). The index has also been used as tool to classify hazards for the manufacture of epichlorohydrin (Khan and Abbasi, 1997). To assess the risk of fire and explosion for operations taking place in the Microbiology Laboratory at the University of Reno Nevada, the Dow Fire and Explosion Index was implemented (Kavitha, 2003).

The limitations of the Dow Fire and explosion are that it only addresses fire and explosion safety concerns but it does not address toxicological data. To address this limitation, Dow Chemical Exposure Index (Dow Chemical Company, 1994) was developed to be incorporated with the Dow Fire and Explosion Index. The Dow Chemical Exposure Index was proposed to measure toxicity risks by using the physical and chemical properties of the material, equipment process information and operating conditions.

3.4.3.2 Mond Fire, Explosion and Toxicity Index

The Mond Index developed at the Mond division of the Imperial Chemical Industries, is used to systematically access the risks of fire, explosion and toxic release in a chemical process (Lewis, 1979; Tyler et al., 1994). The Mond Index is an expansion of the Dow Explosion Index, but other hazard factor such as inventory of material, and a layout hazard and toxicity factors have been incorporated. There are six indices that have been proposed by the Mond group and these include: fire load index, unit toxicity index, major toxicity incident index, explosion index and aerial explosion index.

The Mond index differs from the Dow fire and explosion index in that it can evaluate safety impact of wider ranges of chemicals such as explosive properties and toxicity assessments. The Mond Index also incorporates hazards credits for processes with safety control devices (Khan and Abbasi, 1998). The Mond index like the Dow Fire and Explosion index can be used when plant equipment configuration have been determined and sized.

3.4.3.3 Simulation of Chemical Industrial Accidents Software Package (SCIASP)

The Simulation of Chemical Industrial Accidents Software Package (SCIASP) was developed to evaluate the possible risk of accidents in chemical processes (El Harbawi et al., 2008). This graphical based tool is able to perform hazard analysis that determines risks and damage associated with accidental releases, fires and explosions. This newly developed software is a useful tool for risk assessment because it can be used as a decision making tool to compare the safety risks of different processes.

3.4.3.4 Mortality Index

The Mortality Index was suggested by Marshall (1977) evaluates the fatality of lethal chemical substances. The mortality index is shown in Equation 3.15 below.

$$\text{Mortality Index} = \text{Number of Deaths} / \text{Mass of Toxic Substance} \qquad (3.15)$$

3.4.3.5 The Instantaneous Fractional Annual Loss (IFAL) Index

The Instantaneous Fractional Annual Loss (IFAL) Index, developed to identify hazards from pool fires, vapor fires, uncondensed cloud explosions, condensed cloud explosions and internal explosions is a complicated system that needs to be calculated with a computer (Singh and Munday, 1979; Munday et al., 1980). This index was proposed by the United Kingdom Insurance Technical Bureau, to access hazards for each piece of process equipment in order to estimate insurance rates (Cox, 1982).

3.4.3.6 Hazard Identification and Ranking (HIRA)

The Hazard Identification Racking (HIRA) methodology was developed by Khan and Abbasi to evaluate the risk of fire, explosion and toxic release. This methodology consists of two indices: the fire and explosion damage index and the toxicity damage index. To determine the fire and explosion damage index, a five step procedure has been suggested by Khan and Abbasi (1998). This methodology has been demonstrated on the sulfolane production process and the safety risk was determined. To validate this methodology, results of other indices such as the Dow Fire and Explosion Index, IFAL Index and the Mond Fire and Explosion Index have been compared to the HIRA methodology. The results of the comparison show that HIRA is more sensitive and accurate compared to other methods (Khan and Abbasi, 1998). However, it has some limitations.

One drawback of HIRA is that it does not tell if existing control systems are sufficient or need modifications. It also does not incorporate an emergency response plan such as toxic release control and firefighting equipment into the calculation (Khan et al., 2001). A new tool to improve some of the limitation of HIRA was proposed and this was called the Safety Weighted Hazard Index (sWeHI). The Safety Weighted Hazard Index was developed by Khan et al. (2001) to accurately and precisely address safety concerns in chemical industry while integrating credits for safety measures that are already in place.

3.4.3.7 Maximum Credible Rapid Risk Assessment (MAXCRED)

The Maximum Credible Rapid Risk Assessment (MAXCRED) is a computer software developed by Khan and Abbasi (1999) to simulate accident and damage potential in order to evaluate safety risk of processes in the chemical industry. A number of different risk assessment models for fire, explosion, toxic release and dispersion have been incorporated into MAXCRED.

MAXCRED has been demonstrated on an industrial sulfolene production process. Two different accident scenarios namely boiling liquid / vapor cloud explosion followed by flash fire and confined vapor cloud explosion have been modeled for the British Petroleum Texas City Refinery incident. This was developed to show that hazard assessment can prevent safety incidents and provide adequate emergency response (Khan and Amyotte, 2007). MAXCRED was also used for damage prediction for an oxidation based ethylene oxide plant (Khan et al., 2003).

3.4.3.8 Inherent Safety Index

The Inherent Safety Index was proposed by Heikkila (1999) to evaluate process safety. There are two categories of safety indexes presented by this researcher and they are chemical and process safety index. The summation of these two indices yields the Inherent Safety Index. The chemical index describes how raw materials, products, by-products, and intermediates interactions affect safety of a process. The index evaluates the risk from chemicals with high heats of reaction, flammability, explosiveness, toxicity, corrosiveness, and chemical interactions. While the process safety index depicts how equipment configuration and operating conditions can impact the safety of a process. The index measures the risks from high temperatures, pressures and the type of equipment present in a process and chemical inventory. This Inherent Safety index has several applications such as route selection, flow sheet development, and selection of best operating conditions in order to select the optimum process safe situation.

The limitation of this safety index is that it does not model safety risks resulting from deviations in operating conditions. In spite of its limitation, the Inherent safety Index has been used by other researchers. It was integrated into an expert system called iSafe for ranking safety of process flow sheet structure (Palaniappan et al., 2002). It was used to select the safest production route from 10 different options for acetic acid (Palaniappan et al., 2004). This index was used to access the safety of simulated chemical and mechanical heat pump systems and the safest option was selected based on the inherent safety index (Ajah et al., 2008). This inherent safety methodology has been incorporated into the SUSTAINABILITY EVALUATOR and will be discussed in details in section 5.

3.4.3.9 Summary of Health and Safety Impact Assessment Tools

This section presents two categories of tools for evaluating safety in the chemical industry and the key features are summarize in Table 3.5. The first category is the accidental consequence analysis tools which include SCIASP and MAXCRED. The two tools are intelligent systems that can evaluate accident consequence analysis for a chemical processing plant. The second category of tool are indices such as the Dow Fire and Explosion Index, Dow Exposure Index, Mond Fire, Explosion and Toxicity Index, Mortality, HIRA, IFAL Index, sWeHI and Inherent Safety Index which measure several aspects of safety such as fire, explosion and toxic exposure risks to humans. These indices are not automated and require manual computation by plugging equations into a spreadsheet or a calculator.

Table 3.5: Summary of Safety Impact Assessment Tool

Tools	Type of Impact Assessment	Software	Toxic Release	Fire	Explosion
SCIASP	Accident Consequence Analysis	Yes	✓	✓	✓
MAXCRED	Accident Consequence Analysis	Yes	✓	✓	✓
Dow Fire and Explosion Index	Index System	No		✓	✓
Dow Exposure Index	Index System	No	✓		
Mond Index	Index System	No	✓	✓	✓
Mortality Index	Index System	No	✓		
HIRA	Index System	No	✓	✓	✓
IFAL Index	Index System	No		✓	✓
sWeHI	Index System	No	✓	✓	✓
Inherent Safety Index	Index System	No	✓	✓	✓

3.5 SUMMARY

This chapter presents economic, environmental and health and safety concerns facing the chemical industry. All of these issues discussed are important and it is very critical that they are addressed and incorporated into early stages of process design using user friendly approaches. The tools that are available for evaluating economic, environmental and social concerns for the process industry were presented in this chapter. A summary of the tool discussed are presented in Figure 3.9. The key issue with these tools is that many of them are complicated and only address limited aspect of sustainability. It would be useful to have one tool that can evaluate and incorporate all dimensions of sustainability into process design. The next chapter introduces metrics that address the three sustainability concerns. The applications of this metrics to process design are also discussed.

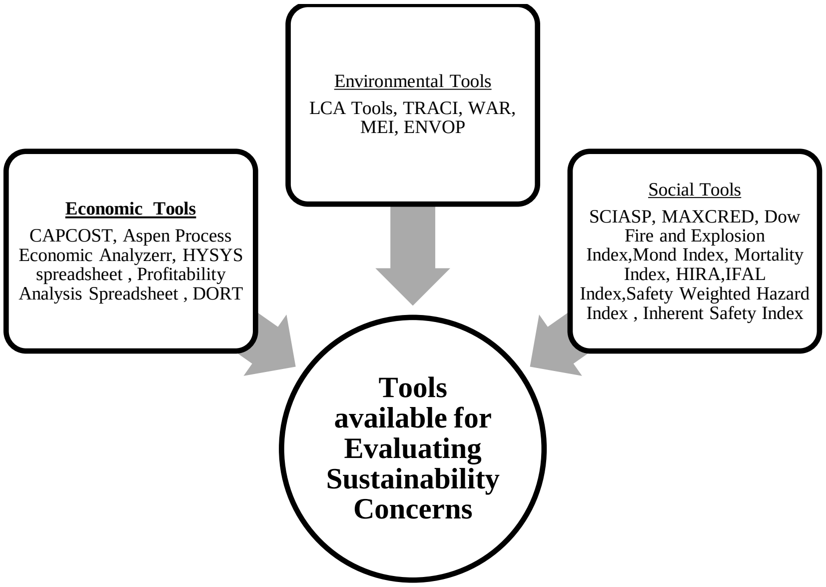

Figure 3.9: Tools Available for Evaluating Sustainability Concerns

CHAPTER IV

SUSTAINABILITY METRICS AND INDICATORS

4.1 INTRODUCTION

The issues driving sustainability as shown in Figure 4.1 can be classified into the following: visible impacts, stakeholder demands, stricter environmental regulations, financial risks, safety and supply chain pressure (Bakshi, 2000; Beloff, 2009).

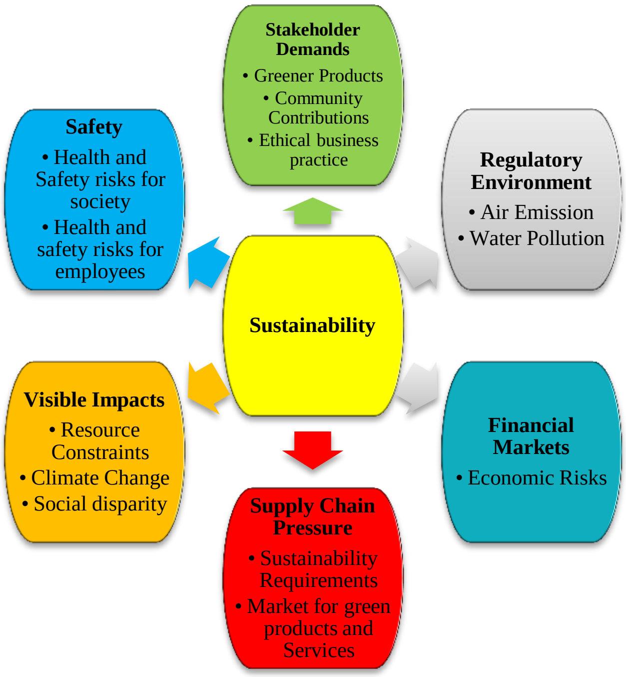

Figure 4.1:Factors Driving Sustainability (Beloff, 2009)

To summarize these issues, society would like to have environmentally friendly processes and products using as little resources as possible while considering health and safety risks. In order to determine if our processes or products are sustainability, we must develop a quantitative or qualitative method to measure progress. As the business adage says, “only what gets measured gets managed,” we must , therefore, have a set of guiding principles towards measuring sustainability (Beloff et al., 2005). One approach to measure sustainability is to use metrics or indicators.

Sustainability metrics and indicators capture environmental, social and economic concerns and transform them into quantitative and or qualitative measures that are useful for making vital decisions (Beloff et al., 2005). Although metrics and indicators are often used interchangeably to quantify sustainability, they are quite different in meaning. According to a document titled “Indicators and Measures of Sustainability,” a sustainability indicator can be defined as “observable world changes that indicate progress towards increased sustainability (Alberta Round Table on the Environment and the Economy, 1993). Tanzil and Beloff (2006) noted that an indicator defines a quantitative measure as well as a narrative description of issues, while metrics refers to “quantitative or semi-quantitative measures.” Sustainability metrics or indicators are quite different from performance goals, which companies have measured for years. Jin and High (2004b) proposed that environmental performance can be converted to environmental sustainability by considering the following:

- Evaluating long term impact versus short term impact.
- Incorporating biological or ecological changes instead of only physical and chemical changes.

- Treating a process or situation as related to the ecosystem as opposed to handling it in isolation from the ecosystem.
- Taking a long term analysis of environmental characteristics versus an immediate analysis of the environment.

When metrics or indicators are aggregated in order to present a simple multidimensional view of a system or process, they are termed a sustainability index or indices (Mayer, 2008). Several researchers have suggested several metrics, indicators and indices to measure progress. The next section discusses the merits and limitations of the work presented by these researchers.

4.2 SURVEY OF SUSTAINABILITY METRICS AND INDICATORS

According to Tanzil and Beloff (2006), sustainability metrics and indicators can be broken into three major categories as shown in Figure 4.2. Socio-economic considerations relate to the economic wellbeing of a society. Socio-environmental considerations link environmental concerns such as resource usage, health and safety concerns that can impact the society. Eco-efficiency, address the use of limited resources in an economic way with reduced environmental impact.

4.2.1 Sustainability Metrics

Understanding the characteristics of sustainability metrics is important in selecting measures for a certain process. Below are few characteristics suggested by (Atlee and Kirchain, 2006):

- Simple and easily accessible by any audience

- Predictive and consistent
- Serve as decision making tool
- Economical efficient: data collection should be easily
- Unbiased
- Applicable to several process

Figure 4.2: Triple Bottom Line of Sustainability (Beloff et al., 2005)

During preliminary process design, it is important to incorporate sustainability concerns into process design. The use of sustainability metrics is a good technique to determine if alternatives are sustainable. Economic, environmental and social metrics could be calculated. For example, decision makers can select between several alternatives by selecting a process or engineering design with a lower sustainability metric. Without going through complicated optimization routines, metrics can be used as a preliminary assessment to determine if a process is sustainable or not.

Sustainability metrics are expressed in ratios. For environmental and economical metrics, the numerator is usually the impact such as resource consumption or pollutant emission while the denominator is usually an impact such as physical or financial. Social metrics developed by the Institute of Chemical Engineers are expressed in percentages such as “benefit as percentage of payroll expense (%), working hours lost as percent of total hours worked, lost time accident frequency (number per million hours worked) and number of complaint per unit value added (Beloff et al., 2005).” A majority of the metric and index systems focus on environmental and economic impacts and do not quantify social concerns. Social concern is an import dimension that must not be left out.

4.2.2 Sustainability Indicators

Sustainability indicators can be useful in reflecting progress over a period of time and monitoring positive or negative change to products and processes. Sustainability indicators must be relevant to the user and the community, be understandable by its intended user, must address long term impact and show linkages between the three dimensions of sustainability. There are three major categories of indicators namely economic, environmental and social. Economic indicators measure economic progress of the society or community being observed. They measure economic improvements that can be tracked over a long period of time. Examples of economic indicators include the following: net job growth, employment diversity, number of jobs with benefits, work required to support basic needs, “percent of tourism dollars that come from recreational uses and number of new businesses that are more environmentally friendly, number of people employed in outdoor recreational businesses and "environmentally-efficient" agriculture e.g. number of acres used for organic farming” (Anderson et al., 2001).

Environmental indicators measure positive environmental progress of the society or community being observed. They target environmental concerns and measure improvements over a period of time. Examples of environmental indicators include the following:

- Measures of ecological health (biodiversity, percent native species, etc.)
- Measure of improved water quality over time (pH, dissolved oxygen, etc.)
- Number of complaints about air quality
- Parts per million of particulate matter in the air
- Number of good air quality days
- Number of asthma-related hospital admissions due to pollution issues
- Number of vehicle miles traveled and the ecological impact of the emissions emitted from the vehicles

Social indicators measure issues that relate to the health, safety and well-being of the society or community being observed. They target social concerns and address societal benefits over a period of time. Examples of social indicators include the following (Anderson et al., 2001):

- Number of health issues as a result of environmental pollutants
- Number of students that are enlightened on environmental issues in an environmental education class
- Number of community members addressing environmental issues such as global warming
- Number of families who are living below the poverty line

Indicators, like metrics, are useful in measuring sustainability progress. Indicators help in explaining sustainability to individuals who might not be very knowledgeable on the subject matter. It can also be used to educate the community on sustainability by linking noticeable progress. With sustainability progress being measured quantitatively, individuals can stay focused and motivated because they are able to see noticeable changes.

4.3 PROPOSED SUSTAINABILITY METRICS AND INDICATOR SYSTEMS

Several indicators and metrics have been proposed by researchers over the years. The limitation with some of these metric systems is that they only cover a certain dimension of sustainability and not all three dimensions. A summary of the key sustainability qualitative assessment systems that have been proposed by researchers is presented in the next sections and in Table 4.1. The table highlights the concerns addressed by qualitative assessments systems.

4.3.1 Sustainability Process Index

Krotscheck and Narodoslawsky (1996; 2000) developed the sustainability process index to evaluate process and product ecological footprint. This index takes into account the process area while evaluating the impact of renewable resource consumption, emission and waste production. The sustainable process index has been used as a decision making tool to determine if a technology is renewable resource friendly (Hertwich et al., 1997). A low value of the index indicates that a process is competitively sustainable. An Excel based tool, SPIonExcel that uses this index to calculate the ecological footprint of a process was developed (Sandholzer and Narodoslawsky, 2007).

Table 4.1: Proposed Sustainability Metric and Indicator Systems

Developer	Metric	Economic	Environment	Social
Narodoslawsky and Krotscheck (1996, 2000)	Sustainable Process Index		✓	
Heikkila (1999)	Inherent Process Safety Index			✓
Afgan, Carvalho and Hovanov (2000)	Sustainability Indicators	✓	✓	✓
AICHE/CWRT (AIChE Center for Waste Reduction Technologies (CWRT), 2000)	ALCHE/ CWRT Sustainability Metrics		✓	
SAM (Knoepfel, 2001)	Dow Jones Sustainability Index	✓	✓	✓
BASF (Saling et al., 2002)	Eco-efficiency Metrics	✓	✓	✓
Constable, Curzons and Cunningham (2002)	Green Metrics		✓	
IChemE Metrics (2002)	IChemE Sustainability Metrics	✓	✓	✓
Krajnc and Glavič (2003)	Indicators of Sustainable Production	✓	✓	✓
Saling, Maisch, Silvani and König (2005)	BASF Socio-Eco-Efficiency Metrics (SEEbalance)	✓	✓	✓
Achour, Haroun, Schult and Gasem (2005)	Global Environmental Risk Assessment (GERA) Index		✓	✓
Tanzil and Beloff, (2006)	BRIDGES Sustainability Index		✓	✓
Martins, Mata, Costa and Sikdar, (2007)	Three Dimensional Sustainability Metrics	✓	✓	✓
Tugnoli, Santarelli and Cozzani, (2008b)	Sustainability Indices	✓	✓	✓
AIChE (2008)	AIChE Sustainability Index ("AIChE Sustainability Index: Strategic Commitment to Sustainability," 2008)	✓	✓	✓

The limitation of this tool is that it only evaluates environmental concern, leaving out the other dimensions of sustainability.

4.3.2 Inherent Process Safety Index

This index system is based on the work suggested by (Heikkila, 1999). This index system addresses the chemical and process risk of a chemical plant (Tugnoli et al., 2008a). The index incorporates operating conditions, nature of chemical reaction, chemical properties inventory and process configuration to evaluate the safety of a process. The efficacy of this index system was demonstrated on an acetic acid production process where the safety risks were identified. The limitation of this metric system is that it only addresses safety concerns in a chemical processes, leaving out other sustainability issues.

4.3.3 Sustainability Indicators

Afgan, Carvalho and Hovanov (2000) developed an indicator system in 2000 that assesses the sustainable energy usage in a process by taking into account resource, environment, economic and social criteria. The resource indicator consists of four metrics namely; fuel resources, stainless steel resource, copper resource and aluminum resource. Environmental indicators suggested by this researcher are carbon dioxide, nitrogen oxide, sulfur dioxide and waste production. Economic indicator proposed includes system efficiency, capital investment, and gross national product. Social indicators recommended include new job creation, standard of living and community benefit. Although this indicator system addresses the three dimension of sustainability, it has limited applications as it has been tailored towards accessing the impact of energy systems.

4.3.4 AIChE/ CWRT Sustainability Metrics

The American Institute of Chemical Engineers/ Center for Waste Management (AIChE/CWRT) (2000) developed six baseline sustainability metrics in 1999 for companies to measure environmental impacts. These metrics are: material intensity, water intensity, energy intensity, toxic release, solid waste and pollutant emission. One limitation of this metric system is that it only addresses one dimension of sustainability, leaving out the other two dimensions. Also, the system categorizes environmental impact of pollution into one metric versus breaking it down into individual concerns such as global warming, atmospheric acidification etc.

4.3.5 Dow Jones Sustainability Index (DJSI)

This index system was developed in 1999 by Sustainable Asset Management (SAM) to track the sustainability performance of companies in 10 market sectors (Knoepfel, 2001). The index system evaluates corporate performance by monitoring issues such as human right issues, illegal corporate activities, discriminatory work place incidents and workplace safety. The assessment criteria for this index system include the following: economic factors such as profit; environmental factors such as environmental reporting, environmental audits and management, environmental profit and loss, environmental performance and eco-design of products and services; and social factors such as employee benefits resolution, occupational health and safety and non-discriminatory work environment. The objective of this indicator is to track financial performance and establish risk for stakeholders. The limitation of this metric system is that most of the indices are qualitative measures and are not applicable to early stages of design.

4.3.6 BASF Socio-Eco-efficiency Metrics

BASF first developed a set of eco-efficiency metrics to evaluate the impact of products and process developed at the company (Saling et al., 2002). These metrics include: raw materials consumption, energy consumption, land use, air and water emissions, solid waste, and potential toxicity. Later on, a set of social metrics were also introduced by the company through the development of SEEBALANCE. SEEBALANCE is a life cycle assessment (LCA) tool that evaluates the impact of products and processes by evaluating its economic, environmental and social performance (Saling et al., 2005). The social metrics developed by this group evaluates the effect of products or processes on the wellbeing of employees, future generation, and consumer as well as local, national and international community. Even though SEEBALANCE is one of the few tools that address social metrics, it requires extensive data and information making it limited for early stages of design. In addition, the social metrics presented, pose difficulty in terms of correlation with process design parameters.

4.3.7 Green Metrics

This metric system was suggested by Constable, Curzons and Cunningham (2002) as a quantitative method to assess the efficiency of chemical synthesis. These metrics include effective mass yield, E-factor, atom economy, mass productivity, mass intensity, reaction mass efficiency and carbon efficiency, energy, ecotoxicity and human health metrics. The metric suggested was used to compare the environmental impacts of various solvents. This would aid manufactures in creating greener solvents. This metric system is limited as it only evaluates resource usage impact and does not incorporate other sustainability issues.

4.3.8 IChemE Sustainability Metrics

The United Kingdom based Institution of Chemical Engineers (IChemE), developed an indicator system in 2002 that could be used to evaluate economic, environmental and social concerns of an operating unit (IChemE Metrics, 2002). Some of the examples of the economic metrics suggested include profit, project investment etc. Environmental metrics include resource usage, emissions, effluents and wastes. Social metrics include workplace benefit package, health and safety at work, number of complaints concerning process facility and products etc. The limitation of this metric system is that for the social metrics presented, it is difficult to correlate them with process design parameters.

4.3.9 Indicator of Sustainable Production

A set of indicators were proposed by Krajnc and Glavič (2003) to assess the sustainability of production processes of companies. The sustainability criteria for this indicator system include: resource usage, product quality, environment impact, economic viability and societal benefit. This group combined the indicators and metrics suggested by several researchers (FEM and FEA, 1997; AIChE Center for Waste Reduction Technologies (CWRT), 2000; Azapagic and Perdan, 2000; Veleva and Ellenbecker, 2001; Holger, 2002). In general, indictor of sustainable production classified sustainability indicators into economic, environmental and social indicators. Economic indicators track financial improvements and expenditure. Environmental indicators measure environmental impact, efficiency and improvements of process and products. Social indicators measure production ethics and societal progress such as income distribution. Although some of the metrics suggested by this researcher are useful, too many metrics were suggested and not all of them are applicable to early stages of design.

4.3.10 Global Environmental Risk Assessment (GERA) Index

This index system was proposed by Achour et al. (2005) and it accesses the environmental and safety risk associated with a process by evaluating the contributions of process streams and units. Indices such as toxicity index, flammability index, reactivity index etc. were assigned different numerical values from 0-4 based on the national fire protection association (NFPA) and hazardous materials identification system (HMIS) hazard codes. An index value of 0 means no risk and a value of 4 means high risk. This group defined an environmental risk index for components present in the inlet and outlet stream of a process. This index system is limited because economic concerns have not been incorporated into the index system. In addition, environmental impacts of emissions have not been incorporated into the GERA Index.

4.3.11 BRIDGES Sustainability Metrics

Tanzil and Beloff (2006) suggested this metric in 2002 and it assesses how impacts can be measured in a production process. The metrics are categorized into socio-economic, socio-environmental and eco-efficiency. Examples of socio-economic metrics include benefits as percentage of payroll expense (%), employee turnover (%). promotion rate (%) and lost-time accident frequency. Socio-environmental metrics include number of citing for toxic industrial emissions and amount of waste released to natural habitats. Eco-efficiency metrics include material intensity, water intensity, energy intensity, toxic release, solid waste and pollutant emission. One limitation of this metric is that it categorizes environmental impact of pollution into one metric versus breaking it down into individual concerns such as global warming and acidification.

4.3.12 Three Dimensional Sustainability Metrics

Martins et al. (2007) presented a three dimensional framework that address sustainability concerns in industrial process. The metrics proposed in this research include material intensity, energy intensity, potential chemical risk, and potential environmental impact. The suggested three dimension metrics can be used to compare the sustainability of processes with alterative production methods. The metrics have been used to compare the sustainability of chlorine production process using three different alternatives; namely mercury cells, diaphragm cells, and membrane cells. The three dimension framework has also been used to compare the sustainability of two acetone/chloroform mixture separation processes. Although two metrics have been presented for environmental impact as well as health risks, safety issues were not addressed.

4.3.13 Sustainability Indices

Tungnoli, Santarelli and Cozzani (2008b) proposed this indicator system and it addresses the three major concerns of sustainability during early stages of design. For social concern, inherent safety index and an occupational index were proposed. To address economic concerns, calculation of the net present value was suggested. For environmental concerns, the impact of air, water and soil emission as well as resource consumption was evaluated. The indicator system is used for comparing alternatives while analyzing the environmental, economic and social impact of each alternative. This metric system is limited in that not all apply to early stages of design.

4.3.14 AIChE Sustainability Index

The American Institute of Chemical Engineers and Golder Associates developed an index system in 2008 to measure sustainability corporate performance. This index looks at the following seven factors: strategic commitment to sustainability, sustainable innovation of products and services, environmental performance, safety performance, product stewardship, value chain management and social responsibility ("AIChE Sustainability Index: Strategic Commitment to Sustainability," 2008). This index system has been used to evaluate the sustainability performance of 11 companies namely; Air Products, Akzo Nobel, Ashland, BASF, Celanese, Dow, DuPont, Eastman, Lyondell, Praxair and Rohm & Hass. This system is limited as most of the suggested indices are qualitative measures and are not applicable to early stages of process design.

4.4 SUMMARY

Sustainability metrics, indicators and indices were introduced in this chapter. Although they are useful in tracking progress, not all of them are applicable to early stages of process design. Table 4.2 summarizes the applications of the metric, indicator and index systems introduced in this chapter.

Table 4.2: Summary of the Metric, Indicator and Index Systems Introduced in this Chapter

System	Applications	Missing Aspects
Sustainable Process Index (Krotscheck and Narodoslawsky, 1996)	Applicable to detailed process design	Although environmental impacts are considered, reaction efficiency has not been incorporated. Not applicable to early stages of design. Also social concerns have not been addressed in this index system.
Inherent Process Safety Index (Heikkila, 1999)	Applicable for assessing the safety of a chemical process at all stages of design	Only addresses safety concerns and the other dimensions of sustainability are not addressed.
Sustainability Indicators (Afgan et al., 2000)	Useful in assessing the sustainability of a chemical process during early stages of design	Indicator system has limited applications as it has been tailored towards accessing the impact of energy systems.
ALCHE/ CWRT Sustainability Metrics (AIChE Center for Waste Reduction Technologies (CWRT), 2000)	Applicable for comparing environmental impact of chemical processes	Only address one dimension of sustainability. Metric categorizes environmental impact of pollution into one metric versus breaking it down into individual concerns such as global warming, acidification. Economic and social concerns are not addressed.
Dow Jones Sustainability Index (Knoepfel, 2001)	Applicable for comparing different companies' performance.	Most of the indices are qualitative measures and are not applicable to early stages of design.
BASF Socio-Eco-efficiency Metrics (Saling et al., 2002)	Useful in evaluate the impact of products and process during detailed design	Requires extensive data and information making it limited for early stages of design. In addition, the social metrics presented, pose difficulty in terms of correlation with process design parameters.
Green Metrics (Constable et al., 2002)	Useful in evaluating the efficiency of chemical reactions	Addresses just resource efficiency but does not incorporate sustainability concerns.

IChemE Sustainability Metrics (IChemE Metrics, 2002)	Useful in assessing the sustainability of production processes	For the social metrics presented, it is difficult to correlate them with process design parameters.
Indicators of sustainable production (Krajnc and Glavič, 2003)	Useful in assessing the sustainability of an operating unit	Although some of the metrics are useful for early stages of design, too many metrics were suggested and not all of them are applicable to early stages of design.
Global Environmental Risk Assessment (GERA) Index (Achour et al., 2005)	Useful in addressing health and safety risks of an operating unit and stream	Economic concerns and environmental impact of emissions has not been incorporated in this system.
BRIDGES to Sustainability Metrics (Tanzil and Beloff, 2006)	Applicable for comparing environmental impact of chemical processes	Only addresses one dimension of sustainability. Metric categorizes environmental impact of pollution into one metric versus breaking it down into individual concerns such as global warming, acidification.
Three Dimensional Sustainability Metrics (Martins et al., 2007)	Useful in evaluating the sustainability of an industrial process	Although two metrics have been presented for environmental impact and health and safety risk, the direct correlation between operating conditions, chemical process risk and environmental impact was not addressed.
Sustainability Indices (Tugnoli et al., 2008b)	Useful in evaluating the sustainability of chemical process alternatives	Not all metrics are applicable to early stages of design.
AIChE Sustainability Index ("AIChE Sustainability Index: Strategic Commitment to Sustainability," 2008)	Applicable for comparing different companies' performance	Most of the indices are qualitative measures and are not applicable to early stages of design.

There is no doubt that sustainability development is very beneficial to our society. The ability to measure sustainability using indicators or metrics are important because it will assist in comparing processes as well as assessing positive change towards sustainability over a period of time. It could be used to evaluate alternatives such as technical alternatives e.g. different raw materials and process improvement options and or business alternatives, for example, different supplier and acquisition options. It can also be used to track performance over time as well as compare facilities or business units and determine what areas of sustainability needs to be improved. Furthermore, it can identify environmental aspects and impacts of industrial operations.

One thing to point out from this study is that it is complex to quantitatively evaluate social sustainability. This is because it is difficult to transform social issues into a scientific vision. As the focus of this research is addressing social, economic and environmental concerns in chemical process design, selected metrics developed by the researchers in this chapter and the ideas from chapters 2-4 have been incorporated into a methodology for designing processes for sustainability.

CHAPTER V

IMPLEMENTING METHODOLOGY FOR DESIGNING PROCESSES FOR SUSTAINABILITY DURING EARLY STAGES OF DESIGN

The first four chapters discussed environmental, economic and social tools that are available for estimating project economics, environmental impacts, health and safety concerns. The previous chapter also introduced sustainability metrics which can be used to address these concerns. This chapter focuses on a methodology that was developed for this PhD work which incorporates sustainability concerns into early stages of design. The framework involves the use of a newly developed novel screening tool, the "SUSTAINABILITY EVALUATOR." This tool identifies sustainability concerns and evaluates improvements after processes have been optimized.

5.1 INTRODUCTION

The design of processes and products for sustainability includes a series of activities that can be executed at all stages of design. Like end of pipe waste treatment methodologies, waiting until the last stage of process design to incorporate sustainability concerns is not economical and resource efficient. Thus, sustainability ideas must be transformed at early stages of design in order to curb the source of concerns. When designing products and processes, engineers must look at the bigger picture, i.e. the economy and environment, instead of merely focusing on the process plant and the economic benefits to the corporation (Bakshi and Fiksel, 2003). In order to design processes for sustainability, the methodology shown in Figure 5.1 is proposed.

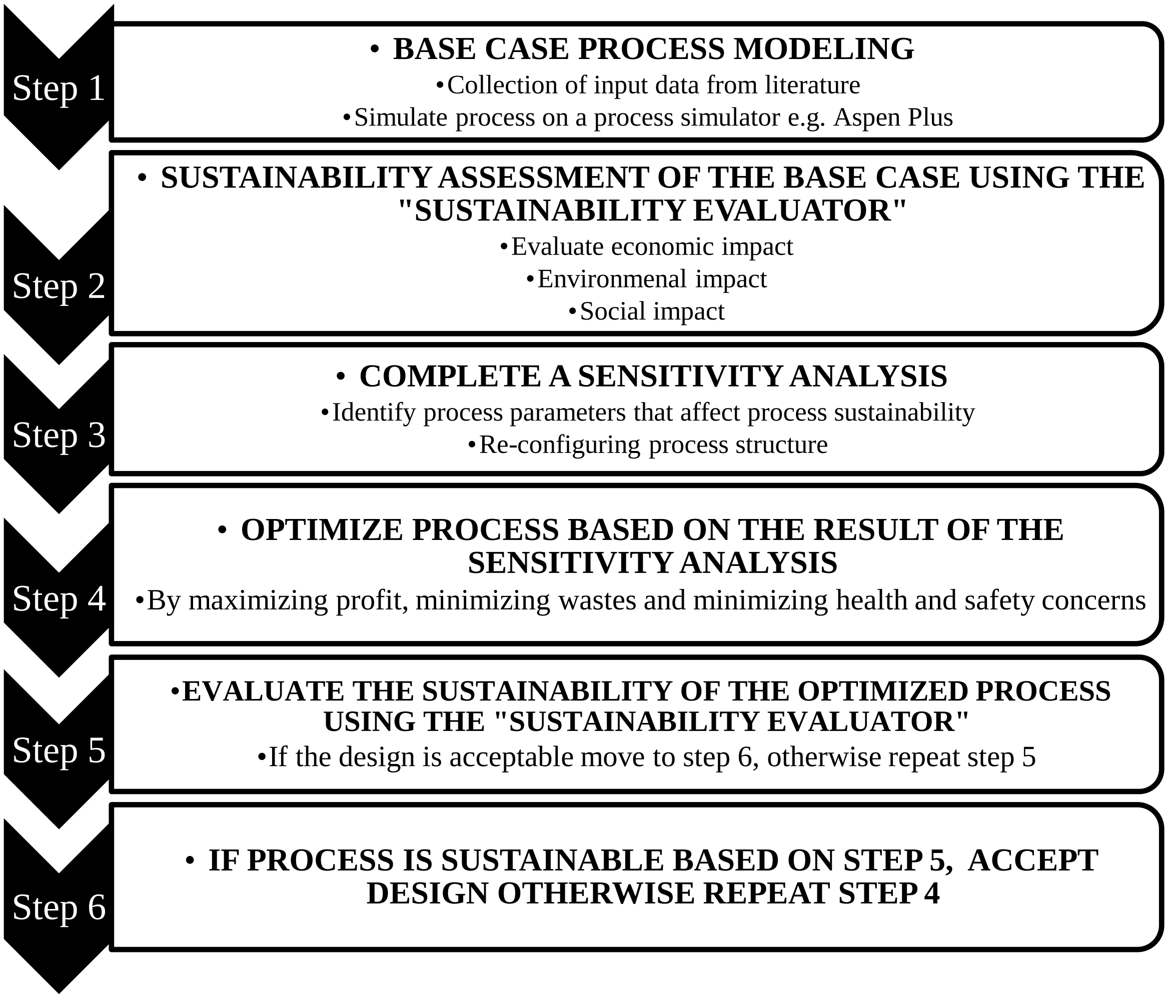

Figure 5.1: Proposed Methodology for Addressing Sustainability Concerns During Early Stages of Design

This methodology includes the following: base case process modeling, sustainability assessment of the base case using the SUSTAINABILITY EVALUATOR, sensitivity analysis to identify process parameters that affect process sustainability, process optimization based on result of sensitivity analysis, and impact assessment of the optimized process using the SUSTAINABILITY EVALUATOR.

5.2 SIMULATION OF THE BASE CASE PROCESS MODEL

The base case model is simulated using information from literature. For this work, the base case was simulated using ASPEN PLUS version 22. This version of ASPEN has a component database which is where the constants that are needed for calculating thermodynamic models are located. Also, it has a solver which contains thermodynamic models that can predict phase behavior. The simulator has a graphic user interface where the designer is able to keep track of selected process equipment and flow streams. There is also a unit operation block solver that has computational blocks for mass and energy balance calculations and other design calculations. The simulator has a data output generator where the result of the simulation run is provided. Lastly it has a flow sheet solver that shows the sequence of how the calculations in the simulation were completed and how well it converged.

For ASPEN PLUS to calculate mass and energy balances for any selected process, the following are the basic inputs into the simulator:

- Chemical component selection
- Feed streams selection with compositions

- Operating conditions such as temperature, pressure etc.
- Selection of thermodynamic models
- Configuration of reactor systems and other processing equipment
- Configuration of separators to separate products and un-reacted raw materials.

The ASPEN process simulator has been chosen because it is readily available at Oklahoma State University and in addition to providing the results of mass and energy balances; it is useful for equipment sizing, economic estimates, sensitivity analysis and optimization. ASPEN PLUS will be used to simulate and optimize chemical processes that will be retrofitted for sustainability constraints.

5.3 ASSESSMENT OF THE PROCESS USING THE SUSTAINABILITY EVALUATOR

The SUSTAINABILITY EVALUATOR is a novel tool that has been developed for evaluating processes for sustainability. This tool uses selected metrics and indices that address economic, environmental, health and safety concerns. The SUSTAINABILITY EVALUATOR is a Microsoft Excel based tool that uses mass and energy flows as inputs to evaluate the sustainability of a process. Some of the concerns that are addressed by this tool include the following as shown in Figure 5.2:

- Economic Concerns: Profit, energy costs, waste treatment costs etc.
- Environmental Concerns: Atmospheric acidification, global warming, environmental burdens, ozone depletion, photochemical smog, resource usage etc.

- Health and Safety Impact: Health and safety risks such as risk of exposure, explosion, flammability etc.

The ultimate goal in every industrial process is to maximize profits; thus a process is not sustainable if it is not economically viable. Therefore, the SUSTAINABILITY EVALUATOR introduces a methodology that involves addressing economic concerns by completing a profitability analysis, addressing environmental concerns by using a set of selected environmental metrics and addressing social concerns by completing a health and safety risk assessment. The SUSTAINABILITY EVALUATOR could be used to evaluate the sustainability of a process and or compare process alternatives to select the most sustainable process. The inputs into this tool as shown in Figure 5.3 are mass flow rates, raw material and product costs, and capital costs from ASPEN PLUS. The outputs of this tool are the selected sustainability metrics as shown in Figure 5.3.

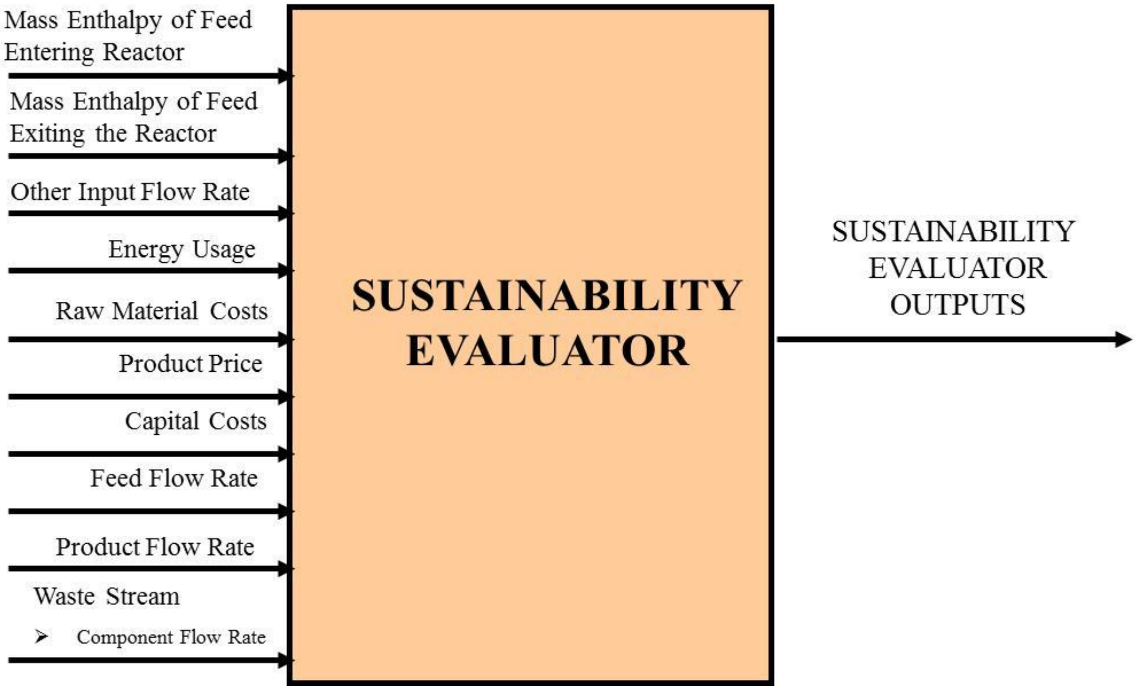

Figure 5.2: Summary of the SUSTAINABILITY EVALUATOR Inputs

The SUSTAINABILITY EVALUATOR, an impact assessment tool is quite novel as there is no other tool that is able to address the three dimensions of sustainability in this fashion. The user manual for the SUSTAINABILITY EVALUATOR is provided in APPENDIX A of this dissertation. The following section describes the metrics that address economic, environmental, health and safety concerns that have been incorporated into this impact assessment tool.

5.3.1 Economic Impact in the SUSTAINABILITY EVALUATOR

The economic benefit for any process is very important because a project that is not profitable is not sustainable. There are several methods that are available for completing the economic analysis of an industrial process as presented by Dantus (1999), Seider et al. (2008) and Turton et al (2009) and in Chapter 3. In this work a set of economic metrics that can be used in evaluating the cost effectiveness of a process is listed below:

1. Product Revenue: This is a measure of the revenue that is generated from the manufactured product and by-products. The higher the product revenue, the more profitable the process will be.
2. Raw Material Costs: This is defined as costs of the raw materials used in manufacturing the product.
3. Waste Treatment Costs: This is defined as the expenses associated with treating wastes generated in a process.
4. Operating costs: This is defined as the costs of energy used in manufacturing a particular product.

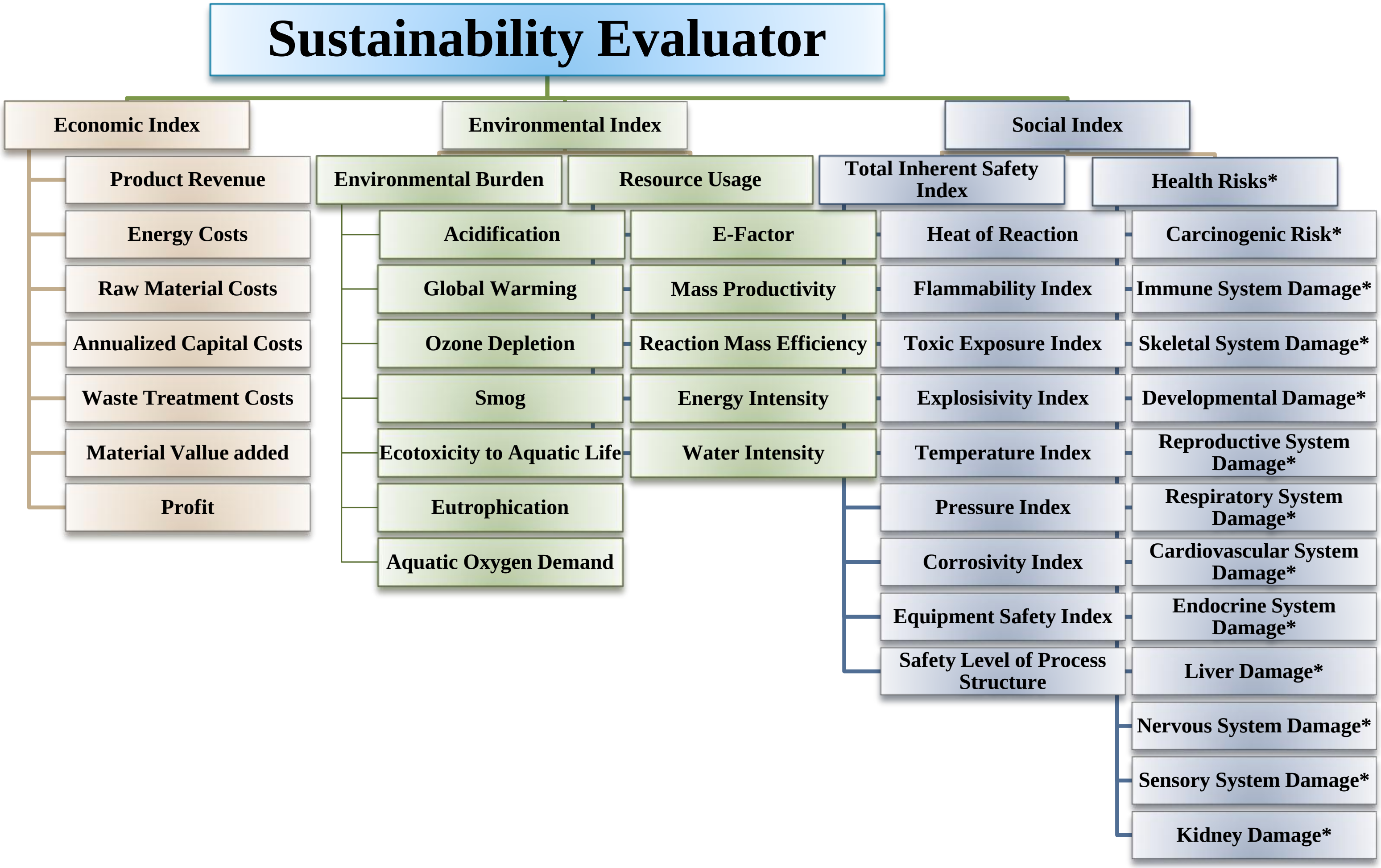

Figure 5.3: Summary of the Concerns Addressed by the SUSTAINABILITY EVALUATOR

5. Material Value Added: This is defined as the difference between the product revenue and the raw material costs (Carvalho et al., 2008).
6. Annualized Capital Costs: This is the conversion of the capital costs to an annual value by multiplying by a capital recovery factor. The capital recovery factor is evaluated using equation 5.1.

$$CRF=\frac{i(1+i)^n}{(1+i)^n-1} \tag{5.1}$$

Where

CRF = Capital Recovery Factor
n = Number of Years
i = Interest Rate

7. Profit: This is defined as shown in Equation 5.2

$$\text{Profit} = \text{Product Revenue} + \text{By-product Revenue} - (\text{Raw Material Cost} + \text{Waste Treatment Cost} + \text{Operating Cost} + \text{Annualized Capital Cost}) \tag{5.2}$$

5.3.2 Environmental Burden in the SUSTAINABILITY EVALUATOR

Once the economics of a process has been evaluated, the next step is to determine the environmental impact. The environmental impact can be evaluated by using metrics developed by Institution of Chemical Engineers (IChemE Metrics, 2002), Green Metrics (Constable et al., 2002) and Bridges to Sustainability (Tanzil and Beloff, 2006). The following nine impact categories listed below are suggested: global warming, stratospheric ozone depletion, photochemical smog, aquatic oxygen demand, atmospheric acidification, aquatic acidification, eco-toxicity to aquatic life, eutrophication and resource usage.

5.3.2.1 Global Warming

This is defined as the increase in the temperature of the earth surface due to activities such as industrial and transportation emissions. Several chemicals cause global warming but carbon dioxide emissions is the major cause. Thus, other substances that lead to global warming are converted to carbon dioxide equivalent by using potency factors shown in Table 5.1.

Table 5.1: Potency Factors for Chemicals that Cause Global Warming (IChemE Metrics, 2002)

Substances	Potency Factor
Carbon dioxide	1
Carbon monoxide	3
Carbon tetrachloride	1400
Chlorodifluoromethane, R22	1700
Chloroform	4
Chloropentafluoroethane, R115	9300
Dichlorodifluoromethane, R12	8500
Dichlorotetrafluoroethane, R114	9300
Difluoroethane	140
Hexafluoroethane	9200
Methane	21
Methylene chloride	9
Nitrogen oxides (NOx)	40
Nitrous oxide	310
Pentafluoroethane, R125	2800
Perfluoromethane	6500
Tetrafluoroethane	1300
Trichloroethane (1,1,1)	110
Trichlorofluoromethane, R11	4000
Trichlorotrifluoroethane, R113	5000
Trifluoroethane, R143a	3800
Trifluoromethane, R23	11700
Volatile organic compounds	11

5.3.2.2 Stratospheric Ozone Depletion

The ozone layer is very important in protecting the earth from ultraviolet rays. Depletion of this layer can result in skin cancer in humans. Examples of chemicals leading to ozone depletion are trichlorofluoromethane and carbon trichloride etc. For this metric, substances that cause ozone depletion are converted to trichlorofluoromethane equivalent by multiplying the mass flow rates of emitted wastes with the potency factors shown in Table 5.2.

Table 5.2: Potency Factors for Chemicals that Cause Stratospheric Ozone Depletion (IChemE Metrics, 2002)

Substances	Potency Factor
Carbon dioxide	1
Carbon monoxide	3
Carbon tetrachloride	1400
Chlorodifluoromethane, R22	1700
Chloroform	4
Chloropentafluoroethane, R115	9300
Dichlorodifluoromethane, R12	8500
Dichlorotetrafluoroethane, R114	9300
Difluoroethane	140
Hexafluoroethane	9200
Methane	21
Methylene chloride	9
Nitrogen oxides (NOx)	40
Nitrous oxide	310
Pentafluoroethane, R125	2800
Perfluoromethane	6500
Tetrafluoroethane	1300
Trichloroethane (1,1,1)	110
Trichlorofluoromethane, R11	4000
Trichlorotrifluoroethane, R113	5000
Trifluoroethane, R143a	3800
Trifluoromethane, R23	11700

5.3.2.3 Photochemical (Smog) Formation

This is a reaction that occurs when photochemical smog causing chemicals such as petrochemicals are reacted with combustive substances leading to a smog like appearance at the right temperature and sunlight (IChemE Metrics, 2002). For this metric, substances that cause photochemical smog formation are converted to ethylene equivalent. Potency factors for chemicals that cause the formation of photochemical smog are shown in Table 5.3.

Table 5.3: Potency Factors for Chemicals that Result in the Formation of Photochemical Smog (IChemE Metrics, 2002)

Substances	Potency Factor
1,1-Dichloroethylene	0.232
1,2,3-Trimethylbenzene	1.245
1,2,4- Trimethylbenzene	1.324
1,3,5- Trimethylbenzene	1.299
1-Butene	1.130
1-Pentene	1.040
2,2-Dimethylbutane	0.321
2,3-Dimethylbutane	0.943
2-Butene	0.990
2-Methylbut-1-ene	0.830
2-Methylbut-2-ene	0.770
2-Methylheptane	0.694
2-Methylhexane	0.719
2-Methylnonane	0.657
2-Methyloctane	0.706
2-Methylpentane	0.778
2-Pentene	0.950
3,5-Diethyltoluene	1.195
3,5-Dimethylethylbenzene	1.242
3-Methylbut-1-ene	1.180
3-Methylhexane	0.730
3-Methylpentane	0.661
Acetaldehyde	0.650
Acetic acid	0.156
Acetone	0.182

Acetylene	0.280
Benzaldehyde	-0.056
Benzene	0.334
Butyl glycol	0.629
Butylene	0.703
Butyraldehyde	0.770
Carbon monoxide	0.027
cis 1,2- Dichloroethylene	0.172
Cyclohexane	0.595
Cyclohexanol	0.622
Cyclohexanone	0.529
Diacetone alcohol	0.617
Dimethyl ether	0.263
Ethane	0.140
Ethyl acetate	0.328
Ethyl alcohol	0.446
Ethylbenzene	0.808
Ethylene	1.000
Formaldehyde	0.554
Formic acid	0.003
i-Butane	0.426
i-Butanol	0.591
i-Butyraldehyde	0.855
i-Pentane	0.599
i-Propanol	0.216
i-Propyl acetate	0.291
i-Propylbenzene	0.744
Isoprene	1.180
Methane	0.034
Methyl acetate	0.046
Methyl alcohol	0.205
Methyl chloride	0.035
Methyl cyclohexane	0.732
Methyl- i -butylketone	0.843
Methyl- t -butyl ether	0.268
Methyl chloroform	0.002
Methylene chloride	0.031
Methylethylketone	0.511
m-Ethyltoluene	0.985
m-Xylene	0.080
n-Butane	0.600

n-Butanol	0.628
n-Butyl acetate	0.511
n-Decane	0.680
n-Dodecane	0.577
n-heptane	0.770
n-Hexane	0.648
Nitric oxide	0.427
Nitrogen dioxide	0.028
n-Nonane	0.693
n-Octane	0.682
n-Pentane	0.624
n-Propyl acetate	0.481
n-Propylbenzene	0.713
n-Undecane	0.616
o- Xylene	0.831
o-Ethyltoluene	0.846
p- Xylene	0.948
p-Ethyltoluene	0.935
Propane	0.411
Propionaldehyde	0.755
Propionic acid	0.035
Propylene	1.080
Propylene glycol methyl ether	0.518
s-Butanol	0.468
s-Butyl acetate	0.452
Styrene	0.077
Sulphur dioxide	0.048
t-Butanol	0.191
Tetrachloroethylene	0.035
Toluene	0.774
trans 1,2- Dichloroethylene	0.101
Trichloroethylene	0.075
Valeraldehyde	0.887
Vinyl chloride	0.272

5.3.2.4 Ecotoxicity to Aquatic Life

This is a measure of an increase in eco-toxicity to aquatic organisms due to the presence of pollutants in water sources. For this metric, all substances that are toxic to aquatic life are converted to copper equivalent using the factors are shown in Table 5.4.

Table 5.4: Potency Factors for Chemicals that Cause Eutrophication (IChemE Metrics, 2002)

Substances	Potency Factor
1,2-Dichloroethane (EDC)	0.50
Ammonia	0.24
Arsenic	0.20
Benzene	0.17
Cadmium	2.00
Carbon tetrachloride	0.42
Chloride	0.50
Chlorobenzene	1.00
Chloroform	0.42
Chromium	0.33
Copper	1.00
Cyanide	1.00
Formaldehyde	1.00
Hexachlorobenzene	166.67
Hexachlorobutadiene	50.00
Iron	0.005
Lead	0.20
Manganese	0.10
Mercury	16.67
Methylene chloride	0.50
Nickel	0.17
Nitrobenzene	0.25
Nitrophenol	0.50
Tetrachloroethylene (PER)	0.50
Toluene	0.13
Trichloroethylene (TRI)	0.50
Vanadium	0.05
Xylenes	0.17
Zinc	0.13

5.3.2.5 Aquatic Oxygen Demand

This is a measure of the increase in oxygen needed by aerobic microorganism due to the presence of pollutants in water sources. For this metric, all substances that cause an increase in aquatic oxygen demand are converted to oxygen equivalent. The potency factors are shown in Table 5.5.

Table 5.5: Potency Factors for Chemicals that Cause Aquatic Oxygen Demand (IChemE Metrics, 2002)

Substances	Potency Factor
Acetic acid	1.07
Acetone	2.09
Ammonium nitrate in solution	0.80
Ammonium sulphate in solution	1.00
Chlorotrifluoroethane	0.54
1,2 – Dichloroethane (EDC)	0.81
Ethylene	1.00
Ethylene glycol	1.29
Ferrous ion	0.14
Methanol	1.50
Methyl methacrylate	1.50
Methylene Chloride	0.47
Phenol	2.38
Vinyl chloride	1.28

5.3.2.6 Atmospheric Acidification

This metric measures the acid increase in the environment when chemicals such as ammonia, sulfuric acid, hydrochloric acid, hydrogen fluoride, nitrogen dioxide and sulfur dioxide are emitted into the atmosphere (IChemE Metrics, 2002; da Costa and Pagan, 2006). To calculate this metric, the mass flow rate of the substance is multiplied by a potency factor for each substance. The potency factor converts, the chemicals to sulfur dioxide equivalent. Potency factors for acidic chemicals are presented in Table 5.6.

Table 5.6: Potency Factors for Chemicals that Cause Atmospheric Acidification (IChemE Metrics, 2002)

Substances	Potency Factor
Ammonia, NH_3	1.88
Sulfuric acid mist, H_2SO4	0.65
Hydrochloric acid, HCL	0.88
Hydrogen fluoride, HF	1.60
Nitrogen dioxide, NO_2	0.70
Sulfur dioxide, SO_2	1.00

5.3.2.7 Aquatic Acidification

This metric measures the acid increase in water sources when chemicals such as acetic acid, hydrochloric acid and hydrogen fluoride etc. are discharged (IChemE Metrics, 2002). To calculate this metric, the mass flow rate of the substance is multiplied by a potency factor for each substance as shown in Table 5.7. The potency factor converts, the chemicals to hydrogen ions.

Table 5.7:Potency Factors for Chemicals that Cause Aquatic Acidification (IChemE Metrics, 2002)

Substances	Potency Factor
Acetic acid	0.020
Hydrochloric acid, HCL	0.027
Hydrogen fluoride, HF	0.050
Sulfuric acid	0.020

5.3.2.8 Eutrophication

This metric is defined as the addition of unwanted nutrients into water sources which leads to the increase in plant growth. For this metric, all substances that cause eutrophication are converted to phosphorus equivalent by using potency factors. The potency factors for this conversion are shown in Table 5.8.

Table 5.8: Potency Factors for Chemicals that Cause Eutrophication (IChemE Metrics, 2002)

Substances	Potency Factor
Ammonia	0.33
COD	0.02
Nitrogen	0.42
Nitrogen dioxide, NO_2	0.20
Nitrogen oxide, NO	0.13
NOx	0.13
Phosphorus	3.06
PO4 (III-)	1.00

5.3.2.9 Resources usage

This metric evaluate resource usage of a chemical process, while addressing energy and water usage as well as reaction efficiency. For more information on these metrics, papers by Constable, Curzons and Cunningham (2002) and Tanzil and Beloff (2006) can be consulted. The sub-metrics under this category include, E-factor, mass productivity, reaction mass efficiency, energy intensity and water consumption. The calculations for these metrics are shown in Equation 5.3-5.8 (Constable et al., 2002; Tanzil and Beloff, 2006).

$$\text{E-Factor} = \frac{\text{Total Waste}}{\text{Kg of Product}} \tag{5. 3}$$

$$\text{Reaction Mass Efficiency} = \frac{\text{Mass of Product}}{\text{Mass of Reactants}} \tag{5. 4}$$

$$\text{Mass Productivity} = \frac{1}{\text{Mass Intensity}} \text{ X } 100 \tag{5. 5}$$

$$\text{Mass Intensity} = \frac{\text{Total Mass used in a Process Step}}{\text{Mass of the Product}} \tag{5. 6}$$

$$\text{Energy Intensity} = \frac{\text{Energy Consumed}}{\text{Mass of Product}} \tag{5. 7}$$

$$\text{Water Intensity} = \frac{\text{Water Consumed}}{\text{Mass of Product}} \tag{5. 8}$$

The interpretation of the environmental impact assessment for any chemical process is as follows:

- When the following metrics have low impact values: atmospheric acidification, global warming, stratospheric ozone depletion, photochemical smog formation, aquatic acidification, aquatic oxygen demand, eco-toxicity to aquatic life, aquatic oxygen demand, eutrophication, E-Factor, mass intensity, energy intensity and water intensity; the chemical process is more environmentally friendly.

- Also, the higher the value of the following metrics: reaction mass efficiency and mass productivity; the chemical process is more environmentally friendly.

5.3.3 Social Concerns in the SUSTAINABILITY EVALUATOR

Social concerns affect society as a whole. These concerns could be how the creation of a new product could create potential job opportunities, societal income as well as process health and safety risks. Or what are the risks involved in manufacturing benzene to plant employees and neighboring inhabitants? It is apparent that several social metrics exist, however for the scope of the proposed research, health and safety metrics were selected. Health and safety has been an area of concern in industry for several years and researchers have put forth efforts towards quantifying it (Heikkila, 1999; Tugnoli et al., 2008b). Therefore, quantitative information on this concern is available. In this work, we focus on evaluating process safety risk by implementing the index developed by Heikkila (1999) and health risk by using data from the International Agency for Research on Cancer (2009) and Score Card (2005). In this section, two categories of metrics as listed below are discussed:

- Process Safety Risks
- Health Risks

5.3.3.1 Process Safety Risk

The following process safety metrics are discussed below: heat of main and side reaction index, flammability index, explosivity index, corrosive index, toxic exposure index, temperature index, pressure index, equipment process safety index and process safety structure index.

5.3.3.1.1 Heat of Main and Side Reaction Index

This metric as shown in Equation 5.9, measures the amount of heat that is released during a chemical reaction. Reactions that generate high quantities of heat could be potentially dangerous due to the potential release of dangerous gases. Many processes have multiple reactions, thus this metric can be used to evaluate both main and side reactions. This metric is calculated by Equation 5.9 below (Heikkila, 1999; Jensen et al., 2003). To interpret the results obtained from this equation, index scores as shown in Table 5.9 have been provided. The index score ranges from 0-8 with 8 being the worse safety scenario as suggested by the author of this dissertation.

$$\Delta H_r = \square_{\text{products}}(H_f)_{\text{products}} - \square_{\text{reactants}}(H_f)_{\text{reactants}} \qquad (5.\ 9)$$

Table 5.9: Index Score for Heat of Reaction

Mass Enthalpy(H_f) (J/g)	Score
≤ 200	0
<600	2
< 1200	4
< 3000	6
3000	8

5.3.3.1.2 Flammability Index

This metric measures the potential for chemicals to burn with air in the event that there is a chemical leak. The flammability index is based on the flash point temperature. In general, the lower the flash points temperature, the more flammable the chemical is. In this work, flash point temperature for chemicals have been obtained from “Chemical Process Safety” (Crowl and Louvar, 1989). The index score for this metric is shown in

Table 5.10. The index score ranges from 0-8 with 8 being the worse safety scenario as suggested by the author of this dissertation.

Table 5.10: Index Score for Flammability Index

Flammability Limits (^oC)	Score
Not Flammable	0
Flash Point > 55	2
Flash Point ≤ 55	4
Flash Point < 21	6
Flash point < 0 & boiling point ≤ 35	8

5.3.3.1.3 Explosivity Index

The metric measures the potential for a gas to form an explosive mixture with air. The explosivity index is calculated by subtracting the upper explosive limit (UEL) from the lower explosive limit (LEL) of chemicals. Substances with a large explosive limit difference tend to be more explosive. UEL and LEL for explosive chemicals have been obtained from Crowl and Louvar (1989), material data safety sheets and Dow Fire & Explosive Hazard Classification (American Institute of Chemical Engineers (AIChE), 1994). The index score for this metric is shown in Table 5.11. The index score ranges from 0-8 with 8 being the worse safety scenario as suggested by the author of this dissertation.

Table 5.11: Index Score for Explosivity Index

Explosiveness Limit	Score
Not Explosive	0
0-20	2
20-45	4
45-70	6
70-100	8

5.3.3.1.4 Corrosive Index

This index measures the possibility for chemicals such as acids, acid anhydrides and bases to corrode plant equipment. The corrosion of plant equipment can be a dangerous situation leading to toxic exposure due to leakages, explosions and fires. Therefore, it is important to select the appropriate material for construction when designing plant equipment to avoid corrosion issues. The corrosive index is based on the material used for construction as shown in Table 5.12. As suggested by the author of this dissertation, the index score ranges from 0-4 with 4 being the worse safety scenario.

Table 5.12: Index Score for Corrosive Index

Material of Construction	Score
Carbon Steel	0
Stainless Steel	2
Better Material Needed	4

5.3.3.1.5 Temperature Index

This is a measure of the potential risk in a process due to the temperature range in the process. Temperature is a very important parameter because high and cryogenic temperatures weaken certain materials of construction leading to other process safety issues. The index score according to the temperature range can be found in Table 5.13. As suggested by the author of this dissertation, the index score ranges from 0-8 with 8 set as the worse safety scenario.

Table 5.13: Index Score for Temperature Index

Temperature (^oC)	Score
< 0	2
0-70	0
70-150	2
150-300	4
300-600	6
>600	8

5.3.3.1.6 Pressure Index

This is a measure of the potential risk in a process due to the pressure range in the process. Pressure is a very important parameter because high pressure conditions affect leakage rates and vessel strength (Heikkila, 1999). The index score according to the pressure range can be found in Table 5.14. As suggested by the author of this dissertation, the index score ranges from 0-8 with 8 set as the worse safety scenario.

Table 5.14: Index Score for Pressure Index

Pressure (bar)	Score
0.5 – 5	0
0-0.5 or 5-25	2
20-25	4
50-200	6
200-1000	8

5.3.3.1.7 Equipment Process Safety Index

This index measures the risk associated with your process based on equipment found in a process. For example, plants that have furnaces and fire heaters have a higher equipment process safety index than plants that have simpler equipment such as storage vessels. The index score according to process equipment can be found in Table 5.15. As suggested by the author of this dissertation, the index score ranges from 0-8 with 8 set as the worse safety scenario.

Table 5.15: Index Score for Equipment Process Safety Index

Type of Equipment	Score
Equipment handling nonflammable, nontoxic materials	0
Heat exchangers, pumps, towers, drums	2
Air coolers, reactors, high hazard pumps	4
Compressors, high hazard reactors	6
Furnaces, fired heaters	8

5.3.3.1.8 Process Safety Structure Index

This index measures the reliability of a process stricture based on industry standard, engineering practice and related incidents. The index score for process safety structure can be found in Table 5.16. As suggested by the author of this dissertation, the index score ranges from 0-10 with 10 set as the worse safety scenario.

Table 5.16: Index Score for Process Safety Structure Index

Process Reliability	Score
Safe	0
Sound Engineering Practice	2
No data	4
Probably Unsafe	6
Minor Accidents	8
Major Accidents	10

5.3.3.1.9 Toxic Exposure Index

This is a measure of the health risk associated with a certain chemical and it is determined by its threshold limit value (TLV). Substances with a lower TLV tend to be more harmful compared to substances with a higher TLV. TLVs can be obtained from the American Conference of Governmental Industrial Hygienists (2009). The index score for this metric is shown in Table 5.17. As suggested by the author of this dissertation, the index score ranges from 0-65 with 65 being the worse safety scenario.

Table 5.17: Index Score for Toxic Exposure Index

Toxic Exposure Limit (ppm)	Score
TLV > 10000	0
TLV ≥ 10000	4
TLV ≤ 1000	8
TLV ≤ 100	12
TLV ≤ 10	16
TLV ≤ 1	20
TLV ≤ 0.1	24
TLV ≤ 0.01	30

5.3.3.1.10 Summary of Safety Metrics

As suggested by Heikkila (1999), an overall safety index can be evaluated by summing each of the ten metrics shown in Table 5.18. A chemical process with a process safety index of 100 has the maximum process safety risk and is an extremely unsafe process.

Table 5.18: Index Score for Process Safety Structure Index

Safety Metric	Index Range
Heat of Main Reaction Index	0-8
Heat of Side Reaction Index	0-8
Flammability Index	0-8
Explosiveness Index	0-8
Corrosiveness Index	0-4
Temperature Index	0-8
Pressure Index	0-8
Equipment Safety Index	0-8
Safety Level of Process Structure Index	0-10
Toxic exposure Index	0-30
Overall Safety Index	0-100

5.3.3.2 Health Risk

The following health metrics are discussed below: carcinogenic health risk, developmental health risk, reproductive health risk, cardiovascular health risk, endocrine system health risk, liver damage health risk, immune system damage health risk, kidney damage health risk, skeletal system damage health risk, neurological damage health risk and respiratory system health risk.

5.3.3.2.1 Carcinogenic Health Index

This index measures the carcinogenic risk of a process based on the chemicals present in the process. Carcinogenic chemicals can be classified into four major categories namely, carcinogenic to humans, probably carcinogenic to humans, possibly carcinogenic to humans, carcinogenic to animals but not humans and probably not carcinogenic to humans (International Agency for Research on Cancer). For this metric, an index score ranging from 0 to 1 were selected by the author as shown in Table 5.19. For each known carcinogen, the index value is multiplied by the amount being emitted to calculate this metric.

Table 5.19: Index Score for Carcinogenic Risk

Type of Carcinogen	Group	Score
Not Carcinogenic	N/A	0
Probably not carcinogenic to humans	4	0.2
Not classifiable as to its carcinogenicity to humans	3	0.4
Possibly carcinogenic	2B	0.6
Probably carcinogenic to humans	2A	0.8
Carcinogenic to humans	1	1

5.3.3.2.2 Developmental Health Risk

This index measures the risks posed to a developing child when a pregnant woman is exposed to toxic chemicals. Developmental problems that can arise include birth defects, low birth weight, biological dysfunctions, psychological or behavioral deficit and even brain damage. For this research, lists of known and suspected developmental toxicants were obtained from Score Card. For this work, suspected and known developmental toxicants were selected by the author and assigned an index value of 0.6 and 1 respectively. These index values were chosen because a value of 0.6 and 1 have been assigned for suspected and known carcinogens, respectively. Therefore because these metric will be compared against each other it was better to use similar index values. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.3 Reproductive Health Risk

This index measures the risks posed to the reproductive system of an adult when they are exposed to reproductive toxicants. Reproductive system problems that can arise include abnormal sexual behavior, decreases in fertility, loss of the fetus during pregnancy. For this research, a list of known and suspected reproductive toxicants was obtained from Score Card. For this work, suspected and known reproductive toxicants were selected and assigned an index value of 0.6 and 1 respectively by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.4 Circulatory System Damage Health Risk

This index measures the risks posed to the circulatory system of an adult after exposure to cardiovascular toxicants. Cardiovascular system problems that can arise include hypertension, arteriosclerosis, cardiac arrhythmia, and decreased coronary ischemia. For this research, a list of suspected reproductive toxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.5 Endocrine System Damage Health Risk

This index measures the risks posed to the endocrine system of an adult after exposure to endocrine toxicants. Endocrine system problems that can arise include hypothyroidism, diabetes mellitus, hypoglycemia, reproductive disorders, and cancer. For this research, a list of suspected endocrine toxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.6 Gastrointestinal and Liver Damage Health Index

This index measures the risks posed to the gastrointestinal tract, liver, or gall bladder of an adult after exposure to toxicants. For this research, a list of suspected toxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.7 Immune System Damage Health Risk

This index measures the risks posed to the immune system after exposure to immunotoxicants. When the immune system has been compromised, there will be an increased rate of infectious diseases and cancer. For this research, a list of suspected immunotoxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.8 Kidney Damage Health Risk

This index measures the risks posed to the kidney, ureter and bladder after toxic exposure. For this research, a list of suspected toxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.9 Skeletal System Damage Health Risk

This index measures the risks posed to the bones, muscles and joint after toxic exposure. Skeletal system damage induced by toxicants includes arthritis, fluorosis and osteomalacia. For this research, a list of suspected toxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.10 Nervous System Damage Health Risk

This index measures the risks posed to the nervous system after toxic exposure. Nervous system damage induced by toxicants includes confusion, fatigue, irritability, brain damage and loss of coordination. For this research, a list of suspected toxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.11 Respiratory System Damage Health Risk

This index measures the risks posed to nasal passages, pharynx, trachea, bronchi, and lungs of an adult when they are exposed to toxicants. Respiratory system damage induced by toxicants includes acute and pulmonary edema, irritation, bronchitis irritations, emphysema, and cancer. For this research, a list of suspected toxicants was obtained from Score Card and was assigned an index value of 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.12 Skin or Sensory Organ Damage Health Risk

This index measures the risks posed to the skin or sensory organ after toxic exposure. Damage to the sensory organ leads to hearing loses, sense of smell, eye irritations etc. For this research, a list of suspected toxicants was obtained from Score Card and was assigned an index value 0.6 by the author. For each known toxicant, the index value is multiplied by the amount being emitted to calculate this metric.

5.3.3.2.13 Summary of Health Metrics

Twelve health metrics were introduced in this section. The index ranges for the metrics are presented in Table 5.20. To determine the health impact associated with a manufacturing process emitting waste, the mass flow rate of the substance being emitted is multiplied by an assigned index value for each metric.

Table 5.20: Index Score for Health Metrics

Health Metric	Index Range
Carcinogenic Risk	0-1
Developmental Damage	0.6 or 1
Reproductive System Damage	0.6
Circulatory System Damage	0.6
Skeletal System Damage	0.6
Endocrine System Damage	0.6
Gastrointestinal and Liver Damage	0.6
Immune System Damage	0.6
Kidney Damage	0.6
Skeletal System Damage	0.6
Nervous System Damage	0.6
Respiratory System Damage	0.6
Sensory System Damage	0.6

5.3.4 Overall Sustainability Impact in the Sustainability Evaluator

Addressing sustainability concerns during early stages of design is a multiple objective optimization problem. In this research, the three major sustainability concerns are weighted and summed up into a single objective resulting in an equation called the "overall sustainability impact" as shown in Equation 5.10. An overall sustainability impact (SUI) was developed by the author based on the economic, environmental and social metrics discussed in the previous sections.

$$SUI = 0.20*EI + 0.40*ENVI + 0.40*SCI \tag{5.10}$$

Where

EI = Economic Impact
ENVI = Environmental Impact
SCI = Social Impact

To determine the overall SUI, weights were assigned to the calculated economic, environmental and social impact. Approaching multiobjective optimization problems using weights has been a conventional approach used by several researchers because it is advantageous in that it is computationally efficient as one final solution is obtained instead of multiple Pareto solutions (Jin et al., 2001; Yaochu et al., 2001).

A weight of 0.20 was assigned to the economic impact while social and environmental impacts were assigned a higher value of 0.4 because when environmental and social risks occur, the overall risks are costly. The objective here was to derive an impact value ranging from 0-1, where processes with overall impact values close to 0 are more sustainable compared with processes with values close to 1. Hence the lower the overall sustainability impact, the more sustainable the process is. Economic, environmental and social metrics were normalized using a ranking system procedure described in the next sections.

5.3.4.1 Economic Impact Normalization

An overall economic impact (EI) was developed based on calculating the profit relative to investment (PRI) as shown in Equation 5.11. The profit relative to investment was the selected metric as this is an important criterion used in making investment decisions. Based on the calculated PRI value, an impact score ranging from 0-1 is assigned as shown in Table 5.21

$$\text{PRI}=\left(\frac{\text{Profit}}{\text{Expenses}}\right)*100 \qquad (5.11)$$

Table 5.21: Score for Economic Impact

PRI	Economic Impact
0	1
5%	0.75
15%	0.5
20%	0.25
>25%	0

As shown in the table, when the calculated PRI is greater than 25% an impact score of 0 is assigned. As the calculated PRI decreases, an impact score is assigned based on ranking so that a process with an economic impact of 1 is not profitable.

5.3.4.2 Environmental Impact Normalization

An overall environmental impact (ENVI) was developed by normalizing both the resource usage and environmental burden metrics and using Equation 5.12.

$$\text{ENVI} = 0.25*\text{RUI} + 0.75*\text{EVI} \qquad (5.12)$$

A value of 0.25 was assigned to resource usage impact because this metric measures one category of environmental concern which is resource depletion, while environmental burdens were assigned 0.75, as this metric measure eight other ecological concerns. The resource usage impact (RUI) was first normalized from 0-1 where each of the individual metric are assigned weights as shown in Table 5.22. The goal here was to ensure that the sum for the worst case scenario would equal 1. As this impact has five sub metrics, each individual concern under resource usage were ranked from 0-0.20 based on the calculated metric as shown in Tables 5.22 and 5.23. Calculated values for mass productivity and reaction mass efficiency were assigned impact values based on Table 5.22, while E-factor, energy intensity and water usage, were assigned values based on Table 5.23.

Table 5.22: Resource Usage Metric Impact Value for Metrics Expressed in percentages

Resource Usage metric (%)	Score
0	0.20
20	0.10
40	0.07
60	0.05
80	0.04
100	0.00

Table 5.23: Resource Usage Metric Impact Value for metrics expressed in Kilogram

Resource Usage Metrics (kg)	Score
0	0.00
0.5	0.03
1	0.04
5	0.05
10	0.07
50	0.10
200	0.20

Next each environmental burden such as global warming, stratospheric ozone depletion, photochemical smog, aquatic oxygen demand, atmospheric acidification, aquatic acidification, eco-toxicity to aquatic life and eutrophication was assigned a value ranging from 0 to 0.125 based on the calculated equivalent value as shown in Table 5.24. The goal here was to ensure that the sum for the worst case scenario would equal 1 as this metric has eight sub metrics.

An impact value of 0 was assigned if that particular metric was not an issue of concern i.e. the calculated impact value is 0 Tones/year equivalent. While it was assigned a value of 0.125 if its calculated impact value was greater than 100,000 Tonnes/year equivalent. For the worst case scenario, where all environmental burdens are an issue of concern and the calculated equivalent impact value is greater than 100,000 Tonnes/year, the EVI is 1.

Table 5.24: Environmental Burden Impact Value

Equivalent Impact (Tonnes/year)	Score
0	0
100	0.041
10000	0.0625
100000	0.125

5.3.4.3 Social Impact Normalization

An overall social impact (SI) was developed based on normalizing the safety impact (SAI) and health impact (HEI) using Equation 5.13. Weights of 0.5 were selected for both indices because they are of equal importance. An overall safety impact (SAI) was developed using the calculated process safety index value. Based on the calculated process safety index, an impact score ranging from 0-1 is assigned as shown in Table 5.25. A process that is assigned an impact of 1 has the highest possible safety risk.

$$SCI = 0.5*SAI + 0.5*HEI \tag{5.13}$$

Table 5.25: Weights for Overall Safety Impact Value

Process Safety Index Value	Score
0	0
25	0.25
50	0.50
75	0.75
100	1.00

For the health impact, the carcinogenic risk was assigned a value ranging from 0 - 0.25 as shown in Table 5.26. The other eleven other health concerns such as developmental health risk, reproductive health risk, cardiovascular health risk, endocrine system health risk, liver damage health risk, immune system damage health risk, kidney damage health risk, skeletal system damage health risk, neurological damage health risk and respiratory system health risk have been assigned a weight of 0-0.068 so that for the worst case scenario, where all health burdens are an issue of concern and the calculated equivalent impact value is greater than 100,000 Tonnes/year, the health impact (HEI) is 1.

Table 5.26: Weights for Carcinogenic Risk

Tonnes/Year Equivalent	Score
0	0
100	0.083
1000	0.125
10000	0.25

A larger weight was assigned to carcinogenic risk as cancer is the most severe health concern. For carcinogen risk, weights were assigned based on Table 5.26, while all other health impacts, were assigned weights s based on Table 5.27. The overall sum of each assigned health impact value for the worst case scenario is 1.

Table 5.27: Weights for other Health Risks

Tonnes/Year Equivalent	Score
0	0
100	0.025
10000	0.05
100000	0.068

5.3.4.4 Validation of Impact Weights

As stated before, a weight of 0.20 was assigned to the economic impact while social and environmental impacts were assigned a higher value of 0.4. To determine if changing the weights for each impact category would affect the overall result, a sensitivity analysis was done on the ally chloride case study (see Chapter 6). In this case study, there are three processes that are evaluated and are compared. These are the base, adiabatic PFR and isothermal PFR cases. The analysis showing the calculated overall sustainability impact for the three cases, when the impact weights are varied, are presented in Table 5.28. As shown in the table, regardless of what weights are selected, the Adiabatic PFR always has the lowest overall sustainability impact value and the base case always had the highest overall sustainability impact value. However, the calculated overall sustainability impact value changed. For this case study, since the impact values were not competing, the selection of weights did not change the overall outcome. Further study should be completed on weight selection.

Table 5.28: Impact Weights Sensitivity Analysis

Case	Economic Weight	Environmental Weight	Social Weight	Base Case*	Adiabatic PFR+	Isothermal PFR
1	0.1	0.1	0.8	0.50	0.35	0.35
2	0.1	0.5	0.4	0.37	0.20	0.23
3	0.2	0.4	0.4	0.45	0.20	0.22
4	0.2	0.5	0.3	0.42	0.16	0.19
5	0.2	0.7	0.1	0.35	0.09	0.13
6	0.3	0.1	0.6	0.59	0.26	0.27
7	0.33	0.33	0.33	0.53	0.16	0.18
8	0.4	0.1	0.5	0.64	0.22	0.22
9	0.4	0.4	0.2	0.54	0.11	0.13
10	0.5	0.2	0.3	0.65	0.14	0.15
11	0.6	0.1	0.3	0.73	0.13	0.14
12	0.6	0.3	0.1	0.67	0.06	0.08
13	0.7	0.1	0.2	0.78	0.09	0.10
14	0.7	0.2	0.1	0.75	0.06	0.07

*Adiabatic PFR case always has the lowest impact value

+ Base case always has the highest impact value

5.4 SENSITIVITY ANALYSIS

A sensitivity analysis is useful in investigating how the variation of one parameter can affect a targeted objective or goal. A sensitivity analysis assists in identifying optimum operating conditions and process configuration. In sensitivity analysis, there are independent and dependent variables. Dependent variables are variables that are being evaluated when independent variables are fluctuated. As the goal of this research is to determine the most sustainable process option, the dependent variables in this work will be the sustainability metrics that were discussed in the previous section, while the independent variables are the parameters that are being investigated such as operating conditions, mass flow rate, reactor temperature and pressure, number of stages in distillation columns, reflux ratio etc.

The sensitivity analysis was carried out using ASPEN PLUS. ASPEN PLUS has a sensitivity analysis model so it was easy to investigate how changes in parameters affected the overall sustainability of a process. Once the sensitivity analysis has been conducted and important variables have been selected, the next step is to reconfigure the process. Process reconfiguration is not process specific and can include a wide range of activities which include the following:

- Incorporating recycle streams
- Adding additional separation equipment
- Including energy efficient technology to the process
- Improving the efficiency of the reactions by considering alternative reaction synthesis
- Modifying reactor operating conditions to improve conversion and reduce the production of by products
- Changing separator mechanics such as reflux ratio

Once the process has been reconfigured, the next step is to optimize the process. The results of the sensitivity analysis will provide reasonable estimates for constraints used in the optimization step of this research.

5.5 PROCESS OPTIMIZATION

After the sensitivity analysis has been completed, the next step is to optimize the process for maximum profit while minimizing wastes and incorporating constraints that have been selected based on the results of the sensitivity analysis. The process optimization was carried out in ASPEN PLUS. ASPEN PLUS has an optimization block that is available for finding optimum conditions in a process. In this research, profit as defined by Equation 5.2 is maximized and the mass flow rates of the streams that are considered wastes are minimized while operating at sustainable safe conditions. Reducing wastes will lessen environmental impact and health risks. Also finding the optimum operating conditions will also improve safety risks. The optimization of this process as described above will lead to an improvement in the overall sustainability impact of the process. The case studies in the next sections will show the objective functions and constraints used in this research.

5.6 SUSTAINABILITY RE-EVALUATION

After process optimization, the newly optimum process is re-evaluated using the "SUSTAINABILITY EVALUATOR." If the design has a low overall sustainability impact, the user can accept the optimized process. However, it is important to note that, the first optimization run might give the optimum sustainable solution. Constraints and parameters might need to be tweaked in order to ensure that the process is as economic, environment friendly and socially acceptable as it could be. Once the process changes have been implemented, the optimization step is repeated and the process is evaluated again using the SUSTAINABILITY EVALUATOR. If there is tremendous improvement, the designer can accept the optimized process otherwise the user will need to keep re-optimizing the process until they are satisfied with the final solution.

5.7 SUMMARY

In this chapter, a novel methodology proposed for this research was presented. A newly developed novel screening tool titled the “SUSTAINABILITY EVALUATOR” was introduced to identify sustainable concerns in a chemical process. The proposed impact assessment methodology is novel for two reasons. The first is that economic, environmental and impact assessments can be evaluated by one tool making it easier for engineers to see how process improvements affect overall sustainability of a process. Secondly the incorporation of social metrics, i.e. health and safety metrics is quite new as many researchers don’t incorporate all three dimensions into process design. Also, an overall sustainability impact was developed. This sustainability impact value provides a quantitative number for process designers to evaluate the sustainability of a process.

In the SUSTAINABILITY EVALUATOR, selected economic, environmental and health and safety metrics have been programmed into the tool. A framework which is useful in identifying and improving sustainability concerns in early stages of design was discussed. The approach proposed can be summarized as follows:

- Simulation of the base case and use of the “SUSTAINABILITY EVALUATOR” to identify the sustainability concerns in the process.
- Complete sensitivity analysis in order to identify parameters that affect and improve the metrics found in the “SUSTAINABILITY EVALUATOR” Process reconfiguration based on the sensitivity analysis.
- Formulate objective functions and constraints based on the results of the sensitivity analysis. Optimization of process to find optimum sustainable conditions.

- Sustainability re-evaluation of the process to ensure it is more sustainable than the base case.

The proposed methodology is implemented and demonstrated on four case studies presented in the next section.

CHAPTER VI

DEMONSTRATION OF THE PROPOSED METHODOLOGY

The previous chapter presented the methodology for this research. This methodology is useful in designing process while incorporating sustainability concerns. This framework uses the SUSTAINABILITY EVALUATOR to screen and evaluate processes for sustainability. The efficacy of the SUSTAINABILITY EVALUATOR is first demonstrated by showing how it can be used to evaluate processes for sustainability.

In this step, an impact assessment of the methyl chloride process is completed with the SUSTAINABILITY EVALUATOR. The results obtained from the SUSTAINABILITY EVALUATOR are compared with the Waste Reduction Algorithm (WAR), an environmental impact assessment tool. Also the SUSTAINABILITY EVALUATOR can be used to select the most sustainable process option when comparing two processing alternatives. The dimethyl ether (DME) production process is used to achieve this step. Once the tool was validated, the overall methodology proposed in Chapter 5 and Figure 5.1 is later tested with two additional production processes namely: acrylonitrile and allyl chloride.

6.1 VALIDATION CASE STUDY: METHYL CHLORIDE PROCESS

Methyl chloride commonly called chloromethane or monochloromethane is a colorless, extremely flammable and toxic gas. This slightly sweet gas has the physical properties shown in Table 6.1.

Table 6.1: Physical Properties of Methyl Chloride

Property	Value
Boiling Point (°C)	-24.2
Melting Point(°C)	-97.7
Solubility in water, 25°C, g/ml	5.325
pH	7-9

Methyl chloride is an important chemical with many applications in industry. It used as a chemical intermediate in the drug industry and in the manufacture of methyl cellulose ether. It is used to synthesize silicone polymers which are used for manufacturing rubber. Methyl chloride is also serves as a chlorinating and methylating agent for several organic chemicals. It also sometimes used as a local anesthetic and as an herbicide. It was also once used as a refrigerant but was banned due to its toxic nature. Although the chemical was once synthesized by the reaction of sodium chloride with methanol in the presence of sulfuric acid, the two major commercial approaches used in creating this chemical is by thermal chlorination of methane and hydro chlorination of methanol (Dantus, 1999; Holbrook, 2000).

The methyl chloride production process is an excellent manufacturing process to test the impact assessment tool because of the tremendous toxic waste streams present in this process. These waste steams pose a threat to the environment and human health. Human exposure to methyl chloride has occurred via contamination of water via hazardous waste sites and occupational exposure. For example, a DuPont methyl chloride leak occurred recently and affected the health of workers at the exposed facility (Ward, 2010).

This chemical is listed in the toxic release inventory compiled by the Environmental Protection Agency, as one on the top toxic chemicals The health threat of this chemical poses a serious issue as methyl chloride is a probable carcinogen and is also linked to other health problems such as nervous system damage and kidney damage etc. Handling waste streams in the methyl chloride process is a challenge that must be handled in a sustainable manner. The SUSTAINABILITY EVALUATOR is used to evaluate the economic, environmental and social impacts of the methyl chloride process.

6.1.1 Brief Description of the Methyl Chloride Process

Methyl chloride is modeled based on literature (AIChE, 1966; Dantus, 1999). The information compiled from literature is simulated in ASPEN PLUS version 22 using the Electrolyte Non-Random Two Liquid model with Redlich-Kwong (ELECNRTL) thermodynamic package. The block flow diagram for the process is shown in Figure 6.1. The input file for this simulated process is available in APPENDIX B.

The methyl chloride production process can be divided into three sections namely thermal chlorination of methane, drying columns and methyl chloride separation. In the thermal chlorination step, methane (CH_4) and chlorine (Cl_2) at 14.7 psia and 77^oF are sent to a Mixer (M-601), which combines the two streams into one stream. The mixture is heated by E-601 to 572^oF. Next it is sent to a continuous stirrer reactor (R-601) where the thermal chlorination of methane takes place as shown in Equation 6.1.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \qquad (6.1)$$

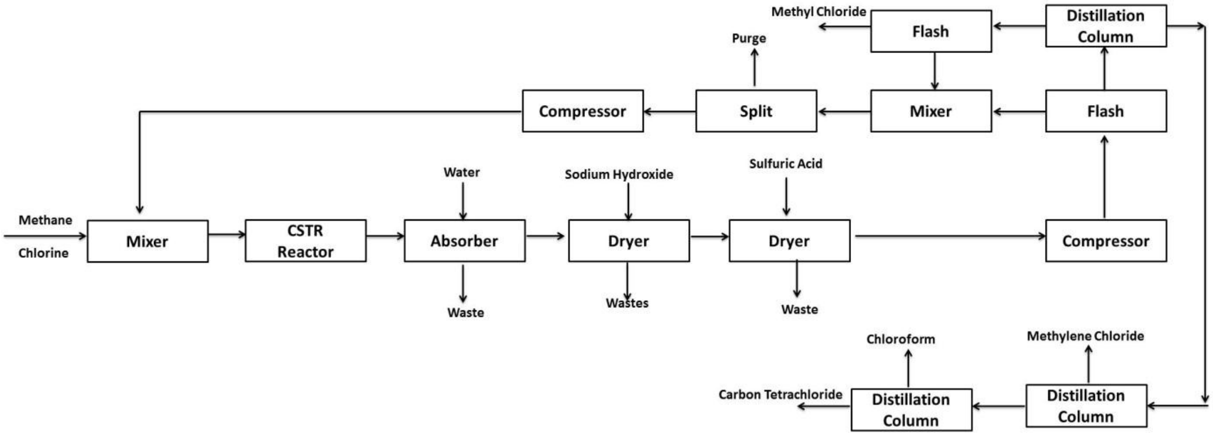

Figure 6.1: Methyl Chloride Block Flow Diagram

Key design consideration must be incorporated when designing this reactor. The first is that for the reactions to take place efficiently, methane and chlorine must be heated above 572°F (Dantus, 1999; Holbrook, 2000). Also the reactor must be operated at a range of 662 to1022°F in order to control the high heat of reaction (Deforest, 1979; Dantus, 1999). Also one of the reactants, methane, must not have impurities of more than 100 ppm to prevent the formation of other by-products such as vinyl chloride, vinylidene chloride, methyl chloroform etc. (Johnson et al., 1959; Dantus, 1999).

The continuous stirred isothermal reactor is operated at 977°F. Although methyl chloride and hydrochloric acid are synthesized in the reactor as shown in Equation 6.1, several side reactions take place resulting in the following by products: methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) as shown in Equation 6.2-6.4. The rate constants for the kinetics for the reactions taking place in the reactor are presented in Table 6.2 and the power law expression is shown in Equation 6.5.

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl \qquad (6.2)$$

$CH_3Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$ (6.3)
$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ (6.4)

Table 6.2: Methyl Chloride Process Kinetic Data (Scipioni and Rapisardi, 1961; Dantus, 1999)[7]

Reaction Number	Activation Energy, E_i KJ/(kg mol)	Pre Exponential Factor $\left(\frac{m^3}{kg\ mol-s}\right)$
1	82000	2.56×10^8
2	71100	6.28×10^7
3	82000	2.56×10^8
4	87200	2.93×10^8

$V = AT^a e\text{-}^{Ea/RT}\Pi(Cn_1)^b$ (AIChE, 1966; Dantus, 1999) (6.5)

Where

V = Rate of reaction
A = Pre- exponential factor
T = Temperature
a = Temperature exponent
E_a = Activation energy
R = Universal Gas Constant
Cn = Concentration
b = Concentration exponent

After the reaction process, the reactor effluent is cooled to 100°F by cooler (E-602). Next the separation of methyl chloride from byproducts and the un-reacted raw materials occurs. First a water stream at 90°F and 14.7 psia is sent along with the cooled effluent to an absorber (T-601). The water aids the removal of hydrogen chloride and chlorine gas. The dissociation reactions are presented in the Equations 6.6-6.9 below.

$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$ (6.6)
$Cl_2 + 2H_2O \leftrightarrow H_3O^+ + Cl + HClO$ (6.7)
$HClO + H_2O \leftrightarrow H_3O^+ + ClO^-$ (6.8)
$2H_2O \leftrightarrow H_3O^+ + OH^-$ (6.9)

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[7] Data obtained from Dantus (1999) based on information reported by Scipioni and Rapisardi (1961)

To prevent corrosion of equipment and the hydrolysis and decomposition of chloromethane, the distillate leaving the absorber is sent to a series of drying towers. In the first drying tower, (T-602) sodium hydroxide is introduced at 86^oF and 14.7 psia and the reactions shown in Equation 6.10 and 6.11 take place.

$$NaOH \leftrightarrow Na^+ + OH^- \qquad (6.10)$$
$$NaCl \leftrightarrow Na^+ + Cl^- \qquad (6.11)$$

Next the distillate leaving the drying tower, T-602 is cooled to 100^oF and 14.7 psia. This cooled stream is sent along with a sulfuric acid stream to a drying tower, T-603, where the following reactions shown in Equations 6.12 and 6.13 take place. Excess water is removed as the bottoms of the drying column, T-603. The distillate from, T-603 is sent to a compressor, C-601 which is operated at 116 psia, then cooled to -58^oF.

$$H_2O + H_2S0_4 \leftrightarrow H_3O^+ + HSO_4^- \qquad (6.12)$$
$$2H_2O \leftrightarrow H_3O^+ + OH^- \qquad (6.13)$$

This cooled stream is sent to a flash column, T-604 at 115^oF. This is where the separation steps take place. The bottom of the flash column is sent to three distillation columns, T-605, T-606 and T-607. In T-605, the separated bottom is sent to T-606 where methyl chloride is separated as the overhead product. The bottoms of T-606 is sent to T-607 where carbon tetrachloride and is separated as the overhead product and the bottoms is considered wastes. The overhead of T-605 is sent to another flash column, T-608. In this flash column, methyl chloride is also separated as the bottoms while the overhead column is combined along with the overhead of flash column T-604 and sent to a mixer.

The mixture which is mostly methane is then sent to a splitter which splits the mixed stream into a purge stream and another stream is sent to a compressor C-602. The compressor, C-602 compresses this methane stream at 45 psia. This compressed stream is later cooled to 77^{o}F before being recycled back to the first mixer, M-301 completing the process cycle. The key input variables for this process adapted from (Dantus, 1999) are summarized in Table 6.3. The schematic for this process, the equipment specification and stream summary tables are presented in Figure C.1, Table C.1 and Table C.2 in APPENDIX C.

Table 6.3: Methyl Chloride Process Key Input Variables (AIChE, 1966; Dantus, 1999)

Variable	Value
Feed Ratio	0.3
Reactor Type	Isothermal, CSTR
Reaction Temperature	977 ^{o}F
Reactor Effluent, cooling temperature	77 ^{o}F
Condenser Temperature	-58 ^{o}F
Condenser Outlet Pressure	114.7 psia

6.1.2 Sustainability Assessment of the Methyl Chloride Process

The economic, environmental and social impacts of the base case methyl chloride process are calculated using the SUSTAINABILITY EVALUATOR. The data used in completing the economic evaluations are presented in Table 6.4. The annual production for the methyl chloride process was set at 31,278 tons/year.

6.1.2.1 Economic Assessment of the Methyl Chloride Process

An economic assessment was completed using the ASPEN Economic Evaluator. The ASPEN Economic Evaluation uses imported data from ASPEN PLUS and estimates capital and operating costs. The capital and operating costs values obtained from the

ASPEN Economic Evaluator, the mass flow rates of the raw material and product stream and the economic data shown in Table 6.4 are inputted into the SUSTAINABILITY EVALUATOR.

Table 6.4: Summary of Economic data for the Methyl Chloride Process

Item	Cost ($)
Chlorine Costs	$0.21/kg (Reed Business Information Limited, 2010b)
Methane	$0.21/kg (Dantus, 1999)[8]
Process Water	$0.00067/kg (Turton et al., 2009)
Sulfuric Acid	$0.081/kg (Reed Business Information Limited, 2010b)
Sodium Hydroxide	$0.441/kg (Reed Business Information Limited, 2010b)
Methyl Chloride	$0.82/kg (Reed Business Information Limited, 2010b)
Methylene Chloride	$1.2/kg (Reed Business Information Limited, 2010b)
Chloroform	$1.014/kg (Reed Business Information Limited, 2010b)
Carbon Tetrachloride	$1.03 (Dantus, 1999)[9]
Hydrogen Chloride	$0.09 (Reed Business Information Limited, 2010b)
Waste Treatment Costs	$0.2/kg (Turton et al., 2009)
Capital Recovery Factor	0.1175

The result of this assessment is shown in Table 6.5. As shown in the table, the estimated annual revenue generated from selling methyl chloride and it's by product is around $50.4 million. The annual expenses for this production process were estimated to be around $66.3 million. The breakdown of the expenses is shown in Figure 6.2. As shown in Figure 6.2, the raw material costs accounts for 91% of the annual operating expenses of the methyl chloride process. Operating cost, which is about5% of the expenses, is the second largest expenditure incurred in manufacturing the products. Several waste streams are present in the methyl chloride process, and must hence be treated.

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[8] Cost obtained from Dantus (1999) and inflated to 2009 prices

The waste treatment cost as shown in Figure 6.2 is around $1.5 million and this is about 2% of the costs. The capital costs for this process is around $9 million but the purpose of calculating profit, the costs were annualized using the capital recovery factor shown in Table 6.4. The annualized capital cost is about 2% of the expenses incurred in this manufacturing process.

Table 6.5: Economic Assessment Results for the Methyl Chloride Process from the SUSTAINABILITY EVALUATOR

Economic Parameters	Base Case (MM)
Revenue	$50.4
Operating Costs	$3.0
Waste Treatment Costs	$1.5
Raw Material Costs	$60.7
Capital Costs	$9.9
Material Value Added	-$10.3
Profit	-$19.2

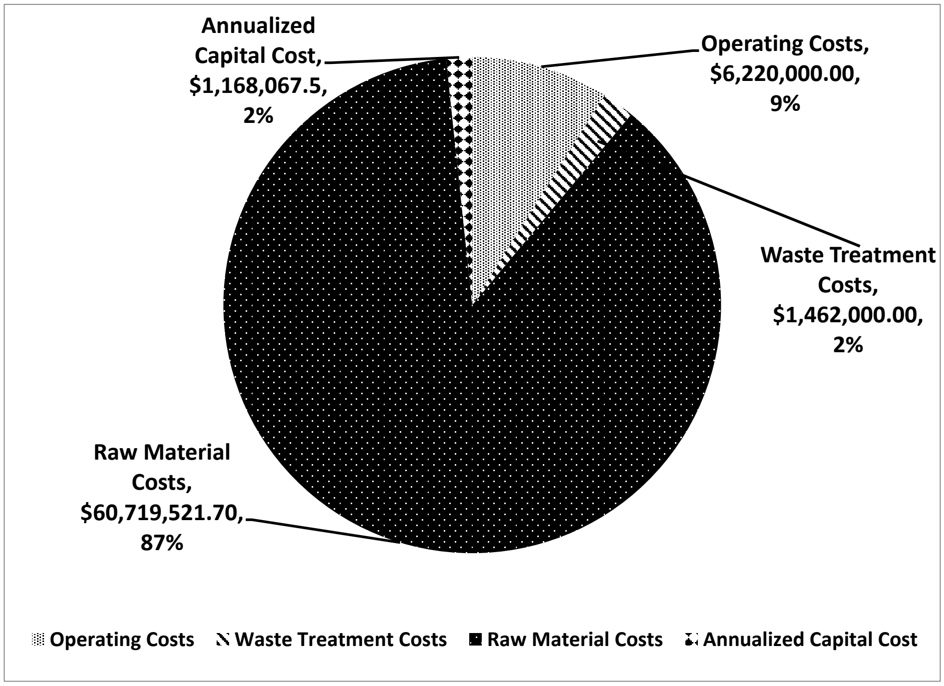

Figure 6.2: Breakdown of Annual Operating Costs for the Methyl Chloride Process from the SUSTAINABILITY EVALUATOR

As shown in Table 6.5, this is not profitable as the process is running at a loss. The reason for this is that the selling price for the raw material is at least $10 million more than the products. The negative profit is probably because the simulated process is based on a 1966 case study and perhaps process improvements have been made over the years leading to a more profitable process. Another reason could be that methyl chloride is used to synthesize other chemicals such as silicone. Perhaps those other final products are more profitable and hence could offset the negative intermediate profit.

6.1.2.2 Environmental Impact Assessment of the Methyl Chloride Process

Once the economics of the methyl chloride process were calculated, the next step was to evaluate the environmental impacts. The environmental impact assessment involved entering the mass flow rates of the waste streams into the SUSTAINABILITY EVALUATOR. The result of the environment assessment is presented in Table 6.6 and Figure 6.3. As shown in table and figure, the methyl chloride process, poses a serious threat to the environment.

Due to the tremendous waste streams the potential environmental burden includes the following concerns: atmospheric acidification, global warming, photochemical smog, stratospheric ozone depletion, aquatic acidification, aquatic oxygen demand, ecotoxicity to aquatic life and eutrophication. The chemicals contributing to each impact category is also presented in Table 6.6. Efforts should be made to reduce the waste streams associated with this production process.

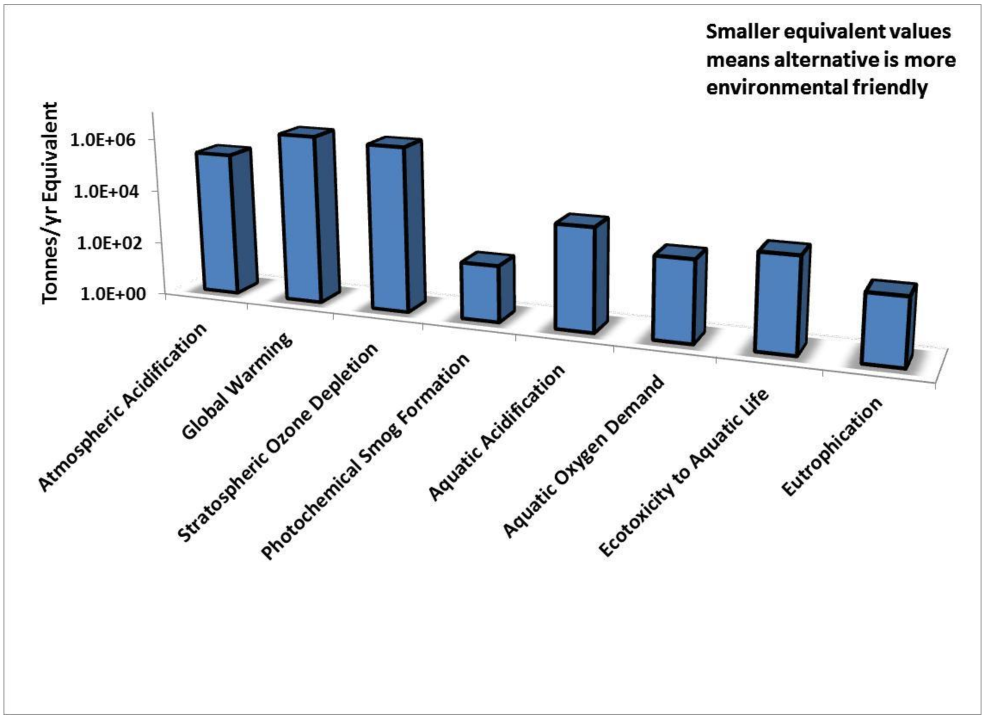

Figure 6.3: Environmental Impact Assessment for the Methyl Chloride Process

Table 6.6: Chemicals in the Methyl Chloride Process Contributing to each Environmental Impact Category

Impact Category	Impact Assessment Value (Tonnes/year)	Chemicals Present
Atmospheric Acidification	2.3E+05	Hydrochloric Acid and Sulfuric Acid
Global Warming	2.0E+06	Methane, Methylene Chloride Chloroform, Carbon Tetrachloride and Methyl Chloride
Stratospheric Ozone Depletion	1.4E+06	Carbon Tetrachloride
Photochemical Smog Formation	1.2E+02	Methylene Chloride and Methyl Chloride
Aquatic Acidification	7.0E+03	Hydrochloric Acid and Sulfuric Acid
Aquatic Oxygen Demand	1.1E+03	Methylene Chloride
Ecotoxicity to Aquatic Life	3.2E+03	Methylene Chloride Chloroform, Carbon Tetrachloride and Chloride
Eutrophication	3.0E+02	Nitrogen

The resource usage efficiency for this process is also evaluated and the results are presented in Table 6.7. As shown in the table, the results of the evaluation show that the methyl chloride production process is not a very resource friendly process. This is because the methyl chloride process is not a single reaction process, several side reactions take place and many unwanted products which are considered wastes are created. The values of the energy intensity, mass productivity, and reaction efficiency are all very low. While the values of the E-Factor, water intensity, and material intensity are all high. Investigating ways to reduce the waste streams and improve reaction efficiency would be important in improving the sustainability of this process.

Table 6.7: Results of Resource Usage Metric Evaluation for the Methyl Chloride Process

Environmental Impact	Value	Units
E-Factor	16.7	Kg/Kg
Mass Productivity	5	%
Reaction Mass Efficiency	28	%
Energy Intensity	0.00062	KW/Kg
Water Intensity	4.6	Kg/Kg

6.1.2.3 Social Impact Assessment of the Methyl Chloride Process

After the environmental impact assessment, the next step was to complete a health and safety impact evaluation using the SUSTAINABILITY EVALUATOR. For the health assessment, the mass flow rate of each specific component found in the waste stream is entered into the SUSTAINABILITY EVALUATOR. As shown in Table 6.8 and Figure 6.4, the methyl chloride process poses a serious health risk in all categories.

Carbon tetrachloride, dichloromethane, and chloroform are group 2b carcinogens. Methyl chloride and hydrochloric acid are considered group 3 carcinogens. Apart from cancer risks, other health threats are eminent; these are shown in Table 6.10. In this table, the chemical contributing to each health impact category is presented. Due to the tremendous health risk, it is therefore vital to ensure that the wastes from this process are handled appropriately and explosions and spills are kept at a minimum.

Table 6.8: Health Impact Assessment Results from the SUSTAINABILITY EVALUATOR for the Methyl Chloride Process

Impact Category	Impact Value (Tonnes/year)	Chemicals Present
Carcinogenic Risk	2.2E+04	Hydrochloric Acid, Carbon Tetrachloride Methylene Chloride Chloroform and Methyl chloride
Immune System Damage	2.7E+04	Hydrochloric Acid
Skeletal System Damage	2.0E+08	Sulfuric Acid
Developmental Damage	3.2E+03	Chloromethane, Chloroform and Carbon Tetrachloride
Reproductive System Damage	4.0E+03	Carbon Tetrachloride Methylene Chloride Chloroform and Methyl chloride
Kidney Damage	2.7E+04	Hydrochloric Acid
Respiratory System Damage	5.1E+04	Hydrochloric Acid, Carbon Tetrachloride Methylene Chloride Chloroform, Sodium Hydroxide, Sulfuric Acid, Chlorine, Nitrogen and Methyl chloride
Cardiovascular System Damage	5.1E+03	Chlorine, Carbon Tetrachloride Methylene Chloride Chloroform and Methyl chloride
Endocrine System Damage	3.1E+03	Carbon Tetrachloride Methylene Chloride and Chloroform
Liver Damage	5.1E+03	Chlorine, Carbon Tetrachloride Methylene Chloride Chloroform and Methyl chloride
Nervous System Damage	5.1E+03	Chlorine, Carbon Tetrachloride Methylene Chloride Chloroform and Methyl chloride
Sensory System Damage	1.9E+05	Hydrochloric Acid, Carbon Tetrachloride Methylene Chloride, Sodium Hydroxide, Sulfuric Acid, Chlorine, and Methyl chloride

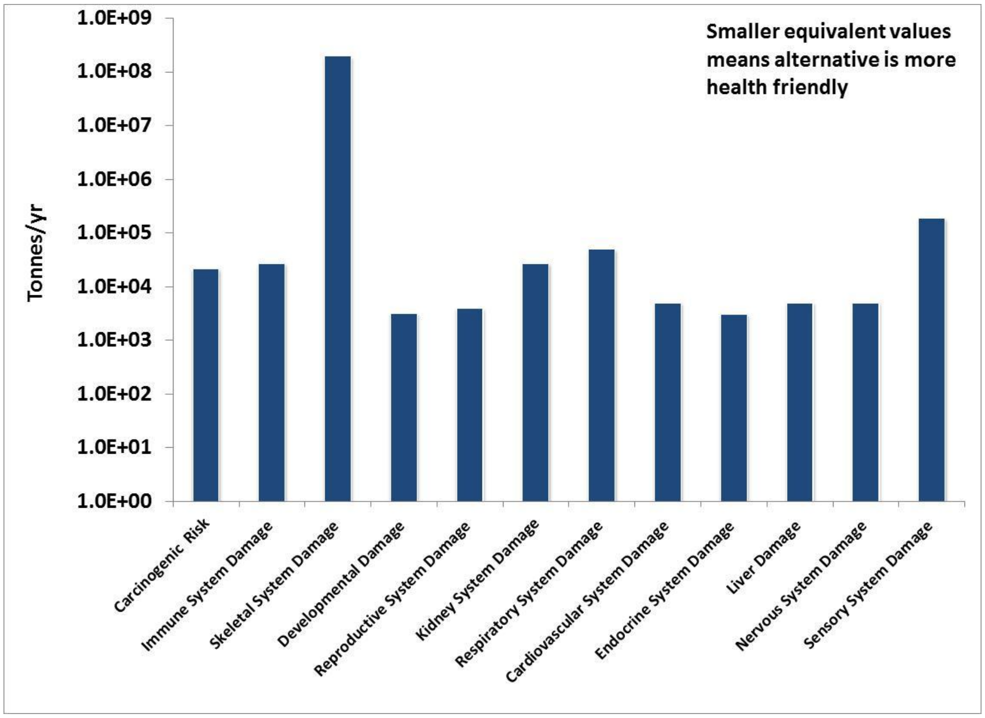

Figure 6.4: Health Impact Assessment for the Methyl Chloride Process

For the safety assessment, the operating conditions, chemicals and equipment present in the process, are selected in the input section of the software. Also, the mass enthalpy is entered to estimate the heat of reaction index. The result of the safety assessment is presented in Table 6.9. The overall total inherent safety index for this process was around 64. The maximum overall safety index i.e. the worst case scenario for any process is 100.

Toxic exposure risks are eminent because the following toxic chemicals are present in the process: methylene chloride, methyl chloride, chloroform, chlorine, carbon tetrachloride and sulfuric acid. Another eminent risk is fire due to flammable chemicals such as methane, methyl chloride and methylene chloride. There are also risks of corrosion since there are strong acids present in the process. The process is also operating at cryogenic temperatures so care must be taken when selecting material of construction to address this issue. Risk of explosion is present in this process because of methyl chloride and methylene chloride. These risks must not be ignored, it is important to investigate ways to ensure safety is not compromised in this process by using appropriate safety measures such as selecting appropriate material of construction as well as incorporating safety devices to this process.

Table 6.9: Safety Assessment Results from the SUSTAINABILITY EVALUATOR for the Methyl Chloride Process

Safety Assessment	Results	Maximum
Heat of main reaction index	2	8
Heat of side reaction index	0	8
Flammability index	8	8
Explosiveness index	6	8
Toxic Exposure Index	24	30
Corrosiveness index	4	4
Temperature index	6	8
Pressure index	2	8
Equipment safety index	4	8
Safety Level of Process Structure index	8	10
Total Inherent Safety index	64	100

6.1.2.4 Summary of Impact Assessment Results

The methyl chloride process presented in this case study is not a sustainable process. As shown in Table 6.10, it is not profitable and hence it has a high economic impact of 1. There are several waste streams leading to several environmental burdens, therefore it has a high environmental impact of 0.54. The safety index for the process is around 64 and there are several health concerns, thus the social impact of 0.59. This process is very unsustainable, with a high overall sustainability impact of 0.65.

Table 6.10: Summary of Impact Assessment Results from the SUSTAINABILITY EVALUATOR for the Methyl Chloride Process

Summary of Results	Methyl Chloride
Profit	$-19.2 (Not profitable)
Economic Impact	1
Environmental Concerns	Global warming, atmospheric acidification, eutrophication, ecotoxicity to aquatic life, aquatic acidification photochemical smog formation and aquatic oxygen demand
Environmental Impact	0.54
Safety Index	64
Health Concerns	Carcinogenic risk, developmental damage, reproductive system damage, circulatory system damage skeletal system damage, endocrine system damage, liver damage, immune system damage, kidney damage, skeletal system damage, nervous system damage, respiratory system damage and sensory system damage
Social Impact	0.59
Overall Sustainability Impact	0.65

6.1.3 Validation of the Results Obtained from the SUSTAINABILITY EVALUATOR using the Waste Reduction Algorithm

The economic section of the SUSTAINABILITY EVALUATOR did not need to be validated because the capital and operating costs were obtained from ASPEN PLUS Economic Analyzer (see chapter 3). ASPEN PLUS Economic Analyzer is a widely used tool used in industry and academia, for evaluating the economics of chemical processes. The ASPEN PLUS Economic Analyzer is robust, efficient and reliable and hence the results obtained from the software are considered valid.

The results obtained from environmental section of the SUSTAINABILITY EVALUATOR are validated with the Waste Reduction Algorithm (WAR). The WAR (see chapter 3) is a publicly available screening tool used to evaluate the potential environment impact and health impact of emission of mass and energy for any simulated process. It is able to evaluate and compare the environmental impact of two or more processes. The impacts categories in the waste reduction algorithm include: acid rain potential (AP), aquatic toxicity potential (ATP), global warming potential (GWP), human toxicity potential by dermal/ inhalation exposure (HTPE), human toxicity potential by ingestion (HTPI), ozone depletion potential (ODP), photochemical oxidation potential (PCOP) and terrestrial toxicity potential (TTP). The software provides the potential environment impact (PEI) in units of (PEI/hr).

For this research, this software is used to validate the environmental portions of the SUSTAINABILITY EVALUATOR. The objective was to check if the WAR would show similar trends as the results provided by the SUSTAINABILITY EVALUATOR developed for this research. Only atmospheric acidification, global warming, ecotoxicity to aquatic Life, stratospheric ozone depletion and photochemical smog formation was selected for this validation because these were the only metrics that were similar to environmental metrics in the SUSTAINABILITY EVALUATOR. The WAR is used to evaluate the environmental impact of the methyl chloride process. To evaluate the impact, the software reads a user specified report file from ASPEN PLUS and the user also inputs the energy usage. The results generated from the WAR and the SUSTAINABILITY EVALUATOR are compared in Figure 6.5 and Table 6.11.

As shown in the Figure 6.5 and Table 6.11, the major concerns for the methyl chloride process are aquatic toxicity potential, global warming potential, photochemical oxidation potential, stratospheric ozone depletion and aquatic acidification. Note that the WAR provides environmental impact results in kg /hr. This unit was converted to Tonnes/year to match the results obtained from the SUSTAINABILITY EVALUATOR.

These results compare well and show similar trends with the environmental impact results provided by the SUSTAINABILITY EVALUATOR. The two tools do not have the same impact assessment values because a different weight and methodology was used in developing the WAR software.

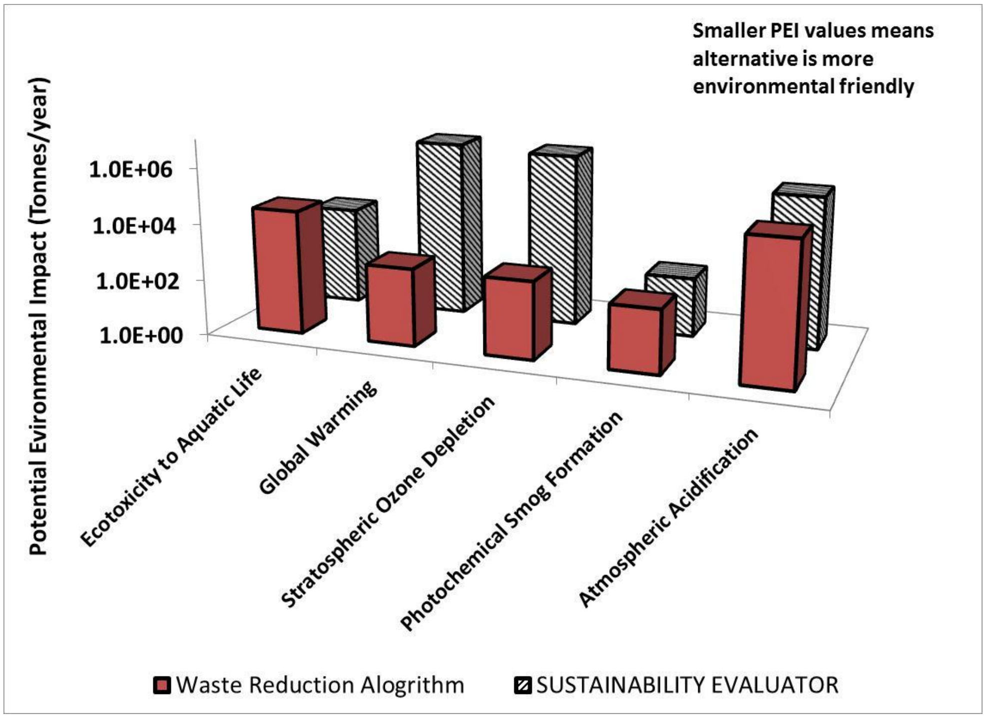

Figure 6.5: Environmental Impact Evaluation from the Waste Reduction Algorithm

Table 6.11: Chemicals in the Methyl Chloride Process Contributing to each Environmental Impact Category

Impact Category	SUSTAINABILITY EVALUATOR Impact Assessment Value (Tonnes/year)	WAR Potential Environmental Impact (Tonnes/year)
Atmospheric Acidification	2.3E+05	9.2E+04
Global Warming	2.0E+06	5.7E+02
Stratospheric Ozone Depletion	1.4E+06	5.6E+02
Photochemical Smog Formation	1.2E+02	1.8E+02
Ecotoxicity to Aquatic Life	3.2E+03	2.6E+04

The safety portion of the software is mostly valid as the methodology was obtained from a reliable PhD dissertation (Heikkila, 1999). The only portion of the tool that was not validated was the health impacts. This is because there are no other health impact assessment tools to compare results in this manner. Now that the SUSTAINABILITY EVALUATOR has been validated and demonstrated as a valid impact assessment tool, the next step of this research was to test the overall methodology on three other industrial processes.

6.2 CASE STUDY: DIMETHYL ETHER PRODUCTION PROCESSES

The SUSTAINABILITY EVALUATOR can be used to compare two process options. This was demonstrated using the Dimethyl Ether (DME) process case study. In this case study, there are two chemistries available for producing DME. These are via dehydration of methanol and via natural gas. The objective is to use the SUSTAINABILITY EVALUATOR to select the most sustainable process option. The results obtained from steps 1 and 2 of the proposed methodology as shown in Figure 5.1 are presented. In this section the following are discussed:

- Brief description of the two DME Processes
- Sustainability evaluation of the two DME Processes
- Selection of the more sustainable DME Process

6.2.1 Brief Description of the DME Production Process

DME is a colorless gas that is used as a propellant and as a fuel additive for diesel engines. DME is considered a greener fuel compared to other hydrocarbons because when it is combusted, it produces minimum amounts of nitrogen oxides, carbon monoxide and it is sulfur free. It is highly flammable but considered nontoxic. The physical properties for DME are illustrated in Table 6.12.

Table 6.12: Physical Properties of Dimethyl Ether

Property	Value
Boiling Point (°C)	-23.6
Freezing Point(°C)	-141.5
Solubility in water, 20°C, g/L	71
Liquid Density, g/L	1.97
Molar Mass, g/mol	46.07

Recently, because of its clean burning nature, several scholars have proposed DME as an alternative fuel for diesel engines, petrol engines and gas turbines (Horstman et al., 2005; Semelsberger et al., 2006; Arcoumanis et al., 2008; Savadkouhi et al., 2010). It could be used as fuel for transportation, power generation, cooking heating etc. (Ogawa et al., 2004). In China and Japan, DME is already being considered as a fuel because of the abundance of coal (Ogawa et al., 2004; Han et al., 2009). DME can be produced by two chemistry pathways namely: DME production via dehydration of methanol and DME production via natural gas.

6.2.1.1 DME Production via Dehydration of Methanol (Option 1)

In this pathway, DME is produced by the catalytic oxidation of methanol to form DME and water as shown in Equation 6.14 below (Turton et al., 2009). The block diagram and the schematic of the process are shown in Figure 6.6 and Figure 6.7 respectively.

$$\underset{\text{methanol}}{2CH_3OH} \rightarrow \underset{\text{DME}}{(CH_3)_2O} + H_2O \tag{6.14}$$

This process is simulated in ASPEN PLUS version 22 using the Universal Functional Activity Coefficient (UNIFAC) thermodynamic package. This thermodynamic package was selected because it predicts the properties of non-ideal mixtures well and it was recommended in literature (Jonasson et al., 1995; Kleiber, 1995). The input file for this simulated process is available in APPENDIX B.

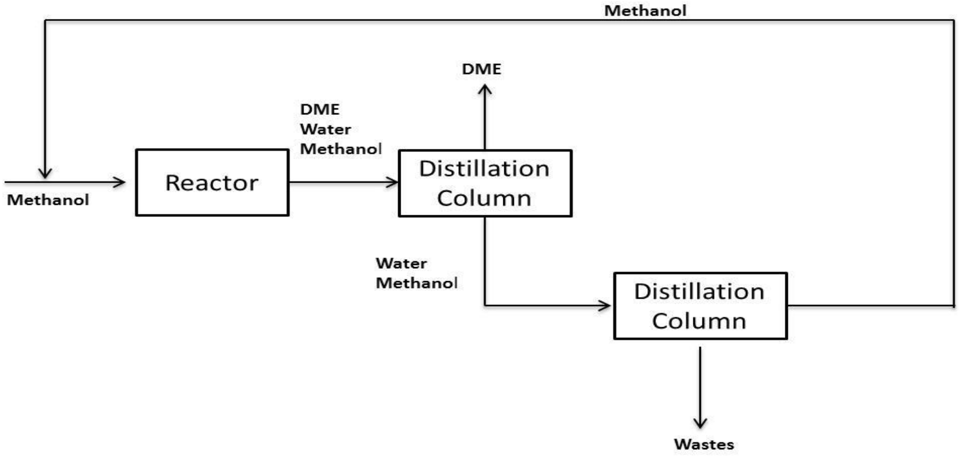

Figure 6.6: Block Diagram of DME Production via Dehydration of Methanol

Methanol (Stream 1) with 99.5% purity at 25°C and 1 bar is fed as a liquid stream and pumped by P-201 at 25 bars and combined with another methanol recycle stream (Stream 13) as shown in Figure 6.7. The combined steams are sent to two heat exchanger E-201 and E-202 where it is heated to 154°C and 220°C respectively before being sent to a reactor. The exothermic reaction taking place is the reactor (R-201) results in 80% conversion of methanol to DME. The products exiting the reactor steam are heated to 364 °C. This exiting stream is cooled down by two coolers E-203 and E-204 to a temperature of 278°C and 100°C respectively, and throttled to 13.4 bar.

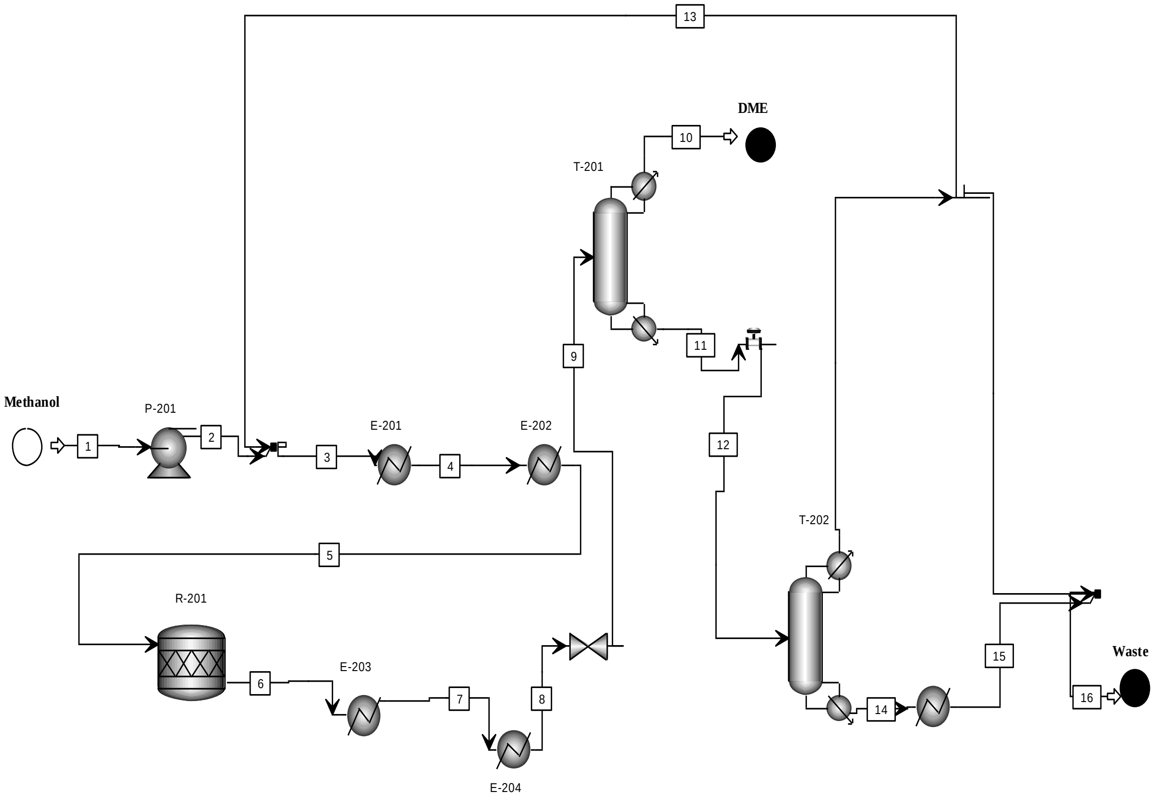

Figure 6.7: Schematic of DME Production via Dehydration of Methanol

This throttled steam is sent to the first distillation column (T-101) where the product DME (stream 10) is separated from the other components. Next the other components (stream 11) are sent to another distillation column (T-102) where methanol (stream 13) and water (Stream 15) are separated. Waste Stream 15 is further cooled to 50^{o}C by cooler E-205. The ASPEN PLUS schematic for this process is show in Figure 6.8. The stream summary and equipment specification tables for this process are presented in Table C.3 and Table C.4 in APPENDIX C respectively.

6.2.1.2 DME Production via Natural Gas

The second option, DME production via natural gas is simulated in ASPEN PLUS version 22 using UNIFAC, the same thermodynamic package as the previous option. The block flow diagram and schematic for this process are shown in Figure 6.8 and Figure 6.9 respectively. The input file for the simulated process is available in APPENDIX B. In this approach, DME is produced by the following steps: steam reforming, methanol synthesis and DME synthesis in three isothermal reactors (Horstman et al., 2005).

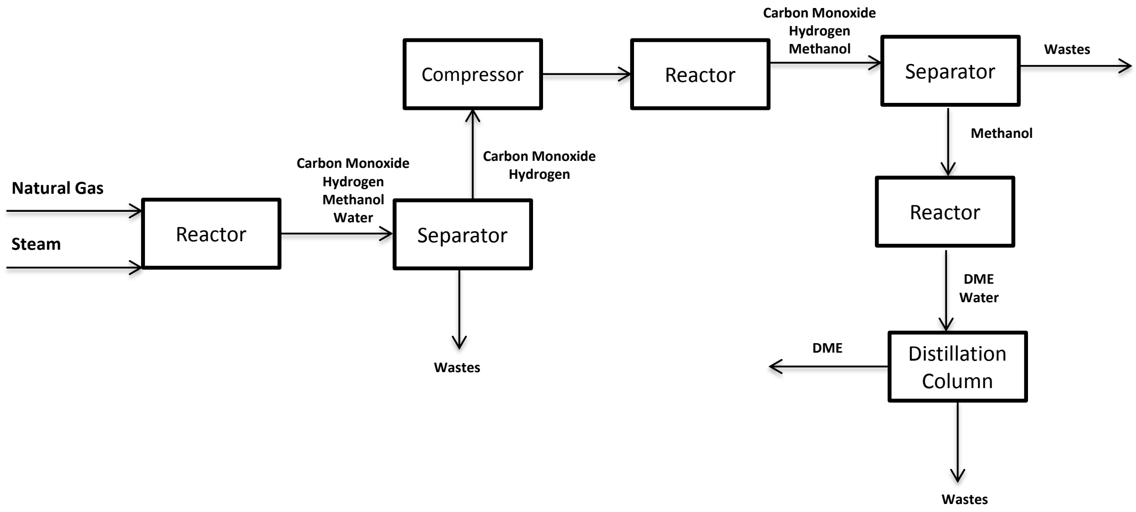

Figure 6.8: Block Diagram of DME Production via Natural Gas

In the steam reforming step, methane (stream 1) with 87.5% purity at 35^{o}C and 1 atm is heated by E-301 to 800^{o}C (stream 2) as shown in Figure 6.9. Water (stream 3) at 35^{o}C and 1atm is also heated by E-302 to 800^{o}C (stream 4). Stream 2 and 4 are fed into reactor (R-301) where natural gas is reacted with steam over nickel or magnesium oxide acting as catalysts to produce synthesis gas (Stream 5) as shown in Equation 6.15.

$$\underset{\text{methane}}{CH_4} + H_2O \rightarrow CO + 3H_2 \tag{6.15}$$

The reaction results in a 96.6% conversion of methane to synthesis gas. The synthesis gas is cooled to 35^oC by E-303 and then sent to a separator to remove excess water (stream 7). The separated synthesis gas (Stream 8) is sent to a compressor where the pressure is increased from atmospheric pressure to 40 atm (stream 9). Next, this stream is sent to a cooler to cool the stream from 644 ^oC to 240 ^oC before being sent to another reactor (R-202).

In this step, methanol is synthesized by reacting carbon monoxide and hydrogen with the aid of carbon dioxide on alumina support as shown in Equation 6.16.

$$CO + 2H_2 \rightarrow \underset{\text{methanol}}{CH_3OH} \tag{6.16}$$

The reaction results in a 75.5% conversion of carbon monoxide to methanol. Next the synthesized stream (stream 11) is compressed shortly before being sent to separator (T-302) where methanol is separated from the syngas mixture. The syngas (stream 14) is heated from 20 ^oC to 240 ^oC shortly before it is sent to the last reactor. Lastly, the methanol is dehydrated in reactor (R-303) to produce DME as shown in Equation 6.17.

$$\underset{\text{Methanol}}{2CH_3OH} \rightarrow \underset{\text{DME}}{CH_3OCH_3} + H_2O \tag{6.17}$$

The reaction results in a 91% conversion of methanol to DAME. The DME mixture is compressed to a lower pressure and sent to distillation column (T-303). The mixture (stream 17) is also separated into two streams, a waste stream (Stream 18) and a DME stream (Stream 19). The schematic of this process is show in Figure 6.9. The equipment specification table and stream summary table for this process are presented in Table C.5 and Table C.6 respectively in Appendix C.

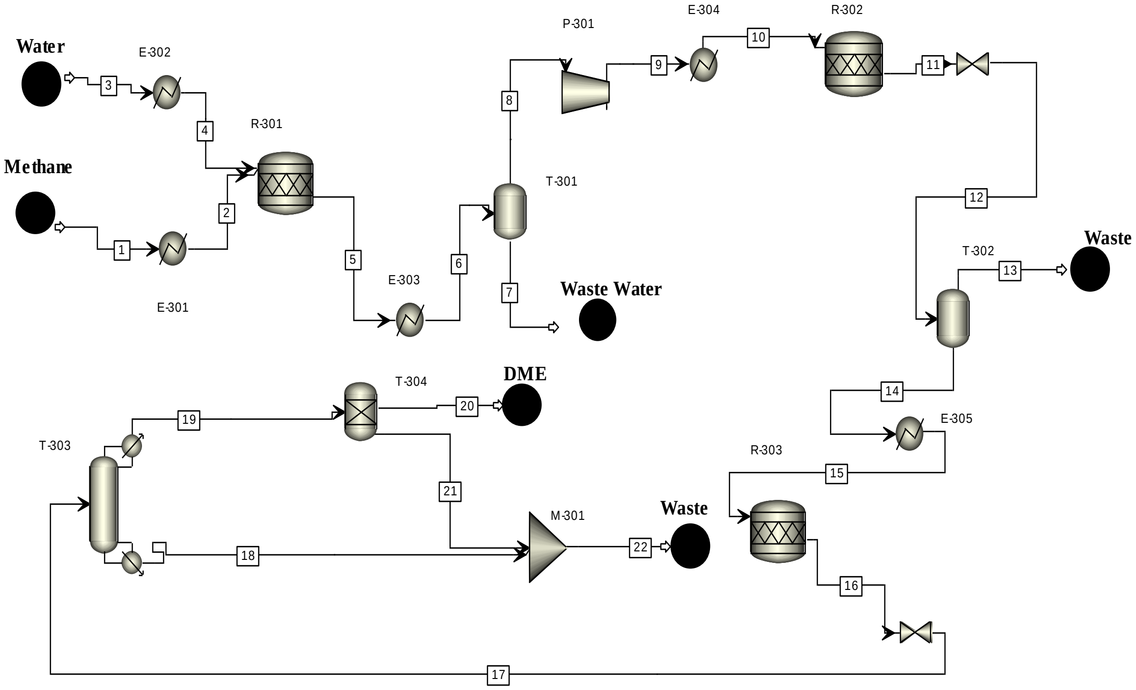

Figure 6.9: Schematic of DME Production via Natural Gas

The DME process is an ideal case study to demonstrate that the SUSTAINABILITY EVALUATOR could be used to compare two process options that differ by reaction pathways. The two DME processes have been simulated on ASPEN PLUS version 22 using data from literature (Horstman et al., 2005; Turton et al., 2009). In this work, the sustainability of the two DME processes are evaluated and compared.

6.2.2 Sustainability Evaluation of the DME Production Process

The two DME base cases were simulated on ASPEN PLUS and set to a production rate of 129.70 kmol/hr and a purity of 99%. The two cases were evaluated for economics, environmental and social concerns. The data used for the economic evaluation is summarized in Table 6.13. The capital and utility costs are evaluated using ASPEN PLUS and the results are inputted into the SUSTAINABILITY EVALUATOR. The raw material and product sale price and the flow rates are imputed as well. The tool outputs the capital costs, annualized capital costs, material value added and profit as shown in Table 6.14.

Table 6.13: Summary of Economic data for the Dimethyl Ether Process

Item	Cost ($)
Methanol	$0.294/kg (Turton et al., 2009)
Industrial Natural Gas	$ 0.21/kg (Dantus, 1999)[9]
Electricity	$0.0717/kilowatt-hour (Energy Information Administration : Official Energy Statistics from the U.S. Government, 2009)
DME	$1.17/kg (Turton et al., 2009)
Process Water	$0.00067/kg (Turton et al., 2009)
Waste Treatment	$0.036/kg (Turton et al., 2009)
Capital Recovery Factor	0.1175

Table 6.14: Comparison of Economic Metrics for the two DME options

Economic Parameters	DME Via Methanol (Option 1) (MM)	DME Via Natural Gas (Option 2) (MM)
Revenue	$61.2	$61.2
Operating Costs	$5.4	$10.0
Waste Treatment Costs	$0.76	$3.4
Raw Material Costs	$21.6	$13.6
Capital Costs	$4.7	$12.0
Annualized Capital Cost	$0.55	$1.4
Material Value Added	$39.7	$47.7
Profit	$32.9	$32.8

The capital recovery factor used for the annualized capital cost is based on 20 years and a 10% interest rate. The results of the economic evaluation for the two DME

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[9] Prices obtained from (Dantus, 1999) but inflated to 2009 costs

production options are compared in Figure 6.6 and Table 6.14. The cylinder in the chart represents option 1 and the box represents Option 2. As shown in the figure both options are economical with profits of $30 million. However, DME via natural gas has higher capital and operating costs.

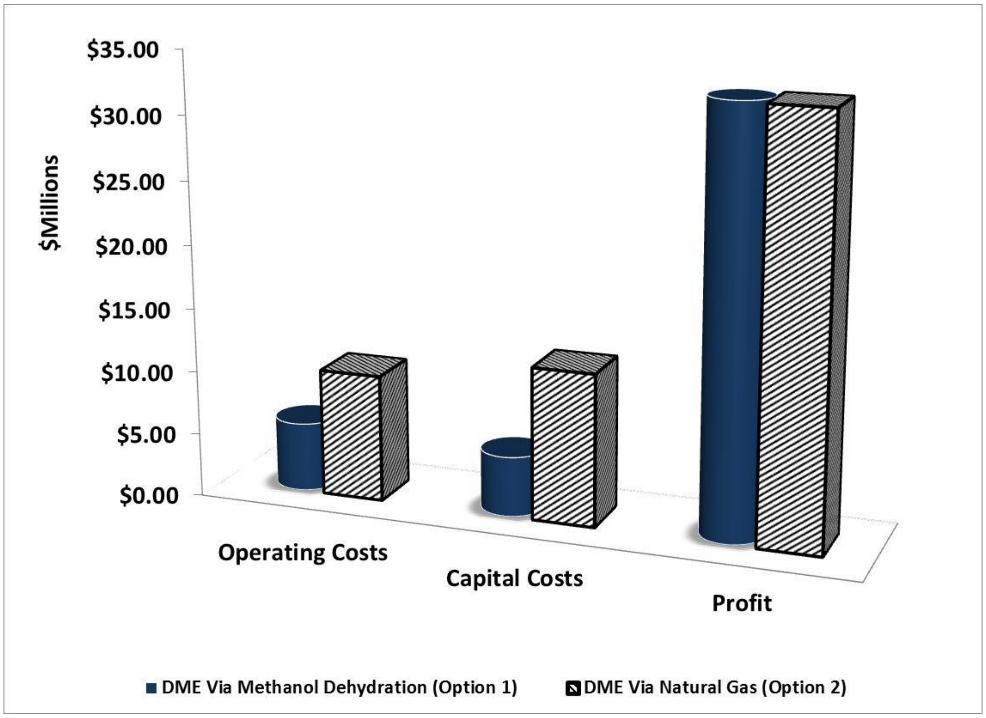


Figure 6.10 : Summary of Economic Results for the two DME Production Options from the SUSTAINABILITY EVALUATOR

The environmental impacts of the two cases are evaluated based on assessing the waste streams for potential land or water impact. The inputs of this evaluation include: mass flow rate of each component in the waste stream. The software supplies the potency factor for each substance and converts it to the right impact unit. The results of comparing the environmental burden of the two processes have been depicted on the bar chart shown in Table 6.15 and Figure 6.11.

Table 6.15: Summary of Chemicals Contributing to Environmental Impact for the Two DME Options

Environmental Impact	Environmental Impact DME Via Methanol (Tonnes/year)	Environmental Impact DME Via Natural Gas (Tonnes/year)	DME Via Methanol	DME Via Natural Gas
Global Warming	2.8E+03	2.8E+05	CH_3OH, DME	CH_4,CO, CH_3OH & C_2H_6, C_3H_8,
Photochemical Smog	5.2E+01	3.0E+03	DAME	CO,C_2H_6, C_3H_8 & CH_4
Aquatic Oxygen Demand	3.7E+02	1.3E+04	CH_3OH	CH_3OH

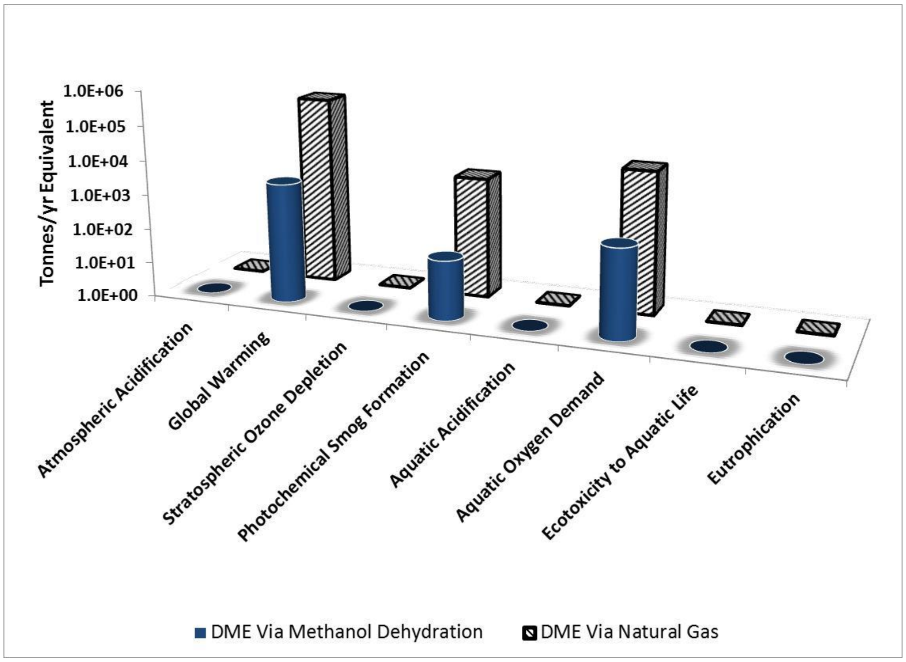


Figure 6.11: Results of Environmental Impacts Assessment from the SUSTAINABILITY EVALUATOR

As shown in Figure 6.11, for both cases, because the waste streams don't have chemicals leading to the following concerns: atmospheric acidification, stratospheric ozone depletion, aquatic acidification, ecotoxicity to aquatic life and eutrophication, the environmental impacts are not depicted on the bar graph. The only environmental concerns for producing DME for both cases are aquatic oxygen demand. Table 6.16

shows a summary of the chemicals contributing to global warming, photochemical smog and aquatic oxygen demand. The efficiency of the reactions used in DME formation and resource usage was also evaluated. The inputs of this evaluation include the following: mass flow rate of product, reactant and waste streams, energy and water consumed by the process. Table 6.16 shows a comparison of the results for each of the different cases.

Table 6.16: Summary of Resource Usage Metrics Results from the SUSTAINABILITY EVALUATOR for the two DME Options

Outputs	DME Via Methanol	DME Via Natural Gas	Units
E-Factor	0.4	1.8	Kg/kg
Mass Productivity	71	35	%
Reaction Mass Efficiency	71	35	%
Energy Intensity/ Fossil Fuel Usage	0.0002	0.002	KW/Kg
Water Intensity	0.0	1.6	Kg/Kg

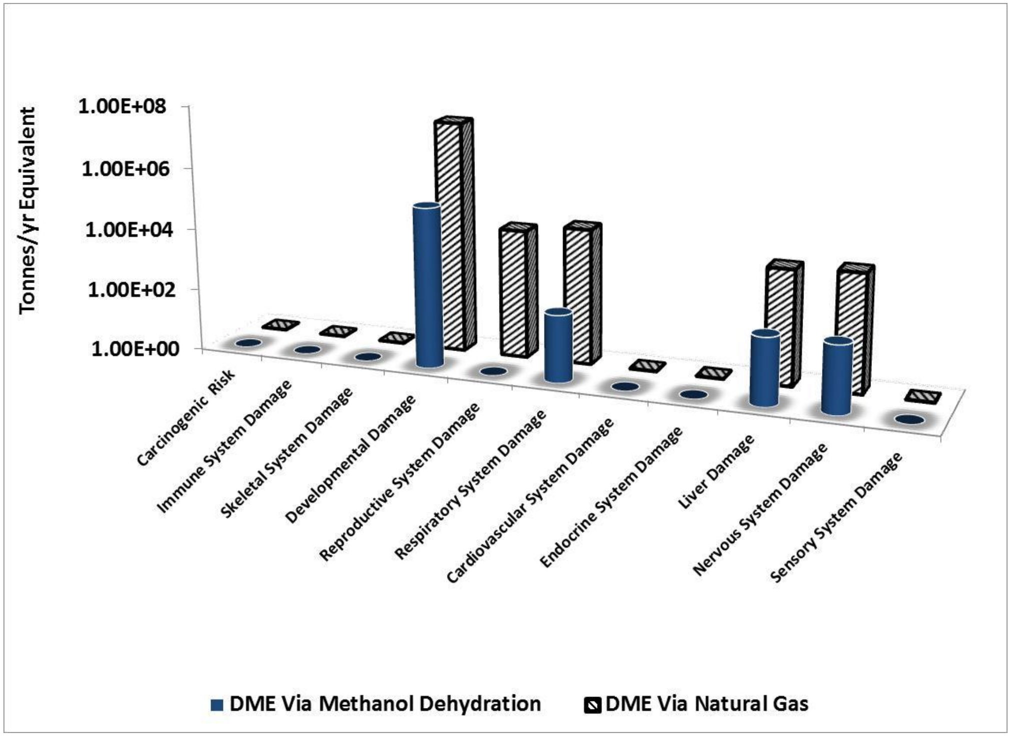


Figure 6.12: Results of Health Impacts Assessment from the SUSTAINABILITY EVALUATOR for the two DME Options

Social concerns are also evaluated for the two processes. Social impact can be categorized into health impact and safety risk. The result of the health impact assessment is depicted in Figure 6.12 and Table 6.17. As shown in the figure, for both options, the major health risks from potential chemical exposure include developmental damage, respiratory system damage, nervous system damage and liver damage. DME production via natural gas has an additional health risk which is reproductive system damage. The chemicals resulting in this health risk are summarized in Table 6.17.

Table 6.17: Summary of Chemicals Contributing to Health Risks for the Two DME Options

Health Impact	Health Impact DME Via Methanol (Tonnes/year)	Health Impact DME Via Natural Gas (Tonnes/year)	DME Via Methanol	DME Via Natural Gas
Developmental Damage	1.5E+05	2.8E+07	CH_3OH	CH_3OH, CO
Reproductive Damage	N/A	1.4E+04	None	CO
Respiratory System Damage	1.5E+02	2.4E+04	CH_3OH	CH_3OH, CO,C_2H_6, CH_4, C_3H_8
Liver Damage	1.5E+02	5.0E+03	CH_3OH	CH_3OH
Nervous System Damage	1.5E+02	6.3E+03	CH_3OH	CH_3OH

The results of the safety metrics for the two cases are presented in Table 6.18. The safety assessments of the two processes are compared in Table 6.18. As shown in the table, DME via methanol has a process safety index of 44 while DME via natural gas has a safety index of 66.

The results of the economic, environmental, social and overall sustainability impact from the SUSTAINABILITY EVALUATOR are presented in Table 6.19. The impact for all categories has been scaled from 0 to 1. The smaller the impact value, the more sustainable the process is.

Table 6.18: Results of Safety Metrics from the SUSTAINABILITY EVALUATOR for the two DME Options

Outputs for Process Safety Evaluation	DME Via Methanol	DME Via Natural Gas
Heat of main reaction index	0	2
Heat of side reaction index	0	4
Flammability index	8	8
Explosiveness index	4	6
Toxic exposure index	12	16
Corrosiveness index	4	4
Temperature index	6	8
Pressure index	2	6
Equipment safety index	4	8
Inputs for safety level of process structure index	4	4
Total inherent safety index	44	66

Table 6.19: Overall Sustainability Impact from the SUSTAINABILITY EVALUATOR for the two DME Options

	DME Via Methanol	DME Via Natural Gas
Economic Impact	0.00	0.00
Environmental Impact	0.09	0.24
Social Impact	0.20	0.36
Sustainable Impact	0.11	0.24

6.2.3 Selection of the More Sustainable DME Production Process

The selection of the most sustainable DME production process is based on the result obtained from the SUSTAINABLE EVALUATOR. In this section, the results of each of the sustainable category are discussed and are summarized in Table 6.20. As shown in Table 6.20, the profits for the cases are similar with a value of $33 million. However, DME production via natural gas has a higher capital and operating costs compared to the first option. For both cases, an economic impact of 0, was obtained, which depicts that the processes are very economical.

Table 6.20: Summary of Impact Assessment Results from the SUSTAINABILITY EVALUATOR for the two DME Options

Summary of Results	DME Via Methanol	DME Via Natural Gas
Profit	$32.9 million	$32.8 million
Economic Impact	0	0
Environmental Concerns	Global warming, photochemical smog formation and aquatic oxygen demand	Global warming, photochemical smog formation and aquatic oxygen demand
Environmental Impact	0.09	0.24
Safety Index	44	66
Health Concerns	Developmental damage, reproductive damage, respiratory system damage, liver damage and nervous system damage	Developmental damage, respiratory system damage, liver damage, reproductive system Damage and nervous system damage
Social Impact	0.20	0.36
Sustainability Impact	0.11	0.24

For environmental impact, DME via methanol is a more environmental friendly process compared to DME via natural gas as presented in Figure 6.11. DME via methanol option is more environmental friendly because intermediate products are not produced and the process also has a methanol recycle stream reducing the amount of wastes from this option. Also as shown in the results presented in Table 6.16, DME production via methanol is more efficient in all categories compared to DME production via natural gas. DME via methanol dehydration is more environmental friendly because it had a lower environmental impact value of 0.09 compared to option 2 which have a value of 0.24.

In terms of social concerns, as shown in Figure 6.12, DME production via natural gas (option 2) has a higher health risk from the following impact categories: developmental damage, respiratory system damage, and liver damage compared to DME production via methanol. The results for safety risk evaluation as shown in Table 6.18, illustrates that DME production via methanol has a process safety index of 44 and is thus a safer process compared to DME production via natural gas which has a process safety index of 66. DME production via natural gas has a higher process safety index value due to the more exothermic reactions taking place in the process, more toxic chemicals, higher process temperature and the presence of compressors and high hazard reactors. DME via methanol dehydration is more socially acceptable because it had a lower social impact value of 0.20 compared to option 2 which have a value of 0.36.

DME via methanol dehydration also had a lower overall sustainable impact value of 0.11 compared to option 2 which had a value of 0.24. Based on the results presented earlier and overall sustainable impact obtained from the SUSTAINABLE EVALUATOR, it can be concluded that the production of DME production via methanol dehydration is the more sustainable production option because it is more economical, environmental friendly and socially acceptable compared to the DME production via natural gas.

6.3 CASE STUDY: ACRYLONITRILE PRODUCTION PROCESS

Acrylonitrile is a colorless liquid with a slightly sharp, irritating odor. Its physical properties are shown in Table 6.21. The chemical is a monomer used in the synthesis of polymers in the chemical industry. These polymers are utilized in the manufacturing of plastics, acrylic fibers, rubber and nylons. It is also used as an intermediate in the manufacture of adiponitrile and acrylamide.

Table 6.21: Physical Properties of Acrylonitrile

Property	Value
Boiling Point (°C)	77
Freezing Point(°C)	-82
Solubility in water, 20°C, g/100ml	7
Viscosity, 25°C (cP)	0.34
pH	6.0 - 7.5

Acrylonitrile is considered one of the top 50 highest volume chemicals produced in the United States (Kanuri, 2000; Fechter et al., 2004). Although the chemical can be synthesized by the acetylene hydrocyanation process, it is mainly produced by the BP America Sohio Process. The Sohio process involves a catalytic gas phase oxidation reaction of ammonia and propylene. The production of acrylonitrile results in several toxic waste streams and byproducts such acetonitrile, acrolein, carbon monoxide and hydrogen cyanide.

The acrylonitrile production is an excellent manufacturing process to demonstrate the proposed methodology because of the tremendous toxic waste streams present in this process. These waste steams pose a threat to the environment and human health. Human exposure to acrylonitrile has occurred via contamination of water via hazardous waste sites and occupational exposure. This chemical is listed in the toxic release inventory compiled by the Environmental Protection Agency, as one on the top toxic chemicals (United States Environmental Protection Agency, 2009).

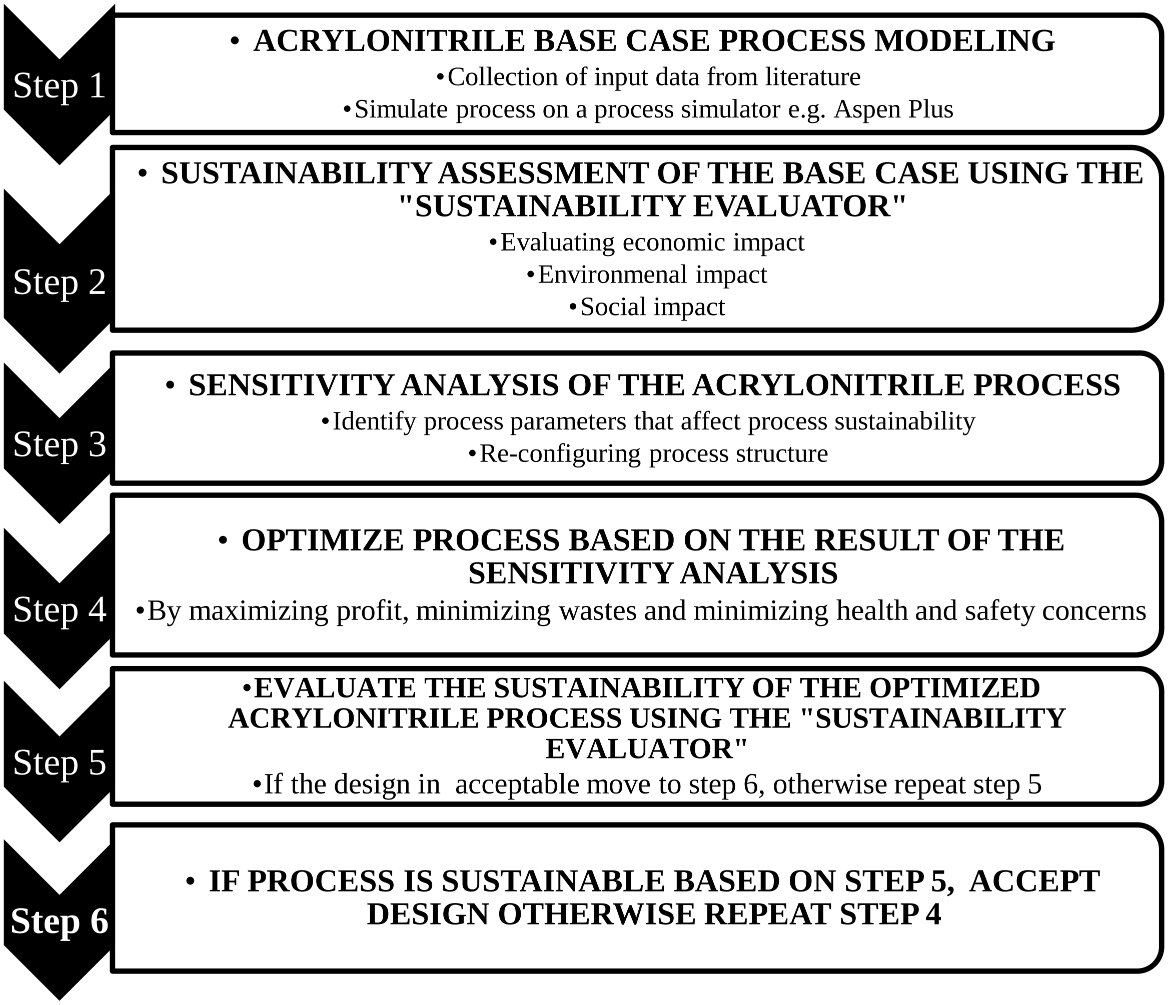


Figure 6.13: Proposed Methodology for Addressing Sustainability Concerns of the Acrylonitrile Process

Also, this chemical polymerizes easily and can become a severe fire and explosion hazard if exposed to light (Reed Business Information Limited). The health threat of this chemical poses a serious issue as acrylonitrile is a suspected carcinogen and is also linked to other health problems such as nervous system damage, kidney damage etc. Handling the waste streams in this process is a challenge that must be handled in a sustainable manner. The methodology discussed in Chapter 5 and presented in Figure 6.13 is applied towards handling the sustainability concerns of the acrylonitrile process.

6.3.1 Acrylonitrile Base Case Process Modeling

The acrylonitrile base case is modeled based on literature data (Venkataraman, 1996; de Haes et al., 1999; Kanuri, 2000). The information compiled from literature is simulated in ASPEN PLUS version 22 using the Electrolyte Non-Random Two Liquid model with Redlich-Kwong (ELECNRTL) thermodynamic package. The block flow diagram and the schematic for this process are shown in Figure 6.14 and Figure C.2 (APPENDIX C) respectively. The ASPEN PLUS input file is shown in APPENDIX B.

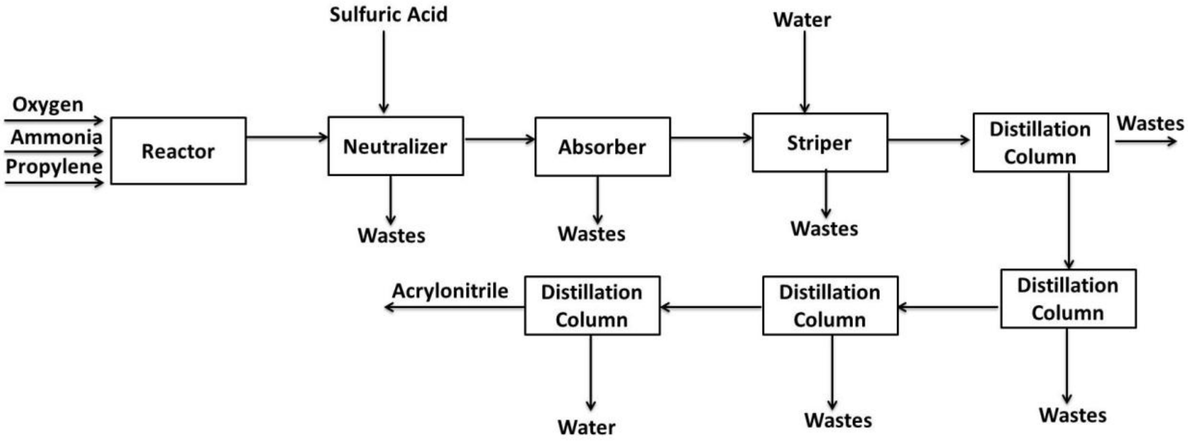


Figure 6.14: Block Flow Diagram for the Base Case Acrylonitrile Process

The production process can be divided into two sections namely propane ammoxidation and acrylonitrile separation. In the propane ammoxidation step, ammonia, propane and oxygen at 14 psia and 80^{o}F are fed to a mixer (M-301), which combines the three streams into one stream. The mixture is sent to R-301, a plug flow reactor (PFR). The PFR is operated at 852 ^{o}F and 28.9 psia. Propylene and ammonia are reacted with oxygen to produce acrylonitrile in the PFR. Although, acrylonitrile is synthesized as shown in Equation 6.18 in this reactor, several side reactions take place resulting in other by products (acetonitrile, arolein, carbon dioxide, carbon monoxide and hydrogen cyanide) as shown in Equations 6.19-6.23. The kinetics or the reactions taking place in the reactor is presented in Table 6.22 and the rate constant are presented in Equation 6.24-6.29.

$$\overset{\text{Propylene}}{C_3H_6} + \overset{\text{Ammonia}}{NH_3} + 3/2\ \overset{\text{Oxygen}}{O_2} \rightarrow \overset{\text{Acrylonitrile}}{C_3H_3N} + 3\,\overset{\text{Water}}{H_2O} \qquad (6.18)$$

$$\overset{\text{Propylene}}{C_3H_6} + O_2 \rightarrow \overset{\text{Acrolein}}{C_3H_4O} + H_2O \qquad (6.19)$$

$$C_3H_6 + NH_3 + 9/4\,O_2 \rightarrow \overset{\text{Acetonitrile}}{CH_3CN} + 1/2\,CO + 1/2\,CO_2 + 3H_2O \qquad (6.20)$$

$$C_3H_4O + NH_3 + 1/2\,O_2 \rightarrow C_3H_3N + 2H_2O \qquad (6.21)$$

$$C_3H_3N + 2\,O_2 \rightarrow CO_2 + CO + HCN + H_2O \qquad (6.22)$$

$$CH_3CN + 3/2\,O_2 \rightarrow CO_2 + HCN + H_2O \qquad (6.23)$$

Table 6.22: Acrylonitrile Process Kinetic Data (Hopper et al., 1993)

Reaction Number	Activation Energy, E_i (cal/mol)	Rate Constant, k_i (sec^{-1}) at 662°F
1	19,000	0.40556
2	19,000	0.00973
3	7,000	0.01744
4	7,000	6.81341
5	19,800	0.16222
6	7,000	0.07300

$$-r_1 = 1.57089E{+}05\ e^{-19000/RT} \qquad (6.24)$$
$$-r_2 = 3.768E{+}03\ e^{-19000/RT} \qquad (6.25)$$
$$-r_3 = 1.99\ e^{-7000/RT} \qquad (6.26)$$
$$-r_4 = 780.07\ e^{-7000/RT} \qquad (6.27)$$
$$-r_5 = 1.08015E{+}05\ e^{-19800/RT} \qquad (6.28)$$
$$-r_6 = 8.357\ e^{-7000/RT} \qquad (6.29)$$

After the reaction process, a sulfuric acid stream at 80 ^{o}F and 14.7 psia is introduced and sent along with the reacted mixture to another mixer (M-302). Next the separation of acrylonitrile from byproducts and the un-reacted raw materials occurs. First the mixture is sent to a neutralizer (R-302), where ammonia reacts with sulfuric acid and ammonium sulfate is produced as shown in Equation 6.30. This reaction aids in the removal of un-reacted ammonia. Next the steam exiting the neutralizer is sent to a separator (T-301) where the ammonium sulfate and sulfuric acid are separated from the mixture as the bottoms of the separator.

$$2NH_3 + H_2SO_4 \rightarrow \overset{\text{Ammonium Sulphate}}{(NH_4)_2SO_4} \tag{6.30}$$

The un-separated distillate stream is cooled via a cooler (E-301) to 40°F and 20 psia and a water stream operating at 161 °F and are sent to an absorber (T-302) , where carbon monoxide, propylene and oxygen are separated as the distillate stream and aqueous solution of acrylonitrile, acetonitrile and hydrocyanic acid are present in the bottoms of the distillation column. The bottoms stream is heated by heat exchanger E-202 to 173 °F and 15 psia. The heated stream is sent to a stripper (T-303) where excess water is removed from the nitrile mixture. The nitrile mixture is cooled to 126 °F and 14.7 psia by heat exchanger E-303. The heated stream is sent to two distillation columns (T-304 and T-305) where waste hydrocyanic acid and acrolein are removed. Finally in the last column (T-306), acrylonitrile is separated from acetonitrile. The schematic for this process, the equipment specification and stream summary tables are presented in Figure C.2, Table C.7and Table C.8 respectively in APPENDIX C.

6.3.2 Sustainability Assessment of the Acrylonitrile Base Case

The economic, environmental and social impact of the base case acrylonitrile process is assessed using the SUSTAINABILITY EVALUATOR. The data used in completing the economic evaluations are presented in Table 6.23. The annual production of 96 weight % acrylonitrile was set at 10,100 tonnes/year.

Table 6.23: Summary of Economic Data for the Acrylonitrile Process

Item	Cost ($)
Ammonia	$0.38/kg (Reed Business Information Limited, 2010b)
Propylene	$0.981/kg (Turton R. et al., 2009)
Oxygen	$0.11/kg (Remediation & Natural Attenuation Services Inc., 2010)
Sulfuric Acid	$0.081/kg (Reed Business Information Limited, 2010b)
Process Water	$0.00067/kg (Turton et al., 2009)
Acrylonitrile	$2.6/ kg (Reed Business Information Limited, 2010a)
Acetonitrile	$2.5/ kg (Reed Business Information Limited, 2010b)
Waste Treatment Costs	$0.12/kg (Turton et al., 2009)
Low Pressure Steam	$14.05/GJ (Turton et al., 2009)
Cooling Water: 30°C	$0.354/ GJ (Turton et al., 2009)
Capital Recovery Factor	0.1175

6.3.2.1 Economic Assessment of the Base Case Acrylonitrile Process

An economic assessment was completed using the ASPEN Economic Evaluator. The ASPEN Economic Evaluation uses imported data from ASPEN PLUS and estimates capital and operating costs. The capital and operating costs values obtained from the ASPEN Economic Evaluator, the mass flow rates of the raw material and product stream and the economic data shown in Table 6.23 are inputted into the SUSTAINABILITY EVALUATOR.

The result of this assessment is shown in Table 6.24. As shown in the table, the estimated annual revenue generated from selling the acrylonitrile is around $23.9 million. The annual expenses for this production process were estimated to be around $18.3 million. The breakdown of the expenses is shown in Figure 6.15. As shown in Figure 6.15, the raw material costs accounts for 78% of the annual operating expenses of the acrylonitrile manufacturing process. Operating cost, which is about 9% of the expenses, is the second largest expenditure incurred in manufacturing the products.

Table 6.24: Economic Assessment Results for the Base Case Acrylonitrile Process from the SUSTAINABILITY EVALUATOR

Economic Parameters	Base Case (MM)
Revenue	$23.9
Operating Costs	$2.1
Waste Treatment Costs	$1.9
Raw Material Costs	$18.3
Capital Costs	$9.2
Material Value Added	$5.6
Profit	$0.43

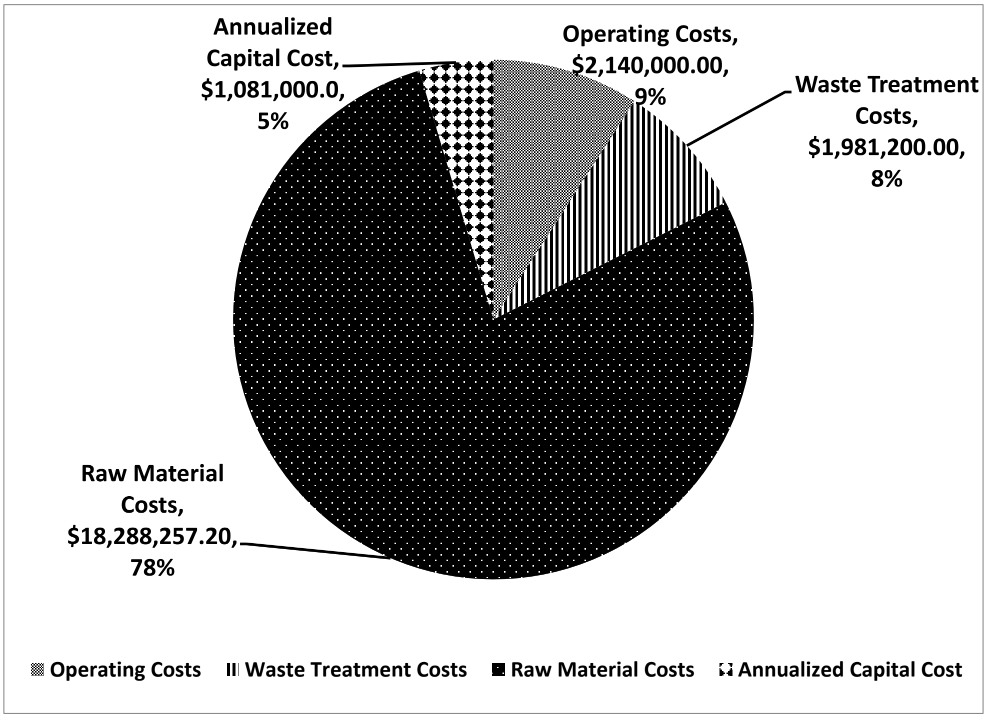


Figure 6.15: Breakdown of Annual Operating Costs for the Base Case Acrylonitrile

Several waste streams are present in the acrylonitrile production process, and must hence be treated. The waste treatment cost as shown in Figure 6.15 is around $1.9 million and this is about 8% of the costs. The capital costs for this process is around $9 million but the purpose of calculating profit, the costs were annualized using the capital recovery factor shown in Table 6.24. The annualized capital cost is about 5% of the expenses incurred in this manufacturing process. As shown in Table 6.24, this is a profitable process in which the estimated annual profit was calculated to be around $0.43 million.

6.3.2.1 Environmental Impact Assessment of the Base Case Acrylonitrile Process

Once the economics of the acrylonitrile process had been calculated, the next step was to evaluate the environmental impacts. The environmental impact assessment involved entering the mass flow rates of the waste streams into the SUSTAINABILITY EVALUATOR. The result of the environment assessment is presented in Table 6.25. As shown in Table 6.25, the acrylonitrile production process, poses a serious threat to the environment.

Table 6.25: Results of Environmental Impact Assessment for the Base Acrylonitrile Process

Impact Category	Impact Assessment Value (Tonnes/year)	Chemicals Present
Atmospheric Acidification	15.5	Ammonia and Sulfuric Acid
Global Warming	11280.5	Carbon dioxide, Carbon Monoxide, Acrolein, Propylene, Acrylonitrile and Acetonitrile
Stratospheric Ozone Depletion	0.0	N/A
Photochemical Smog	291.5	Carbon Monoxide & Propylene
Aquatic Oxygen Demand	0.1	Ammonium Sulphate
Ecotoxcity to Aquatic Life	979.7	Ammonia
Eutrophication	1.4	Ammonia

Due to the tremendous waste streams, the potential environmental burdens include the following: atmospheric acidification, global warming, photochemical smog, aquatic acidification, aquatic oxygen demand, ecotoxicity to aquatic life and eutrophication. The chemicals contributing to each impact category are also presented in Table 6.25. Efforts should be made to reduce the waste streams associated with this production process.

The resource usage efficiency for this manufacturing process is also evaluated and the results are presented in Table 6.26. As shown in the table, the results of the evaluation show that the base case acrylonitrile process is not resource friendly. This is because the formation of acrylonitrile is not a single reaction process. Several side reactions take place and many unwanted products which are considered wastes are created. The values of the, mass productivity, and reaction mass efficiency are all very low, while the values of the E-Factor, water intensity, and energy intensity are all high. Investigating ways to reduce the waste streams and improve reaction efficiency would be important in improving the sustainability of this process.

Table 6.26: Results of Resource Usage Evaluation for the Base Case Acrylonitrile Process

Environmental Impact	Value	Units
E-Factor	1.8	Kg/Kg
Mass Productivity	19	%
Reaction Mass Efficiency	25	%
Energy Intensity	0.0021	KW/Kg
Water Intensity	0.5	Kg/Kg

6.3.2.2 Social Impact Assessment of the Base Case Acrylonitrile Process

After the environmental impact assessment, the next step was to complete a health and safety impact evaluation using the SUSTAINABILITY EVALUATOR. For the health and safety assessment, the mass flow rates of each specific component found in the waste stream are entered into the SUSTAINABILITY EVALUATOR. As shown in Table 6.27, the acrylonitrile process poses a serious health risk in all categories. Acrylonitrile is considered a group 2b, while acrolein is considered a group 3 carcinogen. Apart from cancer risks, other health threats are eminent; these are shown in Table 6.27. In this table, the chemical contributing to each health impact category is presented. Due to the tremendous health risk, it is therefore vital to ensure that the wastes from this process are handled appropriately and explosions and spills are kept at a minimum.

Table 6.27: Results of Health Impact Assessment for the Base Case Acrylonitrile Process

Impact Category	Impact Value (Tonnes/year)	Chemicals Present
Carcinogenic Risk	2.06E+02	Acrolein & Acrylonitrile
Immune System Damage	2.1E+02	Acrylonitrile
Skeletal System Damage	1.2E+02	Sulfuric Acid
Developmental Damage	4.0E+03	Acrolein, Acetonitrile, Acrylonitrile, Ammonia, Carbon Dioxide &Carbon Monoxide
Reproductive System Damage	4.3E+03	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Dioxide, Carbon Monoxide & Hydrogen Cyanide
Kidney Damage	2.1E+02	Acrylonitrile
Respiratory System Damage	9.9E+03	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Dioxide, Carbon Monoxide, Hydrogen Cyanide, propylene, Sulfuric acid & Ammonium Sulphate
Cardiovascular System Damage	2.4E+03	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Monoxide & Hydrogen Cyanide
Endocrine System Damage	1.0E+03	Acrylonitrile
Liver Damage	4.6E+03	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Hydrogen Cyanide, Propylene, Sulfuric acid & Ammonium Sulphate
Nervous System Damage	7.6E+03	Acetonitrile, Acrolein, Acrylonitrile, Ammonia, Carbon Dioxide, Carbon Monoxide, Hydrogen Cyanide & Ammonium Sulphate
Sensory System Damage	1.2E+03	Acrolein, Acrylonitrile & Ammonia,

For the safety assessment, the operating conditions, chemicals present and equipment present are selected in the input section of the software. Also, the mass enthalpy is entered to estimate the heat of reaction index. The result of the safety assessment is presented in Table 6.28. The overall total inherent safety index for this process was around 70. The maximum overall safety index i.e. the worst case scenario for any process is 100. As shown in the table, the obvious safety concerns are flammability, toxic exposure risks and heat of main reaction which are at their maximum index value. Flammable risks are present due to presence of the following chemicals; acetonitrile, acreolin, acrylonitrile, propylene and hydrogen cyanide.

Table 6.28: Safety Assessment Results from the SUSTAINABILITY EVALUATOR for the Base Case Acrylonitrile Process

Safety Assessment	Results	Maximum
Heat of main reaction index	4	8
Heat of side reaction index	4	8
Flammability index	8	8
Explosiveness index	6	8
Toxic Exposure Index	24	30
Corrosiveness index	4	4
Temperature index	6	8
Pressure index	2	8
Equipment safety index	4	8
Safety Level of Process Structure index	8	10
Total Inherent Safety index	70	100

Toxic exposure risks are eminent because the following toxic chemicals that are present in the process: acetonitrile, acrolein, acrylonitrile, ammonia, carbon dioxide, carbon monoxide, hydrogen cyanide and sulfur dioxide. Other eminent risks are heat of side reaction, temperature, and explosive index. The risk level of these index are due to the nature of the reaction taking place in the reactors, the operating temperature in the process and the explosive chemicals present in the process. These risks must not be ignored, it is important to investigate ways to ensure safety is not compromised in this process.

6.3.3 Acrylonitrile Base Case Sensitivity Analysis

After evaluating the sustainability of the base case, it was apparent that it was necessary to optimize the process for economic, environmental, health and safety risk improvements. But before the optimization step, it was essential to identify parameters that affect the selected metrics. In order to identify these parameters, a sensitivity analysis was completed for the acrylonitrile base case. The sensitivity analysis was carried out using ASPEN PLUS. The parameters that were considered were operating conditions, variation of inlet flow-rates and equipment configuration. The above mention parameters are varied and the effect on the following was studied: acrylonitrile mass flow rate, propylene conversion, total waste produced, material value added (revenue-raw-material costs- waste treatment cost) and utility costs.

6.3.3.1 Effect of Varying Inlet Flow rates

The key raw materials involved in the manufacture of acrylonitrile are propylene, ammonia and oxygen. Literature data recommends using the following feed ratio range (Venkataraman, 1996; Kanuri, 2000):

- Propylene / Ammonia : 1-2
- Oxygen / Propylene : 0.5-3

Since this was a range, it was therefore important to investigate how varying the feed ratio affected revenue, material value added, and raw material costs. The inlet feed flow rate were varied as listed below:

Table 6.29: Results of Top 19 cases for Sensitivity Analysis of Varying Feed Ratio

Case	Ammonia Flow rate (Ibmol/hr)	Oxygen Flow rate (Ibmol/hr)	Propylene Flow rate (Ibmol/hr)	Total Waste (Ibmol/hr)	Annual Raw materials Cost ($MM)	Annual Revenue ($MM)	Annual Material Value Added ($MM)	Oxygen /Propylene feed ratio	Propylene /Ammonia feed ratio
Base Case	85	129	85	10885	16.4	19.6	3.2	1.5	1
1	70	140	95	9390	17.2	27.2	9.98	1.47	1.36
2	75	140	95	9559	17.4	27.2	9.79	1.47	1.27
3	70	135	90	9135	16.4	26.0	9.60	1.50	1.29
4	70	135	95	9269	17.2	26.8	9.57	1.42	1.36
5	60	130	75	8439	13.8	23.3	9.55	1.73	1.25
6	65	130	75	8650	13.9	23.4	9.46	1.73	1.15
7	75	135	90	9440	16.6	26.0	9.39	1.50	1.20
8	65	130	80	8789	14.7	24.1	9.38	1.63	1.23
9	75	135	95	9574	17.4	26.8	9.36	1.42	1.27
10	65	140	85	9356	15.6	24.9	9.35	1.65	1.31
11	60	130	80	8593	14.6	23.9	9.32	1.63	1.33
12	80	140	100	11887	18.4	27.6	9.20	1.40	1.25
13	60	125	70	8182	12.9	22.1	9.18	1.79	1.17
14	75	135	100	9719	18.3	27.4	9.17	1.35	1.33
15	80	135	90	9785	16.8	26.0	9.17	1.50	1.13
16	70	130	80	9139	14.9	24.1	9.17	1.63	1.14
17	80	135	95	9919	17.7	26.8	9.14	1.42	1.19
18	70	140	100	9590	18.1	27.1	9.09	1.40	1.43

- Ammonia: 60 -120 lbmole/hr
- Oxygen:60-180 lbmole/hr
- Propylene : 60-120 lbmole/hr

The total number of runs for this analysis was 1378 runs and the results of the 19 best scenarios are presented in Table 6.29. These runs were selected because they had the highest material value added value. The best case scenario, case 1 has a material added value of $9.98M.

6.3.3.2 Effect of Varying Plug Flow Reactor Temperature

The reactor temperature was studied to investigate how variations of it affected propylene conversion and acrylonitrile production. The higher the conversion, the lower waste produced and the higher the acrylonitrile production value would be. According to literature, typical reactor temperature range for the acrylonitrile process ranges from 600-1111 ^{o}F (Kanuri, 2000). Therefore, the reactor temperature was varied at that range as shown in Figure 6.16. As the reactor temperature is varied, propylene conversion increases as well as acrylonitrile formation. However, after 860^{o}F, the increase in both parameters comes to a halt, there by resulting in the conclusion that the optimum temperature range is from 800-860^{o}F, where a maximum conversion of 74% is attained.

6.3.3.3 Effects of Varying Plug Flow Reactor Pressure

The reactor pressure was studied to investigate how variations of it affected propylene conversion. According to literature, typical reactor pressure range for the acrylonitrile production process ranges from 5 -45 psia (Venkataraman, 1996; Kanuri, 2000). Therefore, the reactor pressure was varied at that range as shown in Figure 6.17.

As the reactor pressure is varied, it can be concluded that conversion of propylene to acrylonitrile increases. However, 15 psia is the recommended operating pressure as a maximum conversion of 74% was attained.

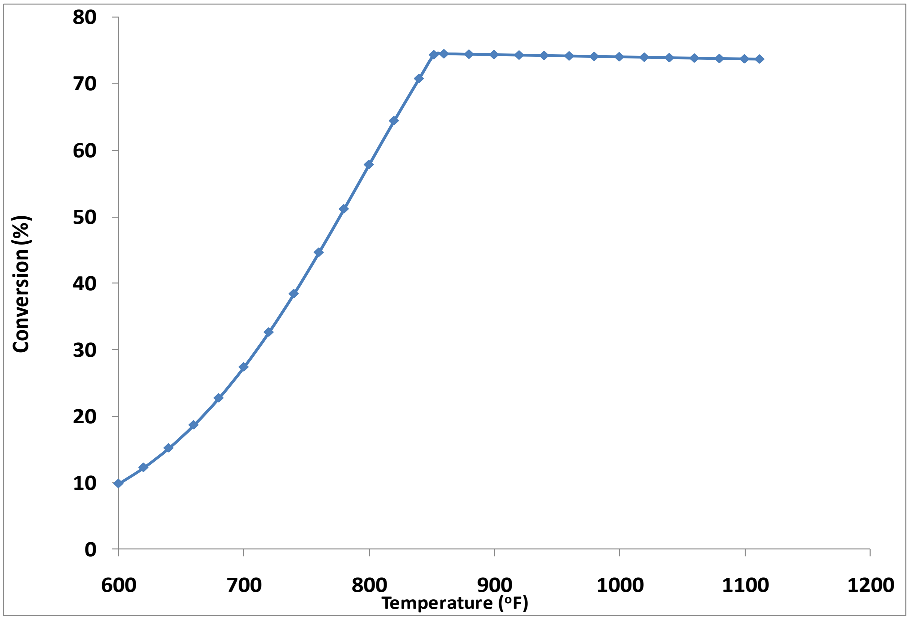


Figure 6.16: Effect of Plug Flow Reactor Temperature on Conversion

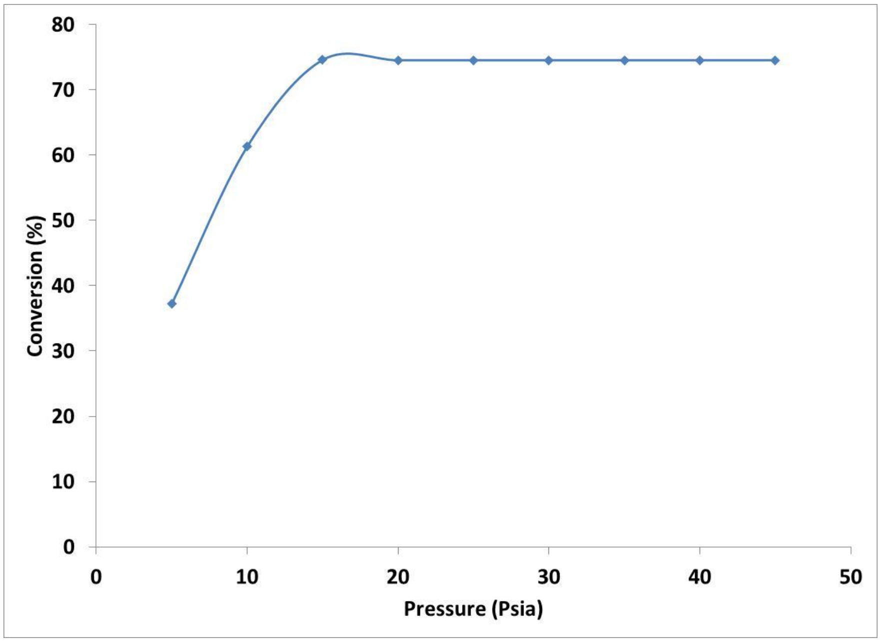


Figure 6.17: Effect of Plug flow Reactor Pressure on Conversion

6.3.3.4 Effect of Varying Plug Flow Reactor Length and Diameter on Conversion

The reactor length is varied from 10-30ft as shown in Figure 6.18. At first, conversion increases from 52-74% the length is varied from 0 -18ft but after 12ft, the conversion remains constant even when the length is increased. The reactor diameter is also varied from 0.5-3ft. As shown in Figure 6.19, as reactor diameter is increased conversion increases until 2ft where the maximum conversion is attained.

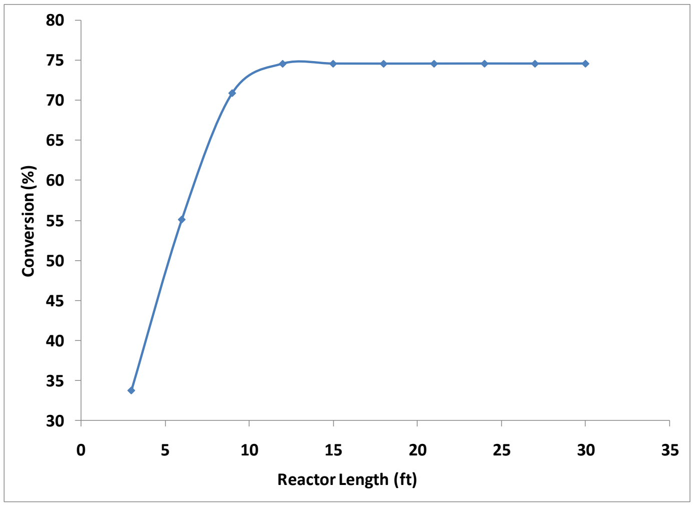


Figure 6.18: Effect of Plug Flow Reactor Length on Conversion

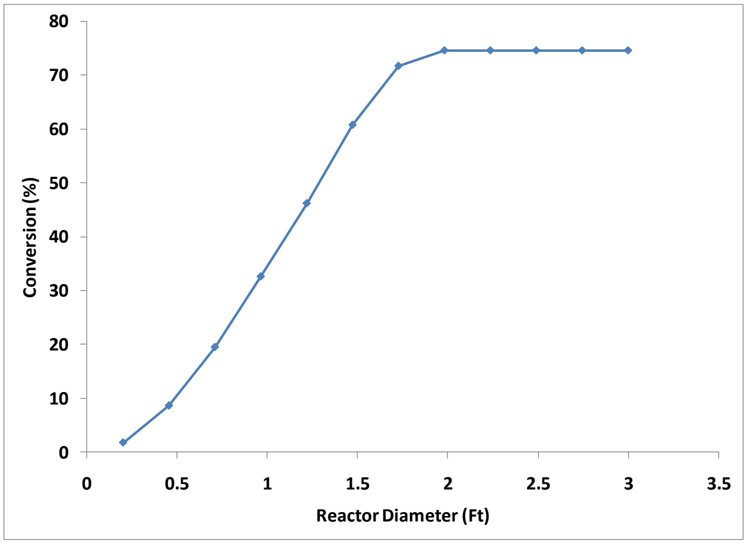


Figure 6.19: Effect of Varying Plug Flow Reactor Diameter on Conversion

6.3.3.5 Effect of Varying Stripper Feed Tray (T- 303)

The objective of the stripper is to remove water from the by-products while ensuring that there is almost complete recovery of acrylonitrile. The feed stage was noticed to impact this objective. The stripper has 30 stages, thus in order to determine the optimum feed stage, it is varied from 2-30. As shown in Figure 6.20, the ideal feed stage was found to be feed stage of 10 with a water removal flowrate of 317 lbmole/hr and acrylonitrile recovery of 99.2%.

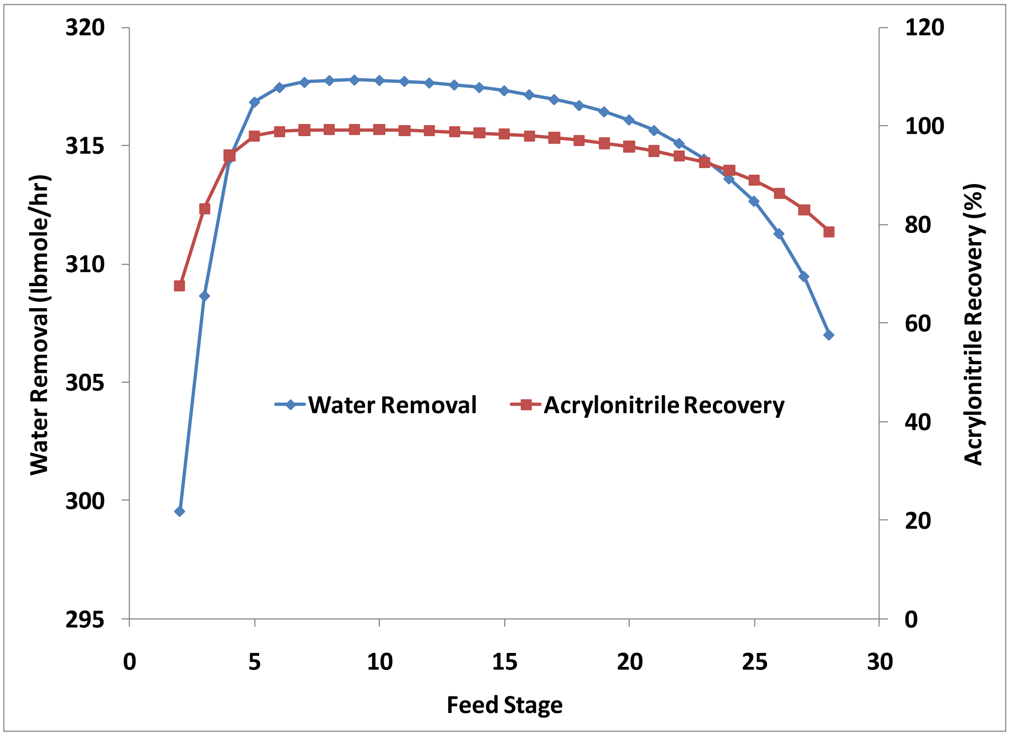


Figure 6.20: Effect of Varying Feed Stage on Water Removal and Acrylonitrile Recovery

6.3.3.6 Effect of Varying Absorber Reflux Ratio (T- 302)

The absorber separates the gases from the liquid products. The absorber reflux ratio was varied from 2 -4 to determine if it had an effect on acrylonitrile recovery. It was noticed that it not have an effect on acrylonitrile recovery but it did have an effect on the condenser and re-boiler duty as shown in Figure 6.21. The lower the reflux ratio, the lower the condenser and re-boiler duty. Hence the optimum re-boiler duty and condenser duty have optimum values at a reflux ratio of 3.

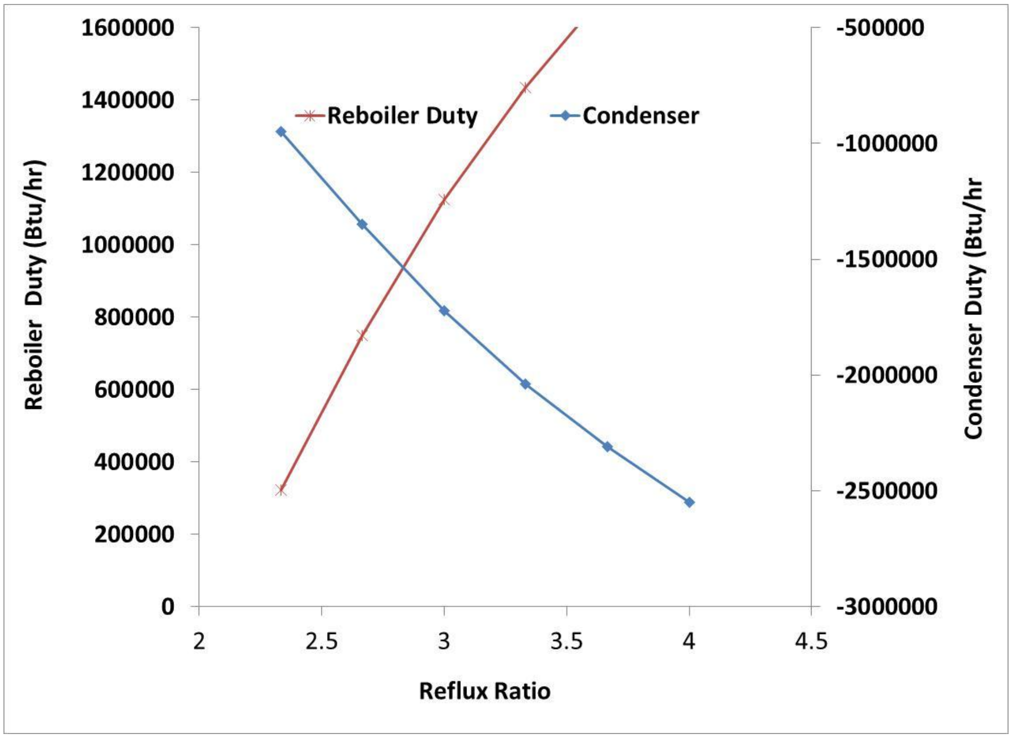


Figure 6.21: Effect of Absorber Reflux Ratio on Condenser and Re-boiler Duty

6.3.3.7 Summary of Sensitivity Analysis

The sensitivity analysis assisted in identifying parameters that affected, profit and waste generation. These parameters include:

- Feed ratio
- Reactor configuration such as temperature, pressure, length and diameter
- Stripper feed stage
- Absorber reflux ratio

The step after completing the sensitivity analysis is process reconfiguration. The first step was to investigate if some of the waste streams could be converted to recycle streams. The elimination of waste streams impacts economics positively because it leads to a reduction in environmental and health impacts as well as waste treatments costs. The acrylonitrile process was reconfigured so that waste stream 10 leaving the absorber (T-302) was separated and then recycled. To aid this objective, two distillation columns are incorporated into the process. The distillate stream leaving the absorber which contains carbon dioxide, carbon monoxide, propylene and hydrogen cyanide are sent to two distillation columns, T-307 and T-308. T-307 separates carbon monoxide and carbon dioxide from the mixture. The bottom stream is sent to T-308 where the recovery of propylene takes place and hydrogen cyanide is also separated. The recovered propylene is recycled back to reactor (R-301). This distillation column (T-307) recovers some of the un-reacted propylene. Since HCN is being recovered in T-307, one of the earlier HCN separator columns, T-304 is eliminated. Since water is being produced in the process, water recovered from the stripper (T-303) is recycled back to the absorber eliminating the need for process stream 6. The modified process is presented in the block flow diagram shown in Figure 6.22. Another important consideration was improving the reaction efficiency. If more of the raw materials are converted to the desired product, less waste would be generated. Once the process had been reconfigured based on the changes described above, it is then optimized in ASPEN PLUS as discussed in the next section.

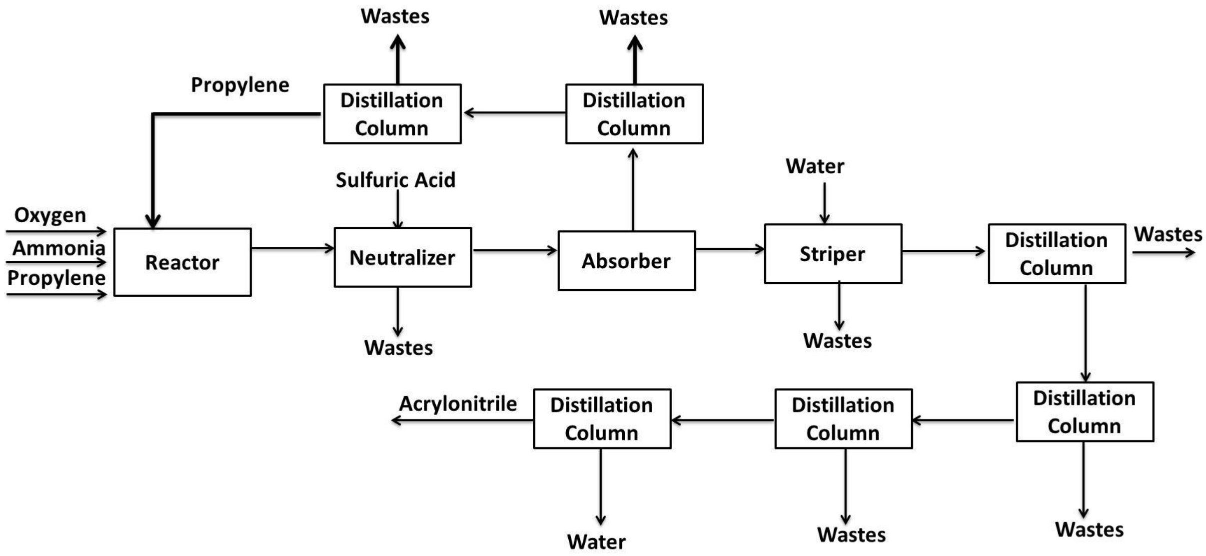


Figure 6.22: Block Flow Diagram of the Reconfigured Acrylonitrile Process

6.3.4 Optimization of the Base Case Acrylonitrile

The key goal in this step is to maximize annual profit (\$/yr) while minimizing waste (kg/yr). Profit is defined by Equation 5.2 shown below. The waste streams as shown in Figure C.2 (Appendix C) include stream 5, 14, 19 and 23. Thus total waste is presented in Equation 6.3.1. Thus the optimization equations for this problem are shown below are described in Equation 6.32-6.36. The process is optimized based on the different ranges shown in Table 6.30.

Profit = Product Revenue + By-product Revenue – (Raw Material Cost + Waste Treatment Cost + Operating Cost +Annualized Capital Cost) (5.2)

Total Waste= Mass Flow Rates of Stream 5+ Mass Flow Rates of Stream 14+ Mass Flow Rates of Stream 19+ Mass Flow Rates of Stream 23 (6.31)

Maximize Profit, Minimize Waste (6.32)

Subject to the following constraints:

Operating Temperature $\leq 600^{o}$C (6.33)
Operating Pressure $\leq$ 25 bar (6.34)
Waste Streams ≤ 4 (6.35)

$$\text{Conversion} \geq 60\% \qquad (6.36)$$

Table 6.30: Variables used in the Optimization of the Acrylonitrile Process

Variable Description	Base Case Value	Optimization Range
Feed Flow Rate	NH_3 = 85 lbmole/hr O_2 = 129 lbmole/hr C_3H_6 = 85 lbmole/hr	NH_3 = 60-90 lbmole/hr O_2 = 120-140 lbmole/hr C_3H_6 = 75-90 lbmole/hr
PFR Reactor Temperature	852 ^oF	800-1112 ^oF
PFR Reactor Pressure	15 psia	10-45 psia
PFR Diameter	1.08ft	1-2ft
PFR Length	19ft	8-20ft
PFR Number of Tubes	17	10-20
H_2SO4 Flow Rate	11.20 lbmole/hr	1-60 lbmole/hr
T-302 (Absorber) Reflux Ratio	4	1-10
T-302 (Absorber) Feed Stage	15	2-14
T-302 (Absorber) Bottoms to Feed Ratio	0.85	0.75-0.85
T-303 (Stripper) Reflux Ratio	7	1-10
T-303 (Stripper) Distillate to Feed Ratio	0.17	0.10-0.20
T-303 (Stripper) Feed Stage	10	2-28
T-305 (Separator) Feed Stage	11	2-11
T-305 (Separator) Reflux Ratio	4	2-10
T-305 (Separator) Distillate to Feed Ratio	0.0015	0.005-0.2
T-306 (Separator) Distillate to Feed Ratio	0.78	0.7-0.9
T-306 (Separator) Reflux Ratio	4	1-5
T-306 (Separator) Feed Stage	15	2-34

The modified optimized acrylonitrile process is presented in the schematic shown in Figure C.3. The stream summary and the equipment specification table for the optimized acrylonitrile process are presented in Table C, 9 and Table C.10 respectively in APPENDIX C. After the optimization of the base case, the next step was to complete an economic assessment using ASPEN Economic Evaluator. Also, the process is evaluated using the SUSTAINABILITY EVALUATOR in order to determine if the process is more economical, environmental friendly and socially acceptable compared to the base case. The results of this assessment are presented in the next section.

6.3.5 Sustainability Assessment of the Optimized Acrylonitrile Process

The optimization of the acrylonitrile process resulted in the changes presented in Table 6.31. The first key change was the reduction in raw material flow rate. This was possible because some of un-reacted raw material was recycled back to reactor (R-301). Another important change was the fact that acrylonitrile production increased from 44 lb -mole/hr to 51.6 lb-mole/hr. The optimization of the acrylonitrile process led to a waste reduction of 43% while profit relative to investment increased to 17%.

Table 6.31: Key Differences between the Base and Optimized Acrylonitrile Processes

Major Change	Base Case Value	Optimized Value
Feed Flow Rate	Ammonia = 85 lbmole/hr Oxygen = 129 lbmole/hr Propylene = 85 lbmole/hr	Ammonia = 67 lbmole/hr Oxygen = 129 lbmole/hr Propylene = 66 lbmole/hr
Sulfuric Acid	11 lbmole/hr	2.097 lbmole/hr
Number of Recycle Streams	0	2 (propylene to the reactor and water to the absorber)
Acrylonitrile Production	44 lb-mole/hr	46.8 lb-mole/hr
Stream Elimination	N/A	Water Stream Elimination
Waste	1.65 E+07 lb/year	9.44 E+06 lb/year
Profit	$0.4MM	$ 3.5MM
Profit Relative to Investment	2%	17%
Sustainability Impact	0.50	0.36

Once the maximum profit and minimum waste had been determined, the next step was to evaluate and compare the sustainability of optimized and base case acrylonitrile processes. The first step was to compare the economics of the two cases. The results of the economic assessment are shown in Table 6.32 and Figure 6.23. As shown in Table

6.32, although the optimized acrylonitrile process has higher operating and capital costs, it has lower raw material and waste treatment costs compared to the base case.

Table 6.32: Comparison of Economic Metrics for the Base and Optimized Acrylonitrile Processes

Economic Parameters	Base Case Acrylonitrile Process (Million)	Optimized Acrylonitrile Process (Million)
Revenue	$23.9	$23.9
Operating Costs	$2.1	$3.9
Waste Treatment Costs	$1.9	$1.1
Raw Material Costs	$18.3	$14.2
Capital Costs	$9.2	$10.1
Material Value Added	$5.6	$9.7
Profit	$0.43	$3.5

The higher operating cost is due to the addition of the distillation columns and the recycle stream. A slight increase in product led to increase in revenue compared to the base case. Also the recycle of propylene back to the reactor and the reduction in ammonia feed rate led to lower raw material costs. This also led to lower waste treatment costs as less wastes were being produced. As shown in Figure 6.23 the optimized acrylonitrile process which has an overall profit of $3.5 million is a more profitable process compared to the base case which has a profit of $0.43 million. The profit relative to investment for the optimized case is around 17% which is higher compared to the base case which has a value of about 2%. Therefore the optimized case had a lower economic impact value of 0.50 compared to the base case which had a value of 0.95.

The environmental impacts of the two cases are evaluated based on assessing the waste streams for potential land or water impact. The results of comparing the environmental burden of the two processes have been depicted on the bar graph shown in Figures 6.24. As shown in Figure 6.24, the optimized acrylonitrile process has a lower environmental impact in all categories compared to the base case. An analysis was completed to investigate the percent reduction for each environmental impact category. As shown in Table 6.33, the percent reduction is significant for all categories. This reduction is as a result of less wastes emission from the process.

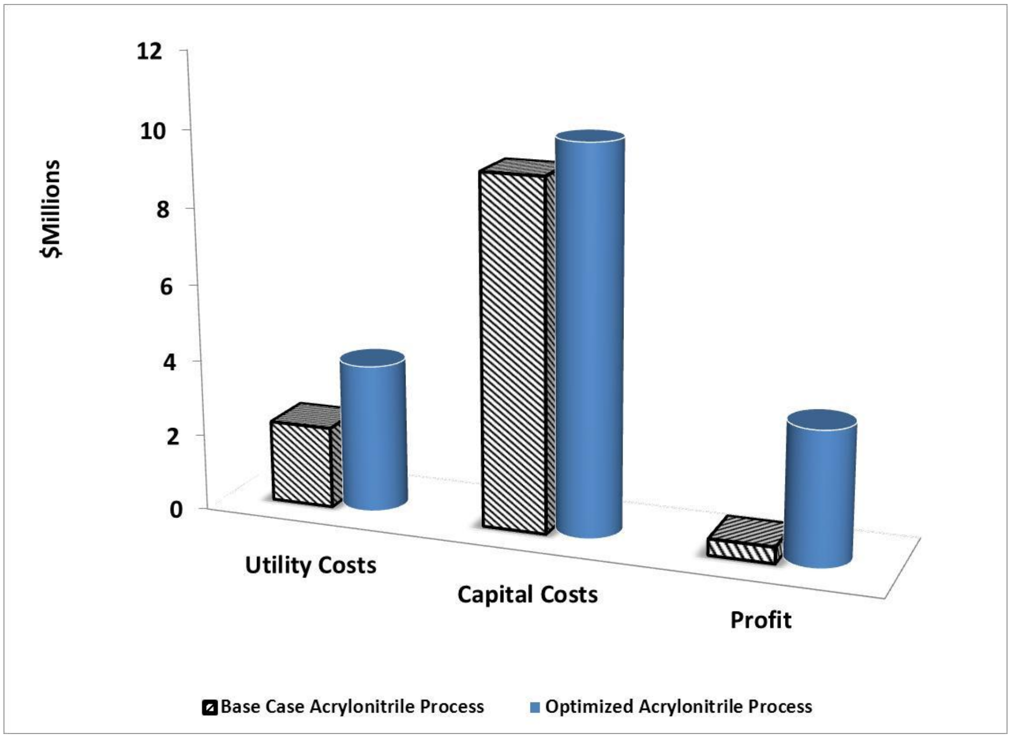


Figure 6.23: Comparison of Economic Assessment of the Base Case and Optimized Acrylonitrile Process

Next the efficiency of the reactions used in acrylonitrile formation and resource usage is evaluated and compared with the base case. Table 6.34 shows a comparison of the results of the two cases. As shown in the table, mass productivity and reaction mass for the optimized case increased to 28%, 29% and 30% respectively. While E-factor, and water intensity reduced to 1 and 0 respectively. Water usage is 0 because of the elimination of the water stream. Rather, water is generated and recycled. The only metric that did not improve was energy usage because of the higher utility needs of the optimized case. In general for all resource usage metrics except energy usage, the optimized acrylonitrile process is more efficient compared to the base case. Also the optimized case is more ecological efficient because it has a lower environmental impact value of 0.17 compared to the base case which was 0.22.

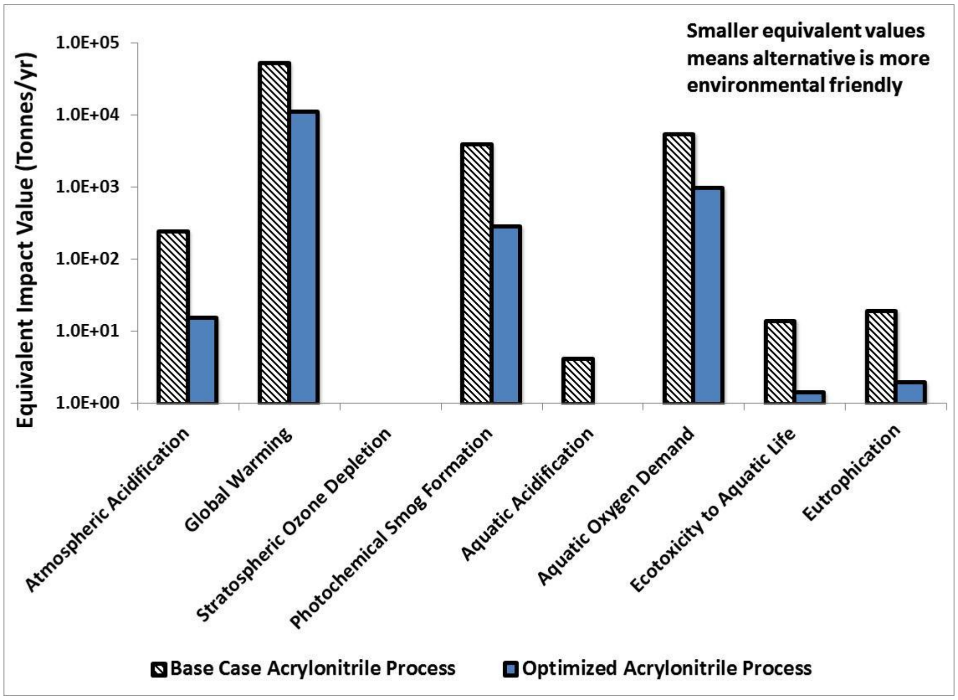


Figure 6.24: Comparison of Environmental Impacts Assessment for the Optimized and Base Case Acrylonitrile Process

Table 6.33: Percent Reduction of the Environmental Impact of the Acrylonitrile Optimized Case relative to the Base Case

Environmental Impacts	Base Case (Tonnes/year)	Optimized Case (Tonnes/year)	Percent Reduction
Atmospheric Acidification	246.0	15.5	94%
Global Warming	52924.4	11280.5	79%
Stratospheric Ozone Depletion	0.0	0.0	N/A
Photochemical Smog Formation	3984.9	291.5	93%
Aquatic Acidification	4.2	0.1	98%
Aquatic Oxygen Demand	5500.0	979.7	82%
Ecotoxicity to Aquatic Life	14.2	1.4	90%
Eutrophication	19.5	2.0	90%

Table 6.34: Resource Usage Metrics Results for the Base and Optimized Acrylonitrile Cases

Outputs	Base Case	Optimized Case	Units
E-Factor	1.8	1.0	Kg/kg
Mass Productivity	19%	28	%
Reaction Mass Efficiency	25%	29	%
Energy Intensity	0.0018	0.0021	KW/Kg
Water Intensity	0.5	0.0	Kg/Kg

The health impact of the optimized acrylonitrile process is also evaluated and compared with the base case and this is presented in Figure 6.25. From the figure, in general the health risk for the optimized case is lower compared to the base case. An assessment was completed to determine the percent reduction for each health impact category. As shown in Table 6.35, the percent reduction is highest for carcinogenic health risk (96%), immune system damage (97%), kidney damage (97%) and skeletal system damage (97%) because of improved recovery of acrylonitrile, reduction in sulfuric acid wastes as well as propylene wastes.

The safety of the optimized acrylonitrile process was also evaluated and compared with the base case. As shown in Table 6.36, the results of the optimized acrylonitrile process shows that there are no changes in overall safety impact. It was difficult to really improve safety impact values because most of the other impact values are based on the chemicals present in the process and the operating temperature and pressure. Changes made to the operating temperature would have affected conversion leading to a loss in product formation. Also the process was not directly optimized for safety, so no improvement in safety was expected. The overall social impact for the optimized case was 0.52 compared to the base case which was 0.62.

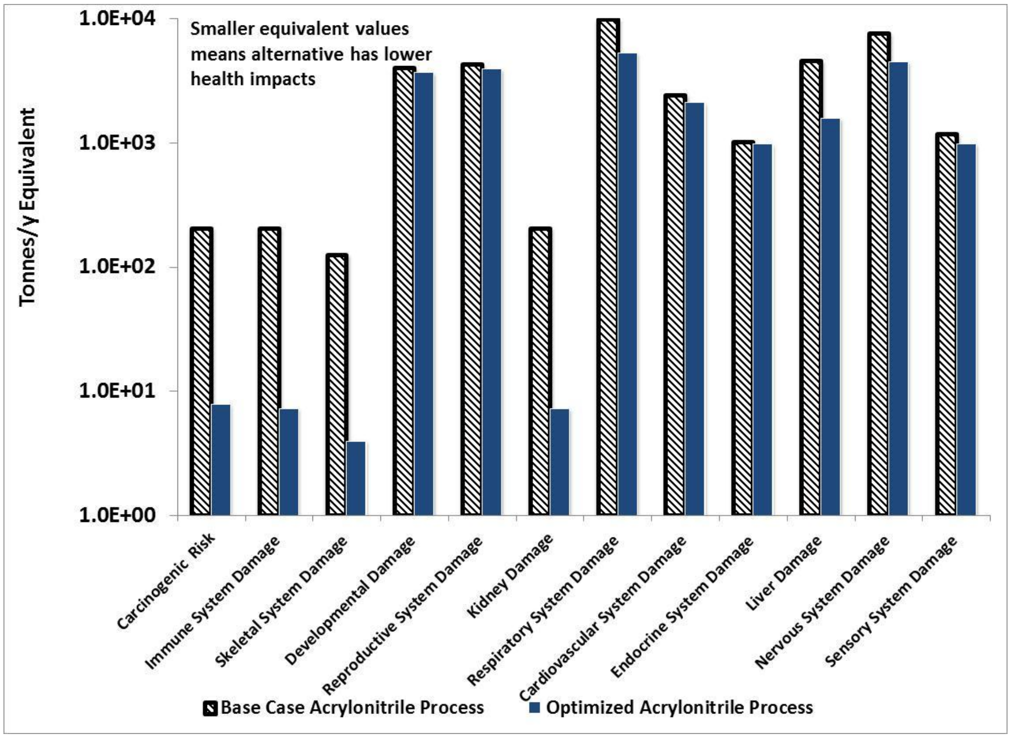


Figure 6.25: Comparison of Health Impacts Assessment the Base and Optimized Acrylonitrile Process

Table 6.35: Percent Reduction of the Health Impact of the Acrylonitrile Optimized Case relative to the Base Case

Health Impacts	Base Case (Tonnes/year)	Optimized Case (Tonnes/year)	Percent Reduction
Carcinogenic Risk	2.1E+02	7.9E+00	96%
Immune System Damage	2.1E+02	7.2E+00	97%
Skeletal System Damage	1.2E+05	4.0E+03	97%
Developmental Damage	4.0E+03	3.7E+03	8%
Reproductive System Damage	4.3E+03	3.9E+03	9%
Kidney Damage	2.1E+02	7.2E+00	97%
Respiratory System Damage	9.9E+03	5.4E+03	45%
Cardiovascular System Damage	2.4E+03	2.1E+03	13%
Endocrine System Damage	1.0E+03	9.8E+02	2%
Liver Damage	4.6E+03	1.6E+03	65%
Nervous System Damage	7.6E+03	4.5E+03	41%
Sensory System Damage	1.2E+03	9.9E+02	18%

Table 6.36: Summary of Results of Safety Metrics for the Base and Optimized Acrylonitrile Processes

Outputs for Process Safety Evaluation	Base case	Optimized Case
Heat of main reaction index	4	4
Heat of side reaction index	4	4
Flammability Index	8	8
Explosiveness Index	6	6
Toxic Exposure Index	24	24
Corrosiveness Index	4	4
Temperature Index	6	6
Pressure Index	2	2
Equipment safety Index	4	4
Inputs for Safety Level of Process Structure Index	8	8
Total Inherent Safety Index	70	70

6.3.6 Summary

The optimized acrylonitrile process differed from the base case because the following changes were made to the process:

- Addition of two distillation columns to aid in the recycle of propylene back to the reactor (R-301)
- Recycling water from the stripper (T-303) which aided in the elimination of process stream 6.
- Optimization of operating conditions

The optimized acrylonitrile process has an economic impact of 0.75 compared to the base case which has a value of 0.95. The optimized case has lower raw material costs and higher revenue. Therefore the profit of the optimized case relative to investment was around 17% compared to the base case value of 2%.

The optimized acrylonitrile process is environment friendly as wastes reduced by 43% compared to the base case. This waste reduction of the optimized case led to improve resource usage metrics and lower environmental impacts resulting in a lower environmental impact of 0.17 compared to 0.22. This happened as a result of the recycle of un-reacted raw material and the elimination of process water. In terms of social concerns, the optimized acrylonitrile case has a lower health risk compared to the base case. There were no changes made to the process safety index. The social impact value of the optimized case is 0.43 compared to the base case which was 0.35.

Therefore, the improvements made to the optimized acrylonitrile process led to a lower overall sustainability impact value of 0.31 compared to the base case which had a value of 0.45. Based on the results obtained from the SUSTAINABLE EVALUATOR, it can be concluded that optimized acrylonitrile process is a more sustainable compared to the base case because it is more economical viable, environmentally friendly and socially acceptable compared to the other option.

6.4 CASE STUDY: ALLYL CHLORIDE PROCESS

Allyl chloride, also known as 3-Chloropropylene, 3-chloro-1-propen and 1-chloro-2 propene, is a colorless organic liquid. This compound is insoluble in water, but miscible in other substances such as chloroform, alcohols and ethers. The physical properties of this extremely flammable and toxic chemical are shown in Table 6.37. The discovery of the synthesis of allyl chloride via substitutive chlorination of propylene was first discovered by Shell Development Corporation in 1930 (Kneupper and Saathoff, 2000). Another approach involves thermal dehydrochloration of 1,2 dichloropropane.

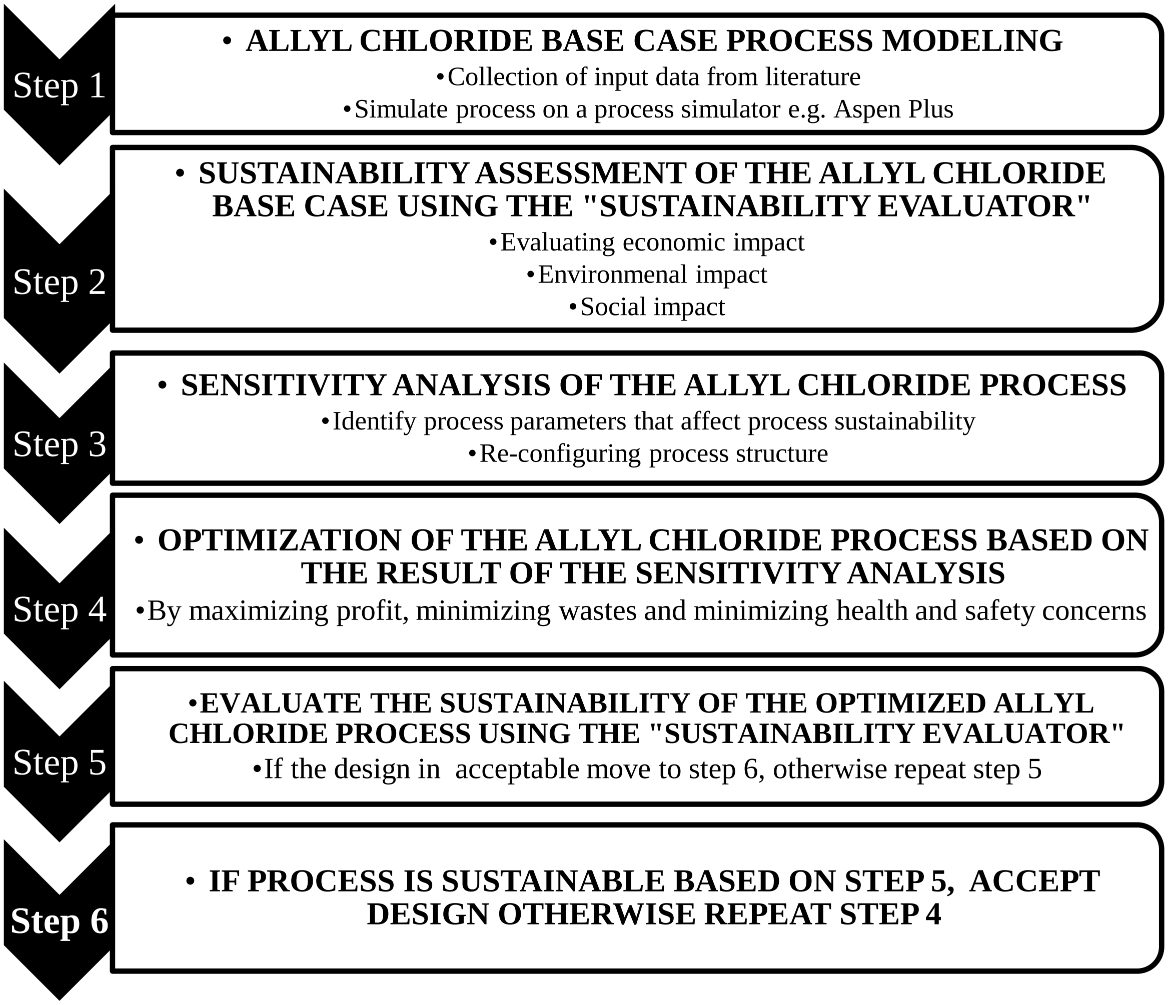
However, allyl chloride via substitutive chlorination of propylene is the more economic approach as thermal dehydrochloration of 1,2 dichloropropane gives by product that are not of economic use (Kneupper and Saathoff, 2000).

Table 6.37: Physical Properties of Allyl Chloride

Property	Value
Boiling Point (°C)	45
Melting Point(°C)	-135
Solubility in water, 20°C, g/L	3.6
Viscosity, 20°C (mPa.s)	0.34
Density (g/L)	0.94

Allyl chloride is an important chemical with many applications in industry. It used as an alkylating agent in many laboratories. It is used as a chemical intermediate in the pharmaceutical industry and in the manufacture of allyl alcohol, allylamine, allyl isothiocyanate. It is used to synthesize other chemicals is used for making pesticides. In most cases, allyl chloride is converted to epichlorohydrin which is used for creating epoxy resins and glycerol. It is also used for synthesizing sodium allyl sulfonate which is used for brightening metals for electroplating baths (Kneupper and Saathoff, 2000).

The allyl chloride production process is an excellent manufacturing process to demonstrate the proposed methodology because of the tremendous toxic waste streams present in this process that are regulated by the Environmental Protection Agency (EPA). These waste steams pose a threat to the environment and human health. According to the EPA, allyl chloride is considered a very volatile hazardous air pollutant that must be disposed of appropriately (United States Environmental Protection Agency, 1992). It is a chemical that must comply with the EPA's Resource Conservation and Recovery Act (Dow Chemical Company, 2006).



• ALLYL CHLORIDE BASE CASE PROCESS MODELING
•Collection of input data from literature
•Simulate process on a process simulator e.g. Aspen Plus

• SUSTAINABILITY ASSESSMENT OF THE ALLYL CHLORIDE BASE CASE USING THE "SUSTAINABILITY EVALUATOR"
•Evaluating economic impact
•Environmenal impact
•Social impact

• SENSITIVITY ANALYSIS OF THE ALLYL CHLORIDE PROCESS
•Identify process parameters that affect process sustainability
•Re-configuring process structure

• OPTIMIZATION OF THE ALLYL CHLORIDE PROCESS BASED ON THE RESULT OF THE SENSITIVITY ANALYSIS
•By maximizing profit, minimizing wastes and minimizing health and safety concerns

•EVALUATE THE SUSTAINABILITY OF THE OPTIMIZED ALLYL CHLORIDE PROCESS USING THE "SUSTAINABILITY EVALUATOR"
•If the design in acceptable move to step 6, otherwise repeat step 5

• IF PROCESS IS SUSTAINABLE BASED ON STEP 5, ACCEPT DESIGN OTHERWISE REPEAT STEP 4

Figure 6.26: Proposed Methodology for Addressing Sustainability Concerns of the Allyl Chloride Process

Workers in allyl chloride processing plants have been exposed to the chemical via breathing contaminated air or skin contact (United States Environmental Protection Agency, 1986). Skin contact with allyl chloride leads to skin irritation and possibly delayed burns. Breathing in vapors of the chemicals, results in severe, eye, noses and throat irritations. Severe exposure to the chemical can even lead to death. There are other long term health risks associated with exposure to allyl chloride. These include cancer, liver and kidney damage, nervous system damage, reproductory system damage and sensory system damage. The two other by products of ally chloride 1, 2 –

dichloropropane and 1, 3-dichloropropene are also volatile hazardous compounds regulated by the EPA. Therefore it is of paramount importance to investigate approaches to handle the allyl chloride process waste streams in a sustainable manner. The methodology discussed in chapter 5 and shown in Figure 6.26 is applied towards handling the sustainability concerns of the allyl chloride process.

6.4.1 Allyl Chloride Base Case Process Modeling

Allyl chloride is modeled based on literature (van der Helm, 1992). The information compiled from literature is simulated in ASPEN PLUS version 22 using the ideal gas model with Raoutls law (SYSOPQ) equation of state thermodynamic package. The block flow diagram of this process is shown in Figure 6.27. The allyl chloride production process can be divided into two main sections namely substitutive chlorination of propylene and purification of allyl chloride.

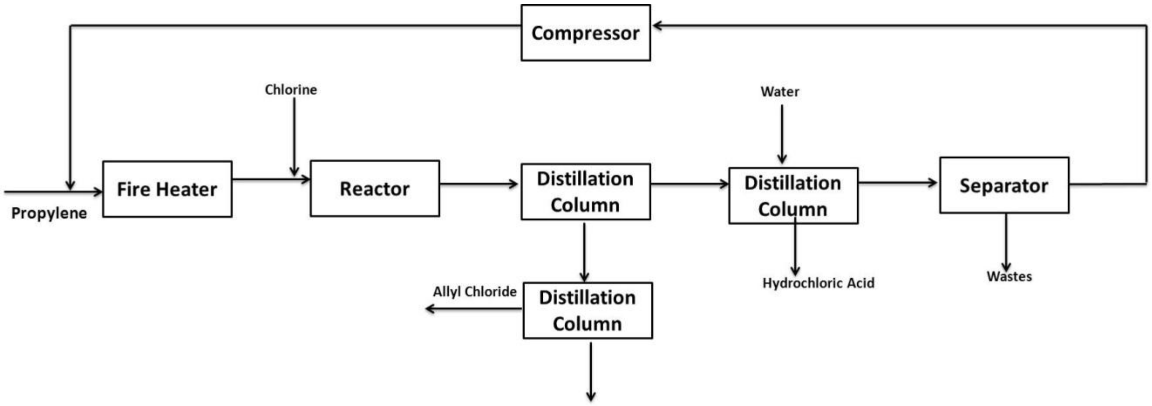


Figure 6.27: Block Flow Diagram of the Allyl Chloride Process

In the substitutive chlorination step, propylene (C_3H_6) at 74.7 psia and 80 ^oF is heated via a heater, E-901 to 730 ^oF. This heated propylene stream is combined by mixer (M-901), with chlorine (Cl_2) at 14.7 psia and 80^oF. Next, the heated stream is sent to an adiabatic plug flow reactor (R-901) where the substitutive chlorination of propylene as shown in Equation 6.37 takes place.

$$\overset{\text{Propylene}}{CH_2 = CH - CH_3} + \overset{\text{Chlorine}}{Cl_2} \rightarrow \overset{\text{Allyl Chloride}}{CH_2 = CH - CH_2\,Cl} + \overset{\text{Hydrochloric acid}}{HCl} \qquad (6.37)$$

Key design consideration must be incorporated when designing this reactor. The first is that for the reactions to take place efficiently, the reactor must be operated at a temperature range of 570-1110 ^{o}F to ensure favorably formation of allyl chloride (van der Helm, 1992). When the reactor is operated below 570 ^{o}F, the formation of one of the byproduct, 1, 2 dichloropropane is favored over allyl chloride formation as shown in Equation 6.38 below. Thus the reaction must be kept above 570 ^{o}F to keep allyl chloride as the major product and 1, 2 dichloropropane as well as cis and trans 1,3 dichloropropane as the byproducts as shown in Equations 6.38 and 6.39. This reaction is highly exothermic, thus it is recommended that these is no heat transfer across the reactor. The rate constants for the kinetics for the reactions taking place in the reactor are presented in Table 6.38.

$$\overset{\text{Propylene}}{CH_2 = CH - CH_3} + Cl_2 \rightarrow \overset{\text{1,2-dichloropropane}}{CH_2Cl - CHCl - CH_3} \qquad (6.38)$$

$$\overset{\text{AllylChloride}}{CH_2 = CH - CH_2\,Cl} + Cl_2 \rightarrow \overset{\text{1,3-dichloropropene}}{CHCl = CH - CH_2Cl} + HCl \qquad (6.39)$$

After the reaction step, the purification of the product from the by product and un-reacted raw material begin. The reactor effluent is cooled to 70^{o}F by cooler (E-602) and sent to a series of separation equipment. In the first distillation column (T-901), hydrochloric acid and propylene are separated as the distillate stream while allyl chloride, 1, 2 dichloropropane and 1, 3 dichloropropene are separated as the bottom steam. The overhead product of T-901 along with a water stream operating at 70^{o}F and 14.7 psia are sent to the second distillation column, T-902. Here propylene and water are separated as the distillate and hydrochloric acid and water are separated as the bottoms stream. The overhead product of T-902 is sent to separator, T-903 where propylene is separated as the distillate and water as the bottoms stream. The recovered propylene is compressed to 90 psia by compressor, C-901 and recycled back to the reactor, R-901.

Table 6.38: Allyl Chloride Process Kinetic Data (van der Helm, 1992)

Reaction Number	Activation Energy, E_i J/(kmol)	Pre Exponential Factor $\left(\frac{m^3}{kg\ mol-s}\right)$
1	7.43E+7	4.04E+7
2	7.11E+4	2.3E+3
3	1.11E+4	9.03E+10

The bottom stream of T-902 is sent to a distillation column, T-904 where water and hydrochloric acid are separated as the overhead product and bottoms stream respectively. The bottom stream of T-901 is sent to a distillation column, T-905 where allyl chloride is separated from 1, 2 dichloropropane and1, 3 dichloropropane as the overhead product and bottom stream respectively. The key input variables for this process adapted from (van der Helm, 1992). The schematic for this process, the equipment specification and stream summary tables are presented in Figure C.4, Table C.11 and Table C.12 in APPENDIX C respectively.

6.4.2 Sustainability Assessment of the Base Case Allyl Chloride Process

The economic, environmental and social impact of the base case allyl chloride process is assessed using the SUSTAINABILITY EVALUATOR. The data used in completing the economic evaluations are presented in Table 6.39. The annual production of pure allyl chloride was set at 20,409 tonnes/year.

Table 6.39: Economic Data for the Allyl Chloride Process

Item	Cost ($/kg)
Allyl Chloride	1.80 (Turton et al., 2009)
Hydrochloric acid (32 Wt%)	0.095 (Turton et al., 2009)
Propylene Costs	0.98 (Turton et al., 2009)
Chlorine Costs	$0.375 (Turton et al., 2009)
Process Water	0.00067 (Turton et al., 2009)
Waste Treatment Costs	$0.2 (Turton et al., 2009)
1,2 Dichloropropane (97wt%)	0.12 (Young et al., 2000)[10]
1,3 Dichloropropane (97wt%)	0.19 (Young et al., 2000)[8]
Capital Recovery Factor	0.1175

6.4.2.1 Economic Impact Assessment of the Base Case Allyl Chloride Process

An economic analysis was completed using the ASPEN Economic Evaluator. The capital and operating costs values obtained from the ASPEN Economic Evaluator, the mass flow rates of the raw material and product stream and the economic data shown in Table 6.39 are entered into the SUSTAINABILITY EVALUATOR. The result of this assessment is shown in Table 6.40 and Figure 6.28. As shown in the table, the estimated annual revenue generated from selling the allyl chloride process is around $41.6 million. The annual expenses for this process are estimated to be around $39.6 million. The breakdown of the expenses is shown in Figure 6.28.

As shown in Figure 6.28, the raw material costs accounts for 80% of the annual operating expenses of the allyl chloride manufacturing process. Toxic waste streams are present in the allyl chloride process, and must hence be treated. The waste treatment cost as shown in Figure 6.32 is around $3.7 million and this is about 2% of the costs. Operating cost, which is about 9% of the expenses, is the third largest expenditure incurred in manufacturing the products. The capital costs for this process is around 6.7 million but the purpose of calculating profit, the costs were annualized using the capital

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[10] Price in Journal article was obtained from Chemical Market reporter. This prices were inflated to 2009

recovery factor shown in Table 6.40. The annualized capital cost is about 2% of the expenses incurred in this manufacturing process. As shown in Table 6.40, this is a profitable process in which the estimated annual profit was calculated to be around $1.6 million.

Table 6.40: Economic Assessment Results for the Base Case Allyl Chloride Process from the SUSTAINABILITY EVALUATOR

Economic Parameters	Base Case (MM)
Revenue	$41.6
Operating Costs	$3.5
Waste Treatment Costs	$3.7
Raw Material Costs	$31.9
Capital Costs	$7.4
Material Value Added	$9.6
Profit	$1.6

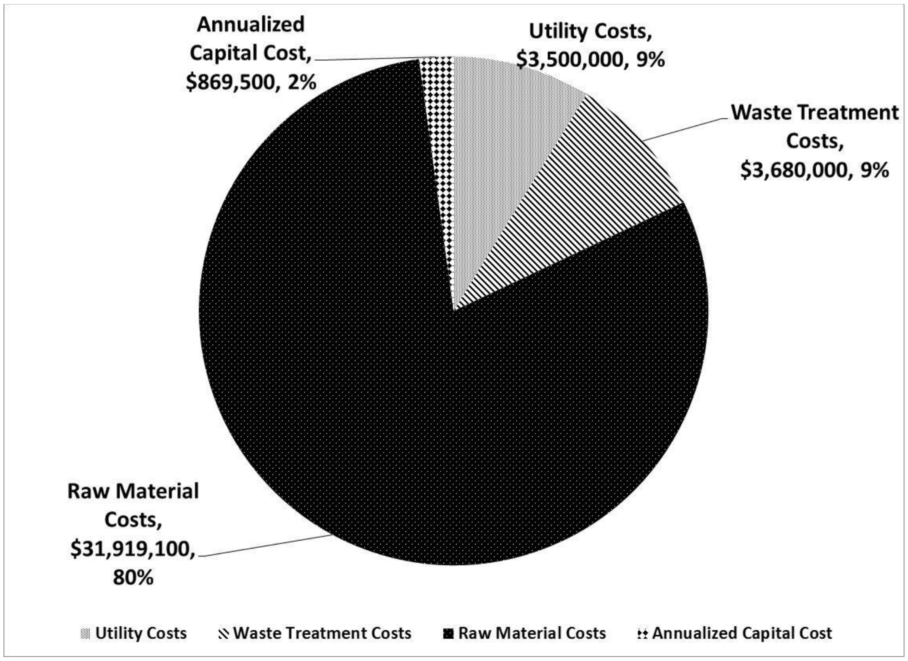

Figure 6.28: Breakdown of Annual Operating Costs for the Base Case Allyl Chloride Process

6.4.2.2 Environmental Impact Assessment of the Base Case Allyl Chloride Process

Once the economics of the allyl chloride process had been calculated, the next step was to evaluate the environmental impacts. The environmental impact assessment involved entering the mass flow rates of the waste streams into the SUSTAINABILITY EVALUATOR. The result of the environment assessment is presented in Figure 6.29 and Table 6.41. As shown in the table, the only threat posed by the allyl chloride process to the environment is global warming.

Table 6.41: Results of Environmental Impact for the Base Case Allyl Chloride Processes

Environmental Impacts	Base Case (Tonnes/year)	Chemicals Present
Global Warming	2.03E5	Allyl chloride, 1,3-dichloropropene and 1,2-dichloropropane.

Next, the resource usage efficiency for the allyl chloride process is also evaluated and the results are presented in Table 6.42. As shown in the table, the base case allyl chloride process is not a very resource friendly process. This is because of the several side reactions taking place leading to two unwanted products which are considered wastes. The values of the effective mass yield, mass productivity, and reaction efficiency are all very low. While the values of the E-Factor, water intensity, and material intensity are all high. Investigating ways to improve reaction efficiency would be important in improving the sustainability of this process.

Table 6.42: Results of Resource Usage Evaluation for the Base Case Allyl Chloride Process

Environmental Impact	Value	Units
E-Factor	0.9	Kg/Kg
Mass Productivity	22	%
Reaction Mass Efficiency	37	%
Energy Intensity	0.00071	KW/Kg
Water Intensity	1.8	Kg/Kg

6.4.2.3 Social Impact Assessment of the Base Case Allyl Chloride Process

After the environmental impact assessment, the next step was to complete a health and safety impact analysis using the SUSTAINABILITY EVALUATOR. For the health assessment, the mass flow rates of each specific component found in the waste stream are entered into the SUSTAINABILITY EVALUATOR. As shown in Table 6.43, the allyl chloride process poses a serious health risk in all categories except skeletal system damage. Allyl chloride and 1,2-dichloropropane are considered group 2b, while 1,3-dichloropropane is considered a group 3 carcinogen.

Table 6.43: Results of Health Impact Assessment for the Base Case Allyl Chloride Process

Impact Category	Impact Value (Tonnes/year)	Chemicals Present
Carcinogenic Risk	9.5E+03	Allyl chloride, 1,2-Dichloropropane & 1,3-Dichloropropene
Immune System Damage	6.5E+06	1,3-Dichloropropene
Skeletal System Damage	0.0E+00	N/A
Developmental Damage	6.2E+01	Allyl chloride
Reproductive System Damage	1.1E+04	1,2-Dichloropropane & 1,3-Dichloropropene
Kidney Damage	6.5E+03	1,3-Dichloropropene
Respiratory System Damage	1.1E+04	1,3-Dichloropropene
Cardiovascular System Damage	4.5E+03	Allyl chloride, 1,2-Dichloropropane & 1,3-Dichloropropene
Endocrine System Damage	4.5E+03	1,2-Dichloropropane
Liver Damage	1.1E+04	Allyl chloride, 1,2-Dichloropropane & 1,3-Dichloropropene
Nervous System Damage	1.1E+04	Allyl chloride, 1,2-Dichloropropane & 1,3-Dichloropropene
Sensory System Damage	1.1E+04	Allyl chloride, 1,2-Dichloropropane & 1,3-Dichloropropene

Apart from cancer risks, other health threats are eminent; these are shown in Table 6.43. In this table, the chemicals contributing to each health impact category as well as the calculated impact value is presented. Due to the tremendous health risk, it is therefore vital to ensure that the wastes from this process are handled appropriately and explosions and spills are kept at a minimum.

For the safety assessment, the operating conditions, chemicals present and equipment present are selected in the input section of the software. Also, the mass enthalpy is entered to estimate the heat of reaction index. The result of the safety assessment is presented in Table 6.44. The overall total inherent safety index for this process was 58. The maximum overall safety index i.e. the worst case scenario for any process is around 100. As shown in the table, the first obvious safety concerns are the flammability, toxic exposure and equipment safety index risks which are at their maximum value.

Table 6.44: Safety Assessment Results from the SUSTAINABILITY EVALUATOR for the Base Case Allyl Chloride Process

Safety Assessment	Results	Maximum
Heat of main reaction index	0	8
Heat of side reaction index	0	8
Flammability index	8	8
Explosiveness index	2	8
Toxic Exposure Index	24	30
Corrosiveness index	4	4
Temperature index	6	8
Pressure index	2	8
Equipment safety index	8	8
Safety Level of Process Structure index	4	10
Total Inherent Safety index	58	100

Flammability risks are eminent due to presence of the following chemicals; allyl chloride, propylene, 1,2-dichloropropane and 1,3-dichloropropene.Toxic exposure risks are prominent because the following toxic chemicals that are present in the process: allyl chloride, 1,3 dichloropropene, 1,2 dichloropropane, chlorine and propylene. The equipment safety index is high because the process has a fired heater and a compressor. Another eminent risk is temperature and corrosion risk. The allyl chloride process is operating at high temperature and corrosive chemicals are present. Hence extra care must be taken when designing equipment. These risks must not be ignored, it is important to investigate ways to ensure safety is not compromised in this process.

6.4.3 Allyl Chloride Base Case Sensitivity Analysis

After evaluating the sustainability of the base case, it was apparent that it was necessary to optimize the process for economic, environmental, health and safety risk improvements. But before the optimization step, it was essential to identify parameters that affect the selected metrics. In order to identify these parameters, a sensitivity analysis was completed for the allyl chloride process. The sensitivity analysis was carried out using ASPEN PLUS. According to literature, there are two key variables that affect allyl chloride formation these are propylene to chlorine feed ratio and reactor temperature (Kneupper and Saathoff, 2000). Another parameter is reactor design, as choice of type of reactor can affect reaction selectivity. Thus the parameters that were considered for the sensitivity analysis were operating conditions, variation of inlet flow rates and equipment configuration. The above mention parameters are varied and the effects on the following were studied: allyl chloride formation and total waste produced.

6.4.3.1 Effect of Varying Inlet Flow Rates for the Base Case Allyl Chloride Process

The raw materials used in the manufacture of allyl chloride are propylene and chlorine. As mentioned earlier, the feed ratio of the raw materials affect ally chloride formation, thus propylene to chlorine ratio was varied from 1 to 12. It was important to investigate how varying the raw material ratio affected conversion and ultimately ally chloride formation. Propylene was varied from 133-1600 lbmole/hr while the chlorine flow rate was kept constant at 133 lbmole/hr. As shown in Figure 6.29, as feed ratio increases from 1-12, allyl chloride formation increases. However there is a trade off because waste increases at first when feed ratio is varied from 1-2, but decreases when it is varied from, 3-10 but later starts increases at a sharp rate when it is varied from 10-12

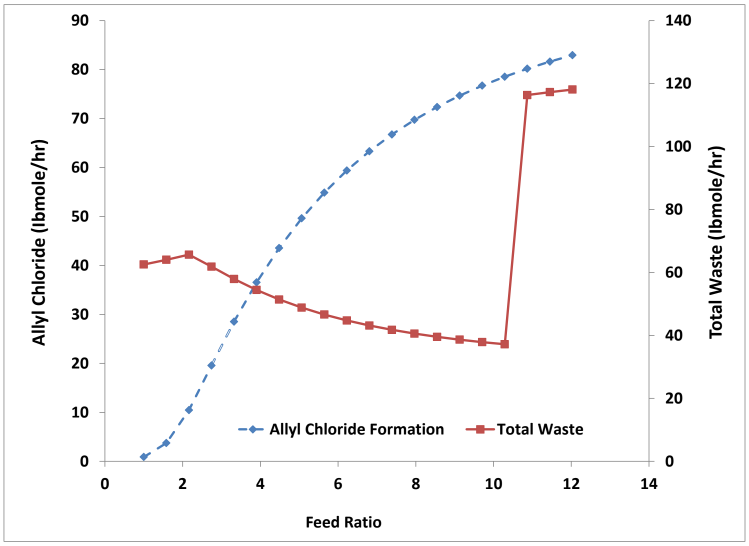

Figure 6.29: Effect of Feed Ratio on the Allyl Chloride Process

6.4.3.2 Effect of Varying Reactor Temperature for the Base Case Allyl Chloride Process

The effect of reaction temperature on allyl chloride formation and total waste is also studied. As discussed earlier, the reaction must operate at temperature range of 570-1110^{o}F to ensure favorably formation of allyl chloride (van der Helm, 1992). Thus the study was completed at this temperature range. As shown in Figure 6.30, when temperature is increased from 570 -650^{o}F, allyl chloride formation increases but after 680^{o}F it begins to decrease. On the other hand, as the temperature is increased from 570-700 ^{o}F, waste production reduces because less of the byproducts (1, 2 dichloropropane and 1, 3 dichloropropane) are being synthesized. When temperature increases from 700 ^{o}F- 1100, the wastes increase as more byproducts are formed.

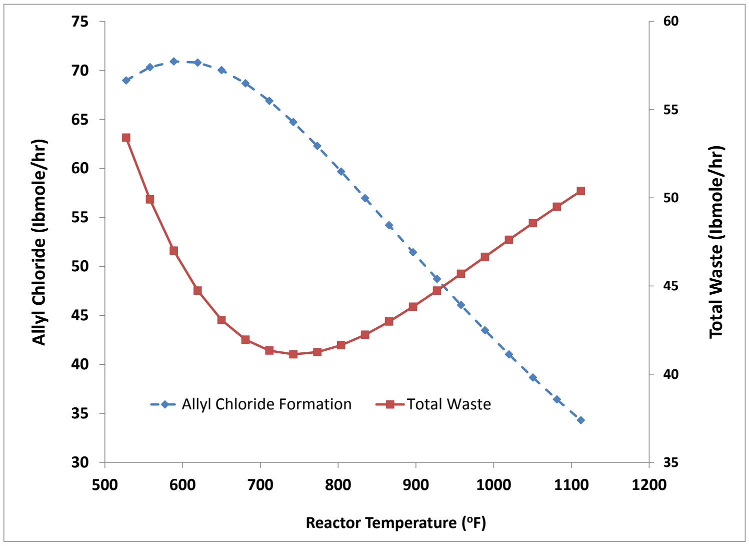

Figure 6.30: Effect of Reactor Temperature on the Allyl Chloride Process

6.4.3.3 Effect of Varying Reactor Residence for the Base Case Allyl Chloride Process

The reactor residence time was varied from 0-16s and as shown in Figure 6.31, residence time does not have significant impact on allyl chloride formation and wastes.

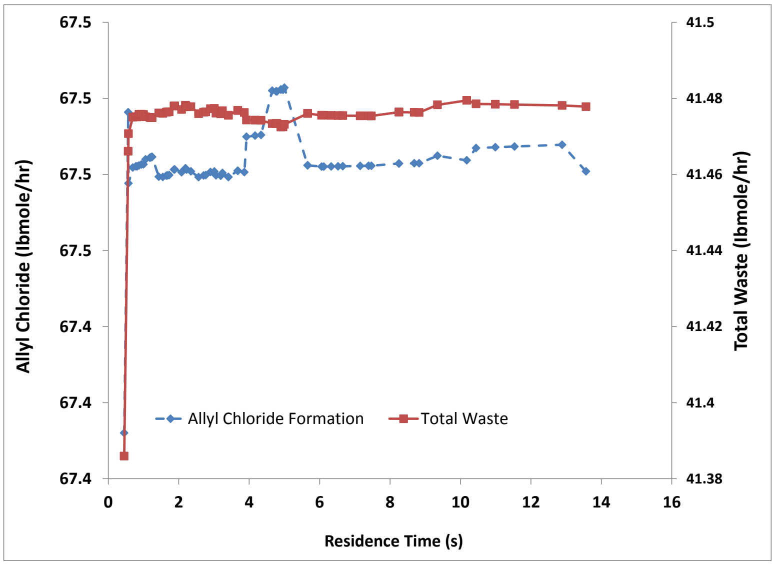

Figure 6.31: Effect of Varying Residence Time on the Allyl Chloride Process

6.4.3.4 Effect of Changing Reactor Specification for the Base Case Allyl Chloride Process

As mentioned earlier, choice of reactor can affect overall reaction selectivity. An isothermal plug flow reactor is also considered for this process. Table 6.45 shows a comparison of key differences of the exit stream of the plug flow reactor and isothermal reactor. As shown in Table 6.45, at isothermal reactor conditions, there is slight variation in product formation and the wastes being formed. At isothermal condition, there is 15% increase in product formation and 6% increase in wastes compared to the adiabatic conditions.

Table 6.45: Comparison of Calculated Parameters for the Adiabatic PFR Case and the Isothermal PFR Case

Reactor Parameters	Adiabatic PFR	Isothermal PFR
Temperature (^{o}F)	937	702.4
Hydrochloric Acid (lb mole/hr)	116.3	100.7
Propylene (lb mole/hr)	891.4	878.5
Allyl Chloride(lb mole/hr)	67.5	77.8
Total Wastes (lbmole/hr)	41.1	43.7

6.4.3.5 Summary of Sensitivity Analysis

The sensitivity analysis assisted in identifying parameters that affected allyl chloride formation and waste generation. The next procedure after completing the sensitivity analysis is process re-configuration. In this step, two distillation columns are placed after waste stream 10, in order to separate byproducts 1, 2 dichloropropane and 1, 3 dichloropropane.

Also the water feed stream 15 was increased to 1000 lbmole/hr. This resulted in the addition of a separator to recover hydrochloric acid. The block flow diagram for the re-configured process is shown in Figure 6.32 and the equipment specification table is shown in Table C.13 in APPENDIX C. After this step, process optimization using ASPEN PLUS is completed as discussed in the next section.

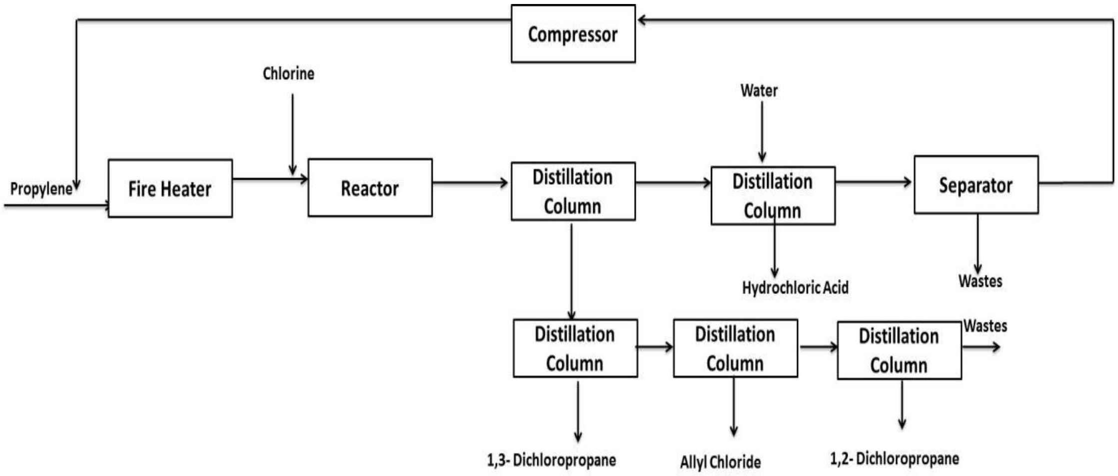

Figure 6.32: Block Flow Diagram of the Reconfigured Allyl Chloride Process

6.4.4 Optimization of the Allyl Chloride Process

Two options are considered for the optimization for the Allyl Chloride Process. Option 1 is the base case in which the reactor is operated at adiabatic conditions. While in option two, the reactor is operated at isothermal conditions. The key goal in this step is to maximize annual profit ($/yr) while minimizing waste (kg/yr). Profit as defined by Equation 5.1 as shown below. Waste is simply the mass flow rate of stream 11. Thus the optimization equations for this problem are shown below. The two options are optimized based on the different ranges shown in Table 6.46.

Profit = Product Revenue + By-product Revenue – (Raw Material Cost + Waste Treatment Cost + Operating Cost +Annualized Capital Cost) (5.2)

Maximize Profit, Minimize Waste (6.40)

Subject to the following constraints:

Operating Temperature $\leq 570^{o}C$ (6.41)
Operating Pressure ≤ 25 psia (6.42)

Allyl Chloride Purity $\geq$ 99% (6.43)
1,2 Dichloropropane Purity $\geq$ 96% (6.44)
1,3 Dichloropropane Purity $\geq$ 96% (6.45)

Table 6.46: Variables Used in the Optimization of the Allyl Chloride Process

Variable Description	Base Case Value	Optimization Range
Feed Flow Rate	Cl = 133 lbmole/hr	Cl = 130-1000 lbmole/h
PFR Reactor Temperature	937 ^oF	200-1100^oF
PFR Reactor Pressure	40 psia	25-50 psia

The stream summary tables of the optimized adiabatic plug flow reactor and the optimized isothermal plug flow reactor cases are shown in Table C.14 and C.15 in APPENDIX C respectively. After optimizing the process, the next step was to complete an economic analysis for both options using the ASPEN PLUS Economic Evaluator. Also, the optimized options are evaluated and compared with the base case using the SUSTAINABILITY EVALUATOR. The results of this assessment are presented in the next section.

6.4.5 Sustainability Assessment of the Optimized Allyl Chloride Processes

The optimization of the acrylonitrile process resulted in the changes presented in Table 6.47. The first key change was a 2% reduction in raw material flow rate of chlorine for both optimized cases. Another important change was an increase in allyl chloride production to 68.7 lbmole/hr and 84.2 lbmole/hr for the optimized adiabatic and isothermal PFR cases respectively.

The reactor temperature reduced to 652.8 ^oF for the optimized adiabatic PFR reactor case but increased to 742.3 ^oF for the optimized isothermal PFR case. The reactor pressure decreased to 39.4 psia for the optimized adiabatic PFR case but increased to 47.1 psia optimized isothermal PFR. The optimization of the allyl chloride process resulted in

88% and 85% waste reduction for both the optimized adiabatic and isothermal PFR cases respectively. Profit increased significantly for the both cases as shown in Table 6.47.

Table 6.47: Key Differences between the Base Case and the Optimized Cases

Major Change	Base Case	Optimized (Adiabatic PFR)	Optimized (Isothermal PFR)
Chlorine Feed Flow Rate (lbmole/hr)	133	130	149.2
Reactor Feed Temperature (^{o}F)	703.4	652.8	742.3
Reactor Pressure (Psia)	40.0	39.4	47.1
Ally Chloride Production (lbmole/hr)	67.1	68.7	84.2
Waste (lbmole/hr)	41.5	4.8	6.0
Profit ($MM/year)	1.6	14.4	19.4

Once the maximum profit and minimum waste had been determined, the next step was to evaluate and compare the sustainability of optimized allyl chloride processes to the base case. The first step was to compare the economics of the three cases. As shown in Table 6.48 and Figure 6.33, the optimized adiabatic PFR case has lower energy cost, capital costs and raw material cost compared to the optimized isothermal case. For both cases, there was an increase in capital and utility costs due to the addition of the one separator and two additional columns to separate the byproducts.

Table 6.48: Comparison of Economic Impact Results for the Base, Optimized Adiabatic and Isothermal Allyl Chloride Processes

Economic Parameters	Base Case (MM)	Optimized Adiabatic Case (MM)	Optimized Isothermal Case (MM)
Revenue	$41.6	$52.9	$64.0
Utility Costs	$3.5	$4.9	$5.4
Waste Treatment Costs	$3.7	$0.44	$0.54
Raw Material Costs	$31.9	$31.9	$37.3
Capital Costs	$7.4	$10.7	$11.3
Material Value Added	$9.6	$21.0	$26.7
Profit	$1.6	$14.4	$19.4

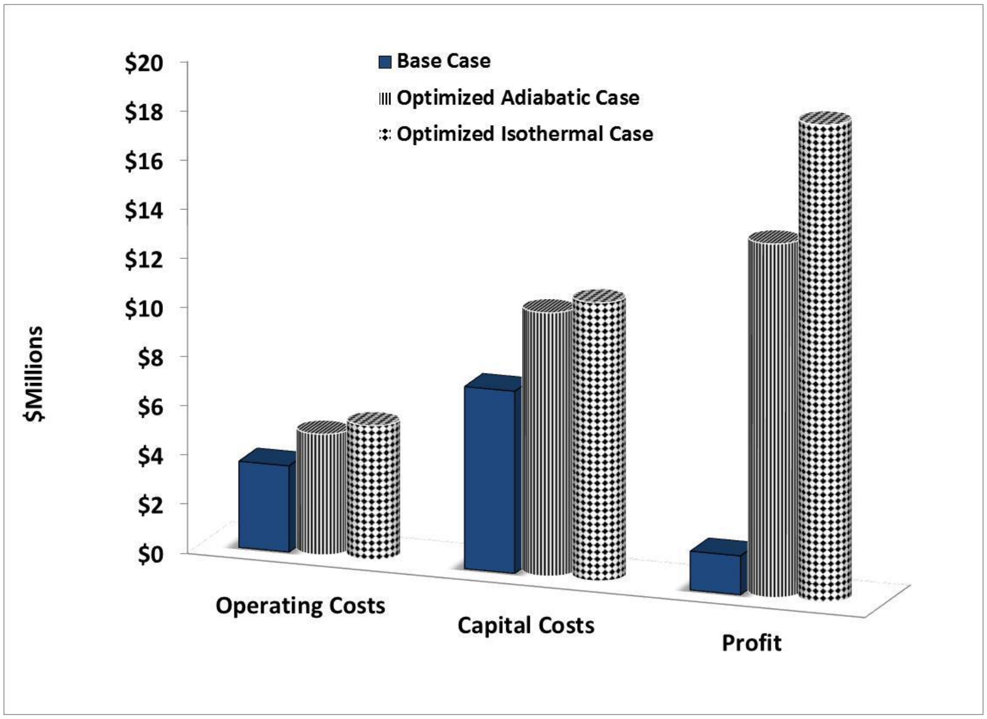

Figure 6.33: Comparison of Economic Assessment of the and Base and Optimized Allyl Chloride Processes

Although both optimized cases had higher operating and capital costs, the waste treatments costs were lower for both cases. The higher capital and operating cost is as result of additional separation equipment to separate the by product. Both cases are more economical compared to the base case and they have an economic impact of 0 compared to the base case which had a value of 0.95. However, the optimized isothermal allyl chloride process is more profitable with a value of $19.2 million.

The environmental impacts of the two optimized cases are evaluated and compared to the base case. The results of comparing the environmental burden of the three options are depicted on the bar chart shown in Figures 6.34 and Table 6.49. As shown in the Figure 6.34, both cases had a significant lower global warming impact compared to the base case. An analysis was completed to investigate the percent reduction for both cases relative to the base case. The adiabatic and isothermal PFR case had 88% and 85% reduction in global warming impact respectively. Hence the adiabatic isothermal PFR case had lower environmental impacts.

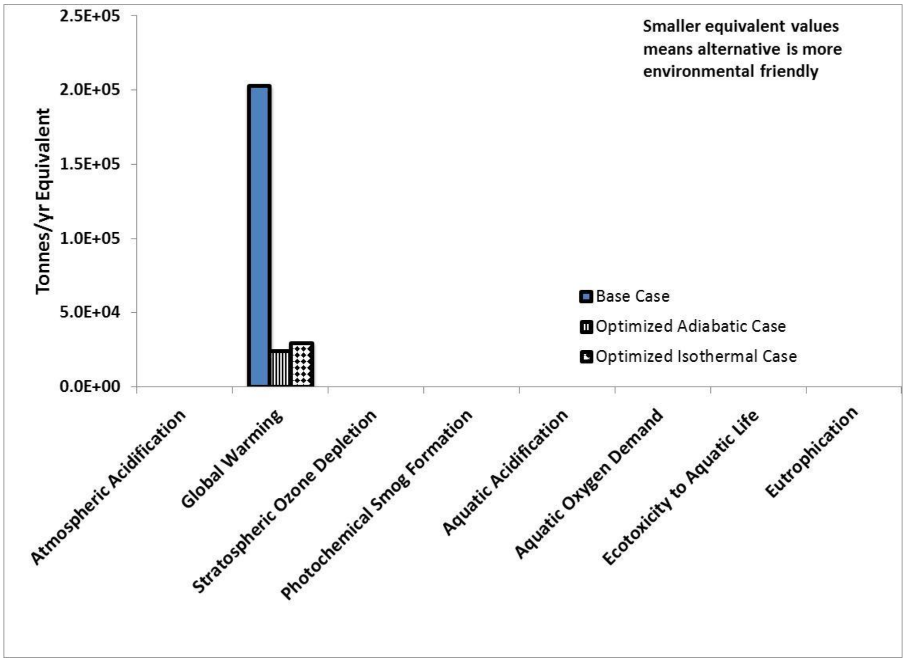

Figure 6.34: Comparison of Environmental Impacts Assessment for the Optimized and Base Cases Allyl Chloride Process

Table 6.49: Environmental Impact Results for Base and Optimized Allyl Chloride Processes

Environmental Impacts	Base Case (Tonnes/year)	Optimized Adiabatic PFR Case	Optimized Isothermal PFR Case
Global Warming	2.03E5	2.4E+04	2.9E+04

The efficiency of the reactions used in ally chloride formation and resource usage for the optimized cases are evaluated and compared with the base case as shown in Table 6.50. As shown in the table, the two optimized cases have a lower E-factor value of 0.1 compared to the base case value which had a value of 0.9. This is because fewer wastes are being produced for the optimized options. The optimized adiabatic PFR case has the highest mass productivity value and lower water intensity because less raw materials and process water were being used to make allyl chloride, while the isothermal PFR case had a higher reaction mass efficiency as smaller amounts raw materials are being used to make allyl chloride.

Table 6.50: Summary of Resource Usage Metrics Results for the Allyl Chloride Base and Optimized Cases

Outputs	Base Case	Optimized Adiabatic PFR Case	Optimized Isothermal PFR Case	Units
E-Factor	0.9	0.1	0.1	Kg/Kg
Mass Productivity	22	34	19	%
Reaction Mass Efficiency	37	38	40	%
Energy Intensity	0.00071	0.0013	0.0012	KW/Kg
Water Intensity	1.8	0.3	2.8	Kg/Kg

Note that energy intensity is higher for the two cases because of the additional separation equipment required to recover the byproducts. Therefore, the optimized adiabatic PFR case is the more efficient process compared to the other two cases. The overall environmental impact for the adiabatic case is 0.10 while the isothermal case is 0.12. This is a substantial improvement because this is lower than the base case which had a value of 0.16.

The health impact of the optimized cases are also evaluated and compared with the base case and this is presented in Table 6.51 and Figure 6.35. From the figure, in general the health risks for the optimized cases are significantly lower compared to the base case. An assessment was completed to determine the percent reduction for each health impact category. As shown in Table 6.51, there is a substantial percent reduction in all categories for both cases. The percent reduction was over 84% for all categories. For both cases, developmental damage had the highest percent reduction of 100% because allyl chloride, the chemical contributing to this health effect is not being emitted

The significant percent reduction is as a result of reducing wastes by a significant amount.

Table 6.51: Comparison of Health Impact Assessment Results from the SUSTAINABILITY EVALUATOR Allyl Chloride Processes

Impact Category	Base Case Impact Value (Tonnes/yr.)	Optimized Adiabatic PFR Impact Value (Tonnes/yr)	Optimized Isotheral PFR Impact Value (Tonnes/yr)	Percent Reduction Adiabatic PFR	Percent Reduction Isothermal PFR
Carcinogenic Risk	9.53E+03	1.11E+03	1.34E+03	88%	86%
Immune System Damage	6.48E+03	7.20E+02	8.46E+02	89%	87%
Skeletal System Damage	0.00E+00	0.00E+00	0.00E+00	N/A	N/A
Developmental Damage	6.16E+01	0.00E+00	0.00E+00	100%	100%
Reproductive System Damage	1.10E+04	1.30E+03	1.59E+03	88%	86%
Kidney Damage	6.48E+03	7.20E+02	8.46E+02	89%	87%
Respiratory System Damage	1.11E+04	1.30E+03	1.59E+03	88%	86%
Cardiovascular System Damage	4.51E+03	5.78E+02	7.44E+02	87%	84%
Endocrine System Damage	4.51E+03	5.78E+02	7.44E+02	87%	84%
Liver Damage	1.11E+04	1.30E+03	1.59E+03	88%	86%
Nervous System Damage	1.11E+04	1.30E+03	1.59E+03	88%	86%
Sensory System Damage	1.10E+04	1.30E+03	1.59E+03	88%	86%

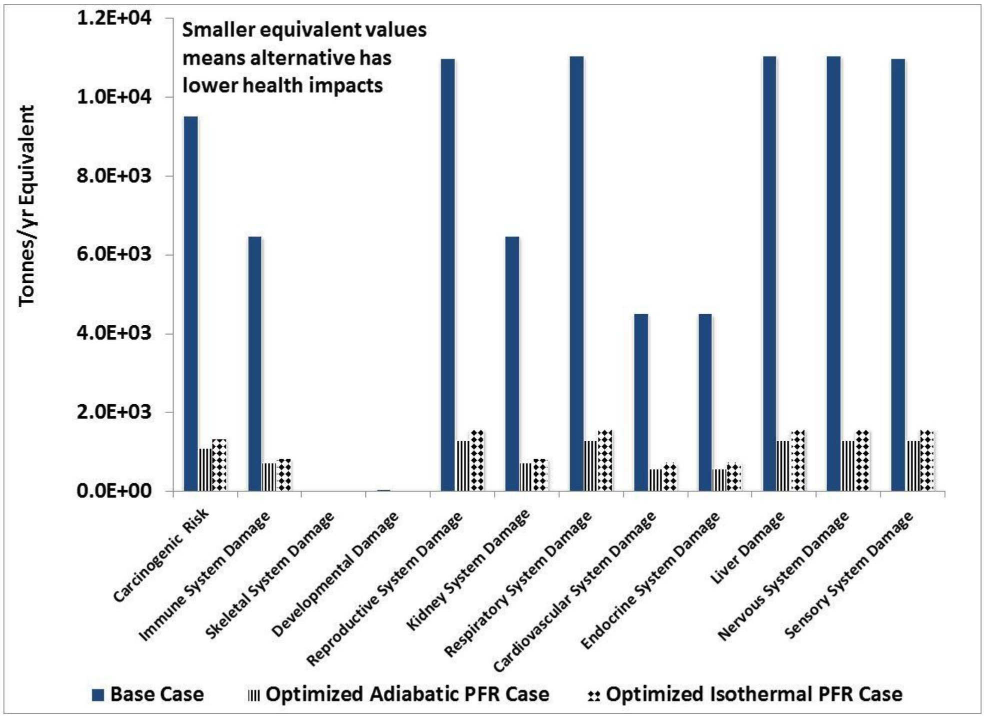

Figure 6.35: Comparison of Health Impacts Assessment the Base and Optimized Allyl Chloride Processes

The safety of the optimized allyl chloride processes was also evaluated and compared with the base case. The process safety index for the base case and the adiabatic PFR case are the same with a value of 58. While the process safety index of the isothermal PFR case increased to 60 because of the higher reaction temperature leading to a larger heat of main reaction index.

It was difficult to really improve the safety index values because this index is based on the chemicals present in the process and the operating temperature and pressure. Significant changes made to the operating conditions would have affected conversion leading to a loss in product formation. Also the process was not directly optimized for safety, so no improvement in safety was expected. An overall social impact was calculated and the optimized cases had a value of 0.43, while the base case had a value of 0.49.

6.4.6 Selection of the Sustainable Allyl Chloride Process

For this study three process options were compared. The first process was the base case allyl chloride process, while the other two options were an optimized modification to the base case. The two optimized cases differed from the base case in that the byproducts were separated through a series of 2 distillation columns and a flash separator. The optimized cases differed from each other by the type of reactor used in the process. The adiabatic PFR case had an overall sustainable impact value of 0.21 while the isothermal PFR case had a value of 0.22. The values calculated for the optimized cases are significantly lower than the base case which has a value of 0.45. Thus the optimized cases are more sustainable compared to the base case. The base case had a profit of $1.6 million but optimization of the process led to improved economics. The optimized isothermal PFR case is more profitable with a value of $19.4 million compared with the adiabatic case which has a value of $14.4 million.

The optimize allyl chloride processes is more environmental friendly because less by products (1, 3-dichloropropene and 1,2-dichloropropane) are produced, thus less wastes. This waste reduction led to improve resource usage metrics and lower environmental impacts. Overall the optimized adiabatic PFR case is more environmental friendly compared to the other two options. In terms of social concerns, the optimized PFR case has a lower health risk compared to the other two cases. Although the isothermal PFR case is 26% more profitable, the optimized adiabatic PFR case is the more sustainable option because it had an overall impact of 0.21 and hence it is more environmental friendly and socially acceptable.

CHAPTER VI

CONCLUSIONS AND FUTURE WORK

7.1 CONCLUSIONS

Adverse environmental changes, stakeholder demands, stricter environmental regulations, financial risks, safety and supply chain pressure have heightened our interest in sustainability. Advancement in industrial activities has led to a threatened environment that affects global sustainability. Hence, the sustainability of processes in industry has gained global attention. There is increasing pressure for processes to become more environmentally friendly and socially acceptable. One way to ensure that the needs of future generations are met and not jeopardized is to ensure that we incorporate sustainability concerns when designing new processes and products.

The perception of how sustainability issues should be addressed in design has changed over time. It is no longer appropriate to evaluate processes for economic feasibility alone; social benefits and environmental impacts must be considered. Addressing sustainability concerns after the fact in chemical process design is no longer acceptable as this could result in more expensive consequences. The ideal approach is to incorporate sustainability concerns into all stages of design to ensure environmental and socially acceptable products and processes. This can be accomplished by evaluating the sustainability of products and processes that are developed as shown in Figure 7.1.

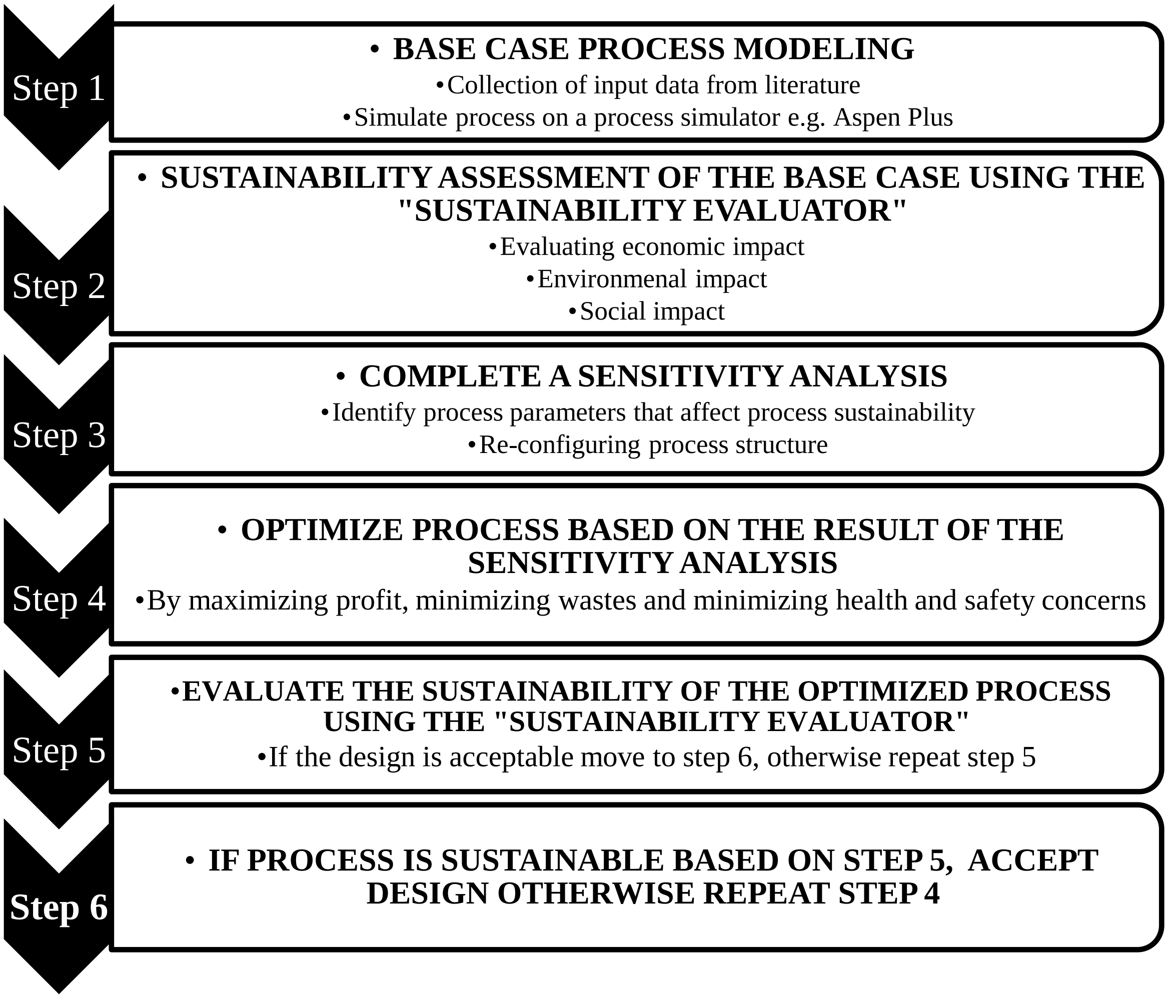

Figure 7.1: Proposed Methodology for Addressing Sustainability Concerns During Early Stages of Design

The main objective of this research was to develop a methodology that incorporates sustainability concerns into chemical process design during early stages. The methodology discussed by this author as summarized in Figure 7.1 and Table 7.1 includes the following: base case process modeling, sustainability assessment of the base case using the SUSTAINABILITY EVALUATOR, completing a sensitivity analysis to identify process parameters that affect process sustainability, process optimization based on the result of sensitivity analysis and impact assessment of the optimized process using the SUSTAINABILITY EVALUATOR.

Table 7.1: Summary of Proposed Methodology

Steps	Action	Tools Used
1	Base Case Process Modeling: In this step, the process is simulated in ASPEN PLUS based on design specification or recommended literature data and mass and energy balances are calculated.	Process Simulator such as ASPEN PLUS
2	Impact Assessment of the Process: In this step, the feed, product and waste streams are identified. Once they have been identified, an impact assessment is completed using the SUSTAINABILITY EVALUATOR. The economic, environmental and social impact of the simulated process is evaluated and an overall sustainability impact is calculated.	SUSTAINABILITY EVALUATOR and ASPEN PLUS
3	Sensitivity Analysis: The objective of this step is to identify parameters that affect the sustainability of a chemical process. Such parameters include varying operating conditions, trying a different type of equipment and process configuration. The goal is to identify parameters that improve profit and reduce waste formation.	ASPEN PLUS
4	Optimization of the Process: After the process has been reconfigured and parameters have been identified, the next step is to optimize the process for sustainability concerns. The goal of the optimization is to maximize profit while minimizing wastes.	ASPEN PLUS
5	Impact Assessment of the Optimized Process: After the process has been optimized it is important to evaluate the process for sustainability and compare the improvements made to the optimized process to the base case. Again an overall sustainability impact is calculated and the value should be lower than the base case	SUSTAINABILITY EVALUATOR
6	Accept Design: If the overall sustainability impact is lower than the base case and the process is economical, the engineer can accept the design. Otherwise the optimization step is repeated.	Designer’s Judgment

The major contribution to this research was the development of a novel impact assessment tool called the SUSTAINABILITY EVALUATOR. This Excel based impact assessment tool was developed based on seven economic metrics, thirteen environmental metrics and twenty one social metrics. The economic, environmental and safety metrics were developed by other researchers Heikkila (1999), Constable et al (2002), IChemE Metrics (2002) but combined in a novel approach.

The novel contribution to the sustainability tool was the introduction of health metrics and the selection of the metrics that apply to process design. Economic, environmental and social indices based on this selected metrics were developed using a ranking approach. Also an overall sustainability impact was developed based on assigning weights to the economic, environmental and social indices. These indices have been incorporated into the impact assessment tool. This impact was normalized from 0 to 1, therefore the lower the impact value, the more sustainable the process is. The impact assessment tool was developed to accomplish the following:

- Evaluate simulated chemical processes for sustainability
- Identify sustainability issues in chemical processes
- Compare processing options and select the most sustainable option
- Determine the overall sustainability impact of an optimized

Apart from the tool’s ability to identify and evaluate sustainability concerns in chemical process, it can also be used to handle both single objective and multiobjective optimization problems in chemical process design. For this research, the tool was used to tackle multiple objective optimization problems by using “a posterior methods implementing scalerization”. This involves combining this multiple objective problem into a single scalar objective by using weight factors.

The proposed impact assessment methodology is innovative for two reasons. The first is that economic, environmental and impact assessments can be evaluated by one tool making it easier for engineers to see how process improvements affect the overall sustainability of a process. Secondly the incorporation of social metrics i.e. health and safety metrics in this way is new as researchers to date haven’t incorporated all three dimensions into process design. Also, an overall sustainability impact was developed. This sustainability index value provides a quantitative number for process designers to evaluate the sustainability of a process.

The impact assessment tool has been used to evaluate the sustainability concerns of the methyl chloride process. In this step, the results from the environmental section of the SUSTAINABILITY EVALUATOR was validated and compared with results obtained from the Waste Reduction Algorithm. This algorithm is a widely accepted screening tool used to evaluate the potential environment impact of chemicals found in a chemical processes. The comparison proved that the two impact assessment tools showed a trend, leading to the conclusion that the SUSTAINABILITY EVALUATOR is a valid environmental impact assessment tool.

After validating the tool, an overall sustainability impact was incorporated into the SUSTAINABILITY EVALUATOR. This overall sustainability impact was developed based on assigning weights to the economic, environmental and social indices. This aids the engineer in having a quantitative number in deciding the sustainability impact of a process. The impact assessment tool is also useful in comparing processes and selecting the best option. This has been demonstrated using the dimethyl ether (DME), acrylonitrile and allyl chloride processes. In the DME case study, two options with different chemistries were evaluated and the most sustainable option was selected. In the acrylonitrile and allyl chloride processes, a sensitivity analysis was first completed to identify parameters that affect the sustainability of the process. Once the parameters have been identified, the processes are optimized with ASPEN PLUS. Next the optimized cases are evaluated and compared with their base cases using the SUSTAINABILITY EVALUATOR. The summary of the results generated for each case study is presented in the next paragraphs.

The SUSTAINABILITY EVALUATOR was used to compare two DME options that differed by reaction pathway and equipment configuration. DME can be manufactured via methanol or via natural gas. The tool was able to assist in selecting the most sustainable process option. DME via methanol dehydration had a lower overall sustainable impact value of 0.11 compared DME via natural gas which had a value of 0.24. The lower impact value was a result of the fact that DME via methanol dehydration had a more efficient reaction process, was safer as less toxic chemicals and less hazardous equipment were present in the process and less wastes were generated in the process. Based on the lower overall sustainable impact obtained from the tool, DME production via methanol dehydration is the more sustainable production option because it is more economical, environmental friendly and socially acceptable compared to the DME production via natural gas.

The overall methodology presented in Figure 7.1 and Table 7.1 was first demonstrated on the acrylonitrile process. The base case acrylonitrile process had several waste streams leading to environmental burdens and health risks. The acrylonitrile process was optimized to maximize profit while minimizing wastes after identifying parameters that affected the sustainability of the process. The optimized acrylonitrile process differed from the base case because the following changes were made to the process: addition of separation equipment to recover raw materials, addition of water recycling stream, reduction of raw material used and optimization of operating conditions. The profit for the base case was \$0.4 million compared to the optimized cases which had a value of \$3.5 million. The improvements made to the optimized acrylonitrile process led to a lower overall sustainability impact value of 0.31 compared to the base case which had a value of 0.45. This impact is calculated based on the results of the economic, environmental and social impacts.

Thus optimized case is more sustainable compared to the base case because less wastes are being generated from the process, the reaction is occurring more efficiently. This aided the conversion to more products using lower quantities of raw materials. This led to an improvement in profit relative to investment, environmental and health impacts, which resulted in a lower overall sustainability impact for the optimized processes. Based on the results obtained from the SUSTAINABLE EVALUATOR, it can be concluded that optimized acrylonitrile process is a more sustainable option compared to the base case because it is more economical viable, environmentally friendly and socially acceptable and has a lower overall sustainability impact value.

The methodology was also demonstrated on the allyl chloride process. The base case process had a waste stream that lead to environmental burdens and health risks. The process was optimized to maximize profit while minimizing wastes after identifying parameters that affected the sustainability of the process. For this study three process options were compared. The first process was the base case allyl chloride process, while the other two options were an optimized modification to the base case. The two optimized cases differed from the base case in that the byproducts were separated through a series of two distillation columns and a flash separator. The optimized cases differed from each other by the type of reactor used in the process. The adiabatic PFR case had an overall sustainable impact of 0.21 while the isothermal PFR case had a value of 0.22.

The sustainability impact value calculated for the optimized allyl chloride cases are significantly lower than the base case which has a value of 0.45. Thus the optimized cases are more sustainable compared to the base case because less wastes are being generated from the process, and the reaction is occurring more efficiently; aiding the conversion to more products using less raw materials. Hence improved profit relative to investment, less environmental and health impacts resulted in lower overall sustainability indices for the optimized processes.

The base case had a profit of $1.6 million but optimization of the process led to improved economics. The optimized isothermal PFR allyl chloride case is more profitable with a value of $19.4 million compared with the adiabatic case which has a value of $14.4 million. The isothermal reactor yielded more products but generated more wastes. Although the isothermal PFR allyl chloride case is 26% more profitable, the optimized adiabatic PFR allyl chloride case is the more sustainable option because it has a lower overall sustainability impact of 0.21 and hence it is more environmental friendly and socially acceptable. This impact is based on the calculated economic, environmental and social impact. The lower overall sustainability impact obtained for the optimized adiabatic PFR case is as a result of less waste emissions.

In summary, this work is significant because a novel framework that incorporates economic, environmental and social concerns into early stages of chemical process design was developed. This framework involved the use of the SUSTAINABILITY EVALUATOR, a newly developed impact assessment tool. This impact assessment tool, established based on metrics, has aided the engineer in identifying and evaluating sustainability concerns during early stages of chemical process design. The tool is useful comparing multiple processes and selecting the most sustainable option. Also it could be used to handle single and multiple objective optimization problems. The proposed methodology also uses ASPEN PLUS to simulate processes, calculate mass and energy balances, complete sensitivity analysis and optimize processes for sustainability. Lastly an overall sustainability impact was developed to quantitatively identify process improvements and select the most sustainable process options.

7.2 FUTURE WORK

Although this work has resulted in significant contributions towards incorporating sustainability concerns into chemical process design, there is still room for improvement in the approaches used in methodology. The following are the suggested research directions to consider:

- Link SUSTAINABILITY EVALUATOR and ASPEN PLUS: Currently the SUSTAINABILITY EVALUATOR is a standalone tool i.e. it has not been linked to ASPEN PLUS. Efforts should be made towards linking the two together by creating a dynamic data exchange link using Fortran and Visual Basic codes. This would make the use of the SUSTAINABILITY EVALUATOR more efficient because the sustainability impact of an ASPEN PLUS simulated process would be automatically calculated when process changes are made. For example, if operating conditions are changed, what is the sustainability impact on the process? This will save time as it will eliminate the need to manually transfer inputs from ASPEN PLUS to the SUSTAINABILITY EVALUATOR.
- Develop an Optimization Framework: The optimization section available in ASPEN PLUS is not robust enough to handle sustainable concerns. This is because only single objective optimization techniques can be solved in ASPEN PLUS. The approach used in this research is single objective optimization where a multiobjective optimization was converted into a single objective by using weights. The problem with this approach is that handling sustainability concerns in chemical process design is a multiobjective optimization problem because there are a wide range of concerns that must be addressed. Converting the problem to a single objective problem might not give optimum results. This was demonstrated in the acrylonitrile and allyl chloride case studies as the safety concerns did not directly improve when the processes were optimized. Therefore, formulating the problem into a multiobjective framework in which economic, environmental and social objectives are formulated is the ideal way to tackle sustainability issues in

process design. As there were forty one different metrics in this research, the next step would be to investigate whether to handle this problem by formulating forty one different objectives functions or whether to consider three major objective functions and thirty eight constraints. To further this work, an improved multiobjective optimization framework that can be connected to the SUSTAINABILITY EVALUATOR and ASPEN PLUS should be developed as shown in Figure 7.2.

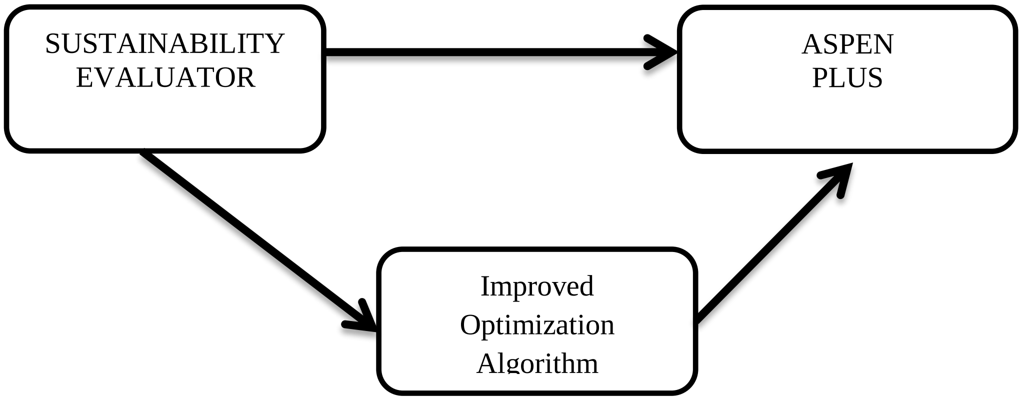

Figure 7.2: Proposed Improved Optimization Framework

- Investigate the sensitivity of the overall sustainability impact: Although an overall sustainability impact was developed, more work should be done to investigate the impact difference that would result in the conclusion that one process is more sustainable than the other. For example, when comparing processes, is there a major difference between processes with an overall sustainability impact difference of 0.01 and or 0.1? What should the impact difference be in order for an engineer to conclude that one process is more sustainable than the other?

- Improve Health Metrics: The author introduced health metrics. The reliability of these metrics has not been validated with a similar tool. Efforts should be made to validate the metrics or improve upon it if needed. Also the method used in handling health concerns is limited in scope as toxicants were classified into only two categories namely, known toxicant or possible toxicant. There are several approaches that could be used to handle health issues in the process industry. These include classifying health risks into chronic versus acute illness. Other approaches could include evaluating the toxicology of chemicals and classifying them into carcinogenic, mutagenic and reprotoxic. The classification of health risks based on illness could also be explored by using information such as inhalation and oral reference concentrations to classify non-carcinogens as well as oral slope factors, oral and inhalation unit risks to classify carcinogens. Efforts should be done to explore other options of handling health risks.
- Improve Impact Assessment Tool: Additional social metrics such as land and water impact according to plant location should be incorporated into the impact assessment tool. Also the scope of the tool is manufacturing focus. Other assessment areas such as cradle to gate assessment should be incorporated. The incorporation of uncertainties should also be investigated. For example, how do changes in certain parameters affect the overall results provided by the SUSTAINABILITY EVALUATOR? Another limitation of this tool is that it does not address scaling effect. For example, how do you compare two production facilities that differ by production rate? More work should be done to investigate how to address this. Lastly, the tool does not evaluate intermediate

streams when assessing safety risks. This is an integral safety issue that should also be addressed.

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APPENDIX A: SUSTAINABILITY EVALUATOR USER MANUAL

SUSTAINABILITY EVALUATOR USER MANUAL

The SUSTAINABILITY EVALUATOR is an impact assessment tool developed for evaluating the sustainability of a process. The metrics that have been used in the sustainability evaluator are described in the “Description of Metrics” section of this manual. This tutorial presents the impact assessment of Dimethyl Ether (DME) production via dehydration of methanol as shown in Equation 1. The schematic for this process is shown below in Figure 1 and the block flow diagram is shown in Figure 2.

$$2\underset{\text{methanol}}{\text{CH}_3\text{OH}} \rightarrow \underset{\text{DME}}{\left(\text{CH}_3\right)_2}\text{O} + \text{H}_2\text{O}$$

(1)

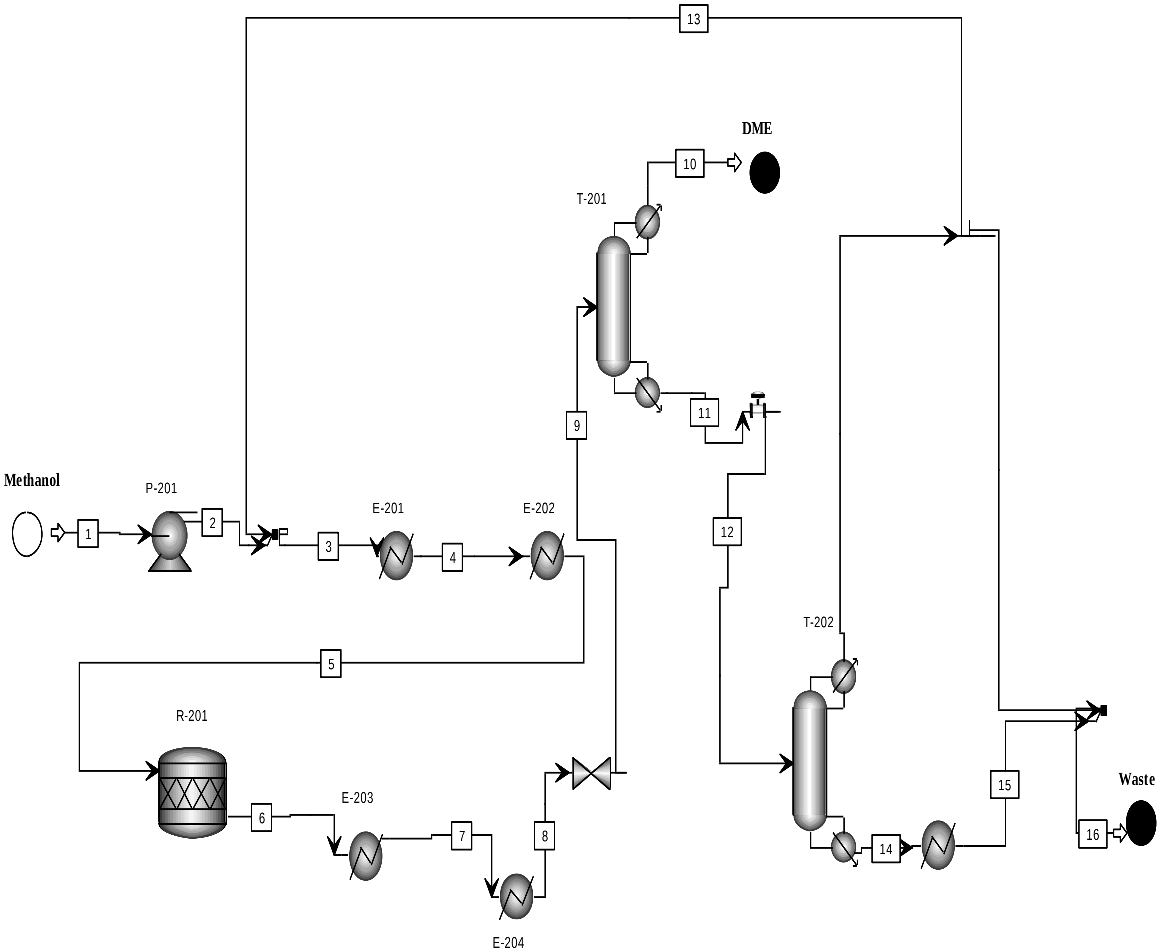


Figure 1: ASPEN Schematic of DME Production via Dehydration of Methanol

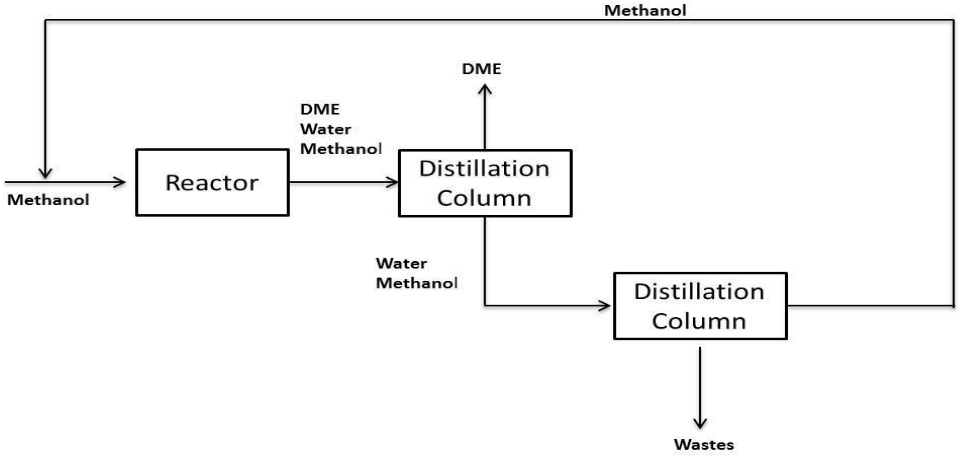


Figure 2: Block flow diagram of DME Production via Dehydration of Methanol

This process is simulated in a chemical process simulator such as ASPEN PLUS. The raw material(s), product(s) and waste streams are identified for this analysis. The identified streams for this process are presented in Table 1. The stream entering and exiting the reactor is identified as well.

Table 1: Identified Raw Material, Product, Waste, Reactor Feed and Exit Streams

	Methanol (Stream 1)	DAME (Stream 10)	Waste (Stream 16)	Reactor In (Stream 5)	Reactor Out (Stream 6)
Temperature (^{o}C)	25.00	46.45	52.33	220.00	364.00
Pressure (bar)	1.00	10.21	1.20	14.70	13.90
Total Flow (kg/year)	7.33E+07	5.23E+07	2.10E+07	9.18E+07	9.18E+07
Mass Flow (kg/year)					
Dimethyl Ether	0.00E+00	5.21E+07	4.34E+03	5.39E+05	5.27E+07
Methanol	7.29E+07	1.68E+05	2.46E+05	9.07E+07	1.81E+07
Water	3.95E+05	8.18E-05	2.08E+07	6.09E+05	2.10E+07
Mass Enthalpy (KJ/Kg)	-7.49E+03	-3.94E+03	-1.57E+04	-6.02E+03	-5.97E+03

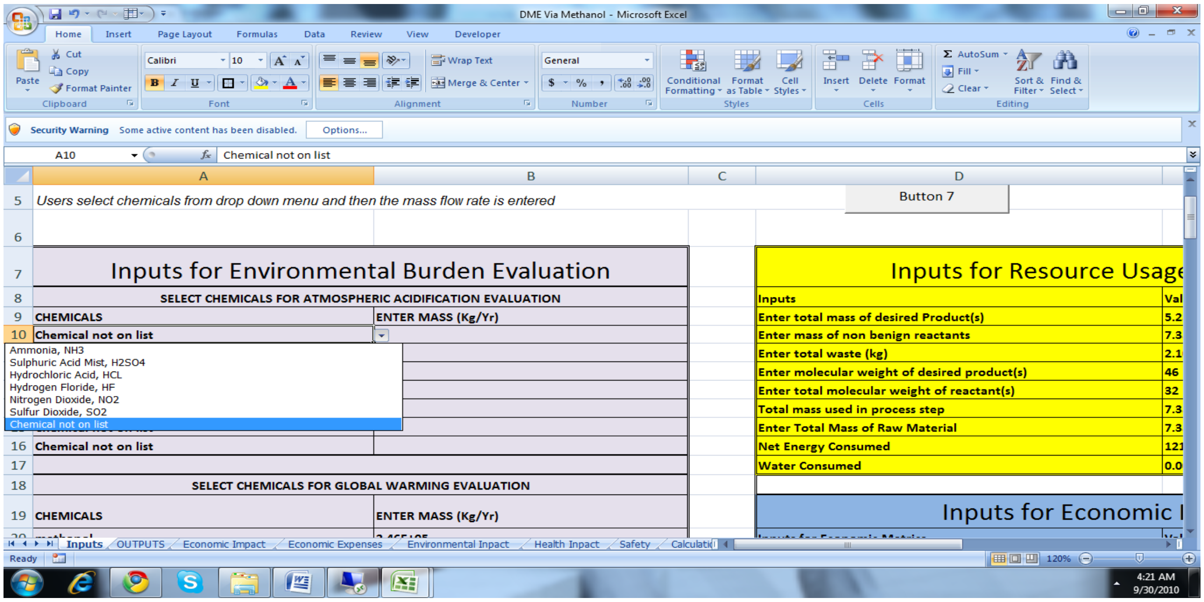
The impact assessment tool is divided into two sections namely Input and Output section.

INPUT SECTION

In the input section, the user selects chemical and inputs mass flow rates, molecular weight, raw material prices etc. The input section is categorized into environmental burden, resource usage, economic impact, health and safety.

<u>Environmental Burden</u>

The environmental burden section is sub divided into eight impact categories. For each category, the chemical(s) contributing to each environmental concern is selected and the mass flow rate in kg/yr is entered as shown in the screen shot in Figure 3. The information on the chemicals is obtained from the waste stream. The steps for completing the environmental impact assessment are described below.



A10 | Chemical not on list

Users select chemicals from drop down menu and then the mass flow rate is entered

Inputs for Environmental Burden Evaluation

SELECT CHEMICALS FOR ATMOSPHERIC ACIDIFICATION EVALUATION

CHEMICALS	ENTER MASS (Kg/Yr)
Chemical not on list	
Chemical not on list	

- Ammonia, NH3
- Sulphuric Acid Mist, H2SO4
- Hydrochloric Acid, HCL
- Hydrogen Floride, HF
- Nitrogen Dioxide, NO2
- Sulfur Dioxide, SO2
- Chemical not on list

SELECT CHEMICALS FOR GLOBAL WARMING EVALUATION

CHEMICALS	ENTER MASS (Kg/Yr)

Inputs for Resource Usage

Inputs	Val
Enter total mass of desired Product(s)	5.2
Enter mass of non benign reactants	7.3
Enter total waste (kg)	2.1
Enter molecular weight of desired product(s)	46
Enter total molecular weight of reactant(s)	32
Total mass used in process step	7.3
Enter Total Mass of Raw Material	7.3
Net Energy Consumed	121
Water Consumed	0.0

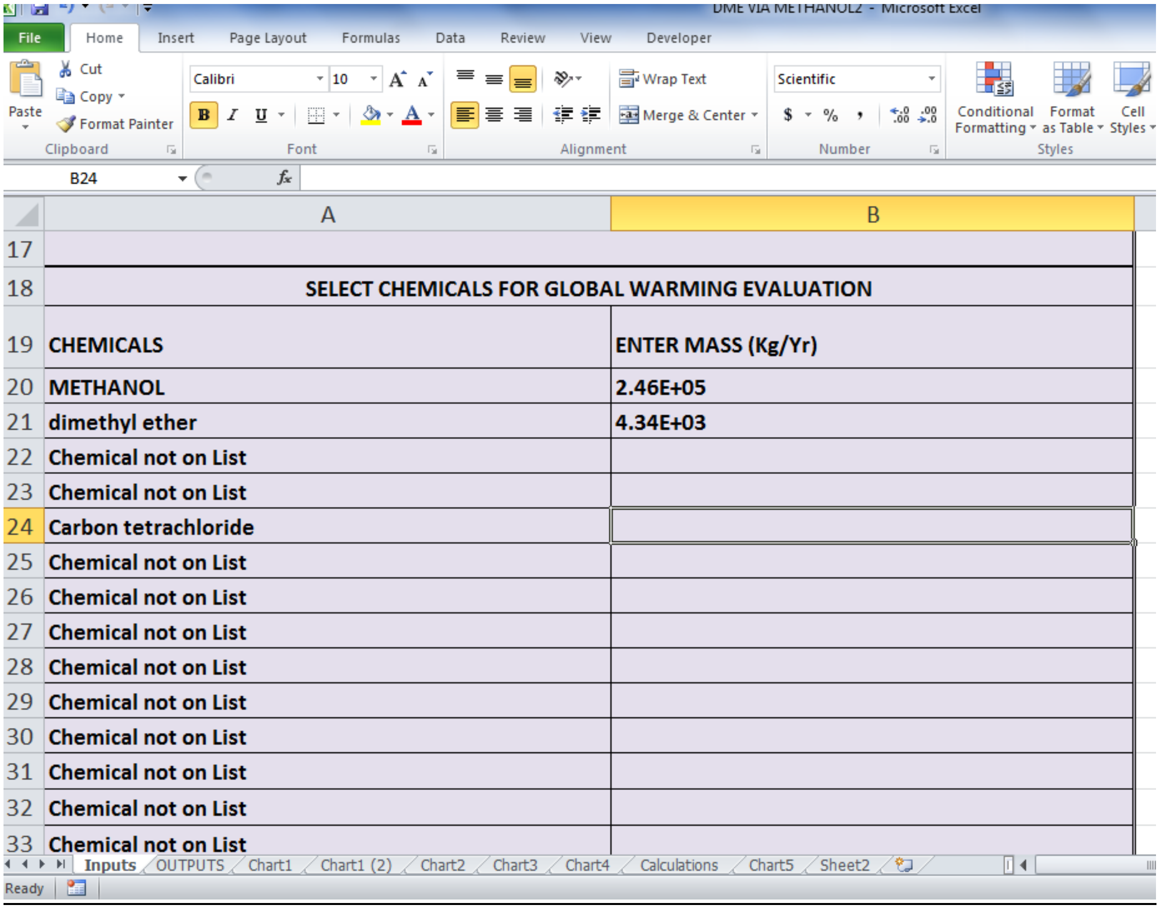
Inputs for Economic I

Figure 3: Screen Shot Demonstrating Selection of Chemicals

Step 1: The first impact category is atmospheric acidification. For this category, because the components present in the waste streams are methanol, DME and water, "chemical not on this list" is selected. This is because the above mentioned chemicals do not lead to atmospheric acidification and therefore the mass flow rate is left blank.

Step 2: The second impact category is global warming. For this category, methanol and DME contribute to global warming. Therefore these two chemicals are selected and the mass flow rate in kg/yr is entered into the tool as shown in the screen shot in Figure 4. This mass flow rates should match with waste stream values shown in Table 1.

Step 3: Repeat steps 1 and 2 for the other six categories. You should have selected chemicals and entered mass flow rates for photochemical smog formation and aquatic oxygen demand.



	A	B
17		
18	SELECT CHEMICALS FOR GLOBAL WARMING EVALUATION	
19	CHEMICALS	ENTER MASS (Kg/Yr)
20	METHANOL	2.46E+05
21	dimethyl ether	4.34E+03
22	Chemical not on List	
23	Chemical not on List	
24	Carbon tetrachloride	
25	Chemical not on List	
26	Chemical not on List	
27	Chemical not on List	
28	Chemical not on List	
29	Chemical not on List	
30	Chemical not on List	
31	Chemical not on List	
32	Chemical not on List	
33	Chemical not on List	

Figure 4: Screen Shot Demonstrating Chemicals that Contribute to Global Warming

Resource Usage

The steps for completing the resource usage assessment are described in the steps below. After completing the steps, your screen should like Figure 5.

Step 1: Enter the total mass flow rate of the desired product shown in Table 1. The desired product is DME and the total mass flow rate is 5.23E+07 kg/yr.

Step 2: Enter the total mass flow rate of non-benign reactant. In this case, the non-benign reactant is methanol and the total mass flow rate is 7.33E+07kg/yr as shown in Table 1.

Step 3: Enter the total waste. In this case total waste mass flow rate 2.10E+07kg/yr as shown in Table 1.

Step 4: Enter the molecular weight of the desired product. In this case the molecular weight of DME is 46 kg/kmol.

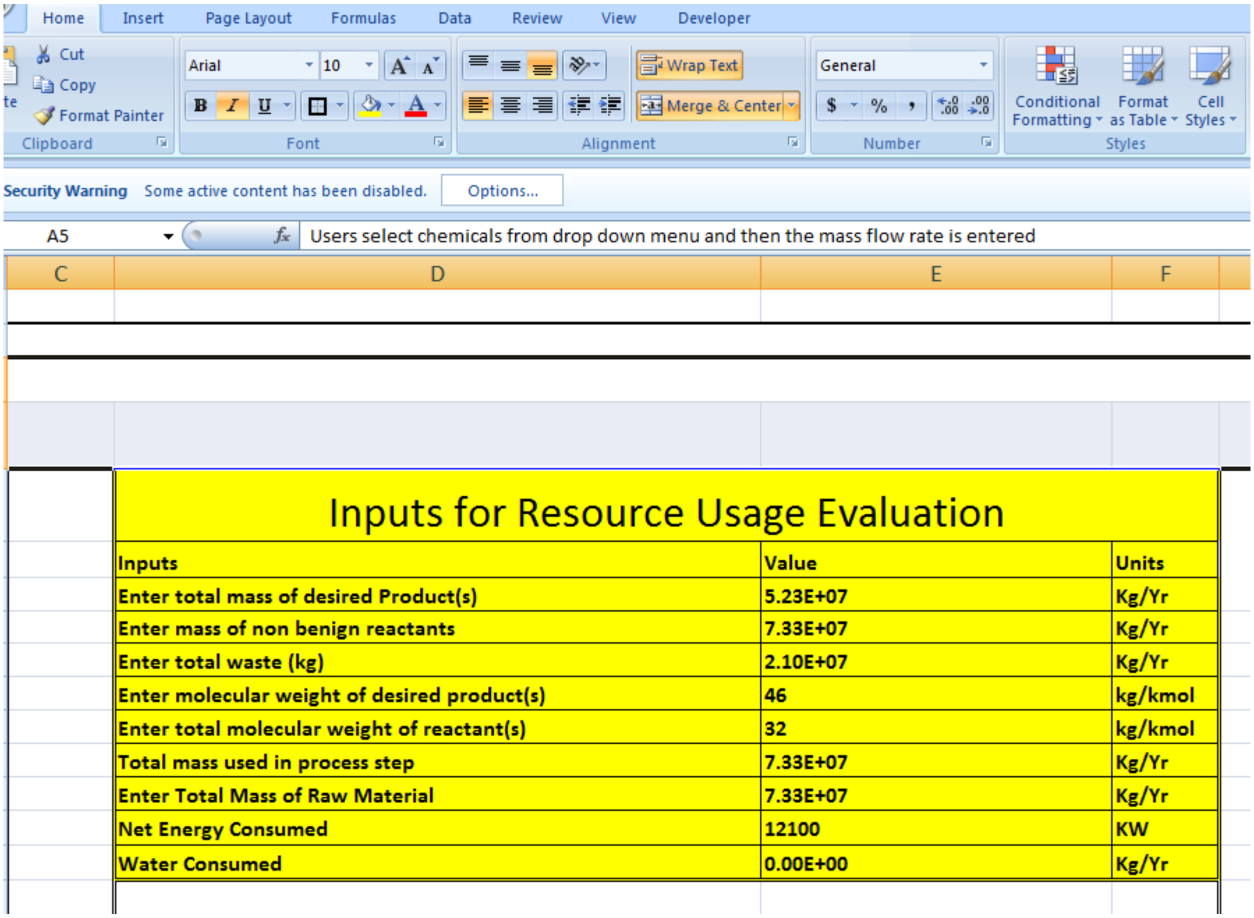
Step 5: Enter the molecular weight of the reactant. In this case the molecular weight of methanol is 32 kg/kmol.

Step 6: Enter total mass used in process steps. These include reactant, solvents or side streams introduced into the process to aid separation of the product. For this process, the total mass used in process step is 7.33E+07kg/yr as shown in Table 1.

Step 7: Enter total mass of raw material. In this case total mass flow rate of methanol is 7.33E+07kg/yr as shown in Table 1.

Step 8: Enter net energy consumed. The net energy consumed is the sum of the energy used by the process equipment. This can be obtained directly from the process simulator. In this case the net energy consumed is 12100KW

Step 9: Enter water consumed. Water is not consumed by this process



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A5 Users select chemicals from drop down menu and then the mass flow rate is entered

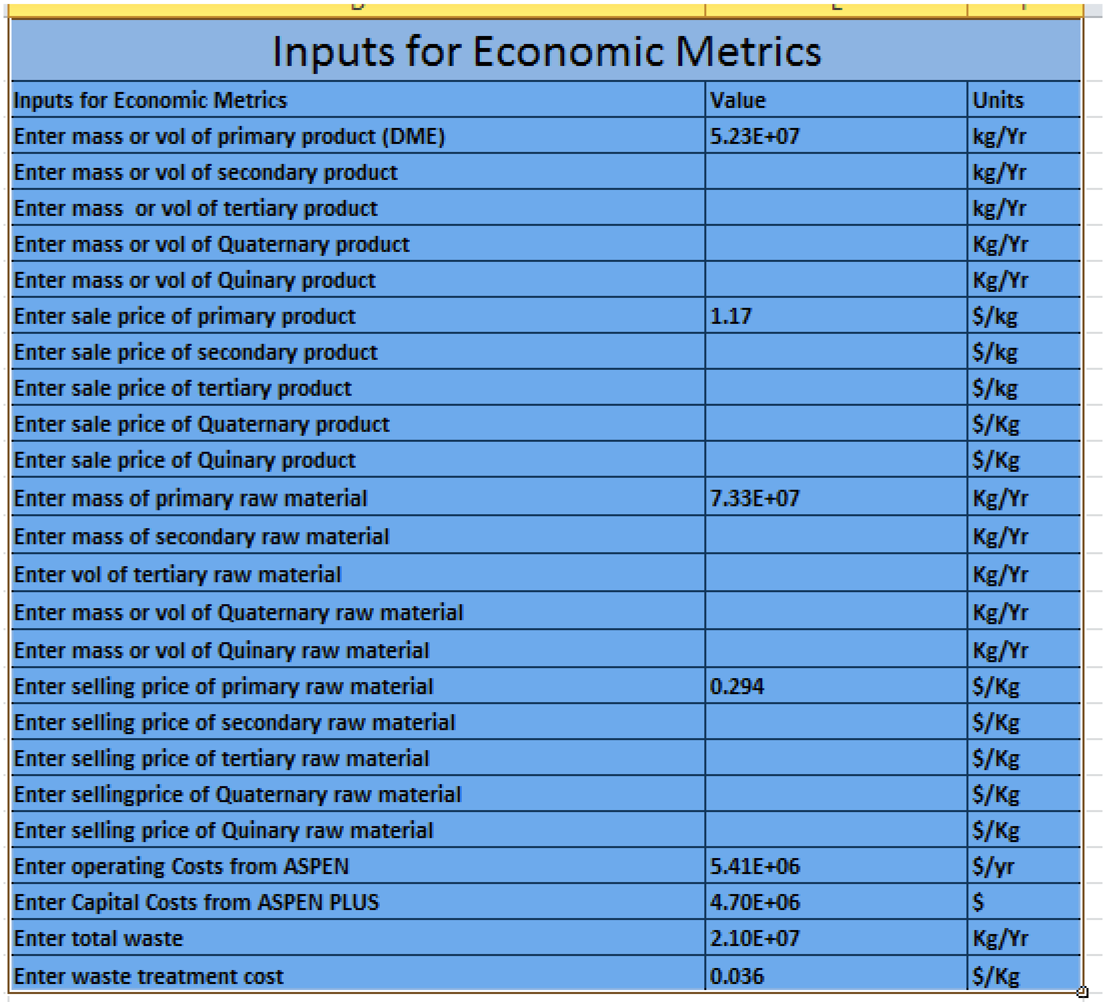
Inputs for Resource Usage Evaluation

Inputs	Value	Units
Enter total mass of desired Product(s)	5.23E+07	Kg/Yr
Enter mass of non benign reactants	7.33E+07	Kg/Yr
Enter total waste (kg)	2.10E+07	Kg/Yr
Enter molecular weight of desired product(s)	46	kg/kmol
Enter total molecular weight of reactant(s)	32	kg/kmol
Total mass used in process step	7.33E+07	Kg/Yr
Enter Total Mass of Raw Material	7.33E+07	Kg/Yr
Net Energy Consumed	12100	KW
Water Consumed	0.00E+00	Kg/Yr

Figure 5: Screen Shot Demonstrating Inputs for Resource Usage

Economics

The steps for completing the economic assessment are described in the steps below. After following the steps, your screen should like the screen shot shown in Figure 6.



Inputs for Economic Metrics

Inputs for Economic Metrics	Value	Units
Enter mass or vol of primary product (DME)	5.23E+07	kg/Yr
Enter mass or vol of secondary product		kg/Yr
Enter mass or vol of tertiary product		kg/Yr
Enter mass or vol of Quaternary product		Kg/Yr
Enter mass or vol of Quinary product		Kg/Yr
Enter sale price of primary product	1.17	$/kg
Enter sale price of secondary product		$/kg
Enter sale price of tertiary product		$/kg
Enter sale price of Quaternary product		$/Kg
Enter sale price of Quinary product		$/Kg
Enter mass of primary raw material	7.33E+07	Kg/Yr
Enter mass of secondary raw material		Kg/Yr
Enter vol of tertiary raw material		Kg/Yr
Enter mass or vol of Quaternary raw material		Kg/Yr
Enter mass or vol of Quinary raw material		Kg/Yr
Enter selling price of primary raw material	0.294	$/Kg
Enter selling price of secondary raw material		$/Kg
Enter selling price of tertiary raw material		$/Kg
Enter sellingprice of Quaternary raw material		$/Kg
Enter selling price of Quinary raw material		$/Kg
Enter operating Costs from ASPEN	5.41E+06	$/yr
Enter Capital Costs from ASPEN PLUS	4.70E+06	$
Enter total waste	2.10E+07	Kg/Yr
Enter waste treatment cost	0.036	$/Kg

Figure 5: Screen Shot Demonstrating Inputs for Economics

Step 1: Enter the total mass flow rate of the primary product. This is obtained from Table 1 and the desired product is DME and the total mass flow rate is 5.23E+07 kg/yr. Note that in many reactions, there might be more than one product. If this is the case, the mass flow rates are also entered.

Step 2: Enter selling price of the primary product(s). In this case the selling price for DME is $1.17/kg. If there are other products, their selling prices are also entered.

Step 3: Enter the total mass flow rate of the primary raw material. In this example, the methanol mass flow rate obtained from Table 1 is 5.23E+07 kg/yr.

Step 4: Enter selling price of the primary raw material. In this case the selling price for methanol is \$0.294/kg. If there are other raw materials or feed streams, their selling prices are also entered.

Step 5: Enter operating costs. The operating cost for the methyl chloride process is obtained from ASPEN PLUS and entered. In this case the value is \$3.20E+06 /yr.

Step 6: Enter capital costs. The capital cost for the methyl chloride process is obtained from ASPEN PLUS and entered. In this case the value is \$4.30E+06 /yr.

Step 7: Enter total waste. In this case total waste mass flow rate 2.10E+07kg/yr as shown in Table 1.

Step 8: Enter waste treatment costs. The waste treatment costs for this process is \$36/1000kg.

Safety Metrics

The steps for completing the safety assessment are described in the steps below. After following the steps described below, your screen should like the screen shot shown in Figure 7.

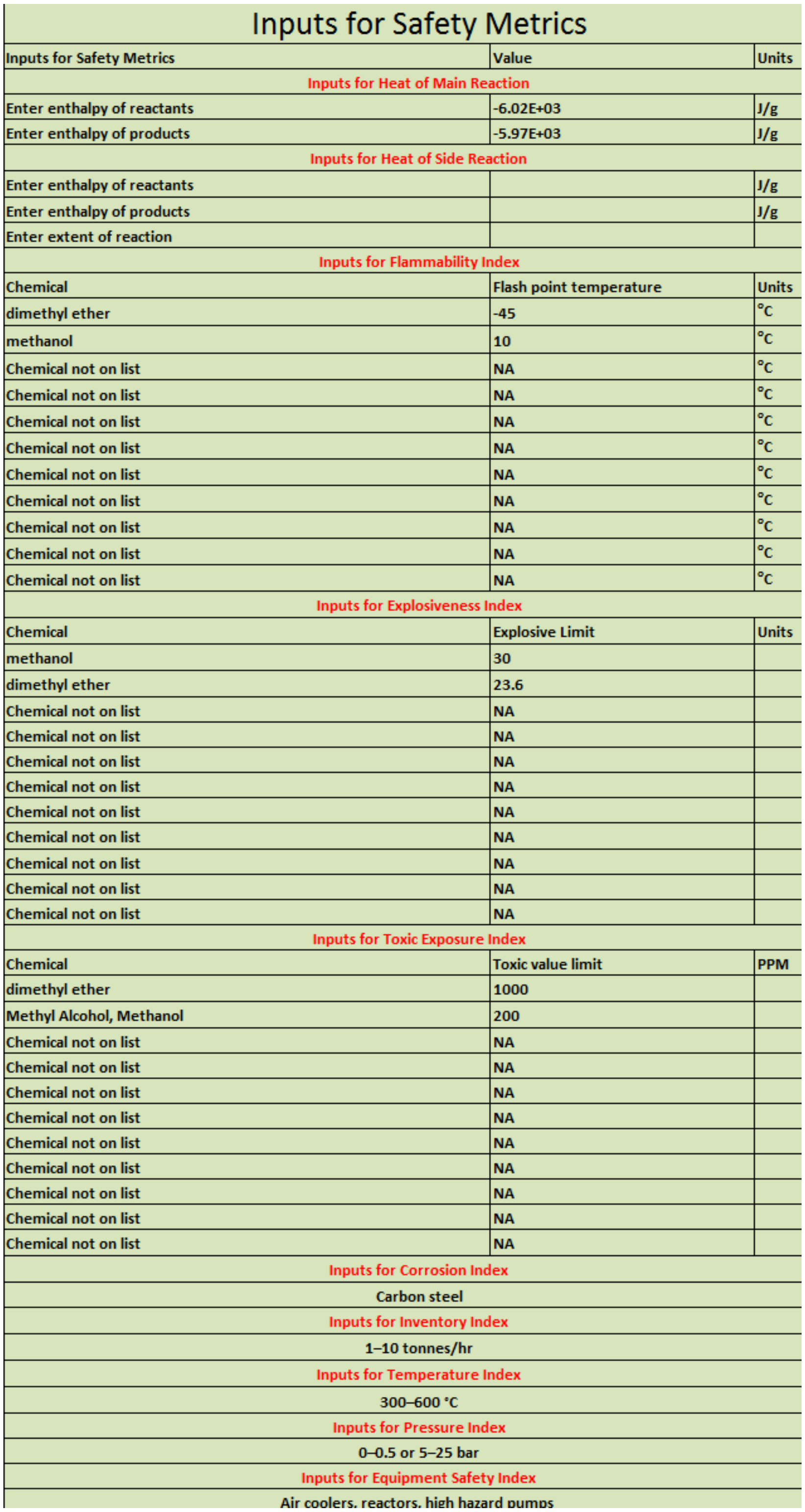
Step 1: Enter the mass enthalpy of the reactants. This information is obtained from the stream entering the reactor. As shown Table 1, the mass enthalpy value is -6.02E+03KJ/KG.

Step 2: Enter the mass enthalpy of the product. This information is obtained from the stream exiting the reactor. As shown Table 1, the mass enthalpy value is 5.97E+03KJ/KG.

Step 1 and 2 are repeated if there are other reactors and inputted in the side reaction section of the SUSTAINABILITY EVALUATOR.

Step 3: Select Chemical for Flammability Index. The chemicals are selected in the drop down menu as shown in Figure 8. For this process, only DME and methanol are flammable, thus they are selected and the flash point temperature is supplied by the tool. If the chemical is not found in the drop down menu, then “chemical not on the list” is selected.

Step 4: Select Chemical for Explosivity Index. The chemicals are selected in the drop down menu. For this process, only DME and methanol are considered to be explosive, thus they are selected and the explosive limit is supplied by the tool. If the chemical is not found in the drop down menu, then “chemical not on the list” is selected.



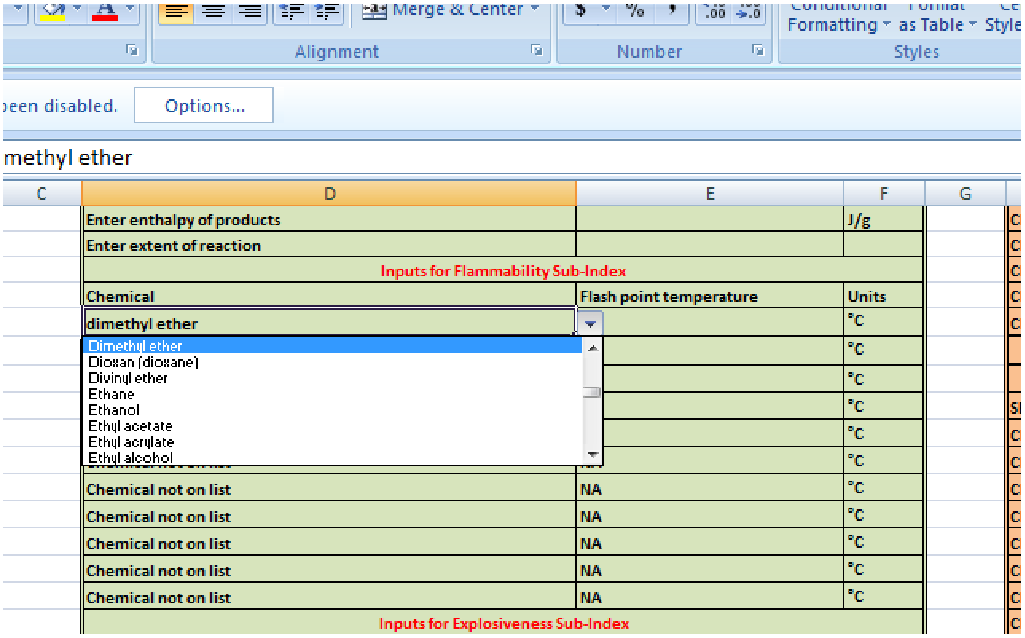
Inputs for Safety Metrics

Inputs for Safety Metrics	Value	Units
Inputs for Heat of Main Reaction		
Enter enthalpy of reactants	-6.02E+03	J/g
Enter enthalpy of products	-5.97E+03	J/g
Inputs for Heat of Side Reaction		
Enter enthalpy of reactants		J/g
Enter enthalpy of products		J/g
Enter extent of reaction		
Inputs for Flammability Index		
Chemical	Flash point temperature	Units
dimethyl ether	-45	°C
methanol	10	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Inputs for Explosiveness Index		
Chemical	Explosive Limit	Units
methanol	30	
dimethyl ether	23.6	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Inputs for Toxic Exposure Index		
Chemical	Toxic value limit	PPM
dimethyl ether	1000	
Methyl Alcohol, Methanol	200	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Chemical not on list	NA	
Inputs for Corrosion Index		
Carbon steel		
Inputs for Inventory Index		
1–10 tonnes/hr		
Inputs for Temperature Index		
300–600 °C		
Inputs for Pressure Index		
0–0.5 or 5–25 bar		
Inputs for Equipment Safety Index		
Air coolers, reactors, high hazard pumps		

Figure 7: Screen Shot of Safety Inputs

Step 5: Select Chemical for Exposure Index. The chemicals are selected in the drop down menu. For this process, only DME and methanol are considered to be chemicals that can harm human health, thus they are selected and the toxic limit value is supplied by the tool. If the chemical is not found in the drop down menu, then "chemical not on the list" is selected.

Step 6: Select material for Corrosion Index. Several chemicals are considered corrosive and strong material of construction might be needed. For example strong acids such as hydrochloric acid can corrode process equipment made from stainless steel or carbon steel. Thus "better material is needed" is selected if this is the case. For this process, DME or methanol are not corrosive thus carbon steel is selected from the drop down menu.



methyl ether

D	E	F
Enter enthalpy of products		J/g
Enter extent of reaction		
Inputs for Flammability Sub-Index		
Chemical	Flash point temperature	Units
dimethyl ether		°C
		°C
		°C
		°C
		°C
		°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Chemical not on list	NA	°C
Inputs for Explosiveness Sub-Index		

Figure 8: Screen Shot Demonstrating Selection of Chemicals for Flammability Index

Step 7: Select inputs for Inventory Index. The range of mass flow rate of the amount of main product being produced is selected in tones/hr. For the DME process, the inventory range is 1-10 tonnes/hr .

Step 8: Select inputs for Temperature Index. The highest operating temperature of the process is selected. For the DME process, the temperature range is between 300-600 ^{o}C.

Step 9: Select inputs for Pressure Index. The highest operating pressure of the process is selected. For the DME process, the temperature range is between 0–0.5 or 5–25 bar.

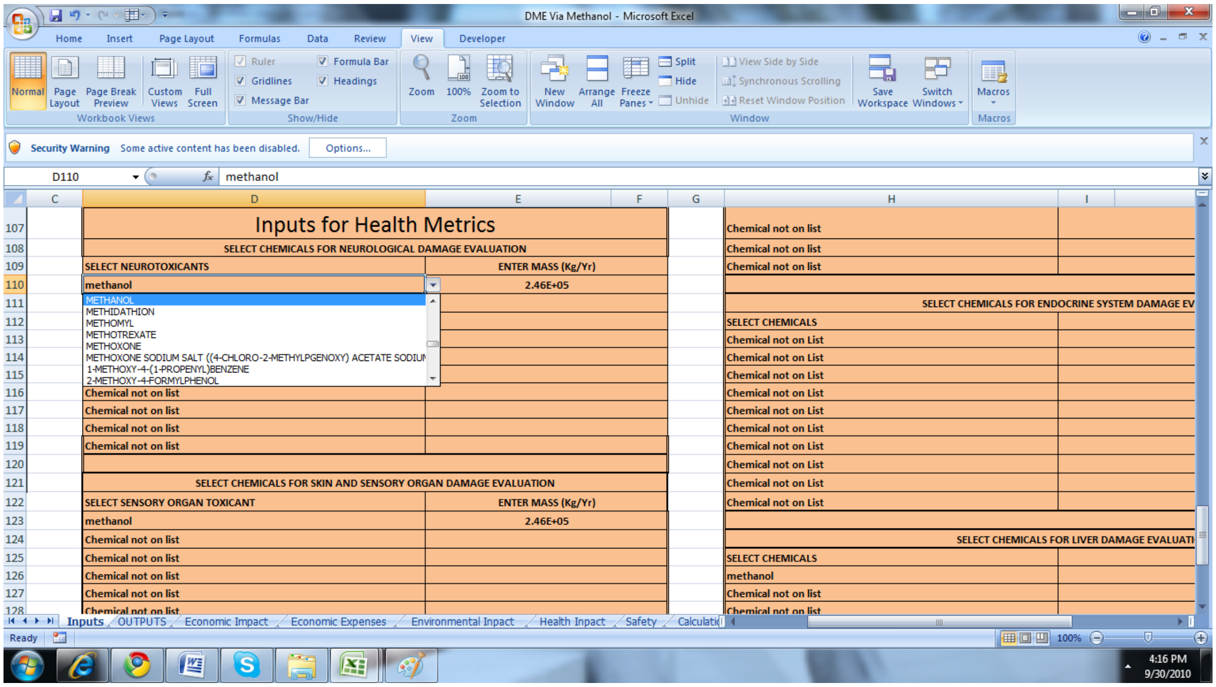
Step 10: Select inputs for Equipment Index: The highest risk equipment present in the process is selected. For this process, “air coolers, reactors, high hazard pumps” is selected because a reactor is present in the process.

Step 11: Inputs for Safety Level of Process Structure Index: Here the safety level is selected and because there is no information of safety incidents relating to DME production, “No data or neutral” is selected.

Health Impact

The health impact is sub divided into eleven impact categories. For each category, the chemical(s) contributing to each health concern is selected and the mass flow rate in kg/yr is entered as shown in the screen shot in Figure 9. The information on the chemicals is obtained from the waste stream. The steps for completing the health impact assessment are described below.

Step 1: The first impact category is Neurological Damage Evaluation. For this category, because the only components present in the waste streams that leads to this health risk is methanol, this chemical is selected from the drop down menu and the mass flow rate is entered as shown in Figure 9.



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D110 methanol

	C	D	E	F	G	H	I
107		Inputs for Health Metrics				Chemical not on list	
108		SELECT CHEMICALS FOR NEUROLOGICAL DAMAGE EVALUATION				Chemical not on list	
109		SELECT NEUROTOXICANTS	ENTER MASS (Kg/Yr)			Chemical not on list	
110		methanol	2.46E+05				
111		METHANOL				SELECT CHEMICALS FOR ENDOCRINE SYSTEM DAMAGE EV	
112		METHIDATHION				SELECT CHEMICALS	
113		METHOMYL				Chemical not on List	
114		METHOTREXATE METHOXONE				Chemical not on List	
115		METHOXONE SODIUM SALT ((4-CHLORO-2-METHYLPGENOXY) ACETATE SODIU 1-METHOXY-4-(1-PROPENYL)BENZENE 2-METHOXY-4-FORMYLPHENOL				Chemical not on List	
116		Chemical not on list				Chemical not on List	
117		Chemical not on list				Chemical not on List	
118		Chemical not on list				Chemical not on List	
119		Chemical not on list				Chemical not on List	
120						Chemical not on List	
121		SELECT CHEMICALS FOR SKIN AND SENSORY ORGAN DAMAGE EVALUATION				Chemical not on List	
122		SELECT SENSORY ORGAN TOXICANT	ENTER MASS (Kg/Yr)			Chemical not on List	
123		methanol	2.46E+05				
124		Chemical not on list				SELECT CHEMICALS FOR LIVER DAMAGE EVALUATI	
125		Chemical not on list				SELECT CHEMICALS	
126		Chemical not on list				methanol	
127		Chemical not on list				Chemical not on list	
128		Chemical not on list				Chemical not on list	

Figure 9: Screen Shot Demonstrating Selection of Chemicals for Health Impact Assessment

This procedure is repeated for the other 10 health impact category. If the chemical is not on the list for any impact category, "Chemical not on the list" is selected. For this assessment you should have selected chemicals and entered inputs for the following: developmental damage, respiratory system damage, liver damage and endocrine damage.

OUTPUT SECTION

The results of the assessments are presented in six tabs namely: Output, Economic Impact Economic expense, Environmental Impact and Health Impact. The output tab provides the results of all the five categories discussed earlier. The results are presented in the screen shot shown in Figure 14. These results are graphed in the other five tabs as shown in Figures 10-13.

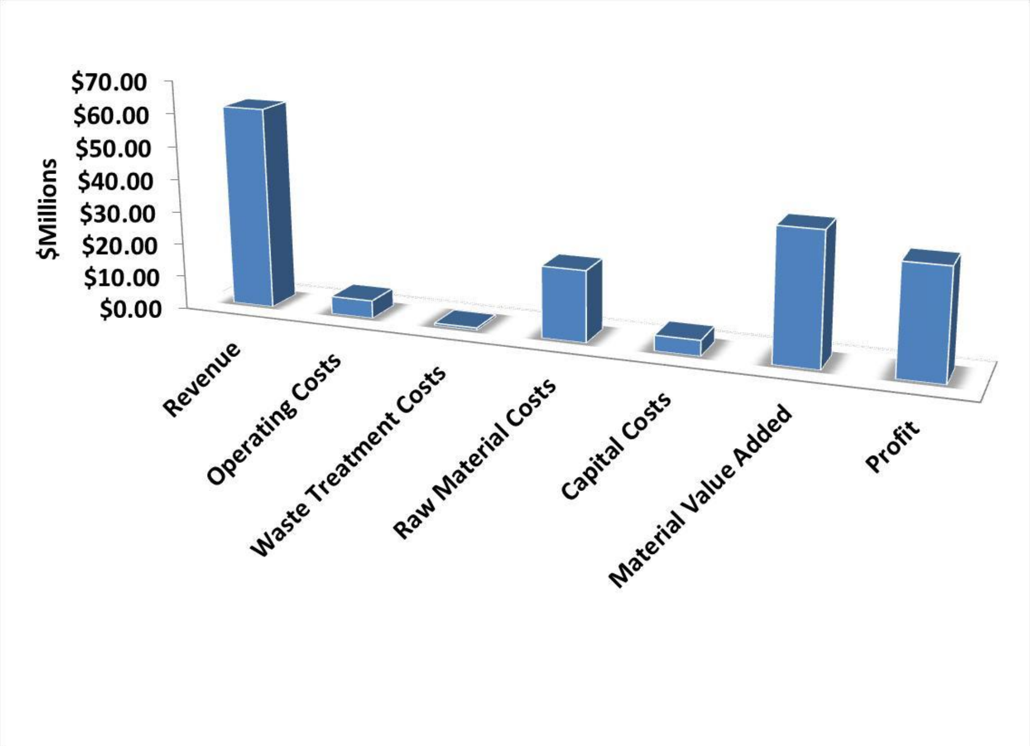


Figure 10: Bar Chart Showing Results Located in the Economic Impact Section of the Tool

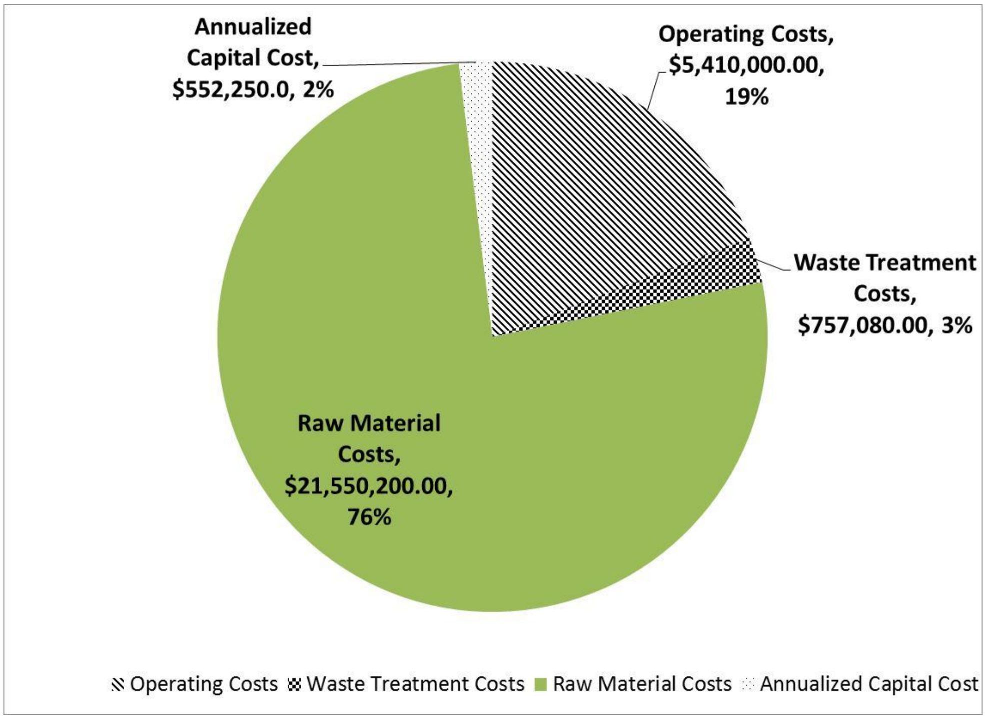


Figure 11: Pie Chart Showing Results Located in the Economic Impact Section of the Tool

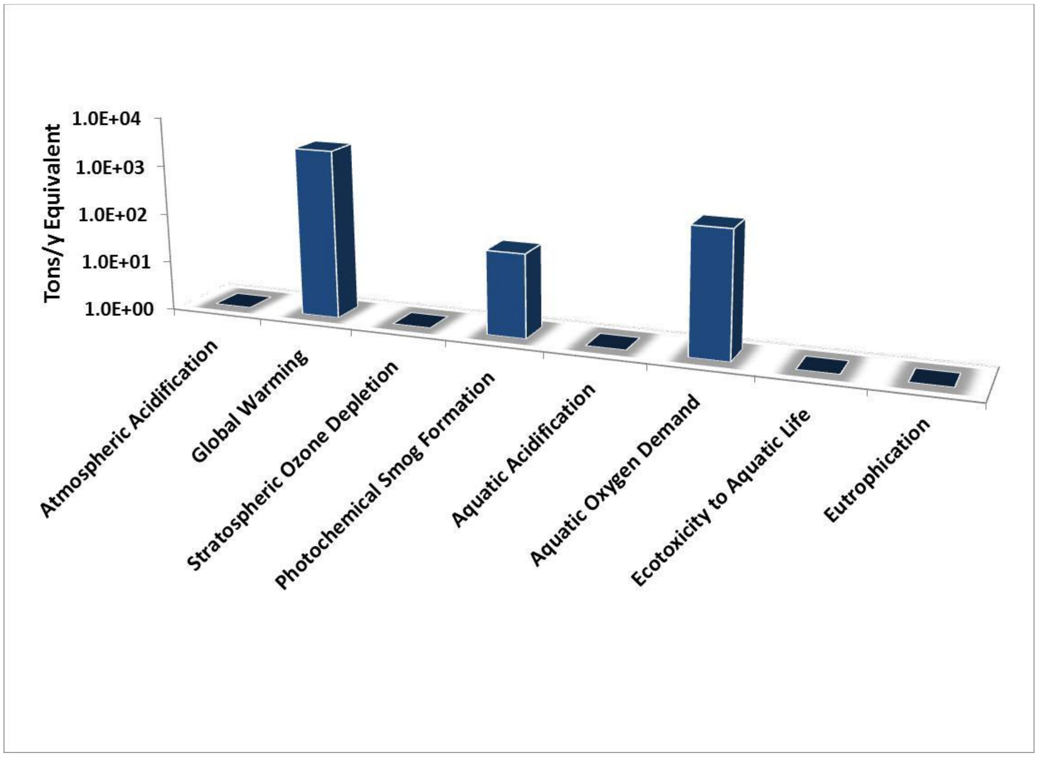


Figure 12: Bar Chart showing Results Located in the Environmental Impact Section of the Tool

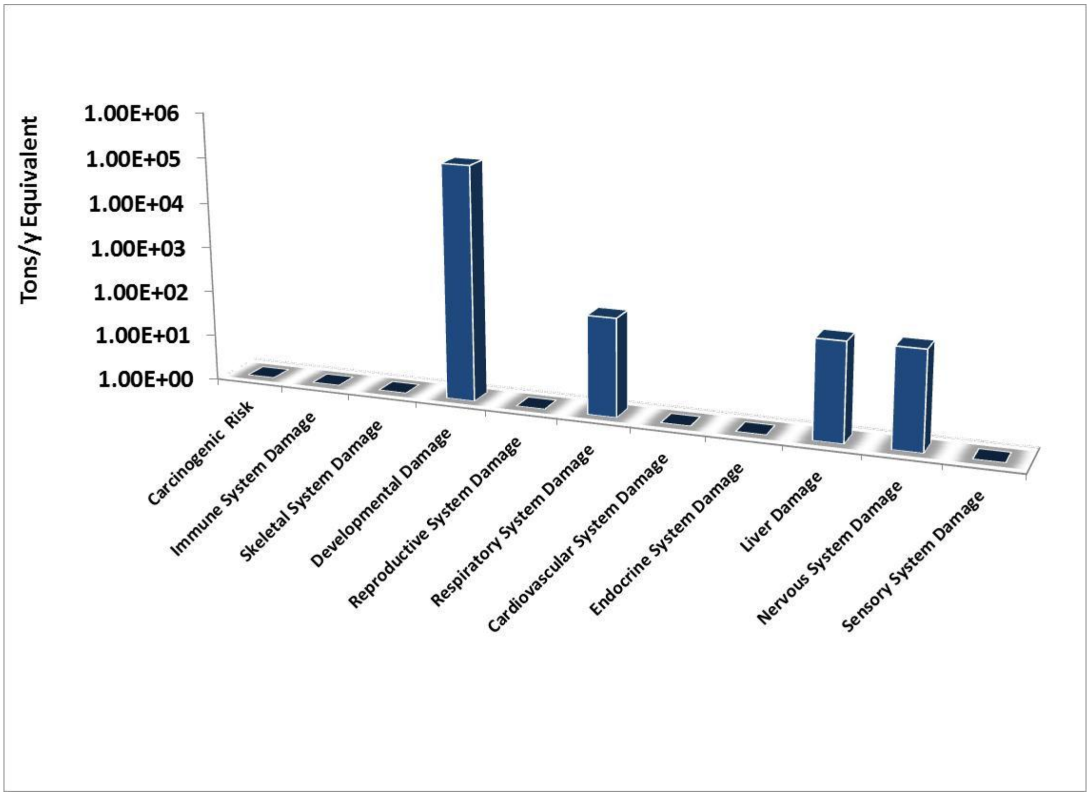
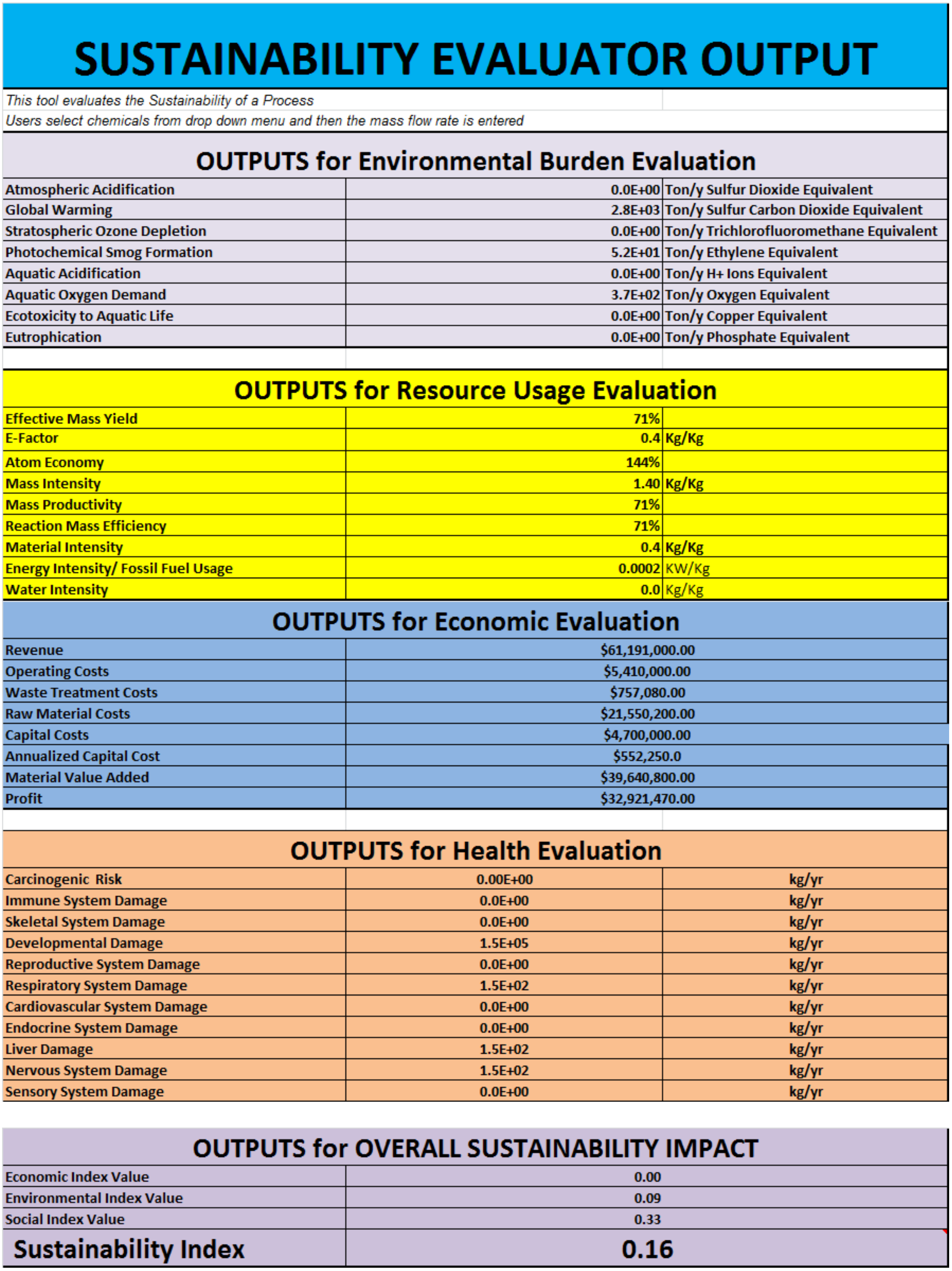


Figure 12: Bar Chart Showing Results Located in the Health Impact Section of the Tool



SUSTAINABILITY EVALUATOR OUTPUT

This tool evaluates the Sustainability of a Process

Users select chemicals from drop down menu and then the mass flow rate is entered

OUTPUTS for Environmental Burden Evaluation

Atmospheric Acidification	0.0E+00	Ton/y Sulfur Dioxide Equivalent
Global Warming	2.8E+03	Ton/y Sulfur Carbon Dioxide Equivalent
Stratospheric Ozone Depletion	0.0E+00	Ton/y Trichlorofluoromethane Equivalent
Photochemical Smog Formation	5.2E+01	Ton/y Ethylene Equivalent
Aquatic Acidification	0.0E+00	Ton/y H+ Ions Equivalent
Aquatic Oxygen Demand	3.7E+02	Ton/y Oxygen Equivalent
Ecotoxicity to Aquatic Life	0.0E+00	Ton/y Copper Equivalent
Eutrophication	0.0E+00	Ton/y Phosphate Equivalent

OUTPUTS for Resource Usage Evaluation

Effective Mass Yield	71%	
E-Factor	0.4	Kg/Kg
Atom Economy	144%	
Mass Intensity	1.40	Kg/Kg
Mass Productivity	71%	
Reaction Mass Efficiency	71%	
Material Intensity	0.4	Kg/Kg
Energy Intensity/ Fossil Fuel Usage	0.0002	KW/Kg
Water Intensity	0.0	Kg/Kg

OUTPUTS for Economic Evaluation

Revenue	$61,191,000.00
Operating Costs	$5,410,000.00
Waste Treatment Costs	$757,080.00
Raw Material Costs	$21,550,200.00
Capital Costs	$4,700,000.00
Annualized Capital Cost	$552,250.0
Material Value Added	$39,640,800.00
Profit	$32,921,470.00

OUTPUTS for Health Evaluation

Carcinogenic Risk	0.00E+00	kg/yr
Immune System Damage	0.0E+00	kg/yr
Skeletal System Damage	0.0E+00	kg/yr
Developmental Damage	1.5E+05	kg/yr
Reproductive System Damage	0.0E+00	kg/yr
Respiratory System Damage	1.5E+02	kg/yr
Cardiovascular System Damage	0.0E+00	kg/yr
Endocrine System Damage	0.0E+00	kg/yr
Liver Damage	1.5E+02	kg/yr
Nervous System Damage	1.5E+02	kg/yr
Sensory System Damage	0.0E+00	kg/yr

OUTPUTS for OVERALL SUSTAINABILITY IMPACT

Economic Index Value	0.00
Environmental Index Value	0.09
Social Index Value	0.33
Sustainability Index	**0.16**

Figure 14: Screen Shot Showing Results Located in the Output Section of the Tool

APPENDIX B: INPUT FILE FOR THE FOLLOWING CASE STUDIES: METHYL CHLORIDE, DIMETHYL ETHER, ACRYLONITRILE AND ALLYL CHLORIDE

DIMETHYL ETHER VIA DEHYDRATION OF METHANOL INPUT FILE

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
      PDROP=bar

DEF-STREAMS CONVEN ALL

SIM-OPTIONS
   IN-UNITS ENG
   SIM-OPTIONS OLD-DATABANK=YES

DESCRIPTION "
   General Simulation with Metric Units :
   C, bar, kg/hr, kmol/hr, Gcal/hr, cum/hr.

   Property Method: None

   Flow basis for input: Mole

   Stream report composition: Mole flow
   "
DATABANKS PURE10  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      NOASPENPCD

PROP-SOURCES PURE10  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
   DIMET-01 C2H6O-1 /
   METHA-01 CH4O /
   WATER H2O

FLOWSHEET
   BLOCK B1 IN=1 OUT=2
   BLOCK E201 IN=3 OUT=4
   BLOCK E202 IN=4 OUT=5
   BLOCK B6 IN=5 OUT=6
   BLOCK E-203 IN=6 OUT=7
   BLOCK B8 IN=7 OUT=8
   BLOCK B9 IN=8 OUT=9
   BLOCK B10 IN=9 OUT=10 11
   BLOCK B13 IN=11 OUT=12
   BLOCK B14 IN=12 OUT=B 14
```

```
    BLOCK B15 IN=14 OUT=15
    BLOCK B2 IN=2 13 OUT=3
    BLOCK B5 IN=B OUT=13 PURGE
    BLOCK B3 IN=15 PURGE OUT=16

PROPERTIES NRTL-RK FREE-WATER=STEAM-TA
    PROPERTIES IDEAL / NRTL / PENG-ROB / SRK / STEAMNBS /
        STMNBS2

PROP-DATA NRTL-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar
    PROP-LIST NRTL
    BPVAL DIMET-01 METHA-01 0.0 -18.93720000 .2951000000 0.0  &
        0.0 0.0 0.0 0.0
    BPVAL METHA-01 DIMET-01 0.0 653.0063000 .2951000000 0.0  &
        0.0 0.0 0.0 0.0
    BPVAL METHA-01 WATER -.6930000000 172.9871000 .3000000000  &
        0.0 0.0 0.0 24.99000000 100.0000000
    BPVAL WATER METHA-01 2.732200000 -617.2687000 .3000000000  &
        0.0 0.0 0.0 24.99000000 100.0000000

PROP-DATA PRKBV-1
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar
    PROP-LIST PRKBV
    BPVAL METHA-01 WATER -.0778000000 0.0 0.0 -273.1500000  &
        726.8500000
    BPVAL WATER METHA-01 -.0778000000 0.0 0.0 -273.1500000  &
        726.8500000

PROP-SET IPE-1
    IN-UNITS ENG
    PROPNAME-LIS MASSVFRA MASSSFRA MASSFLMX VOLFLMX TEMP PRES  &
        MWMX MASSFLOW SUBSTREAM=ALL

PROP-SET IPE-2
    IN-UNITS ENG
    PROPNAME-LIS VOLFLMX MASSFLMX KMX SIGMAMX MUMX CPMX MWMX  &
        UNITS='kJ/kg-K' SUBSTREAM=MIXED PHASE=L

PROP-SET IPE-3
    IN-UNITS ENG
```

```
    PROPNAME-LIS VOLFLMX MASSFLMX KMX MUMX CPMX MWMX UNITS= &
        'kJ/kg-K' SUBSTREAM=MIXED PHASE=V

STREAM 1
    SUBSTREAM MIXED TEMP=25. PRES=1.
    MOLE-FLOW METHA-01 259.7 / WATER 2.5

BLOCK B2 MIXER

BLOCK B3 MIXER

BLOCK B5 FSPLIT
    FRAC 13 0.992

BLOCK B8 HEATER
    PARAM TEMP=100. PRES=13.4

BLOCK B15 HEATER
    PARAM TEMP=50. PRES=1.2

BLOCK E-203 HEATER
    PARAM TEMP=278. PRES=13.8

BLOCK E201 HEATER
    PARAM TEMP=154. PRES=15.1

BLOCK E202 HEATER
    PARAM TEMP=220. PRES=14.7

BLOCK B10 RADFRAC
    PARAM NSTAGE=22 ALGORITHM=STANDARD INIT-OPTION=STANDARD
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 9 12
    PRODUCTS 11 22 L / 10 1 V
    P-SPEC 1 9.2 <barg>
    COL-SPECS MOLE-D=129.7 MOLE-RR=0.6

BLOCK B14 RADFRAC
    PARAM NSTAGE=26
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 12 14
    PRODUCTS B 1 V / 14 26 L
    P-SPEC 1 6.3 <barg>
    COL-SPECS MOLE-D=66.3 MOLE-RR=1.8

BLOCK B6 RSTOIC
    PARAM TEMP=364. PRES=13.9
    STOIC 1 MIXED METHA-01 -2. / DIMET-01 1. / WATER 1.
    CONV 1 MIXED METHA-01 0.8

BLOCK B1 PUMP
```

```
    PARAM PRES=25. EFF=0.6

BLOCK B9 VALVE
    PARAM P-OUT=10.4

BLOCK B13 VALVE
    PARAM P-OUT=7.4

STREAM-PRICE
    STREAM-PRICE STREAM=1 MASS-PRICE=0.0008 <$/kg>

EO-CONV-OPTI
    PARAM SOLVER=DMO

CONV-OPTIONS
    PARAM TEAR-METHOD=DIRECT OPT-METHOD=SQP
    WEGSTEIN MAXIT=50
    DIRECT MAXIT=50
    SECANT MAXIT=50
    BROYDEN MAXIT=50
    NEWTON MAXIT=50

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC PROPERTIES=IPE-1 IPE-2  &
        IPE-3

REACTIONS R-1 GENERAL
    REAC-DATA 1 NAME=1 REAC-CLASS=GLHHW
    RATE-CON 1 PRE-EXP=1210000. ACT-ENERGY=80.4 <kJ/kmol>
    STOIC 1 MIXED METHA-01 -2. / DIMET-01 1. / WATER 1.
    REAC-ACT 1
```

DIMETHYL ETHER VIA NATURAL GAS INPUT FILE

```
DYNAMICS
   DYNAMICS RESULTS=ON
IN-UNITS SI FLOW='kg/hr' MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr'  &
      PRESSURE=atm TEMPERATURE=C DELTA-T=C PDROP=atm

DEF-STREAMS CONVEN ALL

SIM-OPTIONS
   IN-UNITS ENG
   SIM-OPTIONS OLD-DATABANK=YES

DESCRIPTION "
   General Simulation with Metric Units :
   C, bar, kg/hr, kmol/hr, Gcal/hr, cum/hr.

   Property Method: None

   Flow basis for input: Mole

   Stream report composition: Mole flow
   "

DATABANKS PURE10  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      NOASPENPCD

PROP-SOURCES PURE10  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
   DIMET-01 C2H6O-1 /
   METHA-01 CH4O /
   WATER H2O /
   CH4 CH4 /
   OXYGE-01 O2 /
   CO-2 CO2 /
   CO CO /
   H2 H2 /
   C2H6 C2H6 /
   C3H8 C3H8 /
   C4H10 C4H10-1

FLOWSHEET
   BLOCK E-302 IN=3 OUT=4
   BLOCK E-301 IN=1 OUT=2
   BLOCK R-301 IN=4 2 OUT=5
   BLOCK E-303 IN=5 OUT=6
   BLOCK P-301 IN=8 OUT=9
   BLOCK E-304 IN=9 OUT=10
   BLOCK R-302 IN=10 OUT=11
```

```
   BLOCK B9 IN=11 OUT=12
   BLOCK T-302 IN=12 OUT=13 14
   BLOCK E-305 IN=14 OUT=15
   BLOCK R-303 IN=15 OUT=16
   BLOCK B16 IN=16 OUT=17
   BLOCK T-303 IN=17 OUT=19 18
   BLOCK T-301 IN=6 OUT=8 7
   BLOCK B6 IN=19 OUT=20 21
   BLOCK B7 IN=18 21 7 13 OUT=22

PROPERTIES NRTL
   PROPERTIES NRTL-RK / PENG-ROB / SRK

PROP-DATA NRTL-1
   IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
      PDROP=bar
   PROP-LIST NRTL
   BPVAL DIMET-01 METHA-01 0.0 -18.93720000 .2951000000 0.0  &
      0.0 0.0 0.0 0.0
   BPVAL METHA-01 DIMET-01 0.0 653.0063000 .2951000000 0.0  &
      0.0 0.0 0.0 0.0
   BPVAL METHA-01 WATER -.6930000000 172.9871000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL WATER METHA-01 2.732200000 -617.2687000 .3000000000  &
      0.0 0.0 0.0 24.99000000 100.0000000
   BPVAL METHA-01 C4H10 0.0 380.4331000 .3000000000 0.0 0.0  &
      0.0 50.00000000 50.00000000
   BPVAL C4H10 METHA-01 0.0 551.7243000 .3000000000 0.0 0.0  &
      0.0 50.00000000 50.00000000

PROP-DATA PRKBV-1
   IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
      PDROP=bar
   PROP-LIST PRKBV
   BPVAL METHA-01 WATER -.0778000000 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL WATER METHA-01 -.0778000000 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL METHA-01 CO-2 .0230000000 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL CO-2 METHA-01 .0230000000 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL WATER CO-2 .1200000000 0.0 0.0 -273.1500000  &
```

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   726.8500000
BPVAL CO-2 WATER .1200000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CH4 CO-2 .0919000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CO-2 CH4 .0919000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CH4 CO .0300000000 0.0 0.0 -273.1500000 726.8500000
BPVAL CO CH4 .0300000000 0.0 0.0 -273.1500000 726.8500000
BPVAL CH4 H2 .0156000000 0.0 0.0 -273.1500000 726.8500000
BPVAL H2 CH4 .0156000000 0.0 0.0 -273.1500000 726.8500000
BPVAL CO-2 H2 -.1622000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL H2 CO-2 -.1622000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CO H2 .0919000000 0.0 0.0 -273.1500000 726.8500000
BPVAL H2 CO .0919000000 0.0 0.0 -273.1500000 726.8500000
BPVAL METHA-01 C2H6 .0270000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C2H6 METHA-01 .0270000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CH4 C2H6 -2.6000000E-3 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C2H6 CH4 -2.6000000E-3 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CO-2 C2H6 .1322000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C2H6 CO-2 .1322000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CO C2H6 -.0226000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C2H6 CO -.0226000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL H2 C2H6 -.0667000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C2H6 H2 -.0667000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CH4 C3H8 .0140000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C3H8 CH4 .0140000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CO-2 C3H8 .1241000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C3H8 CO-2 .1241000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL CO C3H8 .0259000000 0.0 0.0 -273.1500000 726.8500000
BPVAL C3H8 CO .0259000000 0.0 0.0 -273.1500000 726.8500000
BPVAL H2 C3H8 -.0833000000 0.0 0.0 -273.1500000  &
   726.8500000
BPVAL C3H8 H2 -.0833000000 0.0 0.0 -273.1500000  &
   726.8500000
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  BPVAL C2H6 C3H8 1.10000000E-3 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C3H8 C2H6 1.10000000E-3 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL CH4 C4H10 .0133000000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C4H10 CH4 .0133000000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL CO-2 C4H10 .1333000000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C4H10 CO-2 .1333000000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL H2 C4H10 -.3970000000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C4H10 H2 -.3970000000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C2H6 C4H10 9.60000000E-3 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C4H10 C2H6 9.60000000E-3 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C3H8 C4H10 3.30000000E-3 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C4H10 C3H8 3.30000000E-3 0.0 0.0 -273.1500000  &
    726.8500000

PROP-DATA SRKKIJ-1
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
    VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
    MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
    MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
    PDROP=bar
  PROP-LIST SRKKIJ
  BPVAL CO-2 CO -.0154400000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL CO CO-2 -.0154400000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL CH4 H2 -.0244851000 0.0 0.0 -273.1500000 726.8500000
  BPVAL H2 CH4 -.0244851000 0.0 0.0 -273.1500000 726.8500000
  BPVAL CH4 C2H6 4.21992000E-4 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C2H6 CH4 4.21992000E-4 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL H2 C2H6 .0163828000 0.0 0.0 -273.1500000 726.8500000
  BPVAL C2H6 H2 .0163828000 0.0 0.0 -273.1500000 726.8500000
  BPVAL CH4 C3H8 .0241509000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL C3H8 CH4 .0241509000 0.0 0.0 -273.1500000  &
    726.8500000
  BPVAL H2 C3H8 .1014650000 0.0 0.0 -273.1500000 726.8500000
  BPVAL C3H8 H2 .1014650000 0.0 0.0 -273.1500000 726.8500000
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```
   BPVAL C2H6 C3H8 1.69511000E-3 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL C3H8 C2H6 1.69511000E-3 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL CH4 C4H10 .0226440000 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL C4H10 CH4 .0226440000 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL C2H6 C4H10 5.32194000E-3 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL C4H10 C2H6 5.32194000E-3 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL C3H8 C4H10 -2.0759400E-3 0.0 0.0 -273.1500000  &
      726.8500000
   BPVAL C4H10 C3H8 -2.0759400E-3 0.0 0.0 -273.1500000  &
      726.8500000

PROP-SET IPE-1
   IN-UNITS ENG
   PROPNAME-LIS MASSVFRA MASSSFRA MASSFLMX VOLFLMX TEMP PRES  &
      MWMX MASSFLOW SUBSTREAM=ALL

PROP-SET IPE-2
   IN-UNITS ENG
   PROPNAME-LIS VOLFLMX MASSFLMX KMX SIGMAMX MUMX CPMX MWMX  &
      UNITS='kJ/kg-K' SUBSTREAM=MIXED PHASE=L

PROP-SET IPE-3
   IN-UNITS ENG
   PROPNAME-LIS VOLFLMX MASSFLMX KMX MUMX CPMX MWMX UNITS= &
      'kJ/kg-K' SUBSTREAM=MIXED PHASE=V

STREAM 1
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   SUBSTREAM MIXED TEMP=35. PRES=1. MOLE-FLOW=425.
   MASS-FRAC CH4 0.875 / C2H6 0.075 / C3H8 0.035 / C4H10  &
      0.015

STREAM 3
   IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
      PDROP=bar
   SUBSTREAM MIXED TEMP=35. PRES=1. <atm> MOLE-FLOW=530.
   MASS-FRAC WATER 1.

BLOCK B7 MIXER
```

```
BLOCK B6 SEP
   FRAC STREAM=20 SUBSTREAM=MIXED COMPS=DIMET-01 C2H6 C3H8  &
      FRACS=0.99 0.09 0.09

BLOCK E-301 HEATER
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=800. PRES=1.

BLOCK E-302 HEATER
   IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
      PDROP=bar
   PARAM TEMP=800. PRES=1. <atm>

BLOCK E-303 HEATER
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=35. PRES=1.

BLOCK E-304 HEATER
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=240. PRES=40.

BLOCK E-305 HEATER
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=240. PRES=20.

BLOCK T-301 FLASH2
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=20. PRES=1.

BLOCK T-302 FLASH2
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=20. PRES=20.

BLOCK T-303 RADFRAC
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM NSTAGE=25
   COL-CONFIG CONDENSER=PARTIAL-V
   FEEDS 17 10
   PRODUCTS 19 1 V / 18 25 L
   P-SPEC 1 1.
```

```
   COL-SPECS D:F=0.42 MOLE-RR=4.5

BLOCK R-301 RSTOIC
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=800. PRES=1.
   STOIC 1 MIXED CH4 -1. / WATER -1. / CO 1. / H2 3.
   CONV 1 MIXED CH4 0.966

BLOCK R-302 RSTOIC
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TEMP=240. PRES=4053. <kPa>
   STOIC 2 MIXED CO -1. / H2 -2. / METHA-01 1.
   CONV 2 MIXED CO 0.755

BLOCK R-303 RSTOIC
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
             PARAM TEMP=240. PRES=20.
   STOIC 1 MIXED METHA-01 -2. / DIMET-01 1. / WATER 1.
   CONV 1 MIXED METHA-01 0.91

BLOCK P-301 COMPR
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM TYPE=ISENTROPIC PRES=40. SEFF=0.8

BLOCK B9 VALVE
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM P-OUT=20.

BLOCK B16 VALVE
   IN-UNITS MET FLOW='gm/hr' MASS-FLOW='gm/hr' TEMPERATURE=C  &
      DELTA-T=C
   PARAM P-OUT=8.

EO-CONV-OPTI

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC PROPERTIES=IPE-1 IPE-2  &
      IPE-3

REACTIONS R-1 GENERAL
   IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
      HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
      VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
      MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
      MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
      PDROP=bar
   REAC-DATA 1 NAME=1 REAC-CLASS=GLHHW
```

```
    RATE-CON 1 PRE-EXP=1210000. ACT-ENERGY=80.4 <kJ/kmol>
    STOIC 1 MIXED METHA-01 -2. / DIMET-01 1. / WATER 1.
    REAC-ACT 1

REACTIONS R-2 GENERAL
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar
    REAC-DATA 1 NAME=ATR REAC-CLASS=EQUILIBRIUM
    STOIC 1 MIXED CH4 -2. / OXYGE-01 -1. / CO-2 -1. / CO  &
        3. / H2 3. / WATER 1.
;
;
;
```

ACRYLONITRILE BASE CASE INPUT FILE

```
DYNAMICS
   DYNAMICS RESULTS=ON    ;
IN-UNITS ENG
DEF-STREAMS CONVEN ALL
SIM-OPTIONS RESTART=NO OLD-DATABANK=YES
RUN-CONTROL MAX-TIME=15000 MAX-ERRORS=1000 MAX-FORT-ERR=1000
DATABANKS PURE93  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      ASPENPCD
PROP-SOURCES PURE93  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      ASPENPCD
COMPONENTS
   NH3 H3N /
   H20 H2O /
   HCN CHN /
   CO CO /
   O2 O2 /
   PROPYLEN C3H6-2 /
   CO2 CO2 /
   ACETO C2H3N /
   ACRYLO C3H3N /
   ACROLEIN C3H4O /
   H2S04 H2SO4 /
   AMMSUL "(NH4)2SO4"

FLOWSHEET
   BLOCK M-301 IN=1A 1C 1B OUT=1
   BLOCK M-302 IN=3 2 OUT=2+3
   BLOCK R-302 IN=2+3 OUT=OUT
   BLOCK T-301 IN=OUT OUT=4 5
   BLOCK E-301 IN=4 OUT=6
   BLOCK T-302 IN=6 8 OUT=10 9
   BLOCK E-303 IN=9 OUT=11
   BLOCK T-303 IN=11 OUT=13 12
   BLOCK T-306 IN=16 OUT=18 19
   BLOCK R-301 IN=1 OUT=2
   BLOCK T-305 IN=15 OUT=17 16
   BLOCK E-302 IN=7 OUT=8
   BLOCK T-304 IN=21 OUT=14 15
   BLOCK E-304 IN=14 OUT=20
   BLOCK E-305 IN=13 OUT=21
```

```
   BLOCK B2 IN=5 10 20 17 OUT=22

PROPERTIES ELECNRTL
   PROPERTIES AMINES / IDEAL / NRTL / NRTL-RK / PENG-ROB /
      PITZ-HG / POLYNRTL / PSRK / RK-SOAVE

USER-PROPS DRUSR2 1 2 3
PROP-DATA NRTL-1
   IN-UNITS ENG
   PROP-LIST NRTL
   BPVAL NH3 H20 -.16424220 -1849.5450 .20 .0 .0 .0 32.0  &
      392.0
   BPVAL H20 NH3 -.5440720 3021.2440 .20 .0 .0 .0 32.0  &
      392.0
   BPVAL H20 HCN .0 909.90 .30 .0 .0 .0 50.0 230.0
   BPVAL HCN H20 .0 .0 .30 .0 .0 .0 50.0 230.0
   BPVAL H20 CO2 10.0640 -5882.6430 .20 .0 .0 .0 32.0  &
      392.0
   BPVAL CO2 H20 10.0640 -5882.6430 .20 .0 .0 .0 32.0  &
      392.0
PROP-DATA PRKBV-1
   IN-UNITS ENG
   PROP-LIST PRKBV
   BPVAL NH3 H20 -.2589000000 0.0 0.0 -459.6699923  &
      1340.329993
   BPVAL H20 NH3 -.2589000000 0.0 0.0 -459.6699923  &
      1340.329993
   BPVAL H20 CO2 .1200000000 0.0 0.0 -459.6699923 1340.329993
   BPVAL CO2 H20 .1200000000 0.0 0.0 -459.6699923 1340.329993
   BPVAL PROPYLEN CO2 .0933000000 0.0 0.0 -459.6699923  &
      1340.329993
   BPVAL CO2 PROPYLEN .0933000000 0.0 0.0 -459.6699923  &
      1340.329993

STREAM 1A
   SUBSTREAM MIXED TEMP=80. PRES=14.7 <psi>
   MOLE-FLOW NH3 85.
STREAM 1B
   SUBSTREAM MIXED TEMP=80. PRES=14.7 <psi>
   MOLE-FLOW O2 129.
STREAM 1C
   SUBSTREAM MIXED TEMP=80. PRES=14.7 <psi>
   MOLE-FLOW PROPYLEN 85.
STREAM 3
```

```
    SUBSTREAM MIXED TEMP=86. PRES=14.7 <psi>
    MOLE-FLOW H20 0.21 / H2S04 11.
STREAM 7
    SUBSTREAM MIXED TEMP=45. PRES=1. <atm>
    MOLE-FLOW H20 120.
BLOCK B2 MIXER
BLOCK M-301 MIXER
    PARAM PRES=14.7 <psi>
BLOCK M-302 MIXER

BLOCK E-301 HEATER
    PARAM TEMP=70. PRES=20.

BLOCK E-302 HEATER
    PARAM TEMP=70. PRES=20.

BLOCK E-303 HEATER
    PARAM TEMP=173. PRES=20.
    UTILITY UTILITY-ID=LPSE

BLOCK E-304 HEATER
    PARAM TEMP=70. PRES=15.
    UTILITY UTILITY-ID=LPE

BLOCK E-305 HEATER
    PARAM TEMP=127. PRES=15.
    UTILITY UTILITY-ID=LPE2

BLOCK T-301 FLASH2
    PARAM TEMP=350. PRES=23.99
    UTILITY UTILITY-ID=CWT301

BLOCK T-302 RADFRAC
    PARAM NSTAGE=15
    COL-CONFIG CONDENSER=PARTIAL-V
    RATESEP-ENAB CALC-MODE=EQUILIBRIUM
    FEEDS 6 15 ON-STAGE / 8 1
    PRODUCTS 10 1 V / 9 15 L
    P-SPEC 1 15. / 2 20.
    COL-SPECS B:F=0.85 MOLE-RR=4.
    UTILITIES COND-UTIL=CWRR302 REB-UTIL=CWE2

BLOCK T-303 RADFRAC
    PARAM NSTAGE=30
```

```
    COL-CONFIG CONDENSER=TOTAL
    FEEDS 11 10 ON-STAGE
    PRODUCTS 12 30 L / 13 1 L
    P-SPEC 1 15.
    COL-SPECS D:F=0.17 MOLE-RR=7.
    UTILITIES COND-UTIL=CW-RT303 REB-UTIL=LST-303

BLOCK T-304 RADFRAC
    PARAM NSTAGE=15
    COL-CONFIG CONDENSER=TOTAL
    FEEDS 21 7
    PRODUCTS 14 1 L / 15 15 L
    P-SPEC 1 14.7
    COL-SPECS MASS-D:F=0.08 MOLE-RR=1.18
    UTILITIES COND-UTIL=CWRT304 REB-UTIL=LST-304

BLOCK T-305 RADFRAC
    PARAM NSTAGE=12
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 15 11
    PRODUCTS 16 12 L / 17 1 V
    P-SPEC 1 14.7
    COL-SPECS D:F=0.016 MOLE-RR=4.
    UTILITIES COND-UTIL=CW-RT305 REB-UTIL=LST-305

BLOCK T-306 RADFRAC
    PARAM NSTAGE=35
    COL-CONFIG CONDENSER=TOTAL
    FEEDS 16 15
    PRODUCTS 18 1 L / 19 35 L
    P-SPEC 1 12.
    COL-SPECS D:F=0.78 MOLE-RR=4.
    UTILITIES COND-UTIL=CWRT306 REB-UTIL=LST306

BLOCK R-302 RSTOIC
    PARAM TEMP=170. PRES=15. <psi>
    STOIC 1 MIXED NH3 -2.0 / H2S04 -1.0 / AMMSUL 1.0
    CONV 1 MIXED NH3 .960
    UTILITY UTILITY-ID=CWT-R302

BLOCK R-301 RPLUG
    PARAM TYPE=T-SPEC NTUBE=20 LENGTH=19. DIAM=13. <in>
    T-SPEC 0.0 852.
    REACTIONS RXN-IDS=PLAW-1
```

```
UTILITY CW-RT303 GENERAL
    COST ENERGY-PRICE=0.354 <$/GJ>
    PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=15.  &
        TIN=30. <C> TOUT=93.53 CALOPT=FLASH

UTILITY CW-RT305 GENERAL
    COST ENERGY-PRICE=0.354 <$/GJ>
    PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=14.7  &
        TIN=30. <C> TOUT=154.4 CALOPT=FLASH

UTILITY CWE2 GENERAL
    COST ENERGY-PRICE=14.05 <$/GJ>
    PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=20.  &
        TIN=160. <C> TOUT=195.52 CALOPT=FLASH

UTILITY CWRR302 GENERAL
    COST ENERGY-PRICE=0.354 <$/GJ>
    PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=15.  &
        TIN=30. <C> TOUT=24.56 CALOPT=FLASH

UTILITY CWRT304 GENERAL
    COST ENERGY-PRICE=7.89 <$/GJ>
    PARAM UTILITY-TYPE=REFRIGERATIO PRES-OUT=15. TIN=-20. <C>  &
        TOUT=-46.97 VFRAC=1. CALOPT=FLASH
    COMPOSITION H20 1.

UTILITY CWRT306 GENERAL
    COST ENERGY-PRICE=0.354 <$/GJ>
    PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=14.7  &
        TIN=30. <C> TOUT=160.36 CALOPT=FLASH

UTILITY CWT-R302 GENERAL
    COST ENERGY-PRICE=0.354 <$/GJ>
    PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=15.  &
        TIN=30. <C> TOUT=170. CALOPT=FLASH

UTILITY CWT301 GENERAL
    COST ENERGY-PRICE=0.354 <$/GJ>
    PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=10.  &
        TIN=30. <C> TOUT=350. CALOPT=FLASH

UTILITY LPE GENERAL
    COST ENERGY-PRICE=14.05 <$/GJ>
```

```
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=15.  &
      TIN=160. <C> TOUT=70. CALOPT=FLASH

UTILITY LPE2 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=23.99  &
      TIN=160. <C> TOUT=127. CALOPT=FLASH

UTILITY LPSE GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> TIN=160. <C>  &
      TOUT=120. <C> VFR-OUT=1. CALOPT=FLASH

UTILITY LST-303 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=15.  &
      TIN=160. <C> TOUT=212.77 CALOPT=FLASH

UTILITY LST-304 GENERAL
   COST ENERGY-PRICE=13.28 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
      TIN=160. <C> TOUT=177.7 CALOPT=FLASH

UTILITY LST-305 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
      TIN=160. <C> TOUT=172. CALOPT=FLASH

UTILITY LST306 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
      TIN=160. <C> TOUT=201.94 CALOPT=FLASH

UTILITY U-1 GENERAL
   COST ELEC-PRICE=0.06
   PARAM UTILITY-TYPE=ELECTRICITY

DESIGN-SPEC DS-1
   DEFINE INAMM MOLE-FLOW STREAM=OUT SUBSTREAM=MIXED  &
      COMPONENT=AMMSUL
   DEFINE OUTAMM MOLE-FLOW STREAM=5 SUBSTREAM=MIXED  &
      COMPONENT=AMMSUL
F        RATIO = OUTAMM/INAMM
   SPEC "OUTAMM/INAMM" TO "0.99"
```

```
    TOL-SPEC "0.05"
    VARY BLOCK-VAR BLOCK=T-301 VARIABLE=PRES SENTENCE=PARAM
    LIMITS "0  " "70"

DESIGN-SPEC DS-2
    DEFINE INH20 MOLE-FLOW STREAM=OUT SUBSTREAM=MIXED  &
        COMPONENT=H20
    DEFINE OUTH20 MOLE-FLOW STREAM=4 SUBSTREAM=MIXED  &
        COMPONENT=H20
    SPEC "OUTH20/INH20" TO "0.95"
    TOL-SPEC "0.05"
    VARY BLOCK-VAR BLOCK=T-301 VARIABLE=TEMP SENTENCE=PARAM
    LIMITS "0" "600"

DESIGN-SPEC DS-3
    DEFINE MOLH2 MOLE-FLOW STREAM=3 SUBSTREAM=MIXED  &
        COMPONENT=H2S04
    DEFINE MOLNH3 MOLE-FLOW STREAM=2 SUBSTREAM=MIXED  &
        COMPONENT=NH3
    SPEC "MOLH2" TO "MOLNH3/2"
    TOL-SPEC "5"
    VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=H2S04
    LIMITS "2" "120"

EO-CONV-OPTI

CONV-OPTIONS
    PARAM TOL=.010
    WEGSTEIN MAXIT=200 QMIN=-20.0
    SECANT MAXIT=60 XTOL=1E-03

REPORT UTILITIES ECONOMIC

STREAM-REPOR NOSORT MOLEFLOW MASSFLOW MASSFRAC

ECONOMIC-REP CASH-FLOW=ANNUAL

REACTIONS PLAW-1 POWERLAW
    REAC-DATA 1 PHASE=V
    REAC-DATA 2 PHASE=V
    REAC-DATA 3 PHASE=V
    REAC-DATA 4 PHASE=V
    REAC-DATA 5 PHASE=V
    REAC-DATA 6 PHASE=V
```

```
    RATE-CON 1 PRE-EXP=157498 ACT-ENERGY=34200
    RATE-CON 2 PRE-EXP=3778 ACT-ENERGY=34200
    RATE-CON 3 PRE-EXP=1.99 ACT-ENERGY=12600
    RATE-CON 4 PRE-EXP=780.82 ACT-ENERGY=12600
    RATE-CON 5 PRE-EXP=108308 ACT-ENERGY=35640
    RATE-CON 6 PRE-EXP=8.3658 ACT-ENERGY=12600
    STOIC 1 MIXED PROPYLEN -1 / NH3 -1 / O2 -1.5 / ACRYLO  &
       1 / H20 3
    STOIC 2 MIXED PROPYLEN -1 / O2 -1 / ACROLEIN 1 / H20  &
       1
    STOIC 3 MIXED PROPYLEN -1 / NH3 -1 / O2 -2.25 / ACETO  &
       1 / CO2 .5 / CO .5 / H20 3
    STOIC 4 MIXED ACROLEIN -1 / NH3 -1 / O2 -0.5 / ACRYLO  &
       1 / H20 2
    STOIC 5 MIXED ACRYLO -1 / O2 -2 / CO 1 / CO2 1 /  &
       H20 1 / HCN 1
    STOIC 6 MIXED ACETO -1 / O2 -1.5 / CO2 1 / HCN 1 /  &
       H20 1
    POWLAW-EXP 1 MIXED PROPYLEN 1
    POWLAW-EXP 2 MIXED PROPYLEN 1
    POWLAW-EXP 3 MIXED PROPYLEN 1
    POWLAW-EXP 4 MIXED ACROLEIN 1
    POWLAW-EXP 5 MIXED ACRYLO 1
    POWLAW-EXP 6 MIXED ACETO 1
;
;
;
;
;
```

OPTIMIZED ACRYLONITRILE INPUT FILE

```
DYNAMICS
    DYNAMICS RESULTS=ON
IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS RESTART=NO OLD-DATABANK=YES

RUN-CONTROL MAX-TIME=15000 MAX-ERRORS=1000 MAX-FORT-ERR=1000

DATABANKS PURE93  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        ASPENPCD

PROP-SOURCES PURE93  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        ASPENPCD

COMPONENTS
    NH3 H3N /
    H20 H2O /
    HCN CHN /
    CO CO /
    O2 O2 /
    PROPYLEN C3H6-2 /
    CO2 CO2 /
    ACETO C2H3N /
    ACRYLO C3H3N /
    ACROLEIN C3H4O /
    H2S04 H2SO4 /
    AMMSUL "(NH4)2SO4"

FLOWSHEET
    BLOCK M-301 IN=1A 1C 1B 25 OUT=1
    BLOCK M-302 IN=3 2 OUT=2+3
    BLOCK R-302 IN=2+3 OUT=OUT
    BLOCK T-301 IN=OUT OUT=4 5
    BLOCK E-301 IN=4 OUT=6
    BLOCK T-302 IN=6 19 OUT=8 9
    BLOCK T-303 IN=9 OUT=12 11
    BLOCK T-306 IN=15 OUT=16 17
    BLOCK R-301 IN=1 OUT=2
    BLOCK T-305 IN=12 OUT=14 15
    BLOCK E-302 IN=11 OUT=18
    BLOCK E-303 IN=24 OUT=25
    BLOCK E-304 IN=21 OUT=22
    BLOCK B17 IN=18 OUT=19 39
    BLOCK B19 IN=5 14 20 23 OUT=42
    BLOCK T-307 IN=8 OUT=20 21
    BLOCK T-304 IN=22 OUT=24 23
```

```
PROPERTIES ELECNRTL
   PROPERTIES AMINES / IDEAL / NRTL / NRTL-RK / PENG-ROB /
      PITZ-HG / POLYNRTL / PSRK / RK-SOAVE

USER-PROPS DRUSR2 1 2 3

PROP-DATA NRTL-1
   IN-UNITS ENG
   PROP-LIST NRTL
   BPVAL NH3 H20 -.16424220 -1849.5450 .20 .0 .0 .0 32.0  &
      392.0
   BPVAL H20 NH3 -.5440720 3021.2440 .20 .0 .0 .0 32.0  &
      392.0
   BPVAL H20 HCN .0 909.90 .30 .0 .0 .0 50.0 230.0
   BPVAL HCN H20 .0 .0 .30 .0 .0 .0 50.0 230.0
   BPVAL H20 CO2 10.0640 -5882.6430 .20 .0 .0 .0 32.0  &
      392.0
   BPVAL CO2 H20 10.0640 -5882.6430 .20 .0 .0 .0 32.0  &
      392.0

PROP-DATA PRKBV-1
   IN-UNITS ENG
   PROP-LIST PRKBV
   BPVAL NH3 H20 -.2589000000 0.0 0.0 -459.6699923  &
      1340.329993
   BPVAL H20 NH3 -.2589000000 0.0 0.0 -459.6699923  &
      1340.329993
   BPVAL H20 CO2 .1200000000 0.0 0.0 -459.6699923 1340.329993
   BPVAL CO2 H20 .1200000000 0.0 0.0 -459.6699923 1340.329993
   BPVAL PROPYLEN CO2 .0933000000 0.0 0.0 -459.6699923  &
      1340.329993
   BPVAL CO2 PROPYLEN .0933000000 0.0 0.0 -459.6699923  &
      1340.329993

STREAM 1A
   SUBSTREAM MIXED TEMP=80. PRES=15. <psi>
   MOLE-FLOW NH3 67.

STREAM 1B
   SUBSTREAM MIXED TEMP=80. PRES=15. <psi>
   MOLE-FLOW O2 129.

STREAM 1C
   SUBSTREAM MIXED TEMP=80. PRES=15. <psi>
   MOLE-FLOW PROPYLEN 80.

STREAM 3
   SUBSTREAM MIXED TEMP=86. PRES=14.7 <psi>
   MOLE-FLOW H20 0.21 / H2S04 10.
```

```
BLOCK B19 MIXER

BLOCK M-301 MIXER
   PARAM PRES=14.7 <psi>

BLOCK M-302 MIXER

BLOCK B17 FSPLIT
   MOLE-FLOW 19 120.

BLOCK E-301 HEATER
   PARAM TEMP=170. PRES=20. <psi>
   UTILITY UTILITY-ID=CWE2

BLOCK E-302 HEATER
   PARAM TEMP=170. PRES=20.
   UTILITY UTILITY-ID=CWE2

BLOCK E-303 HEATER
   PARAM TEMP=80. PRES=15.
   UTILITY UTILITY-ID=LPS1

BLOCK E-304 HEATER
   PARAM TEMP=80. PRES=15.
   UTILITY UTILITY-ID=LPS1

BLOCK T-301 FLASH2
   PARAM TEMP=350. PRES=15.
   UTILITY UTILITY-ID=CWT301

BLOCK T-304 DSTWU
   PARAM LIGHTKEY=PROPYLEN RECOVL=0.99 HEAVYKEY=HCN  &
      RECOVH=0.01 PTOP=14.7 PBOT=14.7 NSTAGE=15

BLOCK T-307 DSTWU
   PARAM LIGHTKEY=CO2 RECOVL=0.99 HEAVYKEY=PROPYLEN  &
      RECOVH=0.01 PTOP=14.7 PBOT=14.7 RDV=1.0 NSTAGE=10  &
      PACK-HEIGHT=10. PLOT=YES

BLOCK T-302 RADFRAC
   PARAM NSTAGE=15
   COL-CONFIG CONDENSER=PARTIAL-V
   RATESEP-ENAB CALC-MODE=EQUILIBRIUM
   FEEDS 6 15 / 19 1
   PRODUCTS 8 1 V / 9 15 L
   P-SPEC 1 14.7
   COL-SPECS B:F=0.838888889 MOLE-RR=2.5
   UTILITIES COND-UTIL=CWRR302 REB-UTIL=CWE

BLOCK T-303 RADFRAC
   PARAM NSTAGE=30
```

```
   COL-CONFIG CONDENSER=TOTAL
   FEEDS 9 10
   PRODUCTS 11 30 L / 12 1 L
   P-SPEC 1 14.7 <psi> / 2 14.7
   COL-SPECS D:F=0.16 MOLE-RR=10.5
   UTILITIES COND-UTIL=CW-RT303 REB-UTIL=LST-303

BLOCK T-305 RADFRAC
   PARAM NSTAGE=12
   COL-CONFIG CONDENSER=PARTIAL-V
   FEEDS 12 5
   PRODUCTS 15 12 L / 14 1 V
   P-SPEC 1 14.7
   COL-SPECS D:F=0.025 MOLE-RR=10.
   UTILITIES COND-UTIL=CW-RT305 REB-UTIL=LST-305

BLOCK T-306 RADFRAC
   PARAM NSTAGE=35
   COL-CONFIG CONDENSER=TOTAL
   FEEDS 15 10
   PRODUCTS 16 1 L / 17 35 L
   P-SPEC 1 14.7
   COL-SPECS D:F=0.8 MOLE-RR=3.
   UTILITIES COND-UTIL=CWRT306 REB-UTIL=LST306

BLOCK R-302 RSTOIC
   PARAM TEMP=170. PRES=15. <psi>
   STOIC 1 MIXED NH3 -2.0 / H2S04 -1.0 / AMMSUL 1.0
   CONV 1 MIXED NH3 0.94
   UTILITY UTILITY-ID=CWT-R302

BLOCK R-301 RPLUG
   PARAM TYPE=T-SPEC NTUBE=13 LENGTH=10. DIAM=1.8
   T-SPEC 0.0 852.
   REACTIONS RXN-IDS=PLAW-1

UTILITY CW-RT303 GENERAL
   COST ENERGY-PRICE=0.354 <$/GJ>
   PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=14.7  &
      TIN=30. <C> TOUT=151.25 CALOPT=FLASH

UTILITY CW-RT305 GENERAL
   COST ENERGY-PRICE=0.354 <$/GJ>
   PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=14.7  &
      TIN=30. <C> TOUT=34.66 CALOPT=FLASH

UTILITY CWE GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
      TIN=160. <C> TOUT=199. CALOPT=FLASH
```

```
UTILITY CWE2 GENERAL
   COST ENERGY-PRICE=0.354 <$/GJ>
   PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=20.  &
      TIN=30. <C> TOUT=170. CALOPT=FLASH

UTILITY CWRR302 GENERAL
   COST ENERGY-PRICE=0.354 <$/GJ>
   PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=14.7  &
      TIN=30. <C> TOUT=58. CALOPT=FLASH

UTILITY CWRT306 GENERAL
   COST ENERGY-PRICE=0.354 <$/GJ>
   PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=14.7  &
      TIN=30. <C> TOUT=169.04 CALOPT=FLASH

UTILITY CWT-R302 GENERAL
   COST ENERGY-PRICE=0.354 <$/GJ>
   PARAM UTILITY-TYPE=WATER PRES=1. <atm> PRES-OUT=15.  &
      TIN=30. <C> TOUT=170. CALOPT=FLASH

UTILITY CWT301 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=15.  &
      TIN=160. <C> TOUT=350. CALOPT=FLASH

UTILITY LPS1 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=15.  &
      TIN=160. <C> TOUT=80. CALOPT=FLASH

UTILITY LST-303 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
      TIN=160. <C> TOUT=211.95 CALOPT=FLASH

UTILITY LST-305 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
      TIN=160. <C> TOUT=175.45 CALOPT=FLASH

UTILITY LST306 GENERAL
   COST ENERGY-PRICE=14.05 <$/GJ>
   PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
      TIN=160. <C> TOUT=205.06 CALOPT=FLASH

UTILITY U-1 GENERAL
   COST ELEC-PRICE=0.06
   PARAM UTILITY-TYPE=ELECTRICITY

DESIGN-SPEC DS-1
   DEFINE INAMM MOLE-FLOW STREAM=OUT SUBSTREAM=MIXED  &
```

```
      COMPONENT=AMMSUL
   DEFINE OUTAMM MOLE-FLOW STREAM=5 SUBSTREAM=MIXED  &
      COMPONENT=AMMSUL
F        RATIO = OUTAMM/INAMM
   SPEC "OUTAMM/INAMM" TO "0.99"
   TOL-SPEC "0.05"
   VARY BLOCK-VAR BLOCK=T-301 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "0  " "70"

DESIGN-SPEC DS-2
   DEFINE INH20 MOLE-FLOW STREAM=OUT SUBSTREAM=MIXED  &
      COMPONENT=H20
   DEFINE OUTH20 MOLE-FLOW STREAM=4 SUBSTREAM=MIXED  &
      COMPONENT=H20
   SPEC "OUTH20/INH20" TO "0.95"
   TOL-SPEC "0.05"
   VARY BLOCK-VAR BLOCK=T-301 VARIABLE=TEMP SENTENCE=PARAM
   LIMITS "0" "600"

DESIGN-SPEC DS-3
   DEFINE MOLH2 MOLE-FLOW STREAM=3 SUBSTREAM=MIXED  &
      COMPONENT=H2S04
   DEFINE MOLNH3 MOLE-FLOW STREAM=2 SUBSTREAM=MIXED  &
      COMPONENT=NH3
   SPEC "MOLH2" TO "MOLNH3/2"
   TOL-SPEC "5"
   VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=H2S04
   LIMITS "0.5" "120"

DESIGN-SPEC DS-4
   DEFINE PR2 MOLE-FLOW STREAM=1 SUBSTREAM=MIXED  &
      COMPONENT=PROPYLEN
   SPEC "PR2" TO "85"
   TOL-SPEC "0.1"
   VARY MOLE-FLOW STREAM=1C SUBSTREAM=MIXED COMPONENT=PROPYLEN
   LIMITS "10" "150"

EO-CONV-OPTI
   PARAM SOLVER=DMO

SENSITIVITY FLOWR
   DEFINE WASTE1 STREAM-VAR STREAM=42 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE ACRYL STREAM-VAR STREAM=16 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE NH3 STREAM-VAR STREAM=1A SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE O2 STREAM-VAR STREAM=1B SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE PROP STREAM-VAR STREAM=1C SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
```

```
    DEFINE H20 STREAM-VAR STREAM=39 SUBSTREAM=MIXED  &
       VARIABLE=MASS-FLOW
    DEFINE H2SO4 STREAM-VAR STREAM=3 SUBSTREAM=MIXED  &
       VARIABLE=MASS-FLOW
    DEFINE MNH3 STREAM-VAR STREAM=1A SUBSTREAM=MIXED  &
       VARIABLE=MOLE-FLOW
    DEFINE MO2 STREAM-VAR STREAM=1B SUBSTREAM=MIXED  &
       VARIABLE=MOLE-FLOW
    DEFINE MPROP STREAM-VAR STREAM=1C SUBSTREAM=MIXED  &
       VARIABLE=MOLE-FLOW
    DEFINE ACRYL2 MOLE-FLOW STREAM=2 SUBSTREAM=MIXED  &
       COMPONENT=ACRYLO
    DEFINE MPROP2 MOLE-FLOW STREAM=2 SUBSTREAM=MIXED  &
       COMPONENT=PROPYLEN
    DEFINE WATERR MOLE-FLOW STREAM=11 SUBSTREAM=MIXED  &
       COMPONENT=H20
    DEFINE ACE MOLE-FLOW STREAM=6 SUBSTREAM=MIXED  &
       COMPONENT=ACRYLO
    DEFINE ACE1 MOLE-FLOW STREAM=9 SUBSTREAM=MIXED  &
       COMPONENT=ACRYLO
    DEFINE COND BLOCK-VAR BLOCK=T-302 VARIABLE=COND-DUTY  &
       SENTENCE=RESULTS
    DEFINE REB BLOCK-VAR BLOCK=T-302 VARIABLE=REB-DUTY  &
       SENTENCE=RESULTS
    DEFINE HCN MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
       COMPONENT=HCN
    DEFINE ACET MOLE-FLOW STREAM=17 SUBSTREAM=MIXED  &
       COMPONENT=ACETO
    DEFINE Q3 BLOCK-VAR BLOCK=R-301 VARIABLE=QCALC  &
       SENTENCE=PARAM
    DEFINE Q4 BLOCK-VAR BLOCK=T-304 VARIABLE=REB-DUTY  &
       SENTENCE=RESULTS
    DEFINE Q5 BLOCK-VAR BLOCK=T-304 VARIABLE=COND-DUTY  &
       SENTENCE=RESULTS
    DEFINE Q6 BLOCK-VAR BLOCK=T-307 VARIABLE=REB-DUTY  &
       SENTENCE=RESULTS
    DEFINE Q7 BLOCK-VAR BLOCK=T-307 VARIABLE=COND-DUTY  &
       SENTENCE=RESULTS
F       TWASTE =WASTE1
F       CNH3 = 0.17
F       C02 = 0.05
F       CPROP = 0.44
F       CH2SO4 = 0.037
F       CH2O = 3.039E-5
F       CACRYL = 1.18
F       CACETO = 0.997
F       CWASTE = 0.016364
F
F       RAW = (CNH3*NH3+ CO2*O2+CPROP*PROP+CH2SO4*H2SO4)*24*365
F       REV = (CACRYL*ACRYL+CH20*H20)*24*365
F       MVA = REV -RAW-(CWASTE*TWASTE)
```

```
F
F       OBYP=MO2/MPROP
F       PBYN=MPROP/MNH3
F       OBYN=MO2/MNH3
F
F       CONV=(MPROP-MPROP2)/MPROP*100
F
F
F       ACRR = (ACE/ACE1)*100
F       TOT = (Q5*(8.77E-6)+Q7*(8.77E-6)+Q3*(-8.77E-6))*365*24
F       TOTALQ = (( Q4* (4.31E-6)+Q6*(4.31E-6))*365*24) +TOT
   TABULATE 1 "TWASTE"
   TABULATE 2 "RAW"
   TABULATE 3 "REV"
   TABULATE 4 "MVA"
   TABULATE 6 "ACRYL2"
   TABULATE 7 "CONV"
   TABULATE 8 "WATERR"
   TABULATE 9 "ACRR"
   TABULATE 10 "ACE3"
   TABULATE 11 "ACET"
   TABULATE 12 "HCN"
   TABULATE 13 "COND"
   TABULATE 14 "REB"
   TABULATE 15 "TOTALQ"
   VARY BLOCK-VAR BLOCK=T-306 VARIABLE=STAGE SENTENCE=FEEDS  &
      ID1=15
   RANGE LOWER="2" UPPER="10" INCR="1"

CONV-OPTIONS
   PARAM TEAR-METHOD=BROYDEN TOL=0.01
   WEGSTEIN MAXIT=200 QMIN=-20.0
   SECANT MAXIT=60 XTOL=1E-03

REPORT UTILITIES ECONOMIC

STREAM-REPOR NOSORT MOLEFLOW MASSFLOW MASSFRAC

ECONOMIC-REP CASH-FLOW=ANNUAL

REACTIONS PLAW-1 POWERLAW
   REAC-DATA 1 PHASE=V
   REAC-DATA 2 PHASE=V
   REAC-DATA 3 PHASE=V
   REAC-DATA 4 PHASE=V
   REAC-DATA 5 PHASE=V
   REAC-DATA 6 PHASE=V
   RATE-CON 1 PRE-EXP=157498 ACT-ENERGY=34200
   RATE-CON 2 PRE-EXP=3778 ACT-ENERGY=34200
   RATE-CON 3 PRE-EXP=1.99 ACT-ENERGY=12600
   RATE-CON 4 PRE-EXP=780.82 ACT-ENERGY=12600
```

```
    RATE-CON 5 PRE-EXP=108308 ACT-ENERGY=35640
    RATE-CON 6 PRE-EXP=8.3658 ACT-ENERGY=12600
    STOIC 1 MIXED PROPYLEN -1 / NH3 -1 / O2 -1.5 / ACRYLO  &
        1 / H20 3
    STOIC 2 MIXED PROPYLEN -1 / O2 -1 / ACROLEIN 1 / H20  &
        1
    STOIC 3 MIXED PROPYLEN -1 / NH3 -1 / O2 -2.25 / ACETO  &
        1 / CO2 .5 / CO .5 / H20 3
    STOIC 4 MIXED ACROLEIN -1 / NH3 -1 / O2 -0.5 / ACRYLO  &
        1 / H20 2
    STOIC 5 MIXED ACRYLO -1 / O2 -2 / CO 1 / CO2 1 /  &
        H20 1 / HCN 1
    STOIC 6 MIXED ACETO -1 / O2 -1.5 / CO2 1 / HCN 1 /  &
        H20 1
    POWLAW-EXP 1 MIXED PROPYLEN 1
    POWLAW-EXP 2 MIXED PROPYLEN 1
    POWLAW-EXP 3 MIXED PROPYLEN 1
    POWLAW-EXP 4 MIXED ACROLEIN 1
    POWLAW-EXP 5 MIXED ACRYLO 1
    POWLAW-EXP 6 MIXED ACETO 1
;
;
```

BASE CASE ALLYL CHLORIDE INPUT FILE

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS OLD-DATABANK=YES

RUN-CONTROL MAX-TIME=100000. MAX-ERRORS=500

DESCRIPTION "
   General Simulation with English Units :
   F, psi, lb/hr, lbmol/hr, Btu/hr, cuft/hr.

   Property Method: None

   Flow basis for input: Mole

   Stream report composition: Mole flow
   "

DATABANKS ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      PURE22

PROP-SOURCES ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      PURE22

COMPONENTS
   H2O H2O /
   HCL HCL /
   PROPENE C3H6-2 /
   CHLORINE CL2 /
   AC C3H5CL /
   12DCP C3H6CL2 /
   13DCP-C C3H4CL2-D1 /
   13DCP-T C3H4CL2-D2 /
   H+ H+ /
   CL- CL-

HENRY-COMPS HENRY CHLORINE HCL PROPENE

CHEMISTRY HCL
   STOIC 1 HCL -1 / H+ 1 / CL- 1

FLOWSHEET
   BLOCK E-901 IN=14 OUT=2
```

```
   BLOCK M-902 IN=1 13 OUT=14
   BLOCK M-901 IN=2 3 OUT=4
   BLOCK R-901 IN=4 OUT=5
   BLOCK E-902 IN=5 OUT=6
   BLOCK T-901 IN=6 OUT=8 7
   BLOCK T-904 IN=7 OUT=9 10
   BLOCK T-902 IN=15 8 OUT=16 17
   BLOCK T-903 IN=16 OUT=12 11
   BLOCK C-901 IN=12 OUT=13

PROPERTIES SYSOP0
   PROPERTIES ELECNRTL / UNIQ-RK / UNIQUAC

STRUCTURES
   STRUCTURES 13DCP-C CL1 C2 S / C2 C3 D / C3 C4 S /  &
      C4 CL5 S

ESTIMATE ALL

PROP-DATA PCES-1
   IN-UNITS ENG
   PROP-LIST DGAQHG / DHAQHG / S25HG / OMEGHG / DHVLB /  &
      VB / RGYR / VLSTD
   PVAL CHLORINE 2983.662941 / -10060.18917 / 28.90035349 /  &
      -17580.05159 / 8784.000000 / .7262124822 /  &
      3.2391732E-10 / .8579136616
   PROP-LIST DHVLB / VB / RGYR
   PVAL 13DCP-C 14431.51333 / 1.612466586 / 1.11089239E-9

PROP-DATA HENRY-1
   IN-UNITS ENG
   PROP-LIST HENRY
   BPVAL HCL H2O -49.78140336 2186.999983 8.370700000  &
      -5.3294445E-3 -3.999995968 68.00000346 0.0
   BPVAL CHLORINE H2O -116.9781387 4371.515965 19.18540000  &
      -4.9558834E-3 49.73000360 103.7300032 0.0
   BPVAL HCL 12DCP 10.00798341 -2648.879936 0.0 0.0  &
      -4.269995966 67.73000346 0.0
   BPVAL PROPENE H2O 326.3806995 -28021.26578 -41.73762000 0.0  &
      69.53000344 220.7300022 0.0
   BPVAL PROPENE 12DCP 12.93988341 -3932.459880 0.0 0.0  &
      -4.269995966 67.73000346 0.0

PROP-DATA UNIQ-1
   IN-UNITS ENG
   PROP-LIST UNIQ
   BPVAL H2O AC -4.247000000 2292.652782 0.0 0.0 109.9400031  &
      212.0000023 0.0
   BPVAL AC H2O 15.46800000 -10062.08074 0.0 0.0 109.9400031  &
      212.0000023 0.0
   BPVAL H2O 12DCP 0.0 -539.9468957 0.0 0.0 77.00000338  &
```

```
        77.00000338 0.0
    BPVAL 12DCP H2O 0.0 -2498.536780 0.0 0.0 77.00000338  &
        77.00000338 0.0

PROP-DATA VLCLK-1
    IN-UNITS ENG
    PROP-LIST VLCLK
    BPVAL H+ CL- .5534556926 .2140997389

PROP-DATA GMELCC-1
    IN-UNITS ENG
    PROP-LIST GMELCC
    PPVAL H2O ( H+ CL- ) 41.67400000
    PPVAL ( H+ CL- ) H2O -22.15400000
    PPVAL HCL ( H+ CL- ) 1.00000000E-3
    PPVAL ( H+ CL- ) HCL -1.0000000E-3

PROP-DATA GMELCD-1
    IN-UNITS ENG
    PROP-LIST GMELCD
    PPVAL H2O ( H+ CL- ) 9581.579923
    PPVAL ( H+ CL- ) H2O -3967.379968

PROP-DATA GMELCE-1
    IN-UNITS ENG
    PROP-LIST GMELCE
    PPVAL H2O ( H+ CL- ) -5.404000000
    PPVAL ( H+ CL- ) H2O 5.188000000

PROP-DATA GMELCN-1
    IN-UNITS ENG
    PROP-LIST GMELCN
    PPVAL H2O ( H+ CL- ) .0283500000

PCES-PROP-DATA
    IN-UNITS ENG
    GAMINF H2O 12DCP * * 68 2340 / * * 86 2310 / * *  &
        104 2090

PCES-PROP-DATA
    IN-UNITS ENG
    GAMINF H2O 13DCP-C * * 68 1360 / * * 86 1430 / * *  &
        104 1460

STREAM 1
    SUBSTREAM MIXED TEMP=80. PRES=74.7
    MOLE-FLOW PROPENE 1000.

STREAM 3
    SUBSTREAM MIXED TEMP=80. PRES=74.7
    MOLE-FLOW CHLORINE 133.
```

```
STREAM 15
   SUBSTREAM MIXED TEMP=70. PRES=14.7
   MOLE-FLOW H2O 500.

BLOCK M-901 MIXER
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES

BLOCK M-902 MIXER
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES

BLOCK T-903 SEP
   PARAM
   FRAC STREAM=12 SUBSTREAM=MIXED COMPS=PROPENE FRACS=1.
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITY UTILITY-ID=BOT903

BLOCK E-901 HEATER
   PARAM TEMP=730. PRES=74.7
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITY UTILITY-ID=NAT

BLOCK E-902 HEATER
   PARAM TEMP=70. PRES=74.7
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITY UTILITY-ID=E-902

BLOCK T-901 RADFRAC
   PARAM NSTAGE=15 ALGORITHM=STANDARD INIT-OPTION=STANDARD  &
      MAXOL=150 DAMPING=NONE
   COL-CONFIG CONDENSER=PARTIAL-V
   FEEDS 6 7
   PRODUCTS 8 1 V / 7 15 L
   P-SPEC 1 20. / 15 27.
   COL-SPECS D:F=0.893039 MOLE-RR=0.5
   SPEC 1 MOLE-RECOV 0.9999 COMPS=AC STREAMS=7
   VARY 1 D:F 0.001 0.999
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITIES REB-UTIL=BOT901

BLOCK T-902 RADFRAC
   PARAM NSTAGE=10 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD  &
      MAXOL=100 MAXIL=50
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   FEEDS 15 1 ON-STAGE / 8 10 ON-STAGE
```

```
    PRODUCTS 17 10 L / 16 1 V
    P-SPEC 1 14.7
    COL-SPECS
    T-EST 1 110. / 10 68.
    PROPERTIES ELECNRTL HENRY-COMPS=HENRY CHEMISTRY=HCL  &
        FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=NO

BLOCK T-904 RADFRAC
    PARAM NSTAGE=15
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 7 6
    PRODUCTS 9 1 V / 10 15 L
    P-SPEC 1 16. / 15 25.
    COL-SPECS D:F=0.54 MOLE-RR=4.02554
    SPEC 1 MOLE-RECOV 0.995 COMPS=AC STREAMS=9 BASE-STREAMS=7
    VARY 1 D:F 0.001 0.999
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITIES COND-UTIL=CW904

BLOCK R-901 RPLUG
    PARAM TYPE=ADIABATIC LENGTH=20. DIAM=6. PRES=40.  &
        INT-TOL=1E-005
    COOLANT MAXIT=50
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES / SYSOP0
    REACTIONS RXN-IDS=R-1

BLOCK C-901 COMPR
    PARAM TYPE=ASME-POLYTROP PRES=90.
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITY UTILITY-ID=EC901

UTILITY BOT901 GENERAL
    COST ENERGY-PRICE=14.05 <$/GJ>
    PARAM UTILITY-TYPE=STEAM PRES=5. <barg> PRES-OUT=14.7  &
        TIN=160. <C> VFR-OUT=0. CALOPT=FLASH

UTILITY BOT903 GENERAL
    COST PRICE=0.00245
    PARAM UTILITY-TYPE=WATER PRES=14.7 PRES-OUT=14.7 TIN=115.  &
        VFR-OUT=1. CALOPT=FLASH

UTILITY CW904 GENERAL
    COST ENERGY-PRICE=0.354 <$/GJ>
    PARAM UTILITY-TYPE=WATER TIN=30. <C> TOUT=40. <C> VFRAC=0.  &
        VFR-OUT=0. CALOPT=FLASH

UTILITY E-902 GENERAL
    COST ENERGY-PRICE=4.43 <$/GJ>
```

```
 PARAM UTILITY-TYPE=REFRIGERATIO BASIS=MASS TIN=5. <C>  &
  TOUT=15. <C> VFRAC=0. VFR-OUT=0. CALOPT=FLASH
 COMPOSITION H2O 1.

UTILITY EC901 GENERAL
 COST ELEC-PRICE=0.06
 PARAM UTILITY-TYPE=ELECTRICITY

UTILITY NAT GENERAL
 COST ENERGY-PRICE=11.1 <$/GJ>
 PARAM UTILITY-TYPE=GAS COOLING-VALU=23000. TIN=246.7  &
  TOUT=682.

DESIGN-SPEC FEED
 DEFINE S19C3 MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
  COMPONENT=PROPENE
 SPEC "S19C3" TO "1000"
 TOL-SPEC "0.1"
 VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=PROPENE
 LIMITS "50" "1000"

DESIGN-SPEC RESTM
 DEFINE RESTM BLOCK-VAR BLOCK=R-901 VARIABLE=RES-TIME  &
  SENTENCE=PARAM
 SPEC "RESTM" TO "1.11E-3"
 TOL-SPEC ".0001"
 VARY BLOCK-VAR BLOCK=R-901 VARIABLE=LENGTH SENTENCE=PARAM
 LIMITS "1" "200"

EO-CONV-OPTI

CONV-OPTIONS
 WEGSTEIN MAXIT=100
 SQP MAXIT=100 MAXPASS=1000

TEAR
 TEAR 13

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC

PROPERTY-REP PCES

REACTIONS R-1 POWERLAW
 REAC-DATA 1 PHASE=V
 REAC-DATA 2 PHASE=V
 REAC-DATA 3 PHASE=V
 RATE-CON 1 PRE-EXP=40400000. ACT-ENERGY=74300000. <J/kmol>
 RATE-CON 2 PRE-EXP=2300. ACT-ENERGY=27300000. <J/kmol>
 RATE-CON 3 PRE-EXP=90300000000. ACT-ENERGY=110000000. <J/kmol>
 STOIC 1 MIXED PROPENE -1. / CHLORINE -1. / AC 1. /  &
  HCL 1.
```

```
STOIC 2 MIXED PROPENE -1. / CHLORINE -1. / 12DCP 1.
STOIC 3 MIXED AC -1. / CHLORINE -1. / 13DCP-C 1. /  &
    HCL 1.
POWLAW-EXP 1 MIXED PROPENE 1. / MIXED CHLORINE 1.
POWLAW-EXP 2 MIXED PROPENE 1. / MIXED CHLORINE 1.
POWLAW-EXP 3 MIXED AC 1. / MIXED CHLORINE 1.
```

OPTIMIZED ADIABATIC ALLYL CHLORIDE CASE

```
DYNAMICS
   DYNAMICS RESULTS=ON
IN-UNITS ENG
DEF-STREAMS CONVEN ALL
SIM-OPTIONS OLD-DATABANK=YES

RUN-CONTROL MAX-TIME=100000. MAX-ERRORS=500

DESCRIPTION "
   General Simulation with English Units :
   F, psi, lb/hr, lbmol/hr, Btu/hr, cuft/hr.

   Property Method: None

   Flow basis for input: Mole

   Stream report composition: Mole flow
   "
DATABANKS ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      PURE22
PROP-SOURCES ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      PURE22

COMPONENTS
   H2O H2O /
   HCL HCL /
   PROPENE C3H6-2 /
   CHLORINE CL2 /
   AC C3H5CL /
   12DCP C3H6CL2 /
   13DCP-C C3H4CL2-D1 /
   13DCP-T C3H4CL2-D2 /
   H+ H+ /
   CL- CL-

HENRY-COMPS HENRY CHLORINE HCL PROPENE

CHEMISTRY HCL
   STOIC 1 HCL -1 / H+ 1 / CL- 1
```

```
FLOWSHEET
   BLOCK E-901 IN=14 OUT=2
   BLOCK M-902 IN=1 13 OUT=14
   BLOCK M-901 IN=2 3 OUT=4
   BLOCK R-901 IN=4 OUT=5
   BLOCK E-902 IN=5 OUT=6
   BLOCK T-901 IN=6 OUT=8 7
   BLOCK T-904 IN=7 OUT=9 10
   BLOCK T-902 IN=15 8 OUT=16 17
   BLOCK T-903 IN=16 OUT=12 11
   BLOCK C-901 IN=12 OUT=13
   BLOCK T-905 IN=9 OUT=18 19
   BLOCK T-906 IN=19 OUT=20 21
   BLOCK T-907 IN=17 OUT=22 23
   BLOCK E-903 IN=10 OUT=24
   BLOCK E-904 IN=20 OUT=25
   BLOCK E-905 IN=23 OUT=27
   BLOCK E-906 IN=22 OUT=28
   BLOCK E-907 IN=21 OUT=29

PROPERTIES SYSOP0
   PROPERTIES ELECNRTL / UNIQ-RK / UNIQUAC

STRUCTURES
   STRUCTURES 13DCP-C CL1 C2 S / C2 C3 D / C3 C4 S /  &
      C4 CL5 S

ESTIMATE ALL

PROP-DATA PCES-1
   IN-UNITS ENG
   PROP-LIST DGAQHG / DHAQHG / S25HG / OMEGHG / DHVLB /  &
      VB / RGYR / VLSTD
   PVAL CHLORINE 2983.662941 / -10060.18917 / 28.90035349 /  &
      -17580.05159 / 8784.000000 / .7262124822 /  &
      3.2391732E-10 / .8579136616
   PROP-LIST DHVLB / VB / RGYR
   PVAL 13DCP-C 14431.51333 / 1.612466586 / 1.11089239E-9

PROP-DATA HENRY-1
   IN-UNITS ENG
   PROP-LIST HENRY
   BPVAL HCL H2O -49.78140336 2186.999983 8.370700000  &
      -5.3294445E-3 -3.999995968 68.00000346 0.0
```

```
    BPVAL CHLORINE H2O -116.9781387 4371.515965 19.18540000  &
        -4.9558834E-3 49.73000360 103.7300032 0.0
    BPVAL HCL 12DCP 10.00798341 -2648.879936 0.0 0.0  &
        -4.269995966 67.73000346 0.0
    BPVAL PROPENE H2O 326.3806995 -28021.26578 -41.73762000 0.0  &
        69.53000344 220.7300022 0.0
    BPVAL PROPENE 12DCP 12.93988341 -3932.459880 0.0 0.0  &
        -4.269995966 67.73000346 0.0

PROP-DATA UNIQ-1
    IN-UNITS ENG
    PROP-LIST UNIQ
    BPVAL H2O AC -4.247000000 2292.652782 0.0 0.0 109.9400031  &
        212.0000023 0.0
    BPVAL AC H2O 15.46800000 -10062.08074 0.0 0.0 109.9400031  &
        212.0000023 0.0
    BPVAL H2O 12DCP 0.0 -539.9468957 0.0 0.0 77.00000338  &
        77.00000338 0.0
    BPVAL 12DCP H2O 0.0 -2498.536780 0.0 0.0 77.00000338  &
        77.00000338 0.0

PROP-DATA VLCLK-1
    IN-UNITS ENG
    PROP-LIST VLCLK
    BPVAL H+ CL- .5534556926 .2140997389

PROP-DATA GMELCC-1
    IN-UNITS ENG
    PROP-LIST GMELCC
    PPVAL H2O ( H+ CL- ) 41.67400000
    PPVAL ( H+ CL- ) H2O -22.15400000
    PPVAL HCL ( H+ CL- ) 1.00000000E-3
    PPVAL ( H+ CL- ) HCL -1.0000000E-3

PROP-DATA GMELCD-1
    IN-UNITS ENG
    PROP-LIST GMELCD
    PPVAL H2O ( H+ CL- ) 9581.579923
    PPVAL ( H+ CL- ) H2O -3967.379968

PROP-DATA GMELCE-1
    IN-UNITS ENG
    PROP-LIST GMELCE
    PPVAL H2O ( H+ CL- ) -5.404000000
```

```
   PPVAL ( H+ CL- ) H2O 5.188000000

PROP-DATA GMELCN-1
   IN-UNITS ENG
   PROP-LIST GMELCN
   PPVAL H2O ( H+ CL- ) .0283500000

PCES-PROP-DATA
   IN-UNITS ENG
   GAMINF H2O 12DCP * * 68 2340 / * * 86 2310 / * *  &
      104 2090

PCES-PROP-DATA
   IN-UNITS ENG
   GAMINF H2O 13DCP-C * * 68 1360 / * * 86 1430 / * *  &
      104 1460

STREAM 1
   SUBSTREAM MIXED TEMP=80. PRES=74.7
   MOLE-FLOW PROPENE 1000.

STREAM 3
   SUBSTREAM MIXED TEMP=80. PRES=74.7
   MOLE-FLOW CHLORINE 133.

STREAM 15
   SUBSTREAM MIXED TEMP=70. PRES=14.7
   MOLE-FLOW H2O 1000.

BLOCK M-901 MIXER
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES

BLOCK M-902 MIXER
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES

BLOCK T-903 SEP
   PARAM
   FRAC STREAM=12 SUBSTREAM=MIXED COMPS=PROPENE FRACS=1.
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITY UTILITY-ID=U-1
```

```
BLOCK E-901 HEATER
    PARAM TEMP=730. PRES=74.7
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITY UTILITY-ID=U-1

BLOCK E-902 HEATER
    PARAM TEMP=70. PRES=74.7
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITY UTILITY-ID=U-1

BLOCK E-903 HEATER
    PARAM TEMP=70. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-904 HEATER
    PARAM TEMP=70. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-905 HEATER
    PARAM TEMP=100. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-906 HEATER
    PARAM TEMP=100. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-907 HEATER
    PARAM TEMP=100. PRES=14.7

BLOCK T-907 FLASH2
    PARAM TEMP=201.5 PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK T-901 RADFRAC
    PARAM NSTAGE=15 ALGORITHM=STANDARD INIT-OPTION=STANDARD  &
        MAXOL=150 DAMPING=NONE
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 6 7
    PRODUCTS 8 1 V / 7 15 L
    P-SPEC 1 20. / 15 27.
    COL-SPECS D:F=0.893039 MOLE-RR=0.5
    SPEC 1 MOLE-RECOV 0.9999 COMPS=AC STREAMS=7
```

```
    VARY 1 D:F 0.001 0.999
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK T-902 RADFRAC
    PARAM NSTAGE=10 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD  &
        MAXOL=100 MAXIL=50
    COL-CONFIG CONDENSER=NONE REBOILER=NONE
    RATESEP-ENAB CALC-MODE=EQUILIBRIUM
    FEEDS 15 1 ON-STAGE / 8 10 ON-STAGE
    PRODUCTS 17 10 L / 16 1 V
    P-SPEC 1 14.7
    COL-SPECS
    T-EST 1 110. / 10 68.
    PROPERTIES ELECNRTL HENRY-COMPS=HENRY CHEMISTRY=HCL  &
        FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=NO

BLOCK T-904 RADFRAC
    PARAM NSTAGE=30
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 7 15
    PRODUCTS 10 30 L / 9 1 V
    P-SPEC 1 16. / 15 25.
    COL-SPECS D:F=0.54 MOLE-RR=7.
    SPEC 1 MOLE-FRAC 0.97 COMPS=13DCP-C STREAMS=10
    VARY 1 D:F 0.001 0.999
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK T-905 RADFRAC
    PARAM NSTAGE=30
    COL-CONFIG CONDENSER=TOTAL
    FEEDS 9 15
    PRODUCTS 19 30 L / 18 1 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RR=5.
    SPEC 1 MOLE-RECOV 0.995 COMPS=AC STREAMS=18
    VARY 1 D:F 0.01 0.99
    UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK T-906 RADFRAC
    PARAM NSTAGE=30
```

```
   COL-CONFIG CONDENSER=TOTAL
   FEEDS 19 15
   PRODUCTS 20 1 L / 21 30 L
   P-SPEC 1 14.7
   COL-SPECS D:F=0.01 MOLE-RR=5.
   SPEC 1 MOLE-RECOV 0.9 COMPS=12DCP STREAMS=20  &
      BASE-STREAMS=19
   VARY 1 D:F 0.01 0.99
   UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK R-901 RPLUG
   PARAM TYPE=ADIABATIC LENGTH=20. DIAM=6. PRES=40.  &
      INT-TOL=1E-005
   COOLANT MAXIT=50
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES / SYSOP0
   REACTIONS RXN-IDS=R-1

BLOCK C-901 COMPR
   PARAM TYPE=ASME-POLYTROP PRES=90.
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITY UTILITY-ID=U-1

UTILITY U-1 GENERAL
   COST ELEC-PRICE=0.071
   PARAM UTILITY-TYPE=ELECTRICITY

DESIGN-SPEC FEED
   DEFINE S19C3 MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
      COMPONENT=PROPENE
   SPEC "S19C3" TO "1000"
   TOL-SPEC "0.1"
   VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=PROPENE
   LIMITS "50" "1000"

DESIGN-SPEC RESTM
   DEFINE RESTM BLOCK-VAR BLOCK=R-901 VARIABLE=RES-TIME  &
      SENTENCE=PARAM
   SPEC "RESTM" TO "1.11E-3"
   TOL-SPEC ".0001"
   VARY BLOCK-VAR BLOCK=R-901 VARIABLE=LENGTH SENTENCE=PARAM
   LIMITS "1" "200"
```

```
EO-CONV-OPTI

OPTIMIZATION MAXPROFT
   DEFINE AC9 MASS-FLOW STREAM=18 SUBSTREAM=MIXED COMPONENT=AC
   DEFINE HCL17 MASS-FLOW STREAM=22 SUBSTREAM=MIXED  &
      COMPONENT=HCL
   DEFINE CL3 MASS-FLOW STREAM=3 SUBSTREAM=MIXED  &
      COMPONENT=CHLORINE
   DEFINE PROP1 MASS-FLOW STREAM=1 SUBSTREAM=MIXED  &
      COMPONENT=PROPENE
   DEFINE H2015 MASS-FLOW STREAM=15 SUBSTREAM=MIXED  &
      COMPONENT=H2O
   DEFINE FDHTR BLOCK-VAR BLOCK=E-901 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE REB1 BLOCK-VAR BLOCK=T-901 VARIABLE=REB-DUTY  &
      SENTENCE=RESULTS
   DEFINE REB2 BLOCK-VAR BLOCK=T-904 VARIABLE=REB-DUTY  &
      SENTENCE=RESULTS
   DEFINE COMP BLOCK-VAR BLOCK=C-901 VARIABLE=BRAKE-POWER  &
      SENTENCE=RESULTS
   DEFINE COOLER BLOCK-VAR BLOCK=E-902 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE COND1 BLOCK-VAR BLOCK=T-901 VARIABLE=COND-DUTY  &
      SENTENCE=RESULTS
   DEFINE COND2 BLOCK-VAR BLOCK=T-904 VARIABLE=COND-DUTY  &
      SENTENCE=RESULTS
   DEFINE WASTE STREAM-VAR STREAM=21 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE PROFIT PARAMETER 1 PHYS-QTY=UNIT-PRICE UOM="$/lb"  &
      INIT-VAL=1.
F     REVAC=1.80
F     REVHCL=0.095
F     CSTCL2=0.375
F     CSTPRP= 0.981
F     WASTEC=0.2
F     CWATER = 6.7e-5
F     REVENUE=(REVAC*AC9+REVHCL*HCL17)*24*365
F     RAWCST=(CSTCL2*CL3+CSTPRP*PROP1+CWATER*H2015)*24*365
F     WSTCST=(WASTEC*WASTE)*24*365
F     TOTGAS=FDHTR
F     LOWS =REB1+REB2
F     GASCST=(TOTGAS)*(1.17E-05)*24*365
F     LOWSC = LPWS*(1.48E-05)*24*365
F     ELECST=0.06*COMP
```

```
F    H20BTU=-(COND1+COND2)
F    FLWH20=H20BTU*(3.7349E-07)*24*365
F    H20CST=FLWH20
F    PROFIT=REVENUE-RAWCST-WSTCST-UTLCST
   MAXIMIZE "PROFIT"
   VARY BLOCK-VAR BLOCK=E-901 VARIABLE=TEMP SENTENCE=PARAM
   LIMITS "200" "1000"
   VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CHLORINE
   LIMITS "130" "1000"
   VARY BLOCK-VAR BLOCK=R-901 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "25" "50"

CONV-OPTIONS
   WEGSTEIN MAXIT=100
   SQP MAXIT=100 MAXPASS=1000

TEAR
   TEAR 13

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC

PROPERTY-REP PCES

REACTIONS R-1 POWERLAW
   REAC-DATA 1 PHASE=V
   REAC-DATA 2 PHASE=V
   REAC-DATA 3 PHASE=V
   RATE-CON 1 PRE-EXP=40400000. ACT-ENERGY=74300000. <J/kmol>
   RATE-CON 2 PRE-EXP=2300. ACT-ENERGY=27300000. <J/kmol>
   RATE-CON 3 PRE-EXP=90300000000. ACT-ENERGY=110000000. <J/kmol>
   STOIC 1 MIXED PROPENE -1. / CHLORINE -1. / AC 1. /  &
      HCL 1.
   STOIC 2 MIXED PROPENE -1. / CHLORINE -1. / 12DCP 1.
   STOIC 3 MIXED AC -1. / CHLORINE -1. / 13DCP-C 1. /  &
      HCL 1.
   POWLAW-EXP 1 MIXED PROPENE 1. / MIXED CHLORINE 1.
   POWLAW-EXP 2 MIXED PROPENE 1. / MIXED CHLORINE 1.
   POWLAW-EXP 3 MIXED AC 1. / MIXED CHLORINE 1.
;
;
;
;
;
```

OPTIMIZED ISOTHERMAL ALLYL CHLORIDE CASE

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS OLD-DATABANK=YES

RUN-CONTROL MAX-TIME=100000. MAX-ERRORS=500

DESCRIPTION "
   General Simulation with English Units :
   F, psi, lb/hr, lbmol/hr, Btu/hr, cuft/hr.

   Property Method: None

   Flow basis for input: Mole

   Stream report composition: Mole flow
   "

DATABANKS ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      PURE22

PROP-SOURCES ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      PURE22

COMPONENTS
   H2O H2O /
   HCL HCL /
   PROPENE C3H6-2 /
   CHLORINE CL2 /
   AC C3H5CL /
   12DCP C3H6CL2 /
   13DCP-C C3H4CL2-D1 /
   13DCP-T C3H4CL2-D2 /
   H+ H+ /
   CL- CL-

HENRY-COMPS HENRY CHLORINE HCL PROPENE
```

```
CHEMISTRY HCL
    STOIC 1 HCL -1 / H+ 1 / CL- 1

FLOWSHEET
    BLOCK E-901 IN=14 OUT=2
    BLOCK M-902 IN=1 13 OUT=14
    BLOCK M-901 IN=2 3 OUT=4
    BLOCK R-901 IN=4 OUT=5
    BLOCK E-902 IN=5 OUT=6
    BLOCK T-901 IN=6 OUT=8 7
    BLOCK T-904 IN=7 OUT=9 10
    BLOCK T-902 IN=15 8 OUT=16 17
    BLOCK T-903 IN=16 OUT=12 11
    BLOCK C-901 IN=12 OUT=13
    BLOCK T-905 IN=9 OUT=18 19
    BLOCK T-906 IN=19 OUT=20 21
    BLOCK T-907 IN=17 OUT=22 23
    BLOCK E-903 IN=10 OUT=24
    BLOCK E-904 IN=20 OUT=25
    BLOCK E-905 IN=23 OUT=27
    BLOCK E-906 IN=22 OUT=28
    BLOCK E-907 IN=21 OUT=29

PROPERTIES SYSOP0
    PROPERTIES ELECNRTL / UNIQ-RK / UNIQUAC

STRUCTURES
    STRUCTURES 13DCP-C CL1 C2 S / C2 C3 D / C3 C4 S /  &
        C4 CL5 S

ESTIMATE ALL

PROP-DATA PCES-1
    IN-UNITS ENG
    PROP-LIST DGAQHG / DHAQHG / S25HG / OMEGHG / DHVLB /  &
        VB / RGYR / VLSTD
    PVAL CHLORINE 2983.662941 / -10060.18917 / 28.90035349 /  &
        -17580.05159 / 8784.000000 / .7262124822 /  &
        3.2391732E-10 / .8579136616
    PROP-LIST DHVLB / VB / RGYR
    PVAL 13DCP-C 14431.51333 / 1.612466586 / 1.11089239E-9

PROP-DATA HENRY-1
```

```
    IN-UNITS ENG
    PROP-LIST HENRY
    BPVAL HCL H2O -49.78140336 2186.999983 8.370700000  &
        -5.3294445E-3 -3.999995968 68.00000346 0.0
    BPVAL CHLORINE H2O -116.9781387 4371.515965 19.18540000  &
        -4.9558834E-3 49.73000360 103.7300032 0.0
    BPVAL HCL 12DCP 10.00798341 -2648.879936 0.0 0.0  &
        -4.269995966 67.73000346 0.0
    BPVAL PROPENE H2O 326.3806995 -28021.26578 -41.73762000 0.0  &
        69.53000344 220.7300022 0.0
    BPVAL PROPENE 12DCP 12.93988341 -3932.459880 0.0 0.0  &
        -4.269995966 67.73000346 0.0

PROP-DATA UNIQ-1
    IN-UNITS ENG
    PROP-LIST UNIQ
    BPVAL H2O AC -4.247000000 2292.652782 0.0 0.0 109.9400031  &
        212.0000023 0.0
    BPVAL AC H2O 15.46800000 -10062.08074 0.0 0.0 109.9400031  &
        212.0000023 0.0
    BPVAL H2O 12DCP 0.0 -539.9468957 0.0 0.0 77.00000338  &
        77.00000338 0.0
    BPVAL 12DCP H2O 0.0 -2498.536780 0.0 0.0 77.00000338  &
        77.00000338 0.0

PROP-DATA VLCLK-1
    IN-UNITS ENG
    PROP-LIST VLCLK
    BPVAL H+ CL- .5534556926 .2140997389

PROP-DATA GMELCC-1
    IN-UNITS ENG
    PROP-LIST GMELCC
    PPVAL H2O ( H+ CL- ) 41.67400000
    PPVAL ( H+ CL- ) H2O -22.15400000
    PPVAL HCL ( H+ CL- ) 1.00000000E-3
    PPVAL ( H+ CL- ) HCL -1.0000000E-3

PROP-DATA GMELCD-1
    IN-UNITS ENG
    PROP-LIST GMELCD
    PPVAL H2O ( H+ CL- ) 9581.579923
    PPVAL ( H+ CL- ) H2O -3967.379968
```

```
PROP-DATA GMELCE-1
    IN-UNITS ENG
    PROP-LIST GMELCE
    PPVAL H2O ( H+ CL- ) -5.404000000
    PPVAL ( H+ CL- ) H2O 5.188000000

PROP-DATA GMELCN-1
    IN-UNITS ENG
    PROP-LIST GMELCN
    PPVAL H2O ( H+ CL- ) .0283500000

PCES-PROP-DATA
    IN-UNITS ENG
    GAMINF H2O 12DCP * * 68 2340 / * * 86 2310 / * *  &
        104 2090

PCES-PROP-DATA
    IN-UNITS ENG
    GAMINF H2O 13DCP-C * * 68 1360 / * * 86 1430 / * *  &
        104 1460

STREAM 1
    SUBSTREAM MIXED TEMP=80. PRES=74.7
    MOLE-FLOW PROPENE 1000.

STREAM 3
    SUBSTREAM MIXED TEMP=80. PRES=74.7
    MOLE-FLOW CHLORINE 133.

STREAM 15
    SUBSTREAM MIXED TEMP=70. PRES=14.7
    MOLE-FLOW H2O 1000.

BLOCK M-901 MIXER
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES

BLOCK M-902 MIXER
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES

BLOCK T-903 SEP
    PARAM
    FRAC STREAM=12 SUBSTREAM=MIXED COMPS=PROPENE FRACS=1.
```

```
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITY UTILITY-ID=U-1

BLOCK E-901 HEATER
    PARAM TEMP=730. PRES=74.7
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITY UTILITY-ID=U-1

BLOCK E-902 HEATER
    PARAM TEMP=70. PRES=74.7
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITY UTILITY-ID=U-1

BLOCK E-903 HEATER
    PARAM TEMP=70. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-904 HEATER
    PARAM TEMP=70. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-905 HEATER
    PARAM TEMP=100. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-906 HEATER
    PARAM TEMP=100. PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK E-907 HEATER
    PARAM TEMP=100. PRES=14.7

BLOCK T-907 FLASH2
    PARAM TEMP=201.5 PRES=14.7
    UTILITY UTILITY-ID=U-1

BLOCK T-901 RADFRAC
    PARAM NSTAGE=15 ALGORITHM=STANDARD INIT-OPTION=STANDARD  &
        MAXOL=150 DAMPING=NONE
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 6 7
```

```
   PRODUCTS 8 1 V / 7 15 L
   P-SPEC 1 20. / 15 27.
   COL-SPECS D:F=0.893039 MOLE-RR=0.5
   SPEC 1 MOLE-RECOV 0.9999 COMPS=AC STREAMS=7
   VARY 1 D:F 0.001 0.999
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK T-902 RADFRAC
   PARAM NSTAGE=10 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD  &
      MAXOL=100 MAXIL=50
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   RATESEP-ENAB CALC-MODE=EQUILIBRIUM
   FEEDS 15 1 ON-STAGE / 8 10 ON-STAGE
   PRODUCTS 17 10 L / 16 1 V
   P-SPEC 1 14.7
   COL-SPECS
   T-EST 1 110. / 10 68.
   PROPERTIES ELECNRTL HENRY-COMPS=HENRY CHEMISTRY=HCL  &
      FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=NO

BLOCK T-904 RADFRAC
   PARAM NSTAGE=30
   COL-CONFIG CONDENSER=PARTIAL-V
   FEEDS 7 15
   PRODUCTS 10 30 L / 9 1 V
   P-SPEC 1 16. / 15 25.
   COL-SPECS D:F=0.54 MOLE-RR=7.
   SPEC 1 MOLE-FRAC 0.97 COMPS=13DCP-C STREAMS=10
   VARY 1 D:F 0.001 0.999
   PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
      TRUE-COMPS=YES
   UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK T-905 RADFRAC
   PARAM NSTAGE=30
   COL-CONFIG CONDENSER=TOTAL
   FEEDS 9 15
   PRODUCTS 19 30 L / 18 1 L
   P-SPEC 1 14.7
   COL-SPECS D:F=0.5 MOLE-RR=5.
   SPEC 1 MOLE-RECOV 0.995 COMPS=AC STREAMS=18
   VARY 1 D:F 0.01 0.99
```

```
    UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK T-906 RADFRAC
    PARAM NSTAGE=30
    COL-CONFIG CONDENSER=TOTAL
    FEEDS 19 15
    PRODUCTS 20 1 L / 21 30 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.01 MOLE-RR=5.
    SPEC 1 MOLE-RECOV 0.9 COMPS=12DCP STREAMS=20  &
        BASE-STREAMS=19
    VARY 1 D:F 0.01 0.99
    UTILITIES COND-UTIL=U-1 REB-UTIL=U-1

BLOCK R-901 RPLUG
    PARAM TYPE=T-SPEC LENGTH=20. DIAM=6. PRES=40.  &
        INT-TOL=1E-005
    COOLANT MAXIT=50
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES / SYSOP0
    REACTIONS RXN-IDS=R-1

BLOCK C-901 COMPR
    PARAM TYPE=ASME-POLYTROP PRES=90.
    PROPERTIES UNIQ-RK FREE-WATER=STEAM-TA SOLU-WATER=3  &
        TRUE-COMPS=YES
    UTILITY UTILITY-ID=U-1

UTILITY U-1 GENERAL
    COST ELEC-PRICE=0.071
    PARAM UTILITY-TYPE=ELECTRICITY

DESIGN-SPEC FEED
    DEFINE S19C3 MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
        COMPONENT=PROPENE
    SPEC "S19C3" TO "1000"
    TOL-SPEC "0.1"
    VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=PROPENE
    LIMITS "50" "1000"

DESIGN-SPEC RESTM
    DEFINE RESTM BLOCK-VAR BLOCK=R-901 VARIABLE=RES-TIME  &
        SENTENCE=PARAM
    SPEC "RESTM" TO "1.11E-3"
```

```
    TOL-SPEC ".0001"
    VARY BLOCK-VAR BLOCK=R-901 VARIABLE=LENGTH SENTENCE=PARAM
    LIMITS "1" "200"

EO-CONV-OPTI

OPTIMIZATION MAXPROFT
    DEFINE AC9 MASS-FLOW STREAM=18 SUBSTREAM=MIXED COMPONENT=AC
    DEFINE HCL17 MASS-FLOW STREAM=22 SUBSTREAM=MIXED  &
        COMPONENT=HCL
    DEFINE CL3 MASS-FLOW STREAM=3 SUBSTREAM=MIXED  &
        COMPONENT=CHLORINE
    DEFINE PROP1 MASS-FLOW STREAM=1 SUBSTREAM=MIXED  &
        COMPONENT=PROPENE
    DEFINE H2015 MASS-FLOW STREAM=15 SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE FDHTR BLOCK-VAR BLOCK=E-901 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE REB1 BLOCK-VAR BLOCK=T-901 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE REB2 BLOCK-VAR BLOCK=T-904 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE COMP BLOCK-VAR BLOCK=C-901 VARIABLE=BRAKE-POWER  &
        SENTENCE=RESULTS
    DEFINE COOLER BLOCK-VAR BLOCK=E-902 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE COND1 BLOCK-VAR BLOCK=T-901 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE COND2 BLOCK-VAR BLOCK=T-904 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE WASTE STREAM-VAR STREAM=21 SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE PROFIT PARAMETER 1 PHYS-QTY=UNIT-PRICE UOM="$/lb"  &
        INIT-VAL=1.
F     REVAC=1.80
F     REVHCL=0.095
F     CSTCL2=0.375
F     CSTPRP= 0.981
F     WASTEC=0.2
F     CWATER = 6.7e-5
F     REVENUE=(REVAC*AC9+REVHCL*HCL17)*24*365
F     RAWCST=(CSTCL2*CL3+CSTPRP*PROP1+CWATER*H2015)*24*365
F     WSTCST=(WASTEC*WASTE)*24*365
F     TOTGAS=FDHTR
```

```
F    LOWS =REB1+REB2
F    GASCST=(TOTGAS)*(1.17E-05)*24*365
F    LOWSC = LPWS*(1.48E-05)*24*365
F    ELECST=0.06*COMP
F    H20BTU=-(COND1+COND2)
F    FLWH20=H20BTU*(3.7349E-07)*24*365
F    H20CST=FLWH20
F    PROFIT=REVENUE-RAWCST-WSTCST-UTLCST
   MAXIMIZE "PROFIT"
   VARY BLOCK-VAR BLOCK=E-901 VARIABLE=TEMP SENTENCE=PARAM
   LIMITS "200" "1000"
   VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CHLORINE
   LIMITS "130" "1000"
   VARY BLOCK-VAR BLOCK=R-901 VARIABLE=PRES SENTENCE=PARAM
   LIMITS "25" "50"

CONV-OPTIONS
   WEGSTEIN MAXIT=100
   SQP MAXIT=100 MAXPASS=1000

TEAR
   TEAR 13

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC

PROPERTY-REP PCES

REACTIONS R-1 POWERLAW
   REAC-DATA 1 PHASE=V
   REAC-DATA 2 PHASE=V
   REAC-DATA 3 PHASE=V
   RATE-CON 1 PRE-EXP=40400000. ACT-ENERGY=74300000. <J/kmol>
   RATE-CON 2 PRE-EXP=2300. ACT-ENERGY=27300000. <J/kmol>
   RATE-CON 3 PRE-EXP=90300000000. ACT-ENERGY=110000000. <J/kmol>
   STOIC 1 MIXED PROPENE -1. / CHLORINE -1. / AC 1. /  &
      HCL 1.
   STOIC 2 MIXED PROPENE -1. / CHLORINE -1. / 12DCP 1.
   STOIC 3 MIXED AC -1. / CHLORINE -1. / 13DCP-C 1. /  &
      HCL 1.
   POWLAW-EXP 1 MIXED PROPENE 1. / MIXED CHLORINE 1.
   POWLAW-EXP 2 MIXED PROPENE 1. / MIXED CHLORINE 1.
   POWLAW-EXP 3 MIXED AC 1. / MIXED CHLORINE 1.
```

APPENDIX C: PROCESS FLOW DIAGRAM, STREAM SUMMARY TABLE, EQUIPMENT SPECIFICATION FOR THE FOLLOWING CASE STUDIES: METHYL CHLORIDE, DIMETHYL ETHER, ACRYLONITRILE AND ALLYL CHLORIDE

Table C.1: Methyl Chloride Base Case Equipment Specification

Equipment	Specification in Aspen
Mixer (M-601)	Pressure – 14.7 psia, Phases- Vapor-liquid
Mixer (M-602)	Pressure – 0 psia, Phases- Vapor-liquid
Splitter (M-603)	Stream 32- Split Fraction -0.1
Heater (E-601)	Temperature – 572 ^oF, Pressure – 14.7 psia
Reactor (R-601)	Type – CSTR Constant at specified Temperature – 977 ^oF Valid Phase – Vapor Only Reactor Volume-1600 ft^3 Reaction Type- Power Law
Cooler (E-602)	Temperature – 100^oF, Pressure – 14.7 psia
Absorber (T-601)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-2 Condenser –None Reboiler - None Valid Phases : Vapor - Liquid Feed Stage -1, and 2 Product Stage – 1– Vapor, 2- Liquid Stage 1 Condenser Pressure – 14.7
Dryer (T-602)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-5 Condenser –None Reboiler - None Valid Phases : Vapor - Liquid Feed Stage -1, and 5 Product Stage – 1– Vapor, 5- Liquid Stage 1 Condenser Pressure – 14.7
Cooler (E-603)	Temperature – 100 ^oF, Pressure – 14.7 psia
Dryer (T-603)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-2 Condenser –None Reboiler - None Valid Phases : Vapor - Liquid Feed Stage -1, and 2 Product Stage – 1– Vapor, 2- Liquid Stage 1 Condenser Pressure – 14.7
Multi Stage Compressor (C-601)	Number of Stages -2 Compressor Model - Polytrophic using ASME method Specification Type : Fixed discharge pressure – 115 psia

	Feed Stream – 1 Cool specification – Stage 2 outlet temperature – 275°F Cool specification – Stage 1 outlet temperature – 844°F Compressor Valid Phases – Vapor Only Cooler Valid Phase – Vapor Only
Cooler (E-604)	Temperature – -58 °F, Pressure – 115 psia
Flash Column (T-604)	Pressure – 115 psia, Heat Duty- 0 Btu/hr
Separator (T-605)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-12 Condenser –Partial Vapor Reboiler - Kettle Valid Phases : Vapor - Liquid Distillate to Feed Ratio- 0.5, Reflux Ratio- 1.2 Feed Stage-6 Product Stage – 1– Vapor, 12- Liquid Stage 1 Condenser Pressure – 14.7
Separator (T-606)	Type – Distil, Number of Stage-10 Condenser Type - Total Condenser Pressure –14.7 psia Reboiler Pressure –14.7 psia Light key recovery- 99.9% Chloroform Heavy Key Recovery – 0.001 – Carbon Tetrachloride
Separator (T-607)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-30 Condenser –Total Reboiler - Kettle Valid Phases : Vapor - Liquid Distillate to Feed Ratio- 0.5, Reflux Ratio- 1.5 Feed Stage-10 Product Stage – 1– Vapor, 20- Liquid Stage 1 Condenser Pressure – 14.7
Flash Column (T-604)	Temperature – -100 °F, Pressure- 15 psia
Compressor (C-602)	Type – Polytrophic using ASME method Specification Type – Pressure Increase– 45 psia
Cooler (E-605)	Temperature –77 °F, Pressure – 14.7 psia

.

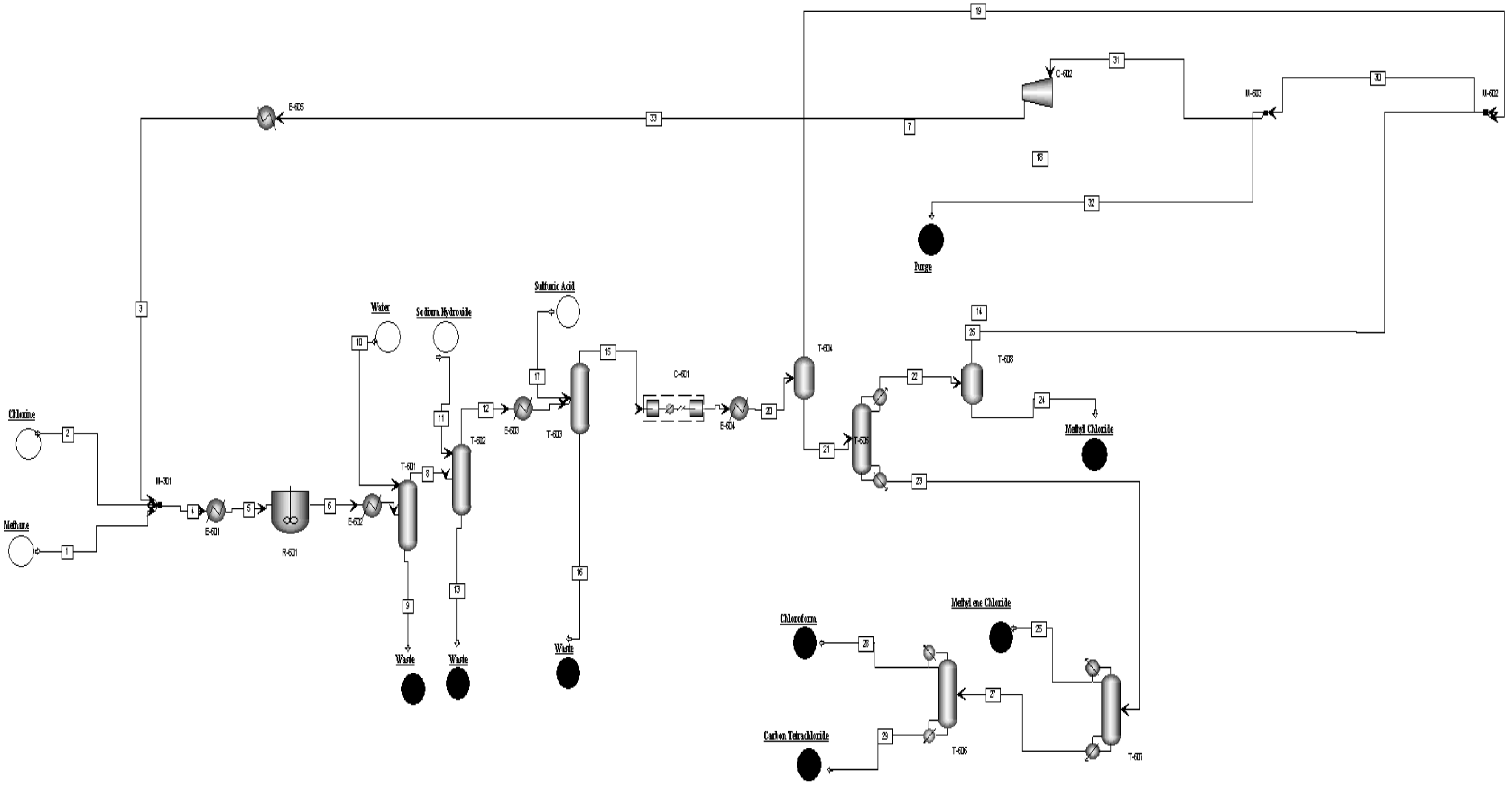

Figure C.1: Schematic of the Methyl Chloride Base Case

Table C.2: Stream Summary Table of the Methyl Chloride Base Case

	1	2	3	4	5	6	7	8	9	10	11
	M-301	M-301	M-301	E-601	R-601	E-602	T-601	T-602		T-601	T-602
			E-605	M-301	E-601	R-601	E-602	T-601	T-601		
Temperature (^{o}F)	77.00	77.00	77.00	76.80	572.00	977.00	100.00	161.40	157.30	86.00	86.00
Pressure (psia)	14.70	14.70	14.70	14.70	14.70	14.70	14.70	14.70	14.70	14.70	14.70
Vapor Frac	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00
Mole Flow (lbmol/hr)	323.00	323.00	780.17	1426.17	1426.17	1426.17	1426.17	1456.39	1994.78	2025.00	200.00
Mass Flow (lb/hr)	5259.14	22902.44	13953.93	42115.52	42115.52	42115.52	42115.52	36008.05	42588.41	36480.94	7999.42
Component Mass Flow lb/hr											
Methane	5078.18	0.00	11255.63	16333.81	16333.81	12632.29	12632.29	12604.05	28.25	0.00	0.00
Chlorine	0.00	22902.44	0.00	22902.44	22902.44	458.63	458.63	440.46	18.17	0.00	0.00
Methyl Chloride	0.00	0.00	1088.82	1088.82	1088.82	9292.84	9292.84	9124.04	168.80	0.00	0.00
Dichloromethane	0.00	0.00	16.48	16.48	16.48	4494.58	4494.58	4021.31	473.27	0.00	0.00
Chloroform	0.00	0.00	1.98	1.98	1.98	1606.52	1606.52	1281.26	325.26	0.00	0.00
Carbon Tetrachloride	0.00	0.00	0.16	0.16	0.16	317.89	317.89	217.21	100.68	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6462.39	30018.55	36480.94	0.00
Hydrogen Chloride	0.00	0.00	0.00	0.00	0.00	11540.95	11540.95	85.84	11455.11	0.00	0.00
Nitrogen	180.97	0.00	1590.85	1771.82	1771.82	1771.82	1771.82	1771.50	0.32	0.00	0.00
Hydronium ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydroclorous Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hypochlorous Ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
hydroxide ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chloride ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7999.42
Sodium Ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sulfuric Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n Sulfate ion											
Sulphate Ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	12	13	14	15	16	17	18	19	20	21	22
	E-603		T-603	C-601		T-603	E-604	M-602	T-604	T-605	T-608
	T-602	T-602	E-603	T-603	T-603		C-601	T-604	E-604	T-604	T-605
	300.30	307.00	100.00	204.20	346.40	90.00	275.00	-58.00	-58.00	-58.00	-23.20
Temperature (^{o}F)	14.70	14.70	14.70	14.70	14.70	14.70	115.00	115.00	115.00	115.00	14.70
Pressure (psia)	1.00	0.00	1.00	1.00	0.00	0.00	1.00	1.00	0.75	0.00	1.00
Vapor Frac	1385.74	270.64	1385.74	1084.96	1033.50	732.71	1084.96	817.56	1084.96	267.39	209.05
Mole Flow (lbmol/hr)	34322.31	9685.16	34322.31	28747.42	77438.97	71864.07	28747.42	14584.08	28747.42	14163.34	8792.23
Mass Flow (lb/hr)											
Component Mass Flow lb/hr	12602.04	2.01	12602.04	12595.20	6.83	0.00	12595.20	11793.36	12595.20	801.85	801.85
Methane	0.00	440.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chlorine	9105.60	18.43	9105.60	9028.95	76.66	0.00	9028.95	1049.36	9028.95	7979.59	7939.69
Methyl Chloride	3999.18	22.12	3999.18	3918.14	81.04	0.00	3918.14	18.31	3918.14	3899.83	0.00
Dichloromethane	1269.99	11.27	1269.99	1227.93	42.06	0.00	1227.93	2.20	1227.93	1225.73	0.00
Chloroform	214.35	2.86	214.35	203.12	11.23	0.00	203.12	0.18	203.12	202.94	0.00
Carbon Tetrachloride	5359.68	1102.71	5359.68	0.45	5359.24	0.00	0.45	0.00	0.45	0.45	0.00
Water	0.00	85.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen Chloride	1771.47	0.03	1771.47	1771.36	0.11	0.00	1771.36	1720.67	1771.36	50.69	50.69
Nitrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydronium ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydroclorous Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hypochlorous Ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
hydroxide ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chloride ion	0.00	7999.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Hydroxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Chloride	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium Hydroxide	0.00	0.00	0.00	2.27	71861.80	71864.07	2.27	0.00	2.27	2.27	0.00
Sulfuric Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hydrogen Sulfate ion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	23	24	25	26	27	28	29	30	31	32	33
	T-607		M-602		T-606			M-603	C-602		E-605
	T-605	T-608	T-608	T-607	T-607	T-606	T-606	M-602	M-603	M-603	C-602
	1.0	-100.0	99.0	145.0	141.8	171.3	-70.0	-70.0	-70.0	157.9	157.9
Temperature (^{o}F)	15.0	15.0	14.7	14.7	14.7	14.7	15.0	15.0	15.0	60.0	60.0
Pressure (psia)	0.0	0.0	1.0	0.0	0.0	0.0	0.0	1.0	1.0	1.0	1.0
Vapor Frac	58.3	159.8	49.3	48.2	10.1	8.8	1.4	866.9	780.2	86.7	780.2
Mole Flow (lbmol/hr)	5370.9	7871.8	920.3	4118.4	1252.5	1046.3	206.2	15504.3	13953.9	1550.4	13953.9
Mass Flow (lb/hr)											
Component Mass Flow lb/hr	0.0	88.9	712.9	0.0	0.0	0.0	0.0	12506.2	11255.6	1250.6	11255.6
Methane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine	39.9	7779.1	160.4	39.9	0.0	0.0	0.0	1209.8	1088.8	121.0	1088.8
Methyl Chloride	3899.7	0.0	0.0	3895.8	3.9	3.9	0.0	18.3	16.5	1.8	16.5
Dichloromethane	1225.7	0.0	0.0	182.5	1043.2	1042.1	1.0	2.2	2.0	0.2	2.0
Chloroform	202.9	0.0	0.0	0.2	202.7	0.2	202.5	0.2	0.2	0.0	0.2
Carbon Tetrachloride	0.4	0.0	0.0	0.0	0.4	0.0	0.4	0.0	0.0	0.0	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Chloride	0.0	3.7	46.9	0.0	0.0	0.0	0.0	1767.6	1590.9	176.8	1590.9
Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydronium ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydroclorous Acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hypochlorous Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
hydroxide ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chloride ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Hydroxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Chloride	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Hydroxide	2.3	0.0	0.0	0.0	2.3	0.0	2.3	0.0	0.0	0.0	0.0
Sulfuric Acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Sulfate ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table C.3: Stream Summary Table for DME Production via Dehydration of Methanol

Stream No.	1	2	3	4	5	6	7	8	9
	P-201	M-201	E-201	E-202	R-201	E-203	E-204	V-201	T-201
		P-201	M-201	E-201	E-202	R-201	E-203	E-204	V-201
Temperature (^{o}C)	25.00	25.96	101.59	154.00	220.00	364.00	278.00	100.00	92.27
Pressure (bar)	1.00	25.00	7.31	15.10	14.70	13.90	13.80	13.40	10.40
Vapor Frac	0.00	0.00	0.00	1.00	1.00	1.00	1.00	0.00	0.06
Total Flow (kg/hr)	8366.39	8366.39	10473.51	10473.51	10473.51	10473.51	10473.51	10473.51	10473.51
Component Mole Flow (kmol/hr)									
Dimethyl Ether	0.00	0.00	1.33	1.33	1.33	130.45	130.45	130.45	130.45
Methanol	259.70	259.70	322.78	322.78	322.78	64.56	64.56	64.56	64.56
Water	2.50	2.50	3.85	3.85	3.85	132.97	132.97	132.97	132.97

Stream No.	10	11	12	13	14	15	16
		V-201	T-202	M-202	E-205		
	T-201	T-201	V-201	M-203	T-202	E-205	M-202
Temperature (^{o}C)	46.45	151.70	139.45	124.82	166.14	50.00	52.33
Pressure (bar)	10.21	10.21	7.40	7.31	7.31	1.20	1.20
Vapor Frac	1.00	0.00	0.04	1.00	0.00	0.00	0.00
Total Flow (kg/hr)	5966.77	4506.74	4506.74	2107.12	2382.63	2382.63	2399.62
Component Mole Flow (kmol/hr)							
Dimethyl Ether	129.10	1.34	1.34	1.33	0.00	0.00	0.01
Methanol	0.60	63.96	63.96	63.08	0.37	0.37	0.88
Water	0.00	132.97	132.97	1.35	131.60	131.60	131.61

Table C.4: ASPEN PLUS Equipment Specification Summary Table for DME Production via Methanol Dehydration

Equipment	Specification in Aspen
Mixer (M-201)	Pressure -0 bar
Mixer (M-202)	Splitter, Stream 13 and 16 Stream 16- Split fraction -0.1
Valve (V-201)	Outlet Pressure -10.4 bar
Valve (V-202)	Outlet Pressure -7.4 bar
Pump (P-201)	Discharge Pressure- 25 bar, Pump Efficiency – 60%
Heater (E-201)	Temperature – 154 ^{o}C, Pressure – 15.1 bar
Heater (E-202)	Temperature – 220 ^{o}C, Pressure – 14.7 bar
Reactor (R-201)	Type – Rstoic Temperature – 364 ^{o}C, Pressure – 13.9 bar Reaction Type- Fractional Conversion (80%) of Methanol
Heater (E-203)	Temperature – 278 ^{o}C, Pressure – 13.8 bar
Heater (E-204)	Temperature –100 ^{o}C, Pressure – 13.4 bar
Columns (T-201)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-22 Condenser –Partial Vapor Distillate Rate- 129.7 Kmol/hr, Reflux Ratio- 0.6 Feed Stage -9, Product Stage – 22 – Liquid, 1- Vapor Pressure- 10.21 bar
Columns (T-202)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-26 Condenser –Partial Vapor Distillate Rate- 66.3 Kmol/hr, Reflux Ratio- 1.8 Feed Stage -14, Product Stage – 26 – Liquid, 1-Vapor Pressure- 7.3 bar
Heater (E-204)	Temperature –50 ^{o}C, Pressure – 1.2 bar

Table C.5: ASPEN PLUS Equipment Specification Summary Table for DME Production Via Natural Gas

Equipment	Specification in Aspen
Heater (E-301)	Temperature – 800 ^oC, Pressure – 1 atm
Heater (E-302)	Temperature – 800 ^oC, Pressure – 1 atm
Heater (E-303)	Temperature – 35 ^oC, Pressure – 1 atm
Heater (E-304)	Temperature – 240 ^oC, Pressure – 40 atm
Heater (E-305)	Temperature – 240 ^oC, Pressure – 20 atm
Mixer (M-301)	Pressure – 0 atm, Valid Phases – Vapor -Liquid
Compressor (C-301)	Type – Isentropic Discharge Pressure – 40 atm Isentropic efficiency – 80%
Reactor (R-301)	Type – Rstoic Temperature – 800^oC, Pressure – 1 atm Reaction Type- Fractional Conversion (96.6%) of Methane
Reactor (R-302)	Type – Rstoic Temperature – 240^oC, Pressure – 4053 kpa Reaction Type- Fractional Conversion (75.5%) of Carbon Monoxide
Reactor (R-303)	Type – Rstoic Temperature – 240 ^oC, Pressure – 20 atm Reaction Type- Fractional Conversion (91 %) of Methanol
Separator (T-301)	Temperature – 20 ^oC, Pressure – 1 atm Valid Phases- Vapor-Liquid
Separator (T-302)	Temperature – 20 ^oC, Pressure – 20 atm Valid Phases- Vapor-Liquid
Columns (T-303)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-45 Condenser –Partial Vapor Distillate Rate- 129.7 Kmol/hr, Reflux Ratio- 4.5 Feed Stage -2, Product Stage – 45 – Liquid, 1- Vapor Pressure- 8 atm
Separator (T-304)	Type- Flash 3 Split fraction – DME 0.99%, Ethane -0.09 &Pentane-0.09
Valve (V-301)	Outlet Pressure – 20 atm
Valve (V-302)	Outlet Pressure- 8 atm

Table C.6: Stream Summary Table for DME Production Via Natural Gas

	1	2	3	4	5	6	7	8	9	10	11
	E-301	R-301	E-302	R-301	E-303	T-301		C-301	E-304	R-302	V-301
		E-301		E-302	R-301	E-303	T-301	T-301	C-301	E-304	R-302
Temperature (^{o}C)	35.0	800.0	35.0	800.0	800.0	35.0	20.0	20.0	643.6	240.0	240.0
Pressure (atm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	40.0	40.0	40.0
Vapor Frac	1.0	1.0	0.0	1.0	1.0	1.0	0.0	1.0	1.0	1.0	1.0
Mole Flow (kg/hr)	425.0	425.0	530.0	530.0	1726.0	1726.0	107.4	1618.6	1618.6	1618.6	1036.6
Mass Flow (kg/hr)	7316.5	7316.5	9548.1	9548.1	16864.6	16864.6	1938.7	14926.0	14926.0	14926.0	14926.0
Component Mole Flow (kmol/hr)											
Dimethyl Ether	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9324.9
Water	0.0	0.0	9548.1	9548.1	2603.4	2603.4	1931.3	672.1	672.1	672.1	672.1
Methane	6402.0	6402.0	0.0	0.0	217.7	217.7	0.0	217.6	217.6	217.6	217.6
Carbon Monoxide	0.0	0.0	0.0	0.0	10797.7	10797.7	0.8	10796.8	10796.8	10796.8	2645.2
Hydrogen	0.0	0.0	0.0	0.0	2331.3	2331.3	0.0	2331.3	2331.3	2331.3	1158.0
Ethane	548.7	548.7	0.0	0.0	548.7	548.7	1.0	547.8	547.8	547.8	547.8
Propane	256.1	256.1	0.0	0.0	256.1	256.1	2.0	254.0	254.0	254.0	254.0
n-Butane	109.7	109.7	0.0	0.0	109.7	109.7	3.4	106.3	106.3	106.3	106.3

	12	13	14	15	16	17	18	19	20	21	22
	T-302		E-305	R-303	V-302	T-303	M-301	T-304		M-301	
	V-301	T-302	T-302	E-305	R-303	V-302	T-303	T-303	T-304	T-304	M-301
Temperature (^{o}C)	240.0	20.0	20.0	240.0	240.0	240.0	150.5	48.5	48.5	48.5	133.2
Pressure (atm)	20.0	20.0	20.0	20.0	20.0	8.0	8.0	8.0	8.0	8.0	8.0
Vapor Frac	1.0	1.0	0.0	1.0	1.0	1.0	0.0	1.0	1.0	0.9	0.1
Mole Flow (kg/hr)	1036.6	702.6	333.9	333.9	333.9	333.9	193.7	140.2	129.1	11.1	204.8
Mass Flow (kg/hr)	14926.0	4721.2	10204.7	10204.7	10204.7	10204.7	3886.1	6318.6	5942.6	376.1	4262.2
Component Mole Flow (kmol/hr)											
Dimethyl Ether	0.0	0.0	0.0	0.0	6019.2	6019.2	39.8	5979.4	5919.6	59.8	99.6
Methanol	9324.9	123.9	9201.1	9201.1	828.1	828.1	798.5	29.6	0.0	29.6	828.1
Water	672.1	2.3	669.8	669.8	3023.6	3023.6	3014.2	9.4	0.0	9.4	3023.6
Methane	217.6	211.4	6.2	6.2	6.2	6.2	0.0	6.2	0.0	6.2	6.2
Carbon Monoxide	2645.2	2615.0	30.2	30.2	30.2	30.2	0.0	30.2	0.0	30.2	30.2
Hydrogen	1158.0	1157.1	0.8	0.8	0.8	0.8	0.0	0.8	0.0	0.8	0.8
Ethane	547.8	432.0	115.8	115.8	115.8	115.8	0.0	115.8	10.4	105.4	105.4
Propane	254.0	115.2	138.9	138.9	138.9	138.9	0.0	138.9	12.5	126.4	126.4
n-Butane	106.3	64.4	41.9	41.9	41.9	41.9	33.6	8.3	0.0	8.3	41.9

Table C.7: Base Case Acrylonitrile Process Equipment Specification

Equipment	Specification in Aspen
Mixer (M-301)	Pressure – 0 psia, Phases- Vapor-liquid
Reactor (R-301)	Type – PFR Constant at specified Temperature – 852 °F Mtultitube reactor Number of Tubes = 20 Tube Length = 19 ft Tube Diameter = 13 in Reaction Type- Power Law
Mixer (M-302)	Pressure – 0 psia, Phases- Vapor-liquid
Reactor (R-301)	Type – Rstoic Temperature – 100 °F, Pressure – 15 psia Reaction Type- Fractional Conversion (96%) of Ammonia
Separator (T-301)	Temperature – 350 °F, Pressure – 10 psia Valid Phases- Vapor-Liquid
Cooler (E-301)	Temperature – 40 °F, Pressure – 20 psia
Columns (T-302)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-15 Condenser –Partial Vapor Bottoms to Feed Ratio- 0.85, Reflux Ratio- 4 Feed Stage -15 and 1, Product Stage – 1– Vapor, 15- Liquid
Heater (E-302)	Temperature –173 °F, Pressure – 15 psi
Columns (T-303)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-30 Condenser –Total Distillate to Feed Ratio- 0.15, Reflux Ratio- 7 Feed Stage -20 Stage 1 Condenser Pressure- 15 psia, Stage 2 Pressure-15 psia
Heater (E-303)	Temperature – 126 °F, Pressure – 14.7 psia
Columns (T-304)	Type –Distl Number of Stage-15 Light Key-HCN, Recovery- 0.95 Heavy key- Acrolein, Recovery – 0.05 Condenser –Total Condenser Pressure- 15 psia, Re-boiler Pressure 15 psia
Columns (T-305)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-12 Condenser –Total Distillate to Feed Ratio- 0.005, Reflux Ratio- 4

	Feed Stage -20 Stage 1 Condenser Pressure- 15 psia
Columns (T-306)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-35 Condenser –Total Distillate to Feed Ratio- 0.96, Reflux Ratio- 4 Feed Stage -15 Stage 1 Condenser Pressure- 15 psia

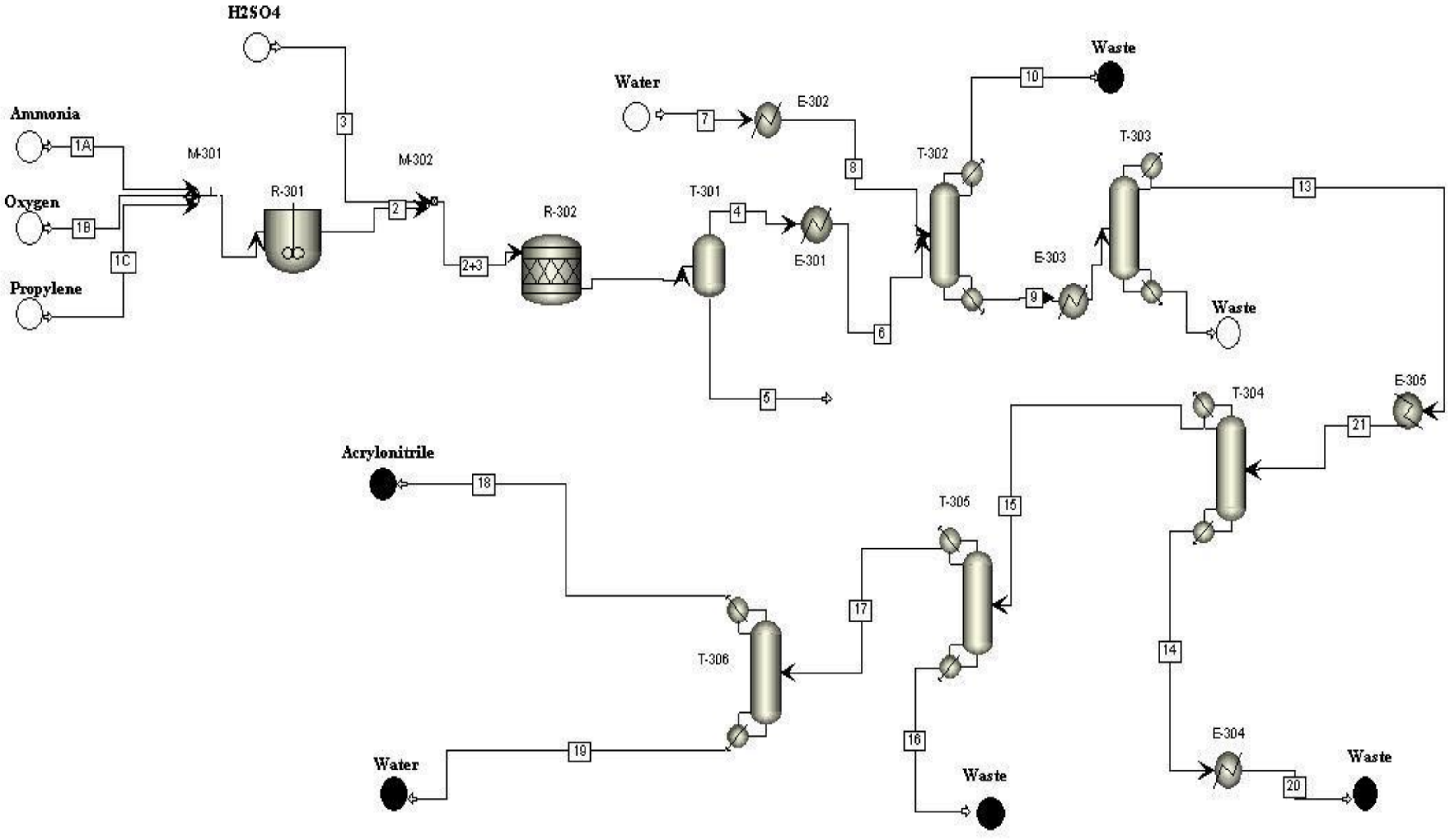

Figure C.2: Schematic of the Acrylonitrile Process Base Case

Table C.8: Base Case Acrylonitrile Process Stream Summary Table

	1	2	3	4	5	6	7	8	9	10
Temperature (^{o}F)	79.70	852.00	86.00	350.00	350.00	40.00	45.00	40.00	195.50	24.60
Pressure (psia)	14.70	14.70	14.70	23.99	23.99	20.00	14.70	20.00	20.00	15.00
Vapor Frac	1.00	347.02	11.21	324.44	12.89	324.44	120.00	120.00	377.78	66.67
Mole Flow (lbmol/hr)	330.00	9152.30	1082.66	8754.60	1480.35	8754.60	2161.83	2161.83	8512.21	2404.23
Mass Flow (lb/hr)	9770.05									
Component Mole Flow (lbmol/hr)		21.77	0.00	0.87	0.00	0.87	0.00	0.00	0.78	0.09
Ammonia	110.00	205.60	0.21	204.32	1.50	204.32	120.00	120.00	324.19	0.13
Water	0.00	15.89	0.00	15.86	0.03	15.86	0.00	0.00	3.37	12.48
Hydrocyanic Acid	0.00	16.93	0.00	16.93	0.00	16.93	0.00	0.00	0.04	16.89
Carbon Monoxide	0.00	0.35	0.00	0.35	0.00	0.35	0.00	0.00	0.00	0.34
Oxygen	135.00	21.74	0.00	21.71	0.04	21.71	0.00	0.00	2.20	19.51
Propylene	85.00	17.37	0.00	17.36	0.01	17.36	0.00	0.00	0.14	17.22
Carbon dioxide	0.00	2.53	0.00	2.51	0.02	2.51	0.00	0.00	2.51	0.00
Acetonitrile	0.00	44.81	0.00	44.50	0.31	44.50	0.00	0.00	44.50	0.00
Acrylonitrile	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.00	0.03	0.00
Acrolein	0.00	0.00	11.00	0.02	0.53	0.02	0.00	0.00	0.02	0.00
Sulfuric Acid	0.00	0.00	0.00	0.00	10.45	0.00	0.00	0.00	0.00	0.00
Ammonium Sulphate	0.00	852.00	86.00	350.00	350.00	40.00	45.00	40.00	195.50	24.60

	11	12	13	14	15	16	17	18	19	20
Temperature (^oF)	173.00	212.80	93.60	-47.00	177.20	178.30	161.40	159.00	201.90	70.00
Pressure (psia)	20.00	15.00	15.00	14.70	14.70	14.70	14.70	12.00	12.00	15.00
Vapor Frac	377.78	313.55	64.22	6.67	57.56	56.64	0.92	44.18	12.46	6.67
Mole Flow (lbmol/hr)	8512.21	5716.02	2796.18	223.69	2572.49	2528.71	43.78	2304.25	224.47	223.69
Mass Flow (lb/hr)										
Component Mole Flow (lbmol/hr)	0.78	0.00	0.78	0.78	0.00	0.00	0.00	0.00	0.00	0.78
Ammonia	324.19	311.54	12.64	0.00	12.64	12.64	0.00	0.18	12.46	0.00
Water	3.37	0.00	3.37	2.89	0.49	0.30	0.19	0.30	0.00	2.89
Hydrocyanic Acid	0.04	0.00	0.04	0.04	0.00	0.00	0.00	0.00	0.00	0.04
Carbon Monoxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	2.20	0.00	2.20	2.20	0.00	0.00	0.00	0.00	0.00	2.20
Propylene	0.14	0.00	0.14	0.14	0.00	0.00	0.00	0.00	0.00	0.14
Carbon dioxide	2.51	0.33	2.18	0.02	2.16	2.14	0.02	2.14	0.00	0.02
Acetonitrile	44.50	1.66	42.84	0.59	42.24	41.53	0.71	41.53	0.00	0.59
Acrylonitrile	0.03	0.00	0.03	0.01	0.02	0.02	0.00	0.02	0.00	0.01
Acrolein	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sulfuric Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonium Sulfate	173.00	212.80	93.60	-47.00	177.20	178.30	161.40	159.00	201.90	70.00

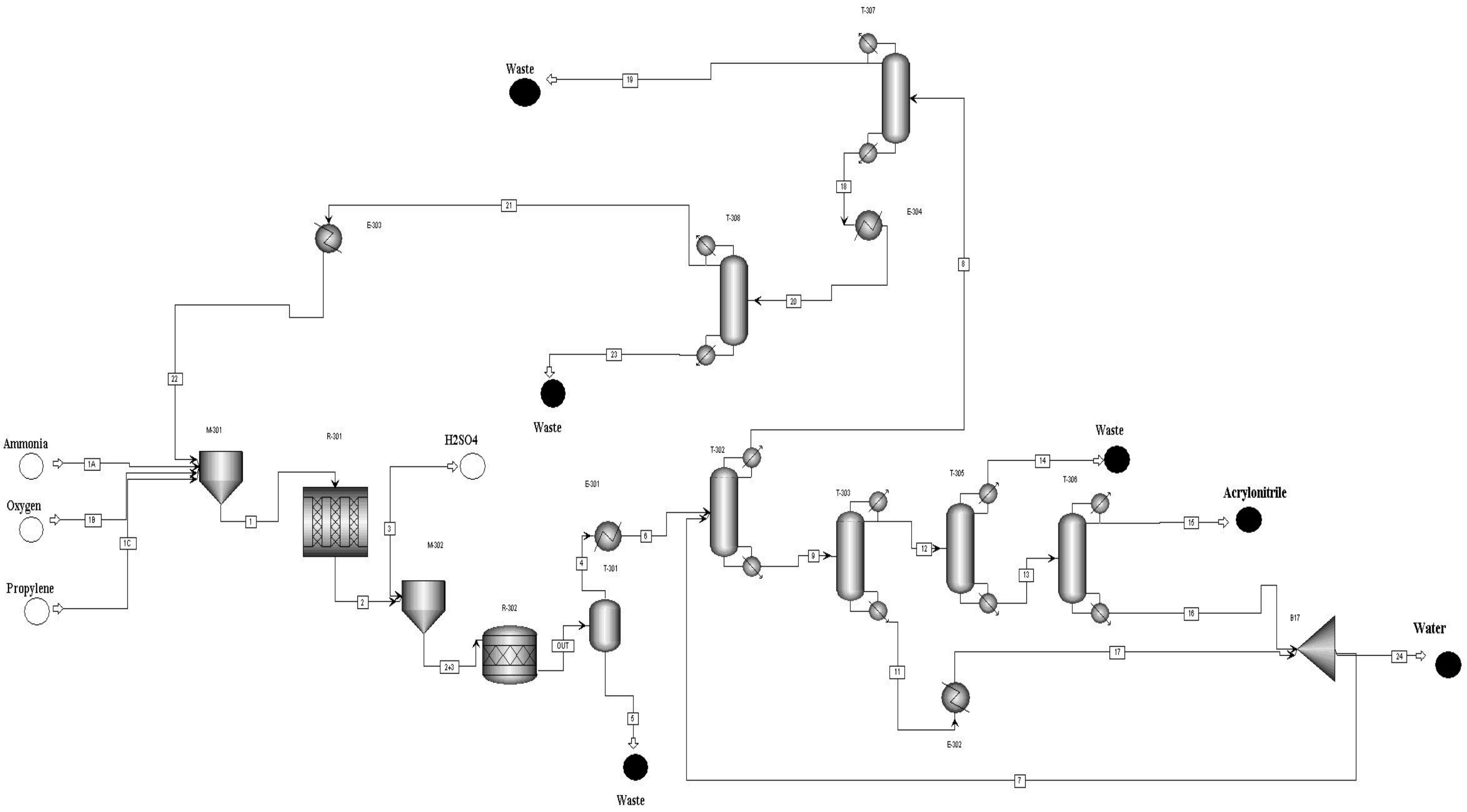

Figure C.3: Schematic of the Optimized Acrylonitrile Process

Table C.9: Optimized Acrylonitrile Process Stream Summary Table

Stream No.	1	2	3	4	5	6	7	8	9	10
Temperature (^oF)	79.60	86.00	350.00	350.00	170.00	170.90	48.80	182.90	212.00	79.60
Pressure (psia)	14.70	14.70	15.00	15.00	20.00	14.70	14.70	14.70	14.70	14.70
Vapor Frac	1.00	0.00	1.00	0.00	0.32	0.00	1.00	0.00	0.00	1.00
Mole Flow (lbmol/hr)	281.23	2.10	325.62	2.06	325.62	120.00	66.84	378.77	318.17	281.23
Mass Flow (lb/hr)	8853.99	188.86	8793.38	249.40	8793.38	2168.84	2409.64	8553.21	5749.01	8853.99
Component Mole Flow (lbmol/hr)										
Ammonia	1141.05	0.00	3.93	0.00	3.93	0.00	0.00	3.93	0.00	1141.05
Water	0.00	3.78	3700.74	2.71	3700.74	2158.16	10.31	5847.99	5723.02	0.00
Hydrocyanic Acid	3.23	0.00	431.74	0.09	431.74	0.00	323.36	108.43	0.00	3.23
Carbon Monoxide	0.00	0.00	473.39	0.00	473.39	0.00	473.32	0.08	0.00	0.00
Oxygen	4127.85	0.00	16.38	0.00	16.38	0.00	16.37	0.01	0.00	4127.85
Propylene	3574.20	0.00	915.04	0.15	915.04	0.00	818.67	96.40	0.00	3574.20
Carbon Dioxide	7.67	0.00	770.87	0.05	770.87	0.00	767.32	3.55	0.00	7.67
Acetonitrile	0.00	0.00	103.60	0.08	103.60	2.25	0.06	106.51	4.61	0.00
Acrylonitrile	0.00	0.00	2374.21	1.68	2374.21	7.33	0.24	2381.74	18.37	0.00
Acrolein	0.00	0.00	1.56	0.00	1.56	0.00	0.00	1.56	0.00	0.00
Sulfuric Acid	0.00	185.08	1.93	6.08	1.93	1.11	0.00	3.01	3.01	0.00
Ammonium Sulfate	0.00	0.00	0.00	238.57	0.00	0.00	0.00	0.00	0.00	0.00

Stream No.	12	13	14	15	16	17	18	19	20	21
Temperature (^oF)	109.70	176.60	69.80	172.10	211.70	170.00	-34.80	-143.70	80.00	-55.60
Pressure (psia)	14.70	14.70	14.70	14.70	14.70	20.00	14.70	14.70	15.00	14.70
Vapor Frac	0.00	0.00	1.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00
Mole Flow (lbmol/hr)	60.60	53.76	6.85	46.77	6.99	318.17	31.98	34.87	31.98	19.36
Mass Flow (lb/hr)	2804.21	2579.56	224.64	2451.85	127.71	5749.01	1152.12	1257.52	1152.12	813.28
Component Mole Flow (lbmol/hr)										
Ammonia	3.93	0.00	3.93	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	124.97	124.97	0.00	0.23	124.74	5723.02	10.31	0.00	10.31	0.00
Hydrocyanic Acid	108.43	0.01	108.43	0.01	0.00	0.00	323.36	0.00	323.36	3.23
Carbon Monoxide	0.08	0.00	0.08	0.00	0.00	0.00	0.00	473.32	0.00	0.00
Oxygen	0.01	0.00	0.01	0.00	0.00	0.00	0.00	16.37	0.00	0.00
Propylene	96.40	0.00	96.40	0.00	0.00	0.00	810.48	8.19	810.48	802.38
Carbon Dioxide	3.55	0.00	3.55	0.00	0.00	0.00	7.67	759.65	7.67	7.67
Acetonitrile	101.90	101.70	0.20	100.22	1.48	4.61	0.06	0.00	0.06	0.00
Acrylonitrile	2363.38	2352.45	10.93	2350.96	1.49	18.37	0.24	0.00	0.24	0.00
Acrolein	1.56	0.44	1.12	0.44	0.00	0.00	0.00	0.00	0.00	0.00
Sulfuric Acid	0.00	0.00	0.00	0.00	0.00	3.01	0.00	0.00	0.00	0.00
Ammonium Sulfate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Stream No.	21	22	24
Temperature (^oF)	80.00	74.00	170.90
Pressure (psia)	15.00	14.70	14.70
Vapor Frac	1.00	0.00	0.00
Mole Flow (lbmol/hr)	19.36	12.62	205.15
Mass Flow (lb/hr)	813.28	338.84	3707.87
Component Mole Flow (lbmol/hr)			
Ammonia	0.00	0.00	0.00
Water	0.00	10.31	3689.60
Hydrocyanic Acid	3.23	320.12	0.00
Carbon Monoxide	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00
Propylene	802.38	8.11	0.00
Carbon dioxide	7.67	0.00	0.00
Acetonitrile	0.00	0.06	3.84
Acrylonitrile	0.00	0.24	12.53
Acrolein	0.00	0.00	0.00
Sulfuric Acid	0.00	0.00	1.90
Ammonium Sulfate	0.00	0.00	0.00

Table C.10: Optimized Acrylonitrile Process Equipment Specification

Equipment	Specification in Aspen
Mixer (M-301)	Pressure – 0 psia, Phases- Vapor-liquid
Reactor (R-301)	Type – PFR Constant at specified Temperature – 852 ^{o}F Mtultitube reactor Number of Tubes = 13 Tube Length = 10 ft Tube Diameter = 1.8 ft Reaction Type- Power Law
Mixer (M-302)	Pressure – 0 psia, Phases- vapor-liquid
Reactor (R-302)	Type – Rstoic Temperature – 170 ^{o}F, Pressure – 15 psia Reaction Type- Fractional Conversion (96%) of Ammonia
Separator (T-301)	Temperature – 350 ^{o}F, Pressure – 15 psia Valid Phases- Vapor-Liquid
Cooler (E-301)	Temperature – 170 ^{o}F, Pressure – 20 psia
Columns (T-302)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-15 Condenser –Partial Vapor Bottoms to Feed Ratio- 0.85, Reflux Ratio- 2.4 Feed Stage -15, and 1, Product Stage – 1– Vapor, 15- Liquid
Heater (E-302)	Temperature –170 ^{o}F, Pressure – 20 psia
Heater (E-303)	Temperature –80^{o}F, Pressure – 15 psia
Columns (T-303)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-30 Condenser –Total Distillate to Feed Ratio- 0.16, Reflux Ratio- 10.5 Feed Stage -10 Stage 1 Condenser Pressure- 15 psia, Stage 2 Pressure-15 psia
Heater (E-304)	Temperature – 80 ^{o}F, Pressure – 15 psia
Columns (T-305)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-12 Condenser – Partial vapor Distillate to Feed Ratio- 0.113, Reflux Ratio- 10 Feed Stage -5 Stage 1 Condenser Pressure- 14.7 psia
Columns (T-306)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-35 Condenser –Total Distillate to Feed Ratio- 0.59, Reflux Ratio- 3 Feed Stage -10 Stage 1 Condenser Pressure- 14.7 psia
Columns (T-307)	Type – DSTWU, Calculation Type- Equilibrium Number of Stage-10 Light Key Component- Carbon Dioxide

	Recovery -99% Heavy Key Component- Propylene Recovery -1%
Columns (T-308)	Type – DSTWU, Calculation Type- Equilibrium Number of Stage-10 Light Key Component- Propylene Recovery -99% Heavy Key Component- Hydrogen Cyanide Recovery -1%

Table C.11: Base Case Allyl Chloride Equipment Specification

Equipment	Specification in Aspen
Mixer (M-901)	Pressure – 0 psia, Phases- Vapor-liquid
Mixer (M-902)	Pressure – 0 psia, Phases- Vapor-liquid
Mixer (M-903)	Pressure – 0 psia, Phases- Vapor-liquid
Mixer (M-904)	Pressure – 0 psia, Phases- Vapor-liquid
Mixer (M-905)	Pressure – 0 psia, Phases- Vapor-liquid
Heater (E-901)	Temperature – 730 ^{o}F, Pressure – 74.7 psia
Cooler (E-902)	Temperature – 70^{o}F, Pressure – 14.7 psia
Cooler (E-903)	Temperature – 70^{o}F, Pressure – 14.7 psia
Cooler (E-904)	Temperature – 100^{o}F, Pressure – 14.7 psia
Cooler (E-906)	Temperature – 70^{o}F, Pressure – 14.7 psia
Reactor (R-901)	Type – Adiabatic Plug Flow Length-20 Diameter-6 Valid Phase – Vapor Only Reactor pressure -40 psia Reaction Type- Power Law
Compressor (C-901)	Type – Polytrophic ASME Method Discharge Pressure -90 Psia
Column (T-901)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-15 Condenser –Partial Vapor Reboiler - Kettle Valid Phases : Vapor - Liquid Reflux Ratio -0.5 Distillate to Feed Ratio -0.893 Feed Stage -7 Product Stage – 1– Vapor, 15- Liquid Stage 1 Pressure – 20, Stage 15 Pressure -27
Dryer (T-902)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-10 Condenser –None Re-boiler - None Valid Phases : Vapor - Liquid

	Feed Stage -1, and 10 Product Stage – 1– Vapor, 10- Liquid Stage 1 Condenser Pressure – 14.7
Separator (T-903)	Type – Sep Split- Propene -1
Column (T-904)	Type – RadFac, Calculation Type- Equilibrium Number of Stage-10 Condenser –Partial Vapor Re-boiler - Kettle Valid Phases : Vapor – Liquid Reflux Ratio-4.02 Distillate to Feed Ratio = 0.54 Feed Stage -6 Product Stage – 1– Vapor, 15- Liquid Stage 1 Pressure – 16 Stage 2 Pressure – 25

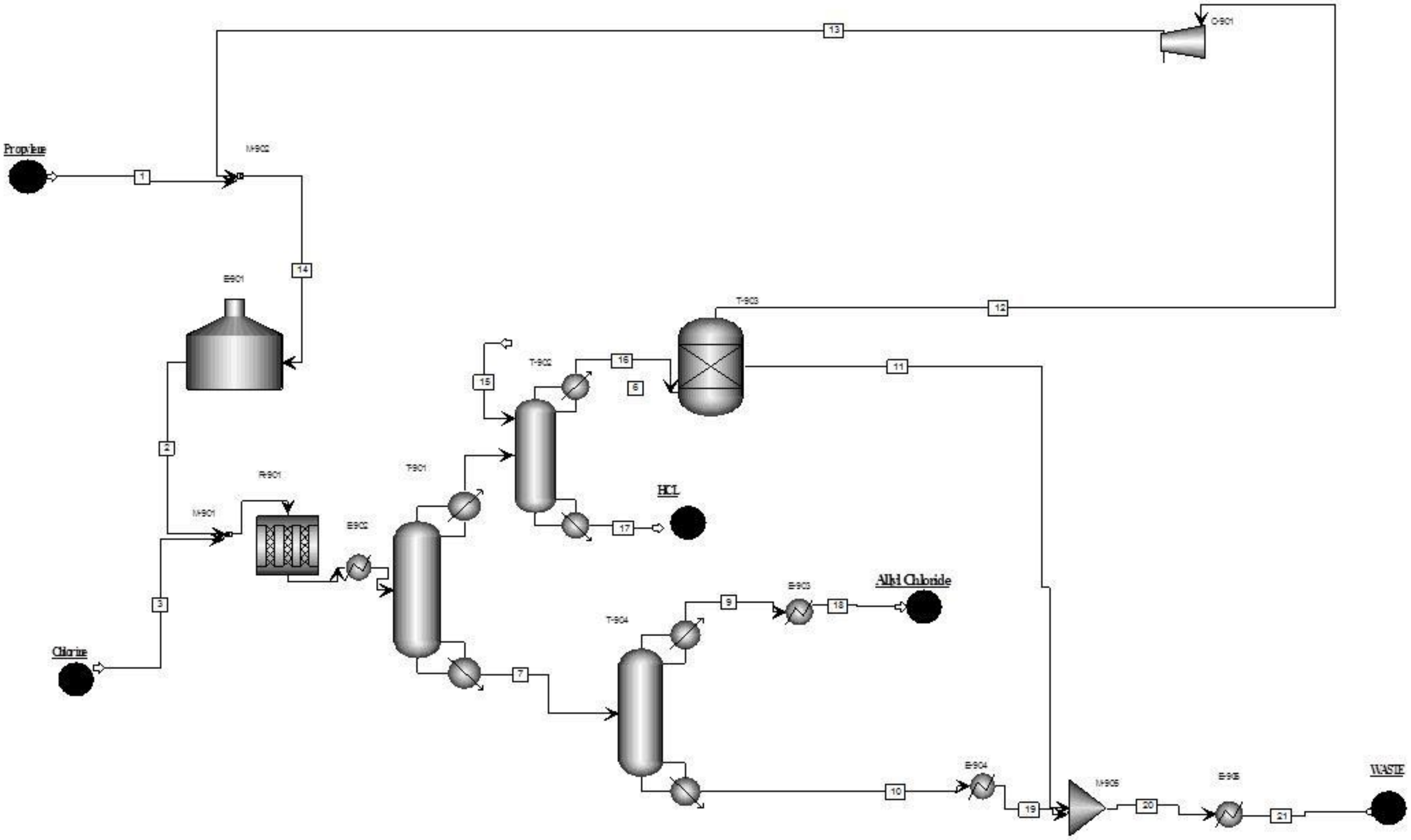

Figure C.4: Schematic of the Base Case Allyl Chloride Process

Table C.12: Base Case Allyl Chloride Process Stream Summary Table

	1	2	3	4	5	6	7	8	9	10	11
	M-902	M-901	M-901	R-901	E-902	T-901	T-904	T-902	E-903	E-904	M-905
		E-901		M-901	R-901	E-902	T-901	T-901	T-904	T-904	T-903
Temperature (^{o}F)	80.0	793.6	80.0	765.8	765.0	70.0	169.9	-45.1	117.9	243.8	72.8
Pressure (Psia)	74.7	74.7	74.7	74.7	40.2	74.7	27.0	20.0	16.0	25.0	14.7
Vapor Frac	1.0	1.0	1.0	1.0	1.0	0.8	0.0	1.0	1.0	0.0	0.0
Mole Flow (lbmol/hr)	113.6	1000.0	130.0	1130.0	1108.7	1108.7	113.6	995.1	75.4	38.1	24.7
Mass Flow (lb/hr)	4779.2	42080.6	9217.7	51298.3	51298.3	51298.3	10033.7	41264.6	5772.8	4260.9	444.8
Component Flow (lb/hr)											
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	444.4
Hydrochloric Acid	0.0	0.0	0.0	0.0	3962.5	3962.5	0.0	3962.5	0.0	0.0	0.0
Propylene	4779.2	42080.6	0.0	42080.6	37301.5	37301.5	0.0	37301.5	0.0	0.0	0.0
Chlorine	0.0	0.0	9217.7	9217.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.0	0.0	0.0	0.0	5802.4	5802.4	5801.8	0.6	5772.8	29.0	0.4
1, 2 dichloropropane	0.0	0.0	0.0	0.0	2408.9	2408.9	2408.9	0.0	0.1	2408.8	0.0
Trans- 1,3 dichloropropane	0.0	0.0	0.0	0.0	1823.1	1823.1	1823.1	0.0	0.0	1823.1	0.0
Cis- 1,3 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	12	13	14	15	16	17	18	19	20	21
	C-901	M-902	E-901	T-902	T-903			M-905	E-906	
	T-903	C-901	M-902		T-902	T-902	E-903	E-904	M-905	E-906
Temperature (^{o}F)	72.8	256.1	236.4	70.0	72.2	83.5	70.0	100.0	93.1	70.0
Pressure (Psia)	14.7	90.0	74.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Frac	1.0	1.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
Mole Flow (lbmol/hr)	886.4	886.4	1000.0	500.0	911.1	584.0	75.4	38.1	62.8	62.8
Mass Flow (lb/hr)	37301.4	37301.4	42080.6	9007.6	37746.3	12526.0	5772.8	4260.9	4705.7	4705.7
Component Flow (lb/hr)										
Water	0.0	0.0	0.0	9007.6	444.4	8563.2	0.0	0.0	444.4	444.4
Hydrochloric Acid	0.0	0.0	0.0	0.0	0.0	3962.5	0.0	0.0	0.0	0.0
Propylene	37301.4	37301.4	42080.6	0.0	37301.4	0.0	0.0	0.0	0.0	0.0
Chlorine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.0	0.0	0.0	0.0	0.4	0.2	5772.8	29.0	29.4	29.4
1, 2 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.1	2408.8	2408.8	2408.8
Trans- 1,3 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1823.1	1823.1	1823.1
Cis- 1,3 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table C.13: Optimized Allyl Chloride Process Equipment Specification

<table>
<tr><th>Equipment</th><th colspan="2">Specification in Aspen</th></tr>
<tr><td>Mixer (M-901)</td><td colspan="2">Pressure – 0 psia, Phases- Vapor-liquid</td></tr>
<tr><td>Mixer (M-902)</td><td colspan="2">Pressure – 0 psia, Phases- Vapor-liquid</td></tr>
<tr><td>Heater (E-901)</td><td colspan="2">Temperature – 730 ^{o}F, Pressure – 74.7 psia</td></tr>
<tr><td>Cooler (E-902)</td><td colspan="2">Temperature – 70^{o}F, Pressure – 74.7 psia</td></tr>
<tr><td>Cooler (E-903)</td><td colspan="2">Temperature – 70^{o}F, Pressure – 14.7 psia</td></tr>
<tr><td>Cooler (E-904)</td><td colspan="2">Temperature – 100^{o}F, Pressure – 14.7 psia</td></tr>
<tr><td>Cooler (E-905)</td><td colspan="2">Temperature – 100^{o}F, Pressure – 14.7 psia</td></tr>
<tr><td>Cooler (E-906)</td><td colspan="2">Temperature – 100^{o}F, Pressure – 14.7 psia</td></tr>
<tr><td>Cooler (E-907)</td><td colspan="2">Temperature – 100^{o}F, Pressure – 14.7 psia</td></tr>
<tr><td>Reactor (R-901)</td><td>Type – Adiabatic Plug Flow
Length-20
Diameter-6
Valid Phase – Vapor Only
Reactor pressure -40 psia
Reaction Type- Power Law</td><td>Type – Isothermal Plug Flow
Specified at Inlet Temperature
Length-20
Diameter-6
Valid Phase – Vapor Only
Reactor pressure -40 psia
Reaction Type- Power Law</td></tr>
<tr><td>Compressor (C-901)</td><td colspan="2">Type – Polytrophic ASME Method
Discharge Pressure -90 Psia</td></tr>
<tr><td>Column (T-901)</td><td colspan="2">Type – RadFac, Calculation Type- Equilibrium
Number of Stage-15
Condenser –Partial Vapor
Reboiler - Kettle
Valid Phases : Vapor - Liquid
Reflux Ratio -0.5
Distillate to Feed Ratio -0.893
Feed Stage -7
Product Stage – 1– Vapor, 15- Liquid
Stage 1 Pressure – 20, Stage 15 Pressure -27</td></tr>
<tr><td>Dryer (T-902)</td><td colspan="2">Type – RadFac, Calculation Type- Equilibrium
Number of Stage-10
Condenser –None
Re-boiler - None
Valid Phases : Vapor - Liquid
Feed Stage -1, and 10
Product Stage – 1– Vapor, 10- Liquid
Stage 1 Condenser Pressure – 14.7</td></tr>
<tr><td>Separator (T-903)</td><td colspan="2">Type – Sep
Split- Propene -1</td></tr>
<tr><td>Column (T-904)</td><td colspan="2">Type – RadFac, Calculation Type- Equilibrium
Number of Stage-30
Condenser –Partial Vapor
Re-boiler - Kettle
Valid Phases : Vapor – Liquid
Reflux Ratio-7</td></tr>
</table>

	Distillate to Feed Ratio = 0.54 Feed Stage -6 Product Stage – 1– Vapor, 30- Liquid Stage 1 Pressure – 16 Stage 2 Pressure – 25 Mole Purity of 1,3 dichloropropene – 97%
Column (T-905)	Type – RadFac, Calculation Type- Equilibrium Number of Stages-30 Condenser –Total Re-boiler - Kettle Valid Phases : Vapor – Liquid Reflux Ratio-5 Distillate to Feed Ratio = 0.5 Feed Stage -10 Product Stage – 30– Liquid, 1- Liquid Stage 1 Pressure – 14.7 Mole Recovery of Allyl Chloride-99%
Column (T-906)	Type – RadFac, Calculation Type- Equilibrium Number of Stages-30 Condenser –Total Re-boiler - Kettle Valid Phases : Vapor – Liquid Reflux Ratio-5 Distillate to Feed Ratio = 0.01 Feed Stage -15 Product Stage – 30– Liquid, 1- Liquid Stage 1 Pressure – 14.7 Mole Recovery of 1,2 dichloropropane-99%
Column (T-906)	Temperature -201.5 ^{o}F Pressure -14.7 psia

Table C.14: Optimized Allyl Chloride Process (Adiabatic PFR) Stream Summary Table

	1	2	3	4	5	6	7	8	9	10	11
	M-902	M-901	M-901	R-901	E-902	T-901	T-904	T-902	T-905	E-903	
		E-901		M-901	R-901	E-902	T-901	T-901	T-904	T-904	T-903
Temperature (^oF)	80.0	677.0	80.0	652.4	891.5	70.0	173.2	-45.1	162.0	253.8	80.7
Pressure (Psia)	74.7	74.7	74.7	74.7	39.4	74.7	27.0	20.0	16.0	25.0	14.7
Vapor Frac	1.0	1.0	1.0	1.0	1.0	0.9	0.0	1.0	1.0	0.0	0.0
Mole Flow (lbmol/hr)	110.6	1000.0	130.0	1130.0	1108.1	1108.1	110.6	997.5	93.8	16.8	32.4
Mass Flow (lb/hr)	4653.9	42080.6	9217.7	51298.3	51298.9	51298.9	9930.9	41368.1	8062.9	1868.0	584.1
Component Flow (lb/hr)											
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	584.1
Hydrochloric Acid	0.0	0.0	0.0	0.0	3940.3	3940.3	0.0	3940.3	0.0	0.0	0.0
Propylene	4653.9	42080.6	0.0	42080.6	37427.2	37427.2	0.0	37427.2	0.0	0.0	0.0
Chlorine	0.0	0.0	9217.7	9217.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.0	0.0	0.0	0.0	5297.0	5297.0	5296.5	0.5	5296.5	0.0	0.0
1, 2 dichloropropane	0.0	0.0	0.0	0.0	2478.8	2478.8	2478.8	0.0	2421.7	57.0	0.0
Trans- 1,3 dichloropropane	0.0	0.0	0.0	0.0	2155.6	2155.6	2155.6	0.0	344.7	1811.0	0.0
Cis- 1,3 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	12	13	14	15	16	17	18	19	20	21	22
	C-901	M-902	E-901	T-902	T-903	T-907		T-906	E-904	E-907	E-906
	T-903	C-901	M-902		T-902	T-902	T-905	T-905	T-906	T-906	T-907
Temperature (°F)	80.7	264.5	244.5	70.0	80.0	90.6	113.3	204.4	202.4	213.0	201.5
Pressure (Psia)	14.7	90.0	74.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Frac	1.0	1.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	1.0
Mole Flow (lbmol/hr)	889.4	889.4	1000.0	1000.0	921.8	1075.7	68.9	24.9	20.1	4.8	560.5
Mass Flow (lb/hr)	37427.1	37426.7	42080.6	18015.3	38011.2	21372.1	5270.0	2792.9	2252.8	540.0	12081.3
Component Flow (lb/hr)											
Water	0.0	0.0	0.0	18015.3	584.1	17431.2	0.0	0.0	0.0	0.0	8160.6
Hydrochloric Acid	0.0	0.0	0.0	0.0	0.0	3940.3	0.0	0.0	0.0	0.0	3920.1
Propylene	37427.1	37426.7	42080.6	0.0	37427.1	0.2	0.0	0.0	0.0	0.0	0.2
Chlorine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.0	0.0	0.0	0.0	0.0	0.5	5270.0	26.5	26.5	0.0	0.4
1, 2 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2421.7	2179.6	242.2	0.0
Trans- 1,3 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	344.7	46.8	297.9	0.0
Cis- 1,3 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	23	24	25	27	28	29
	E-905 T-907	E-903	E-904	E-905	E-906	E-907
Temperature (^{o}F)	201.5	70.0	70.0	100.0	100.0	100.0
Pressure (Psia)	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Frac	0.0	0.0	0.0	0.0	0.2	0.0
Mole Flow (lbmol/hr)	515.1	16.8	20.1	515.1	560.5	4.8
Mass Flow (lb/hr)	9290.9	1868.0	2252.8	9290.9	12081.3	540.0
Component Flow (lb/hr)						
Water	9270.6	0.0	0.0	9270.6	8160.6	0.0
Hydrochloric Acid	20.2	0.0	0.0	20.2	3920.1	0.0
Propylene	0.0	0.0	0.0	0.0	0.2	0.0
Chlorine	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.1	0.0	26.5	0.1	0.4	0.0
1, 2 dichloropropane	0.0	57.0	2179.6	0.0	0.0	242.2
Trans- 1,3 dichloropropane	0.0	1811.0	46.8	0.0	0.0	297.9
Cis- 1,3 dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0

Table C.15: Optimized Allyl Chloride Process (Isothermal PFR) Stream Summary Table

	1	2	3	4	5	6	7	8	9	10	11
	M-902	M-901	M-901	R-901	E-902	T-901	T-904	T-902	T-905	E-903	
		E-901		M-901	R-901	E-902	T-901	T-901	T-904	T-904	T-903
Temperature (^{o}F)	80.0	773.4	80.0	742.3	741.6	70.0	171.5	-45.6	162.8	253.8	84.8
Pressure (Psia)	74.7	74.7	74.7	74.7	47.1	74.7	27.0	20.0	16.0	25.0	14.7
Vapor Frac	1.0	1.0	1.0	1.0	1.0	0.8	0.0	1.0	1.0	0.0	0.0
Mole Flow (lbmol/hr)	130.8	1000.0	149.2	1149.2	1121.2	1121.2	130.9	990.4	115.8	15.1	36.4
Mass Flow (lb/hr)	5504.5	42080.6	10577.7	52658.4	52658.4	52658.4	11664.0	40994.3	9990.2	1673.9	655.8
Component Flow (lb/hr)											
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	655.8
Hydrochloric Acid	0.0	0.0	0.0	0.0	4419.8	4419.8	0.0	4419.8	0.0	0.0	0.0
Propylene	5504.5	42080.6	0.0	42080.6	36573.8	36573.8	0.0	36573.8	0.0	0.0	0.0
Chlorine	0.0	0.0	10577.7	10577.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.0	0.0	0.0	0.0	6473.1	6473.1	6472.4	0.6	6472.4	0.0	0.1
1, 2 Dichloropropane	0.0	0.0	0.0	0.0	3158.9	3158.9	3158.9	0.0	3107.8	51.1	0.0
Trans- 1,3 Dichloropropane	0.0	0.0	0.0	0.0	2032.7	2032.7	2032.7	0.0	409.9	1622.8	0.0
Cis- 1,3 Dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	12	13	14	15	16	17	18	19	20	21	22
	C-901	M-902	E-901	T-902	T-903	T-907		T-906	E-904	E-907	E-906
	T-903	C-901	M-902		T-902	T-902	T-905	T-905	T-906	T-906	T-907
Temperature (^{o}F)	84.8	268.8	245.0	70.0	84.2	97.7	113.3	204.4	202.6	212.7	201.5
Pressure (Psia)	14.7	90.0	74.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Frac	1.0	1.0	1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	1.0
Mole Flow (lbmol/hr)	869.1	869.2	1000.0	1000.0	905.5	1084.8	84.2	31.6	25.7	5.9	629.4
Mass Flow (lb/hr)	36573.7	36576.2	42080.6	18015.3	37229.5	21780.1	6440.1	3550.1	2884.5	665.6	13566.3
Component Flow (lb/hr)											
Water	0.0	0.0	0.0	18015.3	655.8	17359.5	0.0	0.0	0.0	0.0	9163.7
Hydrochloric Acid	0.0	0.0	0.0	0.0	0.0	4419.8	0.0	0.0	0.0	0.0	4402.0
Propylene	36573.7	36576.2	42080.6	0.0	36573.7	0.1	0.0	0.0	0.0	0.0	0.1
Chlorine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.0	0.0	0.0	0.0	0.1	0.6	6440.1	32.4	32.4	0.0	0.5
1, 2 Dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3107.8	2797.0	310.8	0.0
Trans- 1,3 Dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	409.9	55.1	354.8	0.0
Cis- 1,3 Dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	23	24	25	27	28	29
	E-905					
	T-907	E-903	E-904	E-905	E-906	E-907
Temperature (°F)	201.5	70.0	70.0	100.0	100.0	100.0
Pressure (Psia)	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Frac	0.0	0.0	0.0	0.0	0.2	0.0
Mole Flow (lbmol/hr)	455.4	15.1	25.7	455.4	629.4	5.9
Mass Flow (lb/hr)	8213.8	1673.9	2884.5	8213.8	13566.3	665.6
Component Flow (lb/hr)						
Water	8195.8	0.0	0.0	8195.8	9163.7	0.0
Hydrochloric Acid	17.9	0.0	0.0	17.9	4402.0	0.0
Propylene	0.0	0.0	0.0	0.0	0.1	0.0
Chlorine	0.0	0.0	0.0	0.0	0.0	0.0
Allyl Chloride	0.1	0.0	32.4	0.1	0.5	0.0
1, 2 Dichloropropane	0.0	51.1	2797.0	0.0	0.0	310.8
Trans- 1,3 Dichloropropane	0.0	1622.8	55.1	0.0	0.0	354.8
Cis- 1,3 Dichloropropane	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Ion	0.0	0.0	0.0	0.0	0.0	0.0
Chlorine Ion	0.0	0.0	0.0	0.0	0.0	0.0

VITA

OLAMIDE OLAYEMI SHADIYA

Candidate for the Degree of

Doctor of Philosophy

Thesis: SOCIAL, ECONOMIC AND ENVIRONMENTAL METRICS FOR THE SUSTAINABLE OPTIMIZATION OF CHEMICAL AND PETROLEUM PROCESSES

Major Field: Chemical Engineering

Biographical:

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Experience: Internship Experience with Chevron Corporation (summer 2004, 2005, 2006 and 2009), Sabics Innovative Plastics (summer 2008) and Midstates Biodiesel (fall 2005). Employed by Oklahoma State University as a Graduate Assistant from August 2006-December 2010.

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Name: Olamide Olayemi Shadiya　　Date of Degree: December, 2010

Institution: Oklahoma State University　　Location: Stillwater, Oklahoma

Title of Study: SOCIAL, ECONOMIC AND ENVIRONMENTAL METRICS FOR THE SUSTAINABLE OPTIMIZATION OF CHEMICAL AND PETROLEUM PROCESSES

Pages in Study: 357　　Candidate for the Degree of Doctor of Philosophy

Major Field: Chemical Engineering

Scope and Method of Study: This research is focused on adopting a systematic methodology for address sustainability concerns during early stages of engineering design. Traditionally, engineers designed processes to achieve beneficial operations and economic goals. However, given the need to balance the economic benefits of chemical engineering processes, safety, health and environmental impacts, the improved focus on sustainability of production processes has introduced more complex dimensions to consider. When it comes to addressing the three conflicting dimensions of sustainability, there is no well-defined methodology or tool for achieving this. A thorough review was completed to investigate the applications and limitations of existing economic, environmental, health and safety evaluation tools. Therefore, the methodology combines already established approaches, concepts and tools into a novel systematic technique that addresses sustainability concerns during early stages of chemical process design.

Findings and Conclusions: A methodology that involves the use of the SUSTAINABILITY EVALUATOR and ASPEN PLUS was developed for evaluating processes for sustainability. The SUSTAINABILITY EVALUATOR is a novel impact assessment tool developed for this research. This tool applies selected metrics that address economic, environmental as well as health and safety concerns. The SUSTAINABILITY EVALUATOR is a Microsoft Excel based tool that uses mass and energy balance inputs from ASPEN PLUS to evaluate the sustainability of a process. This impact assessment tool equips the process designer with a framework to design industrial processes for sustainability. The objective is for processes designers to use the results generated from the tool to assess and improve the sustainability of a process. The proposed framework involved the use of ASPEN PLUS to simulate processes, calculate mass and energy balances, complete sensitivity analysis and lastly optimize processes An overall sustainability impact which has been incorporated into the SUSTAINABILITY EVALUATOR was developed to quantify sustainability issues in process design. The methodology was demonstrated on two case studies: the acrylonitrile process and the allyl chloride process. The application of the methodology on the two case studies resulted in a more economic, environmental and socially acceptable processes.

ADVISER'S APPROVAL: Dr. Karen High