EVALUATION OF CHEMICAL PROCESSES FOR SUSTAINABLE OPTIMIZATION

By

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EVALUATION OF CHEMICAL PROCESSES FOR

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TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

Regulatory laws to protect the environment and people's lives have been strictly enforced since the Bhopal Union Carbide Plant tragedy in 1984. The Bhopal tragedy is the largest industrial catastrophe to date. It was caused by the leak of the hazardous methyl isocyanate gas resulting in several thousand deaths and injuries including long term environmental and liability issues (Wright 2007). The methyl isocyanate gas is treated with 1-naphthol to produce carbaryl, an insecticide. An alternative chemistry to produce carbaryl is to convert 1-naphthol to chloroformate, which is then treated with methylamine. The alternative chemistry uses exactly the same reagents, but in a different sequence and avoids the synthesis of methyl isocyanate. The alternative chemistry is green as it avoids the hazardous methyl isocyanate gas. Green chemistry is the incorporated in the design of chemical processes to eliminate the generation of hazardous substances. Current industrial focus has shifted from environmental concerns to sustainability concerns. The question is: Is implementing a greener chemistry in the process industry more sustainable? Answering this question is not as simple as it may seem. A well-defined methodology is needed to quantitatively measure sustainability in order to answer this question.

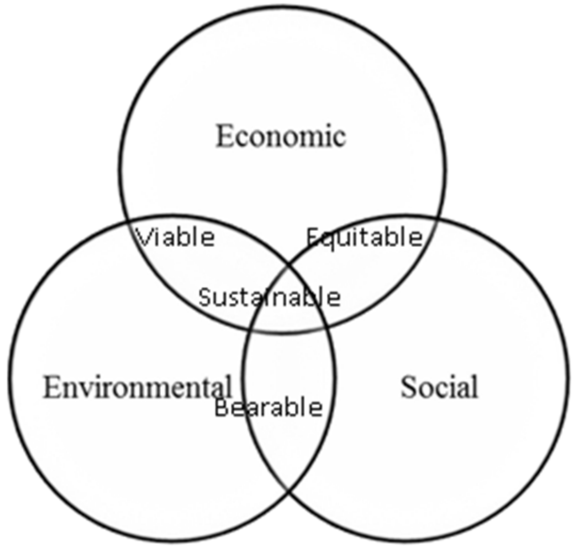

Figure 1.1: Dimensions of Sustainability (Pinter 2005; Adams 2006)

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). In the 21st century industrialists and business leaders are becoming more aware of their role in the environment and society, and people want more environmentally friendly processes. Additionally, manufacturing products that use resources efficiently while considering societal impacts of the processes are highly encouraged. The three dimensions used to classify a process as sustainable are economic, environmental, and social dimensions. As presented in the Venn diagram below in Figure 1.1, a process that addresses economic and environmental concerns is considered viable, a process that addresses environmental and social concerns is considered bearable, and a process that addresses social and economic concerns is considered equitable (Adams 2006). Understanding the driving force behind each of these dimensions is vital to the implementation of the dimensions in process design.

Increasing concerns over global climate change in recent decades due to greater amounts of greenhouse gases in the atmosphere or ozone depletion etc. are leading engineers to address environmental impacts of industrial processes. Environmental concerns are not new; it can be dated back in the United States to 1892 with the establishment of the Sierra Club. The Sierra

Club is one of the first environmental organizations in the United States that has a large influence on the people and the industry. As economics of the industrial processes was initially dictated as the main constraint in the design of chemical process plants, health and safety of the workers and public welfare (social concerns) have only recently become another main constraint. Addressing environmental, social, and economic concerns is important in the evaluation of sustainability of industrial processes. With all these concerns, engineers are developing novel methods to address sustainability in chemical process design.

One method developed recently at the Oklahoma State University is a Microsoft Excel based tool titled “SUSTAINABILITY EVALUATOR” (Shadiya 2010a). The tool evaluates and provides certain metrics under environmental, social, and economic impacts. The objective of this work is to evaluate two different chemistries used to manufacture the same product using the SUSTAINABILITY EVALUATOR. The comparison of sustainability assessment would lead to a better understanding of whether one chemistry is more sustainable than the other. The proposed methodology takes advantage of the Aspen Plus process simulator to model and optimize processes based on the appropriate sustainability concerns associated with the process.

In order to understand the methodology and its implementation better, several topics presented in Table 1.1 will be covered in the subsequent chapters. Chapter Two will discuss the tools available to address economic, social, and environmental dimensions. There are multiple tools that address sustainability. Chapter Three will discuss the methodology for the existing framework used in this work. The fourth chapter will discuss the applicability of the methodology on two case studies. The case studies are of processes manufacturing methyl chloride from two different chemistries. The last chapter will discuss the conclusions and future recommendations.

Table1.1: Summary of the subsequent chapters

Chapter 2	Available tools for evaluating economic, environmental, and social concerns of a process. The advantages, disadvantages, and applicability of using these tools.
Chapter 3	Introduction to the proposed methodology. Detailed description of the steps followed in the evaluating sustainability of a process.
Chapter 4	Discussion of results obtained from following the proposed methodology on two case studies manufacturing the same product, methyl chloride, but using different chemistries.
Chapter 5	Conclusions and future recommendations

This work will exemplify the applicability of using the SUSTAINABILITY EVALUATOR tool in assessing the economic, environmental, and social impacts of chemical processes in the preliminary stages of design. Evaluations such as this one would lead decision makers to choose between the more sustainable options when implementing a process design or to help regulatory organizations in determining the sustainability of various processes.

CHAPTER II

SUSTAINABILITY METRICS AND INDICATORS, AND THE SUSTAINABILITY EVALUATOR TOOL

2.1 SUSTAINABILITY METRICS AND INDICATORS

The current focus of sustainability is on three impact areas: economic, environment, and social, as presented in Figure 2.1. In other words, "people, planet, and profits," as described in the triple bottom line concept (Elkington 1994, 1997). The triple bottom line concept attempts to satisfy the desires of all stakeholders. Sustainability is needed because economics alone cannot dictate the necessary actions to take with respect to the environment or society. Thus, sustainability metrics "measure the immeasurable" (Pinter 2005; Bohringer 2007).

The three dimensions link to address other considerations (Tanzil 2006). The socio-economic aspect addresses the society's financial welfare. The socio-environment addresses the environmental impacts on the society's health and safety. The eco-efficiency addresses the resource usage efficiency with profitability and limited environmental impact. The metrics based on the triple bottom line framework.

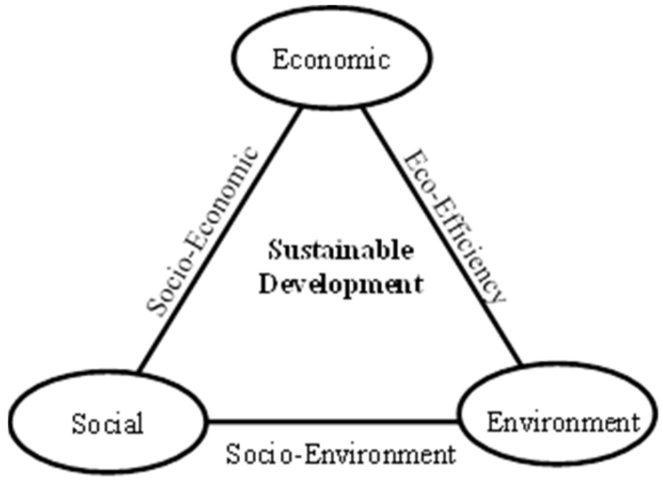

Figure 2.1: Triple bottom line of sustainability (Beloff 2005; Pinter 2005)

Sustainability metrics are used to identify the more sustainable process alternatives. Quantifying sustainability makes that possible. Addressing sustainability concerns in the preliminary stage of design prevent possible future liabilities and responsibilities associated with industrial catastrophes like the Bhopal Union Carbide incident in 1984. Selecting a 'greener' technology or chemistry before implementing it in the industry would prevent such disasters (Allen 2002). Using metrics would aid the decision maker in selecting a process with a lower sustainability impact. In general, metrics are expressed as ratios to make an impact tangible (i.e. physical or financial) (Shadiya 2010a). The social dimension is the most difficult to quantitatively assess because of the metrics indirect nature to be impacted.

There are three categories of indicators: economic, environment, and social. Examples for economic indicators include profit, value, taxes, and investments. Examples for environmental indicators include resource usage, atmospheric, aquatic, and land emissions. Examples for the social indicators include the number of jobs, amount of training, process safety, and society as whole. In order to standardize the decision making of choosing a sustainable option, it is imperative to have the environmental and social dimensions on the same basis as economic (Harmsen 2010). Additionally, this would allow industries to easily assess the sustainability of processes.

Indicators are beneficial because they provide means of quantitatively assessing a particular category in sustainability. Indicators help make addressing sustainability concerns possible. Additionally, they help educate the society on the possible impacts businesses may have on the environment or the health and welfare of people or employment opportunities. As businesses would be able to measure sustainability they would be able to identify the rate of success with respect to profit, social welfare, and environmentally friendly industries. They would be able to quantify any improvements their businesses might make. As a result noticing observable changes would motivate employees do their jobs better

2.2 ECONOMIC, ENVIRONMENTAL, AND SOCIAL EVALUATION

Over the years researchers have proposed different metrics to quantitatively assess and address sustainability concerns. While these tools are successful measures of certain dimensions the problem with them is that they do not address economic, environmental, and social concerns all in one evaluator. Some tools may only address the environment focusing on life cycle assessment for products and processes (Hertwich 1997). Some may only consider economics of a process. However, none of the tools available address the three main dimensions of sustainability. A brief description of the missing aspects of the quantitative assessment metrics available is presented below.

- Sustainable Process Index: Addresses only some aspects of the environmental impact such as ecological impact. It does not address resource usage, economic, and social concerns (Krotscheck 1996; Narodoslawsky 2000).
- Inherent Process Safety Index: Applies to only process safety concerns, not environmental, economic, and health concerns (Heikkila 1999).
- Sustainability Indicators: Limits applicability to assessing energy systems impact during preliminary stages of design (Afgan 2000).

- AIChE/CWRT Sustainability Metrics: Applies only to assessing a general pollution impact category under the environmental concern. It does not address resource usage, economic, and social concerns (AIChE CWRT 2000).
- Dow Jones Sustainability Index: Limits applicability to addressing concerns related to companies' financial performance (Knoepfel 2001).
- BASF Socio-Eco-efficiency Metrics: Limits applicability to detailed stages of design with no correlation to process design parameters (Saling 2002).
- Green Metrics: Applicable to assessing resource usage efficiency of processes' chemical reactions, but not to other environmental, economic, or social concerns (Constable 2002).
- IChemE Metrics: Limited correlation between social concerns and process design parameters making it difficult to improve on the process' social concerns (IChemE Metrics 2002).
- Global Environmental Risk Assessment (GERA) Index: Applicable to social impact assessments, but not economic or environmental evaluations (Achour 2005).
- Indicators of Sustainable Production: Limited applicability to assessing only processes already in operation, however, some metrics may apply to preliminary stages of design (Krajnc 2003).
- BRIDGES to Sustainability Metrics: Useful in only assessing a general pollution impact category under the environmental concern. It does not address resource usage, economic, and social concerns (Tanzil 2006).
- Three Dimensional Sustainability Metrics: Only a couple metrics were addressed under the environmental impact category and there is no correlation between the metrics and process design parameters (Martins 2007).

- Sustainability Indices: Addresses all three dimensions of sustainability, however, has limited applicability to preliminary stages of design because not all metrics are applicable (Tugnoli 2008).
- AIChE Sustainability Index: Only economic concerns are addressed with limited applicability to addressing concerns related to companies' financial performance (AIChE Sustainability Index: Strategic Commitment to Sustainability 2008).

These metrics for sustainability are lacking in one dimension or all or if they are applicable to all three dimensions they are not applicable to preliminary stages of design. To have the ability to measure change in sustainability would help in determining improvements in processes quantitatively. Determining these changes in the early stages of design would be more efficient and effective than during the detailed stages of design. A tool that addresses all three dimensions of sustainability for early stages of design has been developed. The focus of this work will be in applying this tool to a case study.

2.3 CONCERNS ADDRESSED BY THE SUSTAINABILITY EVALUATOR

This work includes applying the SUSTAINABILITY EVALUATOR, an impact assessment tool for the preliminary stages of design, using a case study. This section discusses this tool and the framework for the tool as developed by Shadiya (2010a). The tool addresses economic, environmental, and social concerns using a novel approach (Shadiya 2010c). There is no other tool that is able to address the three dimensions of sustainability in this manner. The metrics used in the SUSTAINABILITY EVALUATOR tool are presented in Figure 2.2.

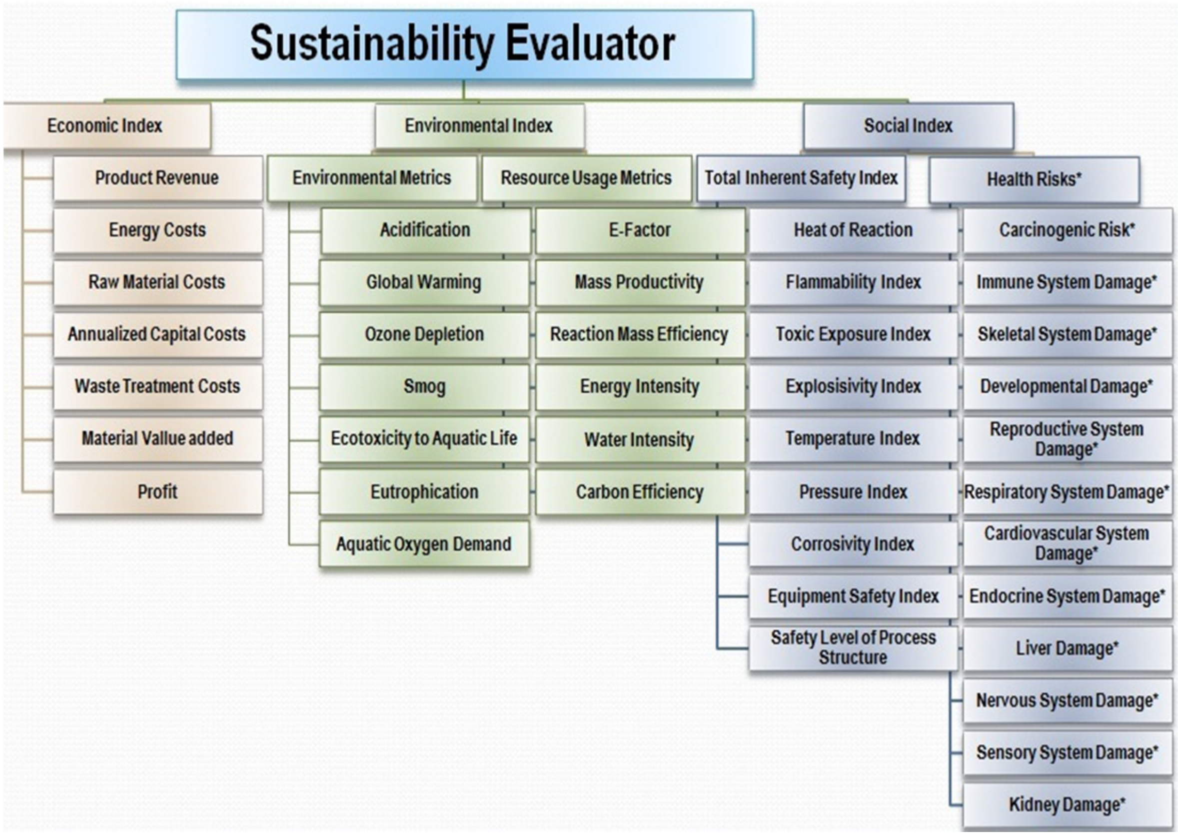

Figure 2.2: Summary of the SUSTAINABILITY EVALUATOR 41 metrics (Shadiya 2010a).

2.3.1 Economic Metrics

The economic metrics used in the SUSTAINABILITY EVALUATOR to quantitative assess the economic dimension includes the following: product revenue, raw material costs, waste treatment costs, operating costs, capital costs, material value added, and profit (Shadiya 2010a). The product revenue and raw material cost is the product or raw material produced or fed in the process multiplied by the selling price. The waste treatment cost is the waste stream multiplied by the cost for treatment. The material value added is the raw material cost subtracted from the product revenue (Carvalho 2008). The operating and capital costs are obtained from Aspen Plus process simulator. The profit is the difference of the total revenue and the total costs. More information on economic analysis is available in Dantus and Seider et al. (Dantus 1996; Seider 2008).

2.3.2 Environmental Metrics

The SUSTAINABILITY EVALUATOR has the following environmental metrics: global warming, atmospheric acidification, aquatic acidification, aquatic oxygen demand, ecotoxicity to aquatic life, eutrophication, photochemical smog formation, and stratospheric ozone depletion. The chemicals impacting these categories were identified and subsequently assigned a value based on the level of chemical's impact on the metric. This was determined by the amount of waste emitted in the process and the amount of the particular chemical in that waste stream (Shadiya 2010a).

The resource usage metrics in the tool include the following: effective mass yield, E-factor, mass intensity, mass productivity, reaction mass efficiency, energy intensity, and water intensity. The following are brief descriptions of these metrics for quantifying the chemistry used in the process (Constable 2002; Tanzil 2006). The effective mass yield is the mass used in the process or process step divided by the mass of reactants entering the process. The E-Factor or the Environmental-Factor is the mass of the total waste divided by the mass of the total product. The reaction mass efficiency is the mass of the products over the mass of the reactants. The mass, energy, and water intensities are the mass used in a process step, energy consumed, and water consumed divided by the mass of the product respectively. The mass productivity is the percentage of the inverse of mass intensity.

2.3.3 Social Metrics

The following are the health risks metrics used in the SUSTAINABILITY EVALUATOR: 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. Chemicals impacting the particular metrics were identified. All metrics have a specific range of index values assigned to them depending on the chemicals impacting. The chemicals impacting the particular metric were assigned an index value depending on the level of risk associated with the amount of a chemical being emitted.

Safety risks metrics in the SUSTAINABILITY EVALUATOR include the following: heat of main reaction, heat of side reaction, flammability index, explosivity index, corrosivity index, temperature index, pressure index, equipment process safety index, process safety structure index, and toxic exposure index. The safety metrics were assigned a range of index values depending on the chemicals impacting or amount of heat released in reactions or operation temperatures or pressures etc. The overall safety index is out of 100, the maximum risk associated with a process.

CHAPTER III

METHODOLOGY

This chapter discusses the methodology used in assessing the applicability of a newly developed tool, the "SUSTAINABILITY EVALUATOR", to chemical processes. The tool measures sustainability concerns in the preliminary stages of design and assesses improvements after optimization of processes.

3.1 INTRODUCTION

Increasing awareness in business leaders thinking that success in the industry alone as a function of profitability is insufficient, is leading companies to assume responsibility of other important factors such as the environment and the society (Bakshi 2003). Industrial emissions and process safety are just two examples of the many influential factors. While waste treatment methodologies are a valuable necessary, the focus of process design also needs inherent waste *reduction* methodologies just like integration of inherent process safety in design. Integrating sustainability concerns after a process is developed is neither economical nor efficient in terms of resource usage. Therefore, these concerns need to be addressed in the early stages of process design.

Designing processes for inherent sustainability is proposed in the following methodology in Figure 3.1:

Base Case Process Simulation

- Aspen Plus Process Simulator

Evaluate Sustainability Using the SUSTAINABILITY EVALUATOR

- Inputs to the SUSTAINABILITY EVALUATOR
- Environmental Impact
- Economic Impact
- Social Impact
- Outputs from the SUSTAINABILITY EVALUATOR

Conduct Sensitivity Analysis to Identify Affecting Parameters

- Fortran Statements Maximizing Profit

Formulate Objective Function

- Single Objective Optimization

Optimize Process Based on Parameters Affecting Sustainability

- Fortran Statements Maximizing Profit

Re-evaluate Sustainability Using the SUSTAINABILITY EVALUATOR

- Decision Maker: Accept results or repeat steps from "Formulate an Objective Function" to re-evaluate the sustainability of the process.

Figure 3.1: Methodology for evaluating sustainability of processes in the preliminary design stages (Shadiya 2010a).

The methodology includes a number of steps before the decision maker can decide whether a process is sustainable. It starts with simulating the base case in Aspen Plus simulator, evaluating the sustainability using the SUSTAINABILITY EVALUATOR, conducting a sensitivity analysis, optimizing the process based on the results of the sensitivity analysis, and finally re-evaluating the sustainability. The steps may be repeated from "Formulate an Objective Function" to optimize based on other possible constraints if in the designer's judgment the process' sustainability results do not meet their requirements.

3.2 BASE CASE PROCESS SIMULATION

The Aspen Plus process simulator is a process modeling tool for designing, optimizing, and monitoring chemical, petroleum, polymeric, coal and mineral processes. Phase equilibrium data is available for regular chemicals, electrolytes, polymers, etc. The pure component and phase equilibria data is from one of the largest databases. The database is regularly updated from the National Institute of Standards and Technology (NIST). Thermodynamic properties could be predicted using the solver for thermodynamic models. Using the simulator engineers can model processes and run a cost analysis to find estimates for capital and operating costs of the plant. Distillation columns, heat exchangers, compressors and other important equipment can be rigorously sized. Sizing equipment manually would be repetitive and time consuming. This is eliminated by using the rigorous computational modeling supported by Aspen Plus. Additionally, it uses various computational modeling tools such as secant method, newton's method, etc. to converge the solutions to the specified stopping and convergence criteria. The simulator could be linked with Microsoft Excel or Visual Basic allowing the user to manipulate equipment (block) inputs for modeling, sizing, and costing.

Some of the inputs to Aspen Plus process modeling tool include the following:

- Listing possible components in the process.
- Choosing the thermodynamic model representation of the molecular behavior of the fluids.
- Selecting the feed flow rates and initial operating conditions such as the temperature and pressure.
- Identifying the necessary unit operation blocks and their inputs including operating conditions.

Aspen Plus was selected for this work because it is useful for sizing unit operations, conducting a cost analysis, and analyzing processes using a variety of model analysis tools where the user can conduct sensitivity analysis and optimize using the built-in process optimizer. The cost evaluator in Aspen Plus uses 2008 US dollars, which is used in evaluating all operating and capital costs. Additionally, this study is conducted using 2009 US dollars. The sensitivity analysis is conducted using sequential-modular (SM) and equation-oriented (EO) strategies. Aspen Plus allows the user to define the sensitivity and optimization blocks by providing optional FORTRAN statements. In this work, Aspen Plus will be used to simulate the processes and optimize based on sustainability.

3.3 ASSESS THE BASE CASE SUSTAINABILITY USING THE SUSTAINABILITY EVALUATOR

The SUSTAINABILITY EVALUATOR is a Microsoft Excel based tool to evaluate the process' environmental burden, economic impact, and social concerns (Shadiya 2010a). The tool uses environmental, economic, and social metrics to address the related concerns. The tool incorporates material and energy flows as inputs and provides the user with the associated impacts from the process.

The inputs to the SUSTAINABILITY EVALUATOR tool are the following.

- Reactor inlet and outlet stream flow rates
- Feed, products, and waste streams flow rates
- Raw material(s) and product(s) prices
- Capital and operating costs
- Total energy usage
- Mass enthalpies of stream entering and exiting the reactor

The SUSTAINABILITY EVALUATOR uses mass and energy flows as inputs. For example, it uses raw material, product, and waste streams flow rates along with economics such as raw material and product prices, capital and operating costs etc. The outputs from the SUSTAINABILITY EVALUATOR are the following:

- Economic evaluation
- Environmental burden evaluation
- Resource usage evaluation
- Process safety evaluation
- Health evaluation
- Overall sustainability impact

A process is sustainable if it environmentally and socially bearable, economically and socially equitable, and environmentally and economically viable. The outputs from the SUSTAINABILITY EVALUATOR are selected metrics and indices that present the impact on environmental, societal, and economical aspects of the process. Since the ultimate objective of any process is economic profitability, the process is not sustainable if it is not economical.

Economic profitability is an important factor in assessing a process' sustainability. If a process is not economical it is not sustainable. There are many different methods that could be used in evaluating a process' profit. In this method the equation to define profit is the following:

$$\text{Profit} = \text{Revenue} - \text{Costs} \tag{3.1}$$

Where:

Revenue = Product revenue + by-product revenue

Cost = Raw material cost + Waste Treatment cost + Energy cost

A process will be more profitable if it is optimized to be operating at the optimum. For example, as the manufactured product or by-products generate greater revenue, the process would achieve greater profit. Additionally, if the costs associated with the process are reduced by making the process as efficient as possible the process would become more profitable. If the process generates the least amount of waste possible the profitability again increases. All these factors play a key role is assessing the process' economic impact. Similarly, addressing the environmental factors will reduce the process' environmental impact.

Increasing concerns over global climate change in recent decades due to greater amounts of greenhouse gases in the atmosphere or ozone depletion etc. are leading engineers to address environmental impacts of industrial processes. The SUSTAINABILITY EVALUATOR evaluates a process' environmental impact on nine different categories using metrics proposed by the Institution of Chemical Engineers (IChemE Metrics 2002). Those nine categories include global warming, stratospheric ozone depletion, photochemical smog, aquatic oxygen demand, atmospheric acidification, aquatic acidification, eco-toxicity to aquatic life, eutrophication, and resource usage. During a process' assessment, if the nine categories have low impact values the process is considered environmentally friendly. Similarly, the social concerns associated with a process are addressed through health and safety impacts.

Health and safety of the workers and public welfare have only recently become another main constraint in establishing the success of a process. The social dimension of sustainability addresses the impact a process might have on the society as a whole. For example, possible job opportunities from implementing a process in the industry, or operating a process plant near a neighborhood etc. While all these concerns are valid, quantification of these has been a challenge. Therefore, the SUSTAINABILITY EVALUATOR addresses only safety and health impacts from a process because of the ability to quantify these. The metrics included are process safety risks (Heikkila 1999) and health risks (International Agency for Research on Cancer 2009;

Score Card 2009). Process safety risks include flammability index, corrosivity index, explosivity index, etc. Health risks include reproductive health risks, cardiovascular health risks, kidney damage health risks etc. All indices are multiplied by the component flow rate from the waste streams to determine the safety and health impacts of the process.

To determine the overall sustainability index of a process, the individual indices from the environmental, social, and economic impacts are added (Shadiya 2010a). Weights were assigned to determine the economic, environmental, and social impacts. The weights assigned may depend on the decision maker. A lesser weight of 0.2 is assigned to the economics because generally they are more quantifiable than environmental and social impacts. The higher weights of 0.4 to the environmental and social impacts are assigned due to the greater uncertainty in determining what may be impacted in the future. The equation used in calculating the overall sustainability index is presented below:

$$SUI = 0.20*EI + 0.40*ENVI + 0.40*SCI \qquad (3.2)$$

Where:

EI: Economic Impact

ENVI: Environmental Impact

SCI: Social Impact

As stated by Shadiya, if the overall impact is zero the process is considered sustainable and if the overall impact is one the process is non-sustainable. The objective of every decision maker using this tool should be to make the overall sustainability index as close to zero as possible. A process is more sustainable if it has a lower overall sustainability impact. Once the sustainability of a base case process has been evaluated a sensitivity analysis is conducted.

3.4 CONDUCT SENSITIVITY ANALYSIS TO IDENTIFY AFFECTING PARAMETERS

A sensitivity analysis is conducted to determine which parameters are affecting the objective. In this analysis, there are independent and dependent variables. Independent variables are the ones that can be varied to determine the effect on the dependent variables. Since the objective is to determine sustainable process options based on profitability and associated environmental and social dimensions, the dependent variable is profit. The independent variables are the parameters that are investigated for example the operating conditions of the process such as the reactor temperature and pressure, the number of stages in a column, the mass flow rates of a specific stream, etc.

Sensitivity analysis is a 'Model Analysis Tool' in the Aspen Plus process simulator. The inputs for the sensitivity analysis tool include a specified objective such as a stream variable or block variable, the tolerance value of the objective, the varying parameter which would again be either a stream variable or block variable, and a given range for varying the parameter. Aspen Plus would output the results in a tabulated format presenting the dependent variable versus the independent variable over the specified range.

3.4.1 FORTRAN Statement Maximizing Profit

When conducting sensitivity analysis, the user may choose the option of including FORTRAN statements to specify the objective. In this work, the objective specified was profit using equation 3.1. An example of the FORTRAN code used is presented in the Appendix Table A1. The outputs from the sensitivity analysis were tabulated with profit, product, and conversion versus the parameters varied within the specified given range.

3.5 FORMULATE OBJECTIVE FUNCTION

In order to improve the sustainability of the process this work used single objective optimization. This kind of problem has a unique or a single solution. While addressing three dimensions of sustainability is a multi-objective optimization problem (Shadiya 2010b), this work was more focused on the applicability of the SUSTAINABILITY EVALUATOR on evaluating process' sustainability. The objective is either minimized or maximized given a set of constraints. For this work, the objective was to maximize the profit. The FORTRAN code for the sensitivity analysis is presented in Appendix A. It was unnecessary to minimize the waste generated to lessen the environmental burden. The equation used in this work to maximize profit is Equation 3.1. Once the objective function is formulated, the next step is to optimize the process based on the sensitivity analysis.

3.6 OPTIMIZE PROCESS BASED ON PARAMETERS AFFECTING SUSTAINABILITY

The optimization was conducted in the Aspen Plus process simulator. Just like the sensitivity analysis, the optimization block is also a 'Model Analysis Tool' and is useful in determining the optimum operating conditions for the process. The inputs for the optimization block include a specified objective function, which in this case is maximizing profit, the convergence criteria for the objective function, the varying parameters such as a stream of block variable, and a specified range for the varying parameters. Unlike the sensitivity analysis, the built-in Aspen Plus optimization may have multiple varying parameters included to determine the optimal point of all varying conditions. The same FORTRAN code used in the sensitivity analysis was used in the optimization. No constraints were added as they were not needed. Aspen Plus would output the results in a tabulated format presenting the dependent variable versus the independent variable over the specified range.

3.7 RE-EVALUATE SUSTAINABILITY USING THE SUSTAINABILTY EVALUATOR

Once the process has been optimized its sustainability is re-evaluated using the SUSTAINABILITY EVALUATOR. If the overall sustainability is acceptable with a value close to zero, the decision maker may choose to accept the optimized process. On the other hand, if the process has a high overall sustainability index with a value close to one, the process is not sustainable, and the decision maker may choose to reconfigure the process based on the sensitivity analysis. After that the decision maker would need to re-optimize the process, and finally re-evaluate the sustainability using the SUSTAINABILITY EVALUTOR. If there is significant improvement in the sustainability the decision maker could choose to accept the re-optimized process, or continue reconfiguration until satisfied with the results.

3.8 SUMMARY

In this chapter, a methodology of applying a newly developed SUSTAINABILITY EVALUATOR tool to a process was introduced. The tool is used to conduct impact assessments or evaluating and improving upon the sustainability of a process in the preliminary stages of design. The approach followed was presented as:

- Simulate a process in Aspen Plus process simulator.
- Evaluate sustainability of the simulated base case process using the SUSTAINABILITY EVALUATOR.
- Conduct sensitivity analysis on the base case process to determine the parameters affecting the objective.
- Formulate the objective function.
- Optimize the process based on the parameters ranges obtained the sensitivity analysis
- Re-evaluate the sustainability using the SUSTAINABILITY EVALUATOR.
- Accept the sustainability results or reconfigure the process and repeat the process until obtaining satisfying results.

In Chapter Four, the methodology was applied to two case studies comparing two different chemistries for manufacturing methyl chloride.

CHAPTER IV

RESULTS AND DISCUSSION

The previous chapter discussed the methodology followed in evaluating processes using the SUSTAINABILITY EVALUATOR. The tool is useful for conducting impact assessments of processes during early stages of design. The methodology involves base case process simulation, sustainability evaluation, sensitivity analysis using Aspen Plus, optimization based on the identified parameters from sensitivity analysis, and finally sustainability re-evaluation. This chapter will discuss the applicability of the tool to two different chemistries manufacturing the same product, methyl chloride, in order to select the most sustainable process alternative. The figures or graphs (other than the sensitivity analysis graphs) are obtained from the output of the SUSTAINABILITY EVALUATOR.

4.1 ABOUT METHYL CHLORIDE

Methyl chloride (or chloromethane or monochloromethane), CH_3Cl, is naturally produced in the ocean daily in large quantities, but produced synthetically for industrial purposes. It is a colorless gas with a mild odor at ambient temperature and pressure. This hazardous and highly flammable colorless gas should be stored and transported with precautions(OxyChem 2009). It is typically transported or stored under pressure to be in the liquid phase.

Methyl chloride has been historically manufactured by the thermal chlorination of methane chemistry, but recently has been manufactured by the hydrochlorination of methanol, oxyhydrochlorination of methane by Dow Corning Corporation (Jarvis Jr. 1995), or from methane over lanthanum-based catalysts (Podkolzin 2008) . This chemical was produced as early as 1835 by Dumas and Peligot and then in the late 1800s to early 1900s for use as starting material for refrigerants, however, it was later banned because of its hazardous nature (Holbrook 2003).

Chloromethane has several important uses in the industry today. One of them is its production as a raw material for manufacturing other chemicals such as methyl cellulose ether. Additionally, it is used in the synthesis of methyl silicone resins, butyl rubber, agricultural chemicals such as herbicide, etc. Most of the methyl chloride produced is used as a chemical intermediate. Some is used for producing ammonium compounds, silicone elastomers, and agricultural chemical (OxyChem 2009).

The manufacturing processes of this chemical are chosen for this work because of its environmental and social impacts. Chloromethane is considered one of the top toxic chemicals by the Environmental Protection Agency. The regulations of Clean Air Act and Clean Water Act list methyl chloride as a hazardous, priority, and regulated air and water pollutant (OxyChem 2009). The chemical is classified as a group 3 chemical signifying as genotoxic for humans or animals and precautions must be taken for the workers handling it (Löf 2000). While the chemical is produced naturally in the oceans, producing it synthetically in the industry causes an effect on the local atmosphere (Löf 2000). The SUSTAINABILITY EVALUATOR tool will be used in conducting an overall sustainability analysis on two methods of producing methyl chloride; first by hydrochlorination of methanol (option 1) and second by chlorination of methane (option 2).

4.2 METHYL CHLORIDE VIA METHANOL PROCESS DESCRIPTION (OPTION 1)

The methyl chloride process is based off of the model found in literature (Dantus 1995). The thermodynamic model chosen for the process is Non-Random Two Liquid model with Redlich-Kwong (NRTL-RK) to handle any non-ideality in the aqueous mixed solution. The input file, stream summaries, and schematics are included in Appendix A and B. The chemistry used for this process is presented below.

$$\mathrm{CH_3OH + HCl \rightarrow CH_3Cl + H_2O} \quad (4.1)$$

$$\mathrm{2CH_3OH + HCl \rightarrow (CH3)_2O + H_2O} \quad (4.2)$$

$$\mathrm{(CH3)_2O\ + 2HCl \rightarrow CHCl_3 + H_2O} \quad (4.3)$$

The main reaction includes methanol and hydrogen chloride reacting to form methyl chloride and water. The other two are side reactions where methanol and hydrogen chloride react to form methyl ether, which in turn reacts with hydrogen chloride to form chloroform. The rates of the side reactions are considered to have negligible effects at the operating temperature. Thus, the side reactions were not included in the chemistry configuration of the isothermal plug flow reactor. As a result, the product composition is mostly methyl chloride and water with some unreacted hydrogen chloride and methanol (GoDove). Studies from the literature presented catalyst γ-alumina to have a greater impact in achieving higher conversion within the operating temperature range; therefore it was used to catalyze the reaction with the properties presented in Table 4.1 (Thyagarajan 1966; Becerra 1992). The power law model in Aspen Plus was used to represent the catalyst system.

Table 4.1: Catalyst γ-Alumina Properties

Activation Energy, E (cal/gram mole)	19,178
Frequency Factor, A (gram moles/hr)	1.816E7
Bulk density (gram per cc)	0.2857

The process follows a series of steps. Figure 4.2 presents the block flow diagram of this process. Methanol and hydrogen chloride feed is preheated up to 675◦F before entering the reactor. The temperature range of the reactor was found from literature to be 572◦F to 734◦F (Thyagarajan 1966). The reactor is operated at 675◦F at ambient pressure in an 8ft (diameter) by 12ft (length) vessel. The reactor effluent is cooled and passed through a series of distillation columns to separate out the product. The reactor effluent is cooled from 675F to 140F and separated in a distillation column. The water and methyl chloride are separated with the water in the bottoms and methyl chloride along with chlorine in the distillate. The bottoms reboiler is operating at 212F and the distillate top stage is at 75F. The distillate is fed to an absorber to separate chlorine from methyl chloride with water from the bottoms of the first tower absorbing the chlorine. The methyl chloride is separated from the light ends and water and chlorine from the heavy ends. The final product purity of methyl chloride is achieved using a flash vessel. The schematic of the process is included in Appendix B.

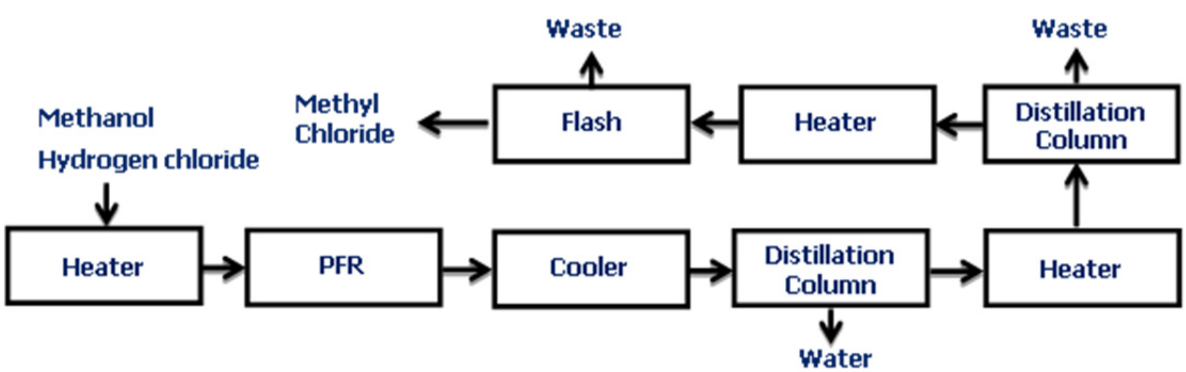

Figure 4.1: Methyl chloride via methanol block flow diagram.

4.2.1 Base Case Sustainability Assessment of the Methyl Chloride via Methanol Process

The SUSTAINABILITY EVALUATOR was used in determining the economic, environmental, and social impacts of the base case methyl chloride via methanol chemistry. The economic impact results will be discussed in the next section.

4.2.1.1 Base Case Economic Assessment of the Methyl Chloride via Methanol Process

The Aspen Plus built-in economic model was used to estimate the capital and operating costs of the process. The economic data used in calculating the associated costs is presented in Table 4.2.

Table 4.2: Summary of economic data for the methyl chloride via methanol process.

Item	Price
Methanol ($/kg)	0.294 (Reed Business Information Limited 2011)
Hydrogen Chloride ($/kg)	0.09 (Reed Business Information Limited 2011)
Process Water ($/kg)	0.00638 (City of Stillwater 2011)
Methyl Chloride ($/kg)	0.82 (Reed Business Information Limited 2011)
Natural Gas ($/ft^3)	0.00451(EIA 2011)
Waste Treatment ($/kg)	0.2 (Turton 2009)

The results from the sustainability evaluator are presented in Table 4.3. The annual revenue from selling methyl chloride is approximate $25.5MM. With all the costs such as the operating cost, waste treatment cost, raw material cost, etc. balancing out the revenue, the profit is about $15.7MM. As presented in Figure 4.3, the raw material cost is the greatest with 82% of all costs. The second highest cost is the operating cost of about 15%. The third highest is the capital cost annualized to about 3% and lastly, the waste treatment cost is a small fraction of all costs. This is probably because this process did not generate much waste. The total waste generated is 2.7E07 lb/year. Analyzing the waste stream, raw material, and products stream components leads to the environmental impact of this process.

Table 4.3: Economic data for the methyl chloride via methanol process.

Economic parameters	Base Case (MM)
Revenue	$25.5
Operating Costs	$1.41
Waste Treatment Costs	$0.315
Raw Material Costs	$8.10
Capital Costs	$2.60
Annualized Capital Cost	$0.31
Material Value Added	$17.5
Profit	$15.7

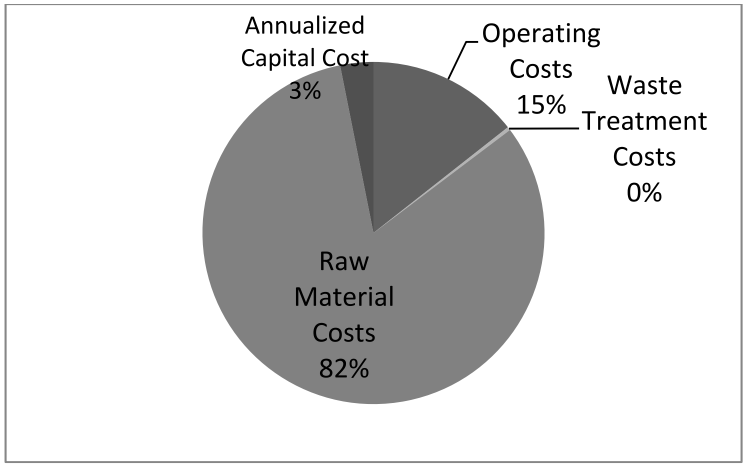

Figure 4.2: Distribution of annualized costs from the SUSTAINABILITY EVALUATOR.

4.2.1.2 Base Case Environmental Assessment of the Methyl Chloride via Methanol Process

The environmental assessment is conducted using the waste streams. As presented earlier in the block flow diagram in Figure 4.2, this particular process has two waste streams. One is from the bottoms of the absorber and the second is from the flash vessel. The component compositions from these streams were used to calculate the environmental impact. The chemicals impacting the environmental metrics are presented in Table 4.4. The results are presented in Figure 4.4. As presented, the most impact this process has is one global warming and atmospheric acidification. The components affecting these two categories are methanol and methyl chloride, and hydrochloric acid respectively. The waste streams need to be reduced in order to minimize the environmental impact.

Table 4.4: Base case environmental impacts for the methyl chloride via methanol process.

Environmental Metrics	Base Case (Tonnes/year)	Chemicals Impacting Metrics
Atmospheric Acidification	1469.5	Hydrogen Chloride
Global Warming	13012.5	Methanol, Methyl Chloride
Stratospheric Ozone Depletion	0.0	None
Photochemical Smog Formation	38.8	Methyl Chloride
Aquatic Acidification	45.1	Hydrogen Chloride
Aquatic Oxygen Demand	113.0	Methanol
Ecotoxicity to Aquatic Life	0.0	None

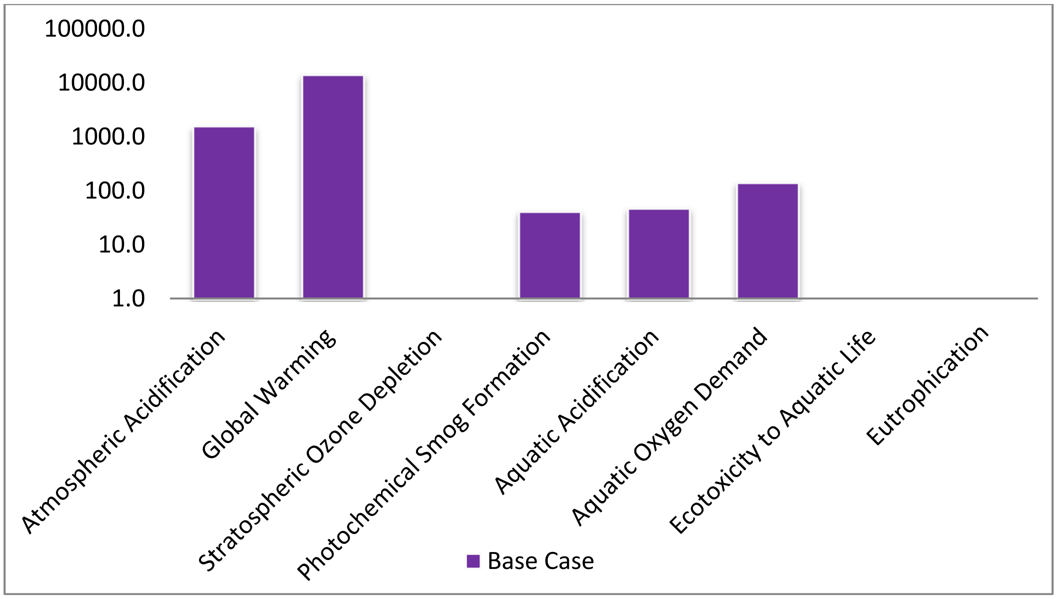

Figure 4.3: Environmental impacts of the base case methyl chloride via methanol option.

In addition to the environmental impact, the resource usage of the process is also estimated using the SUSTAINABILITY EVALUATOR. As presented in Table 4.5, the overall resource usage efficiency seems reasonable; however, there is room for improvement. The efficiency is reasonable because it is a single reaction process. The effective mass yield and reaction mass efficiency could still be improved. Additionally, the material intensity, mass intensity, and water intensity need to be lessened as much as possible. By making the process more efficient and generating less waste the environmental impact would be lessened. The waste stream is also used in determining the social impact of the process.

Table 4.5: Base case resource usage outputs for the methyl chloride via methanol process.

Resource Usage Parameters	Base Case
Effective Mass Yield	71%
E-Factor (kg/kg)	0.1
Mass Intensity (kg/kg)	1.38
Mass Productivity	73%
Reaction Mass Efficiency	71%
Material Intensity (kg/kg)	0.4

4.2.1.3 Base Case Social Assessment of the Methyl Chloride via Methanol Process

The social assessment includes health and safety evaluation using the SUSTAINABILITY EVALUATOR. The waste stream components are used to determine which of the health categories are impacted given the process chemicals. The chemicals affecting the health categories are presented in Table 4.6.

Table 4.6: Base case health impacts for the methyl chloride via methanol process.

Health Impacts	Base Case (Tonnes/year)	Chemicals Impacting
Carcinogenic Risk	6.7E02	Hydrochloric Acid
Immune System Damage	1.0E03	Hydrochloric Acid
Skeletal System Damage	1.0E03	Hydrochloric Acid
Developmental Damage	0.0	None
Reproductive System Damage	0.0	None
Kidney Damage	1.0E03	Hydrochloric Acid
Respiratory System Damage	1.0E03	Hydrochloric Acid, Methanol
Cardiovascular System Damage	0.0	None
Endocrine System Damage	0.0	None
Liver Damage	1.0E03	Hydrochloric Acid, Methanol
Nervous System Damage	4.5E01	Methanol
Sensory System Damage	1.0E03	Hydrochloric Acid, Methanol

The amount of chemicals affecting the health category can be clearly seen in Figure 4.5. The sensory system, liver damage, and skeletal systems are the most impacted. This is because hydrogen chloride and methyl chloride are group 3 carcinogens affecting those categories. The categories impacted most next are skeletal system and the risk of carcinogen from the chemicals. The nervous system is the least impacted because only methanol is impacting.

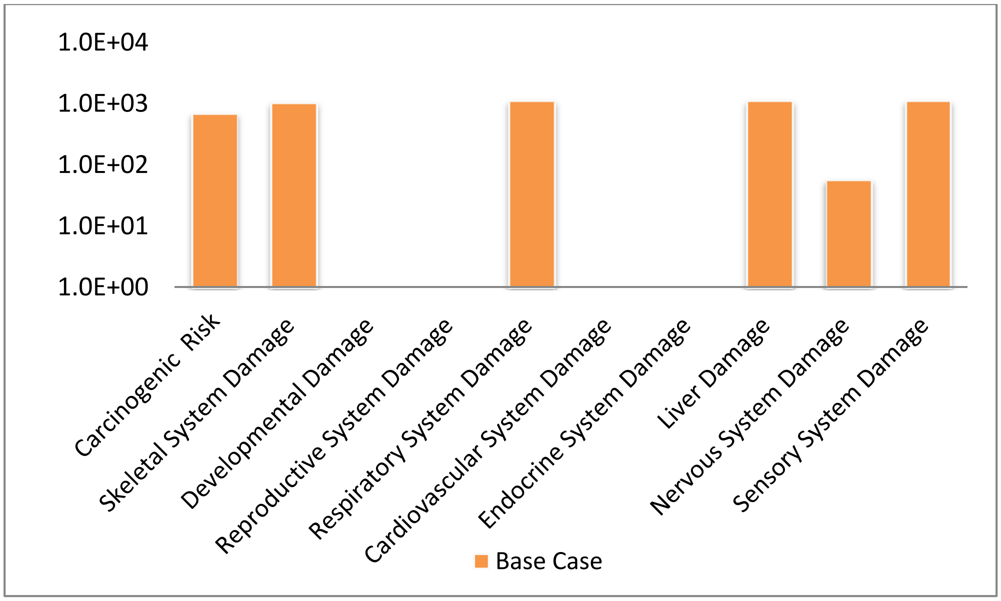

Figure 4.4: Health impacts of the base case methyl chloride via methanol process.

The safety assessment results are presented in Table 4.7. The inputs for the safety assessment include entering flash point temperature of flammable chemicals, explosivity limit, toxicity limit, and corrosivity limit. Operation at high temperatures as well as a risk of corrosion should be considered before determining the material of construction. Additionally, the risk of explosion is present because of methanol. The safety assessment revealed that toxic exposure concern is the most for this process. This is because the chemicals used are highly toxic. The total inherent safety index is 50/100.

Table 4.7: Base case process safety evaluation for the methyl chloride via methanol process.

Process Safety Evaluation	Base Case
Heat of main reaction index	4
Heat of side reaction index	0
Flammability index	6
Explosiveness index	4
Toxic Exposure Index	16
Corrosiveness index	4
Temperature index	6
Pressure index	2
Equipment safety index	4
Safety Level of Process Structure index	4

4.2.1.4 Base Case Sustainability Assessment of Methyl Chloride via Methanol Process Summary

The methyl chloride via methanol process has some sustainability concerns and room for improvement. The economic assessment revealed a zero out of one economic impact, which determines it is a fairly profitable process. The environmental impact revealed 0.15 out of one environmental index, which determines it is somewhat environmental friendly, but still has potential for improvement. The safety index is 50 out of 100 and the overall social index is 0.37 out of one, which determines that the social impacts of this process are the greatest. The overall sustainability impact is 0.21, which is a fairly sustainable process, but has potential for improvement. The summary of this base case sustainability evaluation is presented in Table 4.8. The next step would be to conduct a sensitivity analysis to optimize the process in order to reduce the sustainability impacts of the process.

Table 4.8: Summary of the base case sustainability evaluation of the methyl chloride via methanol process.

Sustainability Evaluation Dimensions	Index
Economic	0.00
Environmental	0.15
Social	0.37
Overall Sustainability	0.21

4.2.2 Base Case Methyl Chloride via Methanol Sensitivity Analysis

Using Aspen Plus built-in model analysis tools block, a sensitivity analysis was conducted on the process to identify parameters affecting the objective function. As the base case sustainability evaluation presented potential for improvement in the process, a sensitivity analysis is necessary for an optimized sustainability evaluation. The variable parameters considered for this process were operating conditions of the reactor and towers and stream component flow rates. The parameters observed for were methanol conversion, product revenue, raw material cost, heat duties cost, waste treatment cost, and profit. Since the observable parameters are not defined in the blocks or streams, a FORTRAN code was written with specific equations to calculate the observable outputs. The FORTRAN code used for the sensitivity analysis is presented in Appendix A. The calculations in the FORTRAN statements were outputted with each varying parameter in the sensitivity analysis to observe the effects.

Three parameters were varied to identify the variables that affect the performance of the hydrochlorination of methanol. The first parameter varied is the feed ratio (methanol/hydrogen chloride). The results are presented in Figure 4.5. As presented, the feed ratio increases from 0.7 to 3.4 while the methanol conversion decreases from 1.0 to 0.3. The second parameter varied is the plug flow reactor temperature. The results are presented in Figure 4.6. As the temperature increases from 570F to 730F, the methyl chloride production increases from 8800lb/hr to 7600lb/hr. The third parameter varied is the plug flow reactor length. The results are presented in Figure 4.7. The reactor length increases from 8ft to 43ft affecting the methyl chloride production to increase 8600lb/hr to 9000lb/hr. These ranges would be used in determining the optimum conditions when optimizing the process.

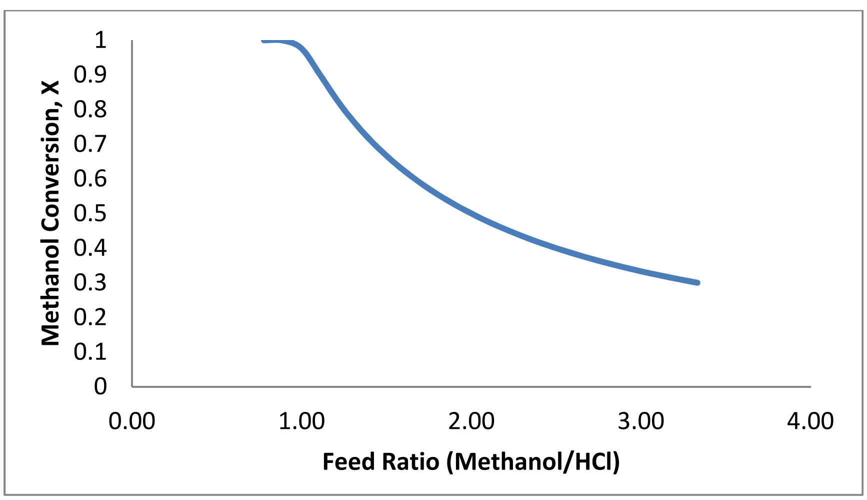

Figure 4.5: Effect of feed ratio sensitivity analysis

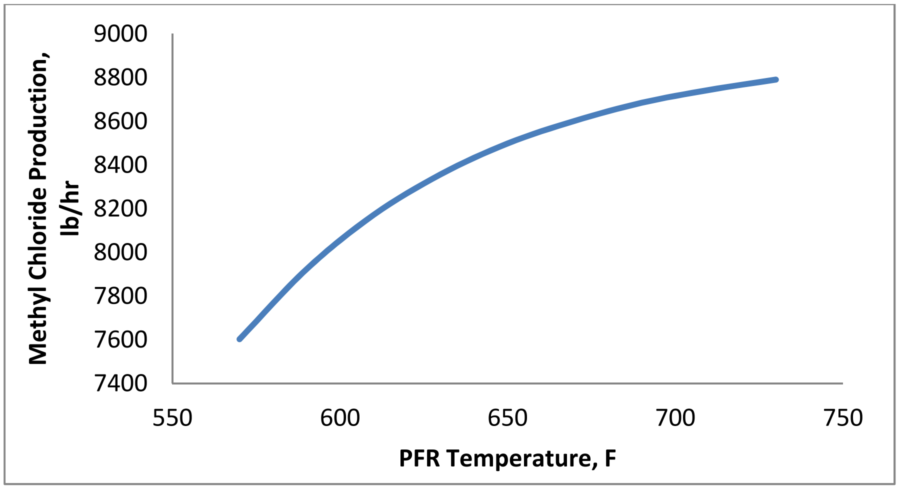

Figure 4.6: Effect of reactor temperature sensitivity analysis.

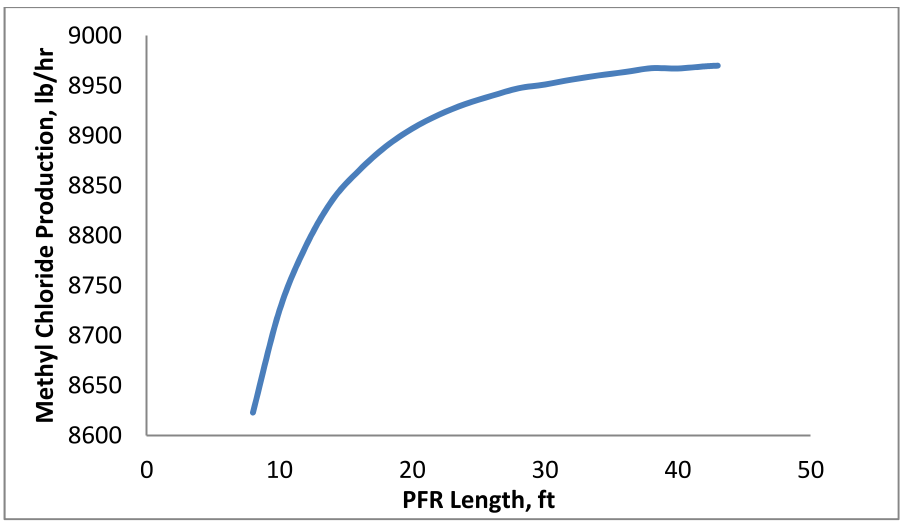

Figure 4.7: Effect of reactor length sensitivity analysis.

4.2.3 Base Case Methyl Chloride via Methanol Optimization

After the sensitivity analysis, optimization of the process was completed using the Aspen Plus built-in 'Model Analysis tools' block. The objective of the optimization was to maximize profit while minimizing waste. The equation used for calculating profit was included in the FORTRAN statements in the sensitivity analysis. The same FORTRAN statements were used in the optimization block. The equation to calculate profit and waste is presented in Equation 3.1 and 4.1 respectively. The variable parameters ranges determined from the sensitivity analysis are used in optimizing the process. These ranges are presented in Table 4.9. Once the optimization is complete, the sustainability of the process is re-evaluated to determine if the sustainability has improved from the base case.

Profit = Revenue – Costs (3.1)

Where:

Revenue = Product revenue + by-product revenue

Cost = Raw material cost + Waste Treatment cost + Energy cost

Total Waste = Mass flow rate of Stream 7 + Mass flow rate of Stream 12 (4.1)

Table 4.9: Variable ranges used in Optimization of Methyl Chloride via Methanol Process

Variable	Base Case Value	Optimization Range
Feed Ratio (Methanol/Hydrogen Chloride)	0.85	0.8-3.0
PFR Temperature, °F	675	570-730
PFR Length, ft.	12	8-43

4.2.3 Optimized Case Sustainability Assessment of Methyl Chloride via Methanol Process

The final optimum values of the variables from the sensitivity analysis and other key changes from the base case in the optimized case are presented in Table 4.10. The amount of waste generated reduced by 2.9% in the optimized case. With the significant reduction in the waste generated the overall sustainability index reduced significantly to 0.13. A comparison of the economic metrics of the base and optimized cases would further help in understanding the lower overall sustainability index.

Table 4.10: Comparison of optimized and base case variable values of the methyl chloride via methanol process.

Items	Base Case Value	Optimized Value
Feed Ratio (Methanol/Hydrogen Chloride)	0.85	1.0
PFR Temperature, °F	675	650
PFR Length, ft.	12	23
Waste generated	27.7E06	26.9E06
Profit, $	15.7	16.1
Overall sustainability index	0.21	0.17

The base and optimized cases economic impacts of the process are presented in Table 4.11. As presented, the major changes are in the revenue, waste treatment costs, and the material value added costs. The revenue increased by $0.6MM as the product generated increased by 2.3%. The waste treatment costs decreased as the waste generated reduced. The decrease in waste treatment cost and increase in revenue increased the profit by 2.5%.

Table 4.11: Comparison of optimized and base case economic metrics of the methyl chloride via methanol process.

Economic parameters	Base Case (MM)	Optimized Case (MM)
Revenue	$25.5	$26.1
Operating Costs	$1.41	$1.40
Waste Treatment Costs	$0.315	$0.307
Raw Material Costs	$8.10	$8.27
Capital Costs	$2.60	$2.60
Annualized Capital Cost	$0.31	$0.31
Material Value Added	$17.5	$17.9
Profit	$15.7	$16.1

The base case and optimized case capital and operating costs along with profit are presented in Figure 4.8. While the capital and operating costs remained almost the same in both cases because there was no equipment re-configuration the profit did in fact slightly increase, which is visible in the slightly taller cylindrical bar. The economic sustainability index for both the cases is zero, which means it is sustainable. The environmental metrics will discuss the chemicals impacting in both the base and optimized cases.

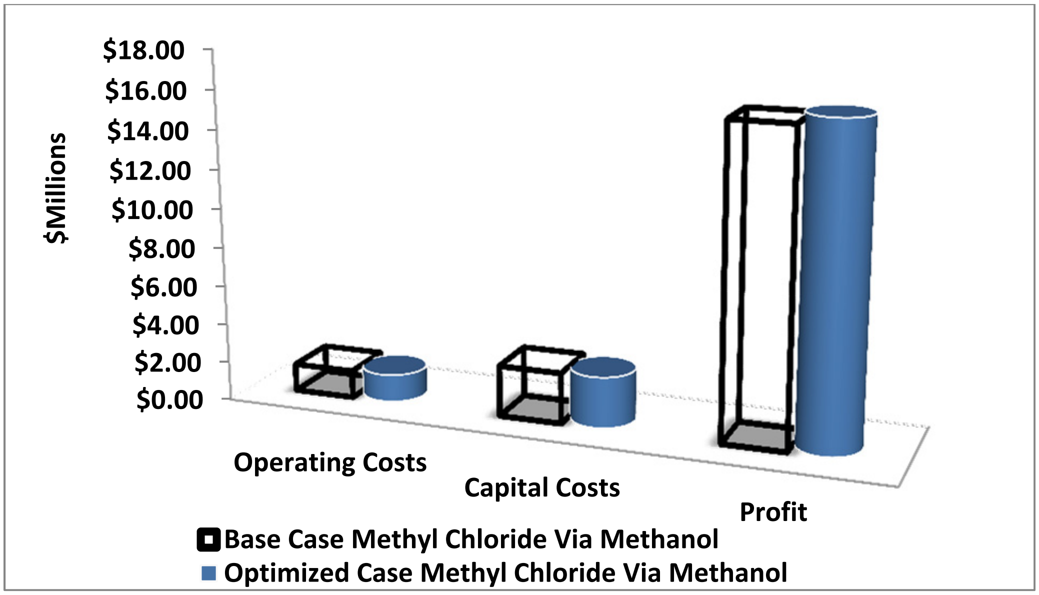

Figure 4.8: Economic metrics of the base and optimized cases of the methyl chloride via methanol process.

The environmental impacts for the base case and optimized case are presented in Table 4.12. The only three categories that are not impacted by this process at all are stratospheric ozone depletion, ecotoxicity to aquatic life, and eutrophication. As presented the atmospheric acidification and aquatic acidification percent reduction of the impact is 100%. This is due to the waste generation reduction in the optimized case. On the other hand global warming, aquatic oxygen demand, and photochemical smog increased due to the increase in the chemicals impacting those categories.

As can be observed, these impacts are more visible in Figure 4.9. The three categories that have greater impacts in the optimized case can be clearly observed from the figure. The increase again is due to the fact that methyl chloride and methanol are present in significant amounts in this process. Further environmental metrics studied for the process include resource usage and efficiency.

Table 4.12: Base case and optimized case environmental impact outputs from the SUSTAINABILITY EVALUATOR

Environmental parameters	Base Case (Tonnes/year)	Optimized Case (Tonnes/year)	Percent Reduction
Atmospheric Acidification	1469.5	0.0	100%
Global Warming	13012.5	18682.8	0%
Stratospheric Ozone Depletion	0.0	0.0	N/A
Photochemical Smog Formation	38.8	51.4	0%
Aquatic Acidification	45.1	0.0	100%
Aquatic Oxygen Demand	113.0	343.2	0%
Ecotoxicity to Aquatic Life	0.0	0.0	N/A
Eutrophication	0.0	0.0	N/A

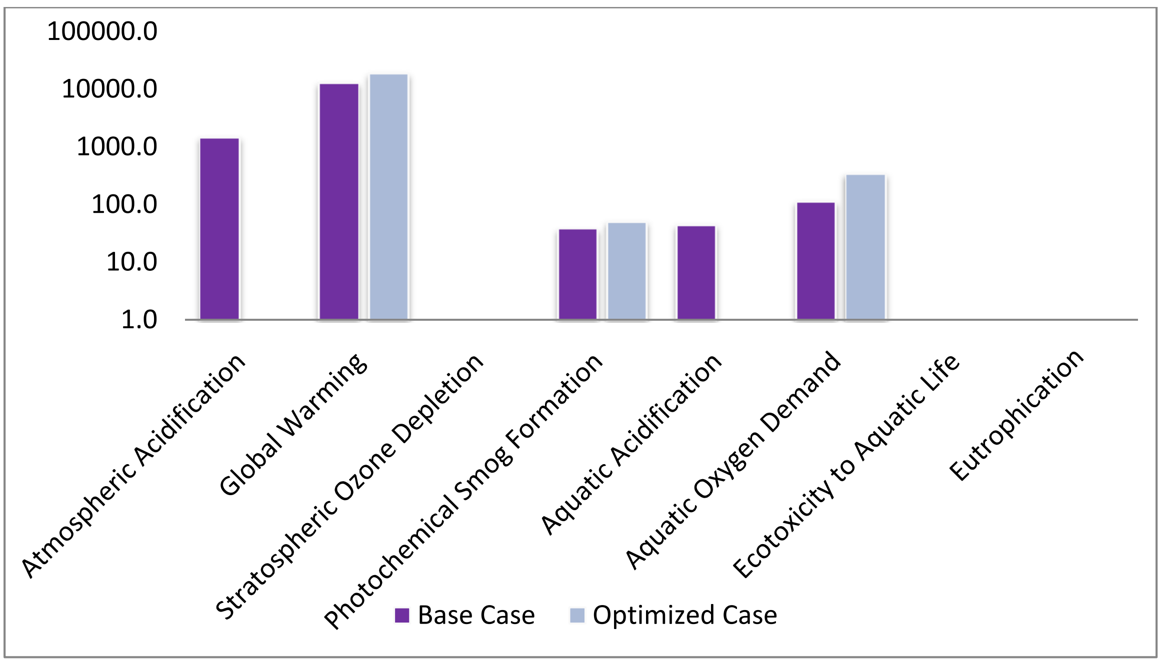

Figure 4.9: Environmental metrics of the base and optimized cases of the methyl chloride via methanol process

The resource usage and efficiency of the reactions for the base and optimized cases is presented in Table 4.13. The reaction mass efficiency, and the effective mass yield increased by 1% in the optimized case. The E-factor, mass, energy, and water intensities decreased in the optimized case. While the mass productivity and material intensity remained the same. All the resource usage metrics improved in the optimized case from the base case. Additionally, the optimized case is more efficient and has a lower environmental impact value of 0.08 and the base case value was 0.15.

Table 4.13: Base case and optimized case resource usage outputs from the SUSTAINABILITY EVALUATOR.

Resource Usage Parameters	Base Case	Optimized Case
Effective Mass Yield	71%	72%
E-Factor (kg/kg)	0.1	0.0
Mass Intensity (kg/kg)	1.38	1.37
Mass Productivity	73%	73%
Reaction Mass Efficiency	71%	72%
Material Intensity (kg/kg)	0.4	0.4
Energy Intensity/ Fossil Fuel Usage (kW/kg)	0.2688	0.2607
Water Intensity (kg/kg)	10	9.7

The health impacts of the optimized and base case processes are presented in Table 4.14 and Figure 4.10. The four metrics that were not impacted by this process at all are developmental, endocrine, reproductive, and cardiovascular system damages. This is as a result of the process chemicals not directly affecting these categories. As presented, the carcinogenic risk, kidney damage, immune, and skeletal system damages reduced by 100%. The respiratory, liver, and sensory system damages are reduced by 86% in the optimized case. The significant reduction on the impacts caused by this process is again because of the lesser waste generation in the optimized case. Evidently, the optimized case health metrics are significantly more sustainable.

The safety assessment of the base and optimized cases are presented in Table 4.15. As presented, there are no changes in process safety from the optimize case. This is mainly due to the fact the process was not optimized for safety as it is difficult to do so. Optimizing for safety would include operating under conditions with low temperatures, which in return would affect the conversion and separation of the chemicals to obtain the necessary product. However, the overall health and safety impacts did reduce to 0.30 in the optimized case from 0.37 in the base case.

Table 4.14: Base and optimized cases health impacts for methyl chloride via methanol process.

Health Impacts	Base Case (Tonnes/year)	Optimized Case (Tonnes/year)	Percent Reduction
Carcinogenic Risk	6.7E02	0.0	100%
Immune System Damage	1.0E03	0.0	100%
Skeletal System Damage	1.0E03	0.0	100%
Developmental Damage	0.0	0.0	N/A
Reproductive System Damage	0.0	0.0	N/A
Kidney Damage	1.0E03	0.0	100%
Respiratory System Damage	1.0E03	1.4E02	86%
Cardiovascular System Damage	0.0	0.0	N/A
Endocrine System Damage	0.0	0.0	N/A
Liver Damage	1.0E03	1.4E02	86%
Nervous System Damage	4.5E01	1.4E02	0%
Sensory System Damage	1.0E03	1.4E02	86%

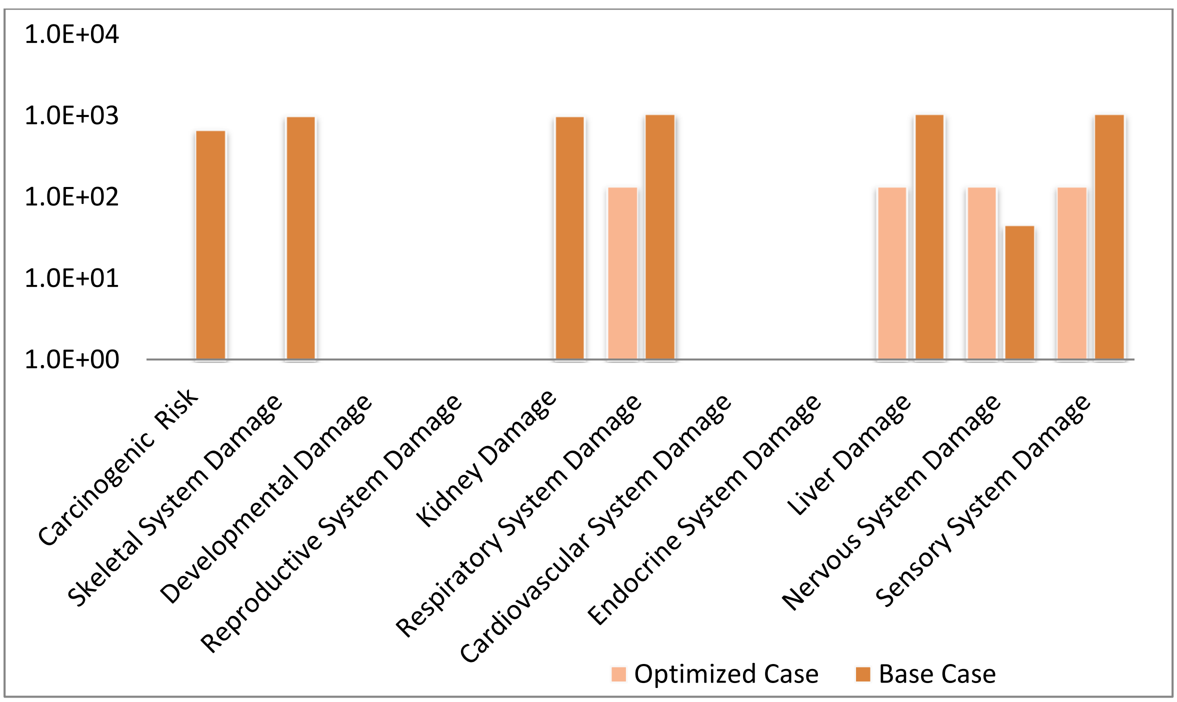

Figure 4.10: Health metrics of the base and optimized cases of the methyl chloride via methanol process.

Table 4.15: Base case and optimized case process safety metrics for methyl chloride via methanol process.

Process Safety Evaluation	Base Case	Optimized Case
Heat of main reaction index	4	4
Heat of side reaction index	0	0
Flammability index	6	6
Explosiveness index	4	4
Toxic Exposure Index	16	16
Corrosiveness index	4	4
Temperature index	6	6
Pressure index	2	2
Equipment safety index	4	4
Safety Level of Process Structure index	4	4
Total Inherent Safety index	50	50

4.2.4 Summary of the Methyl Chloride via Methanol Option Sustainability Evaluation

The base case methyl chloride via methanol option was improved in the optimized case. The sustainability evaluation is summarized in Table 4.16. The following major changes were observed:

- The economic impacts of the both the base and optimized cases were zero because they are both profitable processes; however, the optimized case was 2.5% more profitable than the base case. The optimized case had greater revenue and lower waste treatment cost.
- The environmental impact categories were reduced in the optimized case due to the reduction of waste generation (2.9% reduction). Additionally, the resource usage metrics were improved making the optimized case environmentally friendly than the base case.
- The social impact was divided into the health and safety metrics. The health impact was significantly reduced due to the lessened waste generation as well. The safety impact, however, remained the same since the process was not optimized for addressing process safety directly. Addressing safety would include reducing the operating temperature which would affect the conversion and product separation.

Table 4.16: Summary of the base and optimized case sustainability evaluation of the methyl chloride via methanol option.

Sustainability Evaluation Dimensions	Base Case Index	Optimized Case Index
Economic Impact	0.00	0.00
Environmental Impact	0.15	0.12
Social Impact	0.37	0.30
Overall Sustainability Impact	0.21	0.17

The optimized case of methyl chloride via methanol option is more sustainable than the base case. The next section will discuss the second chemistry process, methyl chloride via methane sustainability evaluation. The comparison of the study of both optimized process chemistries would lead to the choice of the more sustainable option.

4.3 METHYL CHLORIDE VIA METHANE PROCESS DESCRIPTION (OPTION 2)

The manufacture of methyl chloride via methane process is simulated using the design basis available in the literature (AIChE 1966; Dantus 1999). The Electrolyte Non-Random Two Liquid model (ELECNRTL) is chosen to model the phase behavior of this process to handle the non-ideality from the mixed aqueous solutions. The input file, stream summaries, and the schematic are included in the Appendix A and B.

The chemistry of this process is presented in Equations 4.4 to 4.7. The main reaction that takes place is methane and chlorine reacting to form the product methyl chloride. There are three side reactions. The first one is chloromethane reacting with chlorine to form dichloromethane. The second is dichloromethane reacting with chlorine to form chloroform. The fourth one is chloroform reacting with chlorine to form carbon tetrachloride. The kinetic data for the reactions obtained from the literature is presented in Table 4.17.

$$\mathrm{CH_4 + Cl_2 \rightarrow CH_3Cl + HCl} \quad (4.4)$$

$$\mathrm{CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl} \quad (4.5)$$

$$CH_3Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl \quad (4.6)$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl \quad (4.7)$$

Table 4.17: Methyl chloride via methane process kinetic data (Dantus 1999). The pre-exponential factor obtained from the literature was converted from (sec lbmol / ft3)-1 to SI units to include in Aspen Plus.

Reaction	Activation Energy, E, Btu/lbmol	Pre-exponential Factor, A (m^3/Kg-mol sec)
Main Reaction, Equation 4.4	35260	2.56E8
Side Reaction, Equation 4.5	30580	6.28E7
Side Reaction, Equation 4.6	35260	2.56E8
Side Reaction, Equation 4.7	37490	2.93E8

The process follows a series of steps. A block flow diagram is presented in Figure 4.12. This process includes heat exchangers, a reactor, absorbers, distillation towers, flash vessels, and compressors. As presented in Figure 4.11, methane and chlorine mixed feed at ambient temperature and pressure are fed to the Continuous Stirred Tank Reactor (CSTR). The CSTR is operated at 977°F at ambient pressure. The reactor effluent is cooled and washed with water to remove the generated hydrogen chloride. The chloromethanes mixture is then dried in two dehumidification towers to remove water by using sodium hydroxide and sulfuric acid. Water must be removed to prevent corrosion and decomposition of the chloromethanes. From the absorber, sodium hydroxide and sulfuric acid are separated as products from the other components creating two other waste streams. Additionally, the absorber (T-601) generates a waste stream. The distillate from the second dryer (T-603) is compressed (C-601) and cooled before entering the flash vessel (T-604), where the separation of the product and byproducts begins.

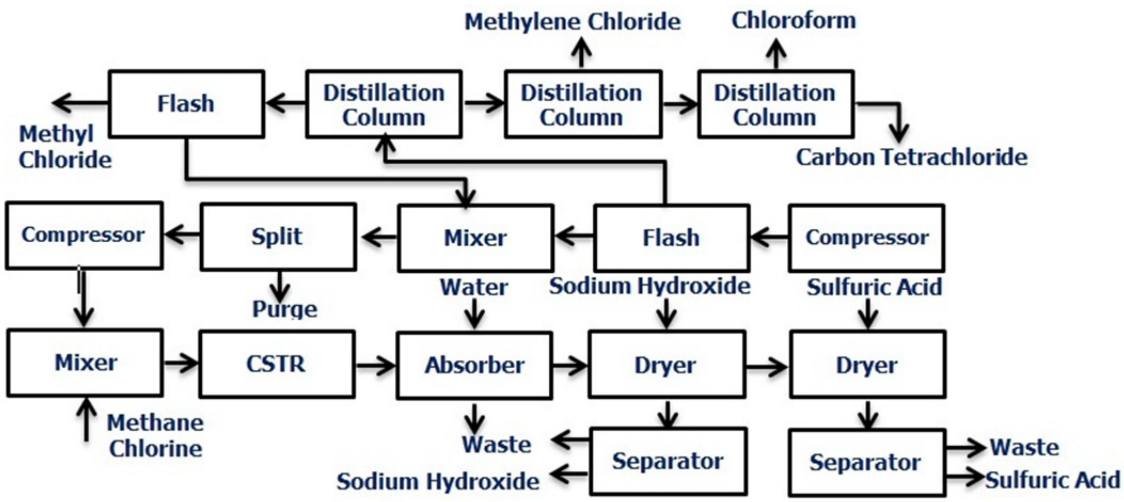

Figure 4.11: Methyl chloride production via methane process block flow diagram.

The bottoms from the flash vessel are sent to a series of distillation columns to separate out the products. The first column (T-605) separates out methyl chloride in the distillate and chloroform, dichloromethane, and carbon tetrachloride in the bottoms. The bottoms are then further separated in a column (T-607) with dichloromethane in the distillate and chloroform and carbon tetrachloride in the bottoms. The bottoms from this tower are further separated in T-606 with chloroform in the distillate and carbon tetrachloride in the bottoms. The methyl chloride from T-605 distillate is fed to a flash vessel with the product separated in the bottoms. The overhead from the flash vessels (T-608 and T-604) is split with a purge stream and methane stream, which is compressed and recycled back to the reactor pre-heater. The process flow diagram and the input summary are presented in the Appendices A and B.

4.3.1 Base Case Methyl Chloride via Methane Sustainability Assessment Summary

A summary of the base case methyl chloride via methane option is presented in this section. The economic parameters such as the raw material and product prices for this process are presented in Table 4.18. These prices were used in conducting the cost analysis.

Table 4.18: Economic parameters summary for the methyl chloride production via methane.

Item	Price
Methane ($/kg)	0.21 (Reed Business Information Limited 2011)
Chlorine ($/kg)	0.21 (Reed Business Information Limited 2011)
Sodium Hydroxide ($/kg)	0.441 (Reed Business Information Limited 2011)
Sulfuric Acid ($/kg)	0.081 (Reed Business Information Limited 2011)
Hydrogen Chloride ($/kg)	0.09 (Reed Business Information Limited 2011)
Process Water ($/kg)	0.00638 (City of Stillwater 2011)
Methyl Chloride ($/kg)	0.82 (Reed Business Information Limited 2011)
Methylene Chloride ($/kg)	1.2 (Reed Business Information Limited 2011)
Carbon Tetrachloride ($/kg)	1.03(Dantus 1999)
Chloroform ($/kg)	1.014 (Reed Business Information Limited 2011)
Natural Gas ($/ft^3)	0.00451(EIA 2011)
Waste Treatment ($/kg)	0.2 (Turton 2009)

The key points of the base case analysis summary obtained from the SUSTAINABILITY EVALUATOR are presented in Table 4.19. As presented this process generates revenue of $54.2MM and is profitable ($24.8MM). One of the key reasons of the process' profitability is separating sulfuric acid and sodium hydroxide as products instead of waste from the dryers. The waste generated in this process is 4.48E8 lb/year from four different waste streams as observed in the process description. This large quantity of waste is used in determining the components impacting the various categories in the SUSTAINABILITY EVALUATOR. These categories are listed in the environmental and health concerns in Table 4.19. Since the chemicals such as hydrogen chloride, methylene chloride, chloroform etc. in this process are mostly in the top hazardous chemicals list the impact on the environment and society is significant. The environmental impact is 0.42 out of 1 and the social impact is 0.41 out of 1. The safety index is 58 out of 100, which is the maximum. With all these outputs from the SUSTAINABILITY EVALUATOR it is evident this process is not as sustainable with an overall sustainability index of 0.33 out of 1. The next steps would be to conduct a sensitivity analysis and optimize the process based on the parameters found affecting the objective, which is to minimize waste and maximize profit. Once the process is optimized it would be re-evaluated to determine its sustainability.

Table 4.19: Sustainability evaluation summary of base case methyl chloride via methane process.

Summary of Base Case Results	Base Case: Methyl Chloride via Methane
Waste generated, lb/year	4.48E08
Revenue, $	54.2MM
Profit, $	24.8 MM
Economic impact	0.00
Environmental concerns	Global warming, eutrophication, ecotoxicity to aquatic life, photochemical smog formation, aquatic oxygen demand, stratospheric ozone depletion
Environmental impact	0.42
Health concerns	Carcinogenic risk, developmental damage, reproductive system damage, respiratory system damage, cardiovascular system damage, endocrine system damage, liver damage, nervous system damage, sensory system damage
Process safety index	58
Social impact	0.41
Overall sustainability index	0.33

4.3.2 Base Case Methyl Chloride via Methane Sensitivity Analysis

The parameters considered for this process were operating conditions of the reactor, towers, and certain stream flow rates. The parameters observed were chlorine conversion and the products flow rate. A FORTRAN code was written with specific equations to calculate the observable outputs. The FORTRAN code is present in Table A2 in Appendix A.

Three parameters were varied to identify the variables that affect the performance of the chlorination of methane. The parameters varied were the feed ratio, CSTR temperature, and CSTR residence time. The results are presented in Figures 4.12 to 4.14. As presented in Figure 4.12, the feed ratio (chlorine/methane) increases from 0.5 to 8.0 affecting the chlorine conversion to first increase drastically and then gradually decrease and level off. In Figure 4.13, the CSTR temperature increases drastically from 800F to 1400F as does the production for the main product, methyl chloride. Specifically, the methyl chloride flow rate increases from 7,200lb/hr to 8,700lb/hr. Dichloromethane, a byproduct, decreases from 4,000lb/hr to 3,300lb/hr. Carbon tetrachloride increases from 120lb/hr to 300lb/hr and chloroform increases from 890lb/hr to 980lb/hr. In Figure, 4.14, as the CSTR residence time increases from 0.0003hr to 0.5hr, the production of methyl chloride and the byproducts increases up to a certain point after which it levels off. These ranges for optimization are presented in Table 4.20.

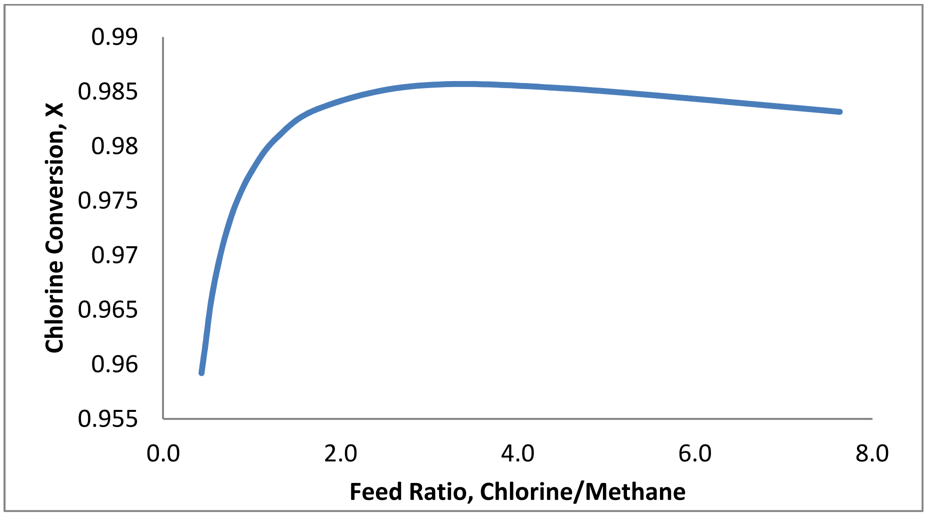

Figure 4.12: Effect of feed ratio on chlorine conversion.

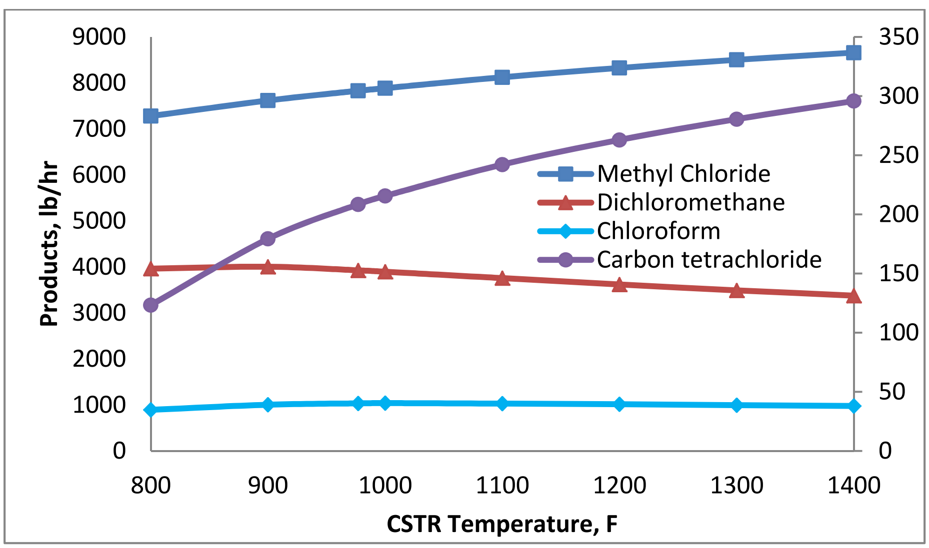

Figure 4.13: Effect of CSTR temperature on chlorine conversion.

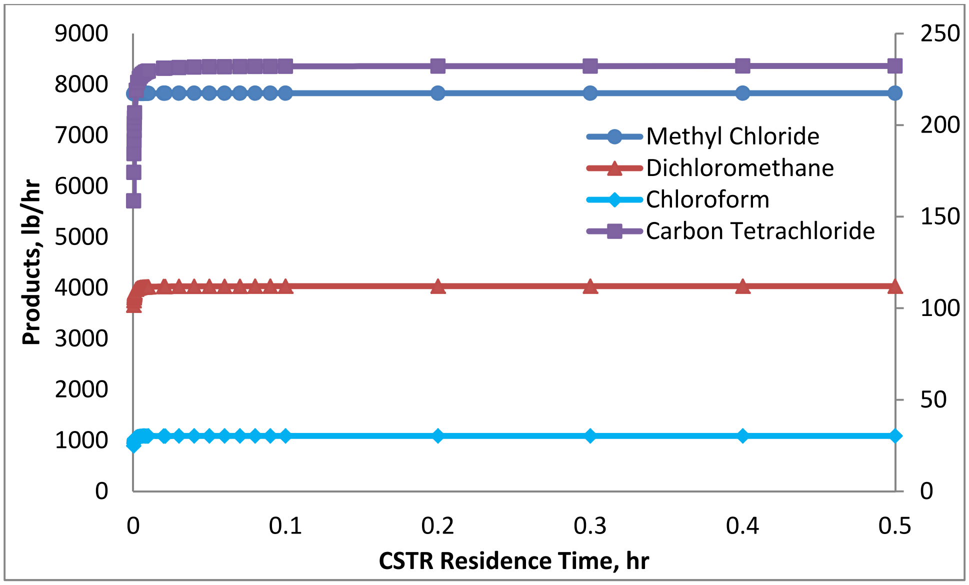

Figure 4.14: Effect of CSTR volume on chlorine conversion.

Table 4.20: Variable ranges used in Optimization of Methyl Chloride via Methane Process

Variable	Base Case Value	Optimization Range
Feed Ratio (Chlorine/Methane)	4.5	0.5-8.0
CSTR Temperature, ◦F	977	800-1400
CSTR residence time, hr	0.021	0.003-0.5

After the sensitivity analysis, optimization of the process was completed using the ranges of the variable parameters presented in Table 4.20. The objective of the optimization was to maximize profit and minimize the waste generated. FORTRAN statements written for the sensitivity analysis were used also used in the optimization block. The equation to calculate profit and waste is presented in Equation 3.1 and 4.2 respectively. Once the optimization is complete, the sustainability of the process is re-evaluated to determine if it has improved from the base case.

$$\text{Profit} = \text{Revenue} - \text{Costs} \tag{3.1}$$

Where:

Revenue = Product revenue + by-product revenue

Cost = Raw material cost + Waste Treatment cost + Energy cost

Total Waste = Mass flow rate of (Stream 9 + Stream 32 + Stream 36 + Stream 38) (4.2)

4.3.3 Optimized Case Methyl Chloride via Methane Sustainability Assessment

The optimum values of the variables from the sensitivity analysis and other key changes from the base case in the optimized case are presented in Table 4.21. The amount of waste generated reduced by 0.3% in the optimized case. The profit per pound of product also increased by 0.06 in the optimized case. With the little reduction in the waste generated the overall sustainability index reduced to 0.32 from 0.33. Even though the reduction in waste generation seems insignificant, a sustainability evaluation of the optimized case and comparison with the base case would present the impacts on the different categories. This in turn would help compare the two chemistries, methyl chloride production via methanol or methane, to determine the more sustainable process.

Table 4.21: Comparison of optimized and base case variable values (option 2).

Items	Base Case Value	Optimized Value
Feed Ratio (Chlorine/Methane)	4.5	4.3
CSTR Temperature, ◦F	977	935
CSTR residence time, hr	0.021	0.53
Product, lb/year	6.8E7	7.0E7
Waste generated, lb/year	4.47E8	4.46E8
Profit, $	24.8MM	25.2MM
$Profit/lb of product	0.076	0.081
Overall sustainability index	0.33	0.32

The base and optimized cases economic impacts of the process are presented in Table 4.22. As presented, the revenue increases by $0.3MM as the product generated increased by 2% (presented in Table 4.21). The operating cost and raw material cost decrease by $0.1MM. The waste treatment costs decreased as the waste generated reduced. The decrease in waste treatment cost and increase in revenue increased the profit by 1.6%.

Table 4.22: Comparison of optimized and base case economic metrics of the methyl chloride via methane process.

Economic parameters	Base Case ($MM)	Optimized Case ($MM)
Revenue	54.2	54.5
Operating Costs	4.51	4.50
Waste Treatment Costs	0.51	0.50
Raw Material Costs	23.5	23.4
Capital Costs	7.33	7.33
Annualized Capital Cost	0.86	0.86
Material Value Added	30.7	31.00
Profit	24.8	25.20

The base case and optimized case capital and operating costs along with profit are presented in Figure 4.15. While the capital and operating costs remained the same in both cases because there was no equipment re-configuration the profit increased as observable in the slightly taller bar. The economic sustainability index for both the base and optimized cases is zero, which means it is sustainable. The environmental metrics will discuss the chemicals impacting in both the base and optimized cases.

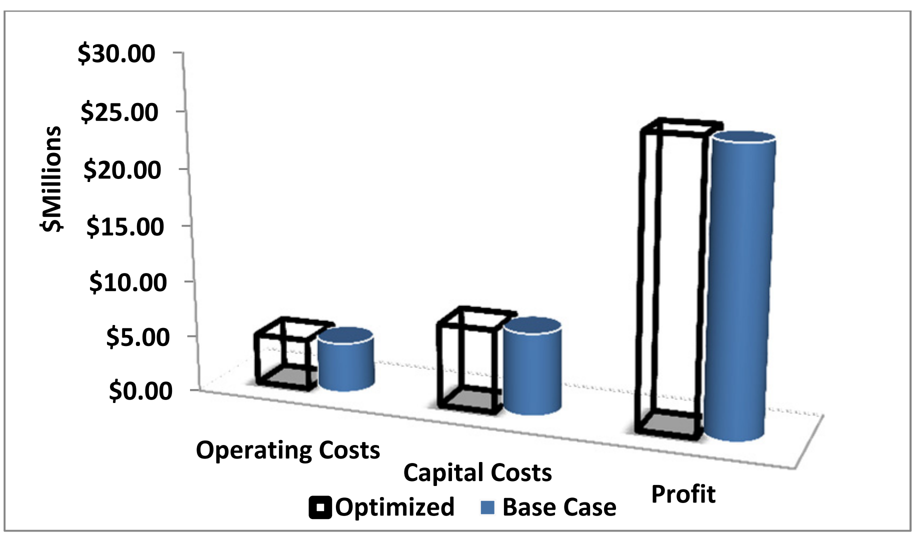

Figure 4.15: Base and optimized cases economic impact outputs of the methyl chloride via methane option from the SUSTAINABILITY EVALUATOR.

The environmental impacts for the base case and optimized case are presented in Table 4.23. The two categories that are not impacted by this process at all are atmospheric acidification and aquatic acidification. As presented the stratospheric ozone depletion and global warming have the highest percent reduction of 21.7% and 19.4% respectively. This is due to the waste generation reduction in the optimized case. The next highest percent reduction of the impact is on photochemical smog formation and ecotoxicity to aquatic life with approximately 5 to 6% reduction.

As can be observed, these impact reductions are more visible in Figure 4.16. The two categories that did not have a significant percent reduction are eutrophication and aquatic oxygen demand. This is due to the fact that methylene chloride and nitrogen are present in significant amounts in this process. Further environmental metrics studied for the process include resource usage and efficiency.

Table 4.23: Base case and optimized case environmental impact outputs from the SUSTAINABILITY EVALUATOR.

Environmental parameters	Base Case (Tonnes/year)	Optimized Case (Tonnes/year)	Percent Reduction
Atmospheric Acidification	0	0	N/A
Global Warming	2,018,377	1,626,934	19.4%
Stratospheric Ozone Depletion	1,329,768	1,040,688	21.7%
Photochemical Smog Formation	636	600	5.77%
Aquatic Acidification	0	0	N/A
Aquatic Oxygen Demand	2,220	2,199	0.92%
Ecotoxicity to Aquatic Life	4,278	4,047	5.41%
Eutrophication	652	650	0.27%

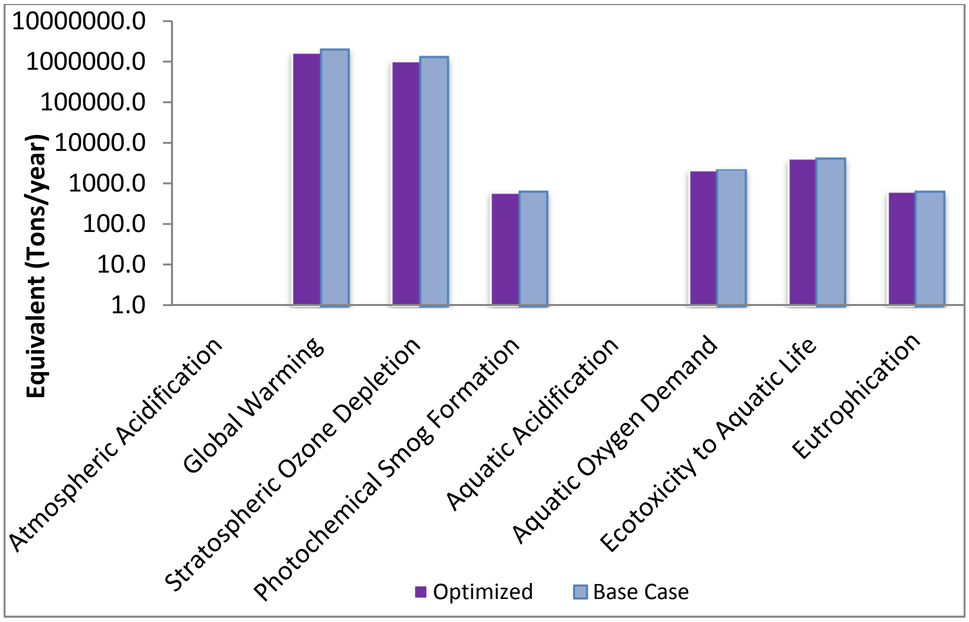

Figure 4.16: Environmental metrics of the base and optimized cases of the methyl chloride via methane process.

The resource usage and efficiency of the reactions for the base and optimized cases is presented in Table 4.24. The reaction mass efficiency did not change at all in the optimized case. The effective mass yield increased by 1% in the optimized case. The E-factor, mass productivity, material intensity, energy intensity, and water intensity decreased in the optimized case. All the resource usage metrics improved in the optimized case from the base case. Additionally, the optimized case is more efficient and has a lower environmental impact value of 0.40 while the base case value was 0.42.

Table 4.24: Base case and optimized case resource usage outputs from the SUSTAINABILITY EVALUATOR.

Resource Usage Parameters	Base Case	Optimized Case
Effective Mass Yield	28%	29%
E-Factor (kg/kg)	6.5	6.4
Mass Productivity	3.34	3.31
Reaction Mass Efficiency	30%	30%
Material Intensity (kg/kg)	20%	21%
Energy Intensity/ Fossil Fuel Usage (kW/kg)	4.0	3.8
Water Intensity (kg/kg)	0.6004	0.5514

The health impacts of the optimized and base case processes are presented in Table 4.25 and Figure 4.17. The three metrics that were not impacted by this process at all are immune system damage, skeletal system damage, and kidney damage. This is because the process chemicals are not affecting these categories. As presented, the sensory system damage and liver damage had the greatest percent reduction (51%) in risk because the amount of chlorine and carbon tetrachloride in the waste streams reduced. The cardiovascular, respiratory, and nervous system damages percent reduction is 34%, 29%, and 22% respectively. The reduction on the impacts caused by this process is because of the lesser waste generation in the optimized case. As evidenced, the optimized case health metrics are more sustainable.

The safety assessment of the base and optimized cases are presented in Table 4.26. As presented, there are no changes in process safety from the optimized case. This is because the process was not optimized for safety as there is no set way of quantifying safety precautions other than operating as ambient temperatures and pressures. Optimizing for safety would include operating under lower temperatures than needed for the required conversion to occur in the CSTR. This in return would affect the separation of the chemicals to obtain the product.

Table 4.25: Base case and optimized case health impacts for methyl chloride via methane process

Health Impacts	Base Case (Tonnes/year)	Optimized Case (Tonnes/year)	Percent Reduction
Carcinogenic Risk	5.57E+03	5.25E+03	6%
Immune System Damage	0.00E+00	0.00E+00	N/A
Skeletal System Damage	0.00E+00	0.00E+00	N/A
Developmental Damage	2.74E+03	2.44E+03	11%
Reproductive System Damage	5.57E+03	5.25E+03	6%
Kidney Damage	0.00E+00	0.00E+00	N/A
Respiratory System Damage	6.08E+03	4.33E+03	29%
Cardiovascular System Damage	5.15E+03	3.40E+03	34%
Endocrine System Damage	5.57E+03	5.25E+03	6%
Liver Damage	3.14E+03	1.53E+03	51%
Nervous System Damage	7.98E+03	6.20E+03	22%
Sensory System Damage	3.14E+03	1.53E+03	51%

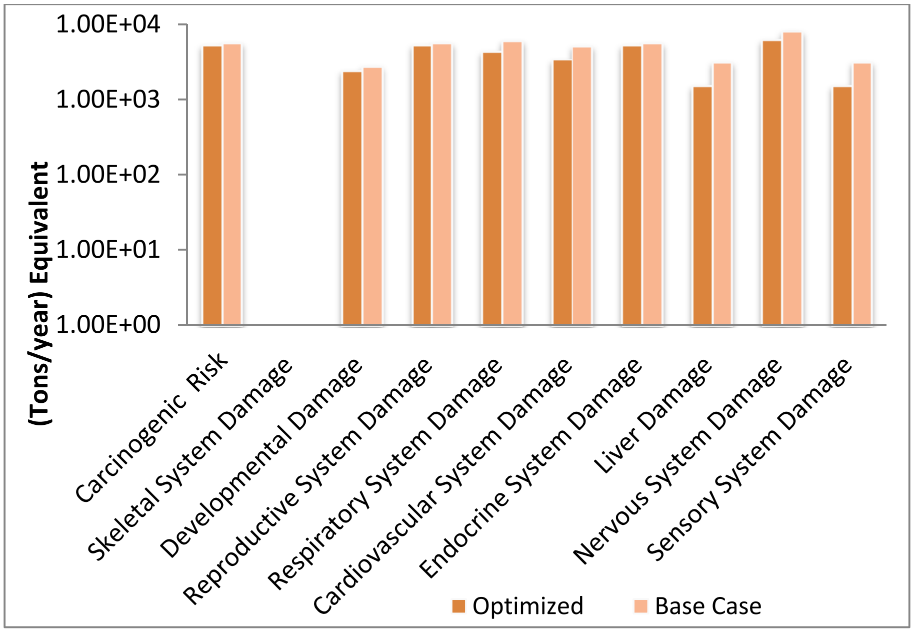

Figure 4.17: Health metrics of the base and optimized cases of the methyl chloride via methane process.

Table 4.26: Base case and optimized case process safety metrics for methyl chloride via methanol process.

Process Safety Evaluation	Base Case	Optimized Case
Heat of main reaction index	0	0
Heat of side reaction index	0	0
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
Safety Level of Process Structure index	4	4
Total Inherent Safety index	58	58

The overall health and safety impacts did not change in the optimized case from the base case even though there are slight observable changes in Figure 4.18. The percent reductions are insignificant to make a great impact in calculating the social index. The social impact in both the cases is 0.41.

4.3.4 Summary of the Methyl Chloride via Methane Sustainability Evaluation

The base case methyl chloride via methane option was slightly improved in the optimized case. The sustainability evaluation is summarized in Table 4.27. The following observations were made:

- The economic indices of the both the base and optimized cases were zero because they are profitable; however, the optimized case was 1.6% more profitable than the base case. The optimized case had greater revenue and lower waste treatment cost.
- The environmental impact categories were reduced in the optimized case due to the reduction of waste generation (0.3% reduction). Additionally, the resource usage metrics were improved making the optimized case environmentally friendly than the base case.
- The social impact includes health and safety categories. The health impact was slightly reduced due to the lessened waste generation, however, not enough to make a difference in the overall social index. The safety impact remained the same since the process was not optimized for addressing safety directly.

Overall optimizing this process did not have a significant improvement in the sustainability. This suggests that this process is not inherently as sustainable probably because of the chemicals involved in the chemistry. All the chemicals are highly hazardous and toxic. Handling the waste streams is a challenge as it must be done in a sustainable manner. The next section will discuss which process (methyl chloride production via methanol or via methane) is more sustainable.

Table 4.27: Summary of the base and optimized case sustainability evaluation of the methyl chloride via methane option.

Sustainability Evaluation Dimensions	Base Case Index	Optimized Case Index
Economic	0.00	0.00
Environmental	0.42	0.40
Social	0.41	0.41
Sustainability	0.33	0.32

4.4 OPTIMIZED CASES COMPARISON OF THE METHYL CHLORIDE PRODUCTION VIA METHANOL AND METHANE PROCESSES

The main objective of this work was to apply the SUSTAINABILITY EVALUATOR tool to determine the greener chemistry for the methyl chloride production process and whether or not the greener chemistry would actually be more sustainable. This section will discuss the optimized cases of the methyl chloride via methanol (option 1) and via methane (option 2). The key changes between the two options are presented in Table 4.28. The amount of waste generated and the waste treatment cost in Option 1 is 94% less than Option 2. The amount of methyl chloride produced in is the same in both options. Option 2 is more profitable than Option 1. With the lesser amount of waste generation in Option 1, the overall sustainability index is 0.17 while Option 2 is 0.32.

Table 4.28: Optimized cases key items: methyl chloride via methanol (option 1) and methane (option 2) processes.

Items	Option 1 (methanol)	Option 2 (methane)
Methyl chloride produced, lb/year	70.0MM	70.0MM
Waste generated	2.69E07	4.46E8
Waste treatment cost, $	30,669	508,510
Profit, $	16.1MM	25.2MM
Overall sustainability index	0.17	0.32

The comparison of the economic metrics of the two options is presented in Figure 4.18. As presented, option 2 (via methane) is evidently more economical with higher revenue and profit, however all the costs are greater too. The capital, operating, waste treatment, and raw material costs are all higher for option 2. The profit is 36% greater for option 2 than option 1 (via methanol). However, sustainability accounts for not only the economics, but also the environmental and social dimensions. A closer look at those two dimensions would help in determining the greener chemistry and whether is it sustainable.

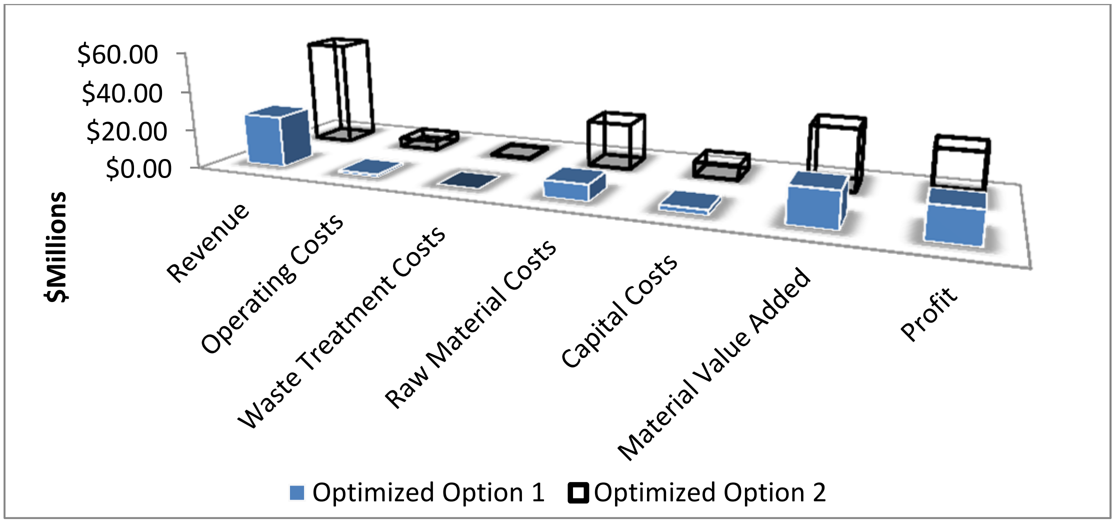

Figure 4.18: Optimized cases economic dimension comparison of methyl chloride via methanol (option 1) and via methane (option 2).

The environmental impacts for the optimized cases of the two options are presented in Figure 4.19. The only three categories that are impacted by Option 1 (via methanol) are global warming, photochemical smog formation, and aquatic oxygen demand. The impact on these three categories is less than 10,000 tons/year. On the other hand option 2 (via methane) impacts six categories with amounts ranging from 1,000 tons/year to 1,000,000 tons/year. These six categories are global warming, stratospheric ozone depletion, photochemical smog formation, aquatic oxygen demand, ecotoxicity to aquatic life, and eutrophication. Option 2 has a greater impact on the environment because it has more chemicals as a result of the chemistry involved and because all those chemicals are highly hazardous. Further environmental metrics studied for the process include resource usage and efficiency.

The resource usage and efficiency of the reactions for the two options optimized cases are presented in Table 4.28. The effective mass yield, mass productivity, and reaction mass efficiency for option 1 are at least twice as more efficient than option 2. The E-factor, mass, energy, and water intensities are significantly lower for option 2 than option 1. All the resource usage metrics are significantly more efficient for option 1 (via methanol) than option 2 (via methane). Additionally, option 1 has a lower environmental impact value of 0.12 while option 2 has a value of 0.40.

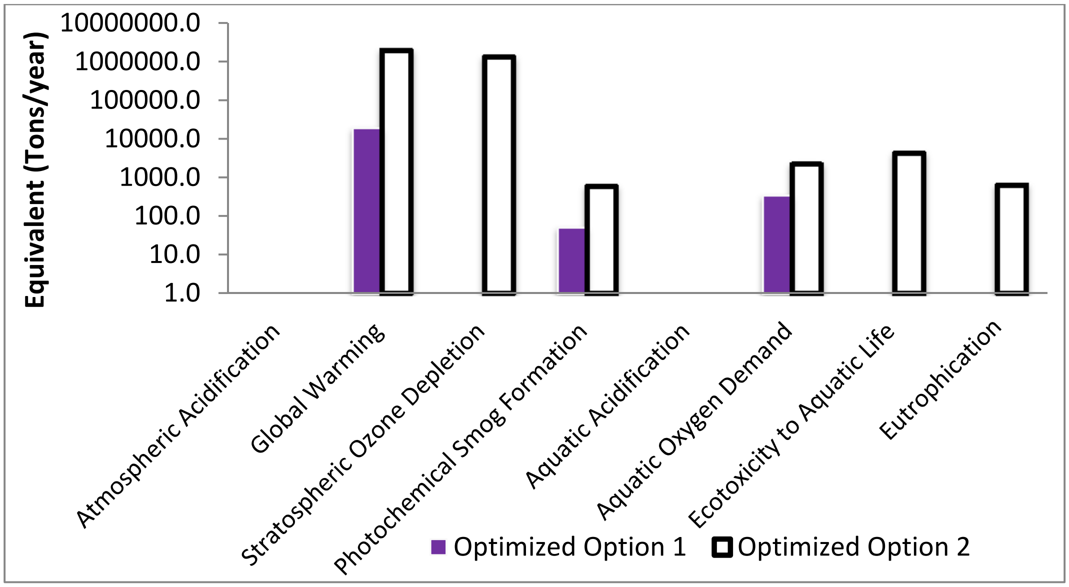

Figure 4.19: Optimized cases environmental dimension comparison of methyl chloride via methanol (option 1) and via methane (option 2).

Table 4.29: Optimized cases resource usage comparison of methyl chloride via methanol (option 1) and via methane (option 2).

Resource Usage Parameters	Option 1 (methanol)	Option 2 (methane)
Effective Mass Yield	72%	29%
E-Factor (kg/kg)	0.0	6.4
Mass Productivity	73%	30%
Reaction Mass Efficiency	72%	21%
Material Intensity (kg/kg)	0.4	3.8
Energy Intensity/ Fossil Fuel Usage (kW/kg)	0.2607	0.5514
Water Intensity (kg/kg)	9.7	35.2

The health impacts of the two options optimized cases are presented in Figure 4.20. The four metrics that were impacted by option 1(via methanol) process are respiratory, liver, nervous, sensory systems damages. Approximately 10 tons/year generated from the process impacts each of those four categories. On the other hand option 2 (via methane) impacts nine different categories with the maximum of 1,000 tons/year. The significantly lower impact from option 1 is because of the lesser waste generation. Evidently, option 1 health metrics are significantly more sustainable.

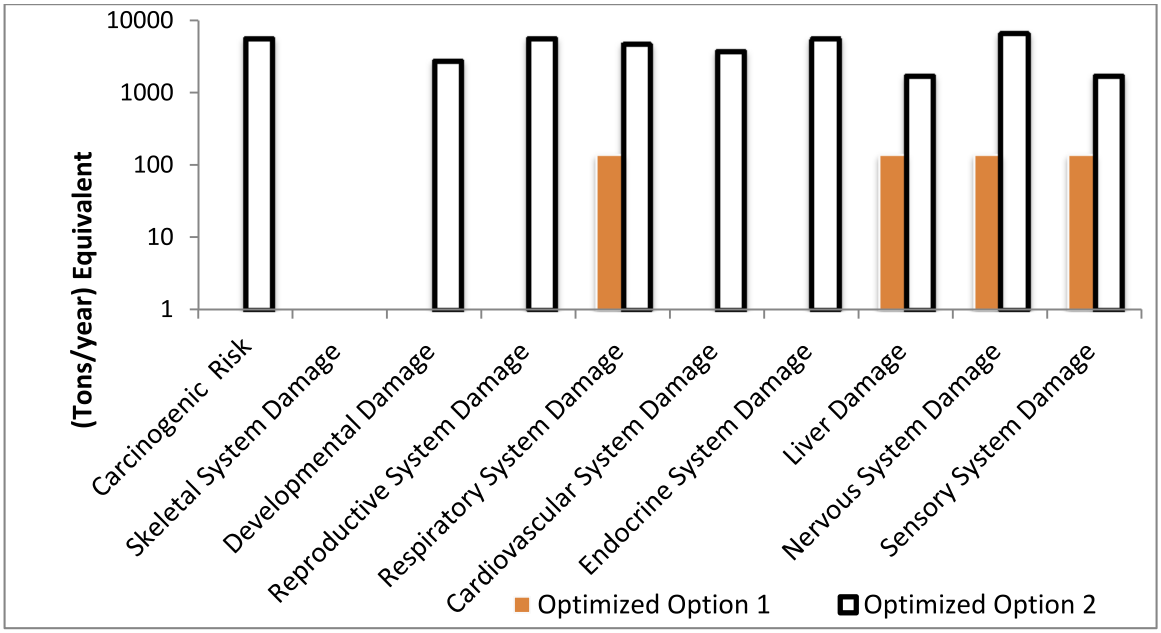

Figure 4.20: Optimized cases health dimension comparison of methyl chloride via methanol (option 1) and via methane (option 2).

The safety assessment of the two options optimized cases are presented in Table 4.30. As may be recalled in the previous sections it was mentioned that the optimized cases had no change in process safety from the base cases because the process was not optimized for safety. Optimizing for safety would include operating under conditions with low temperatures affecting the conversion and separation of the chemicals to obtain the necessary product. Flammability, explosiveness, and toxic exposure indices are lower for option 1 (via methanol) than option 2 (via methane). The heat of main reaction is the only metric that is greater for option 1 than option 2 and the heat of side reactions is the same for both of them. All the other metrics have same level of risks associated with both the processes. The toxic exposure risk is significantly lower for option 1 because it has less toxic chemicals involved. Overall the social impact for option 1(via methanol) is 0.30 and option 2 (via methane) is 0.41. This confirms that option 1 is more socially viable than option 2. The next section will discuss the conclusions that can be drawn from the results obtained from this study.

Table 4.30: Process safety comparison of methyl chloride via methanol (option 1) and via methane (option 2).

Process Safety Evaluation	Option 1 (methanol)	Option 2 (methane)
Heat of main reaction index	4	0
Heat of side reaction index	0	0
Flammability index	6	8
Explosiveness index	4	6
Toxic Exposure Index	16	24
Corrosiveness index	4	4
Temperature index	6	6
Pressure index	2	2
Equipment safety index	4	4
Safety Level of Process Structure index	4	4
Total Inherent Safety index	50	58

CHAPTER V

CONCLUSIONS AND FUTURE DIRECTIONS

5.1 CONCLUSIONS

A methodology was developed to evaluate the sustainability of processes in the preliminary stages of design or retrofit existing processes. The methodology was aimed at evaluating the sustainability and optimizing the process to reduce waste generation in order to satisfy the environmental and social dimensions while remaining profitable. The objective of this work was to test the applicability of the SUSTAINABILITY EVALUATOR on a specific case study with two different chemistries to help the decision maker determine the more sustainable process chemistry.

In the previous chapter, the proposed methodology presented in Figure 5.1 was implemented and the results were evaluated. The methodology involved simulating a base case process in Aspen Plus, evaluating the sustainability of the base case using the SUSTAINABILITY EVALUATOR, conducting a sensitivity analysis and optimizing the process in Aspen Plus, and then re-evaluating the sustainability of the optimized process using the

SUSTAINABILITY EVALUATOR. This methodology was applied to a case study involving two different ways of producing the same product, methyl chloride. The first process option was the methyl chloride production via methanol and the second option was methyl chloride production via methane.

Base Case Process Simulation

- Aspen Plus Process Simulator

Evaluate Sustainability Using the SUSTAINABILITY EVALUATOR

- Inputs to the SUSTAINABILITY EVALUATOR
- Environmental Impact
- Economic Impact
- Social Impact
- Outputs from the SUSTAINABILITY EVALUATOR

Conduct Sensitivity Analysis to Identify Affecting Parameters

- Fortran Statements Maximizing Profit

Formulate Objective Function

- Single Objective Optimization

Optimize Process Based on Parameters Affecting Sustainability

- Fortran Statements Maximizing Profit

Re-evaluate Sustainability Using the SUSTAINABILITY EVALUATOR

- Decision Maker: Accept results or repeat steps from "Formulate an Objective Function" to re-evaluate the sustainability of the process.

Figure 5.1: Methodology for evaluating sustainability of processes in the preliminary design stages (Shadiya 2010a).

The above methodology was applied to methyl chloride production via methanol (option 1). The base case process had an overall sustainability index of 0.21. The optimized case was 2.5% more profitable than the base case and had a 2.9% waste reduction with an overall sustainability of 0.13. The economic indices for both base and optimized cases were zero. The environmental indices of the base and optimized case were 0.15 and 0.12 respectively. The social index of the base case was 0.37 and the optimized case was 0.30. The lower the index values the more sustainable the process.

The same methodology was applied to the second option, methyl chloride production via methane. The overall sustainability of the base case process was 0.33. The optimized case was 1.6% more profitable than the base case. Additionally, it had a 0.3% waste reduction and ended with a 0.32 overall sustainability index. The environmental index of the base case was 0.42 and the optimized case was 0.40. The social indices for both optimized and base cases remained the same as the waste reduction in the optimized case did not have a significant impact. The social indices for both were 0.41.

A comparison of the optimized cases of methyl chloride via methanol (option 1) and via methane (option 2) revealed that the first option has a lower sustainability impact. This would help a decision maker choose and decide on one option over the other as deemed necessary. While option 2 is 36% more profitable than option 1, the first option generates lesser waste than option 2. A summary of the three dimensions of the optimized cases is presented below and in Table 5.1.

- The economic impacts of both optimized cases options were zero because they are both profitable processes; however, methyl chloride via methane (option 2) was 36% more profitable than methyl chloride via methanol (option 1). All the costs associated with option 1 were significantly lower than option 2.
- The environmental impact categories were significantly lower in option 1 than option 2 due to the lower waste generation (94% lower than option 2). Additionally, the resource usage metrics were more efficient for option 1 making it more environmentally friendly than the option 2.
- The social impact was divided into the health and safety metrics. The health and safety impacts was significantly lower in option 1compared to option 2 due to the lessened waste generation and because option 1 inherently a greener process.

In conclusion, the methyl chloride production via methanol process (option 1) has a lower sustainability impact than methyl chloride production via methane (option 2) process. The byproducts generated in option 2 are highly regulated chemicals because of their hazardous and toxic nature whereas the methyl ether byproduct in option 1 is not regulated by the Environmental Protection Agency. In this study, the side reactions in option 1 were not included in simulating the process because the literature found advised the formation of methyl ether did not proceed in measurable quantities. The kinetics of the side reactions were reported to have negligible effects on the operating temperature.

Table 5.1: Optimized cases sustainability dimensions comparison of methyl chloride via methanol (option 1) and via methane (option 2).

Sustainability Evaluation Dimensions	Option 1 (via methanol)	Option 2 (via methane)
Economic Impact	0.00	0.00
Environmental Impact	0.12	0.40
Social Impact	0.30	0.41
Sustainability Impact	0.17	0.32

5.2 FUTURE DIRECTIONS

While this methodology would be helpful in evaluating process' sustainability, it could be improved upon. The future research work to be considered for the future are:

- Develop a rigorous model for the kinetics of methyl chloride production via methanol including the formation of methyl ether. Including methyl ether would provide a complete picture when comparing the two process chemistries. Or assume that the reactions are at equilibrium and then determine the amount of reaction 2 and 3 at equilibrium compositions.
- Construct a multi-objective optimization methodology including economics, environment, and social dimensions as objectives and their metrics as constraints.

- Determine a more efficient and effective way of entering inputs for the SUSTAINABILITY EVALUATOR from Aspen Plus such as linking the tool with Aspen Plus using visual basic for applications.
- Validate the economic, environmental, and social impacts for both chemistries using another tool and compare the results obtained from this study.
- Include long term effects of chemicals in the health and environmental categories in the SUSTAINABILITY EVALUATOR.
- Include the plant cost of a case study when assessing the economic viability using the SUSTAINABILITY EVALUATOR. Develop a way of presenting differences in profitability when assigning weights for the overall economic impact so if one process is more profitable than the other it shows in the economic impact and does not automatically assign a zero for both profitable processes.

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APPENDIX A: FORTRAN STATEMENTS AND INPUT FILES FOR METHYL CHLORIDE PRODUCTION VIA METHANOL (OPTION 1) AND METHYL CHLORIDE PRODUCTION VIA METHANE (OPTION 2)

INPUT FILE FOR BASE CASE METHYL CHLORIDE PRODUCTION VIA METHANOL (OPTION 1)

```
DYNAMICS
   DYNAMICS RESULTS=ON
IN-UNITS ENG
DEF-STREAMS CONVEN ALL
SIM-OPTIONS OLD-DATABANK=YES
DATABANKS PURE22  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      NOASPENPCD

PROP-SOURCES PURE22  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
   METHANOL CH4O /
   HYDRO-01 HCL /
   METHY-01 CH3CL /
   WATER H2O /
   SULFU-01 H2SO4 /
   H+ H+ /
   CL- CL- /
   OH- OH-

HENRY-COMPS HC-1 HYDRO-01

CHEMISTRY C-1
   STOIC 1 HYDRO-01 -1. / H+ 1. / CL- 1.
   STOIC 4 H+ -1. / OH- -1. / WATER 1.

FLOWSHEET
```

```
    BLOCK B1 IN=1 OUT=2
    BLOCK B2 IN=2 OUT=3
    BLOCK B3 IN=3 OUT=4
    BLOCK B4 IN=4 OUT=5
    BLOCK B5 IN=5 OUT=14 15
    BLOCK B7 IN=14 13 OUT=6 7
    BLOCK B8 IN=15 OUT=10 9
    BLOCK B6 IN=16 OUT=11 12
    BLOCK B10 IN=9 OUT=13
    BLOCK B11 IN=6 OUT=16
    BLOCK B9 IN=12 7 OUT=8

PROPERTIES NRTL-RK
    PROPERTIES ELECNRTL

PROP-DATA HENRY-1
    IN-UNITS ENG
    PROP-LIST HENRY
    BPVAL HYDRO-01 METHANOL -49.26816209 2958.840065 7.527300000  &
        0.0 35.78000371 93.56000325 0.0
    BPVAL HYDRO-01 WATER -49.78140336 2186.999983 8.370700000  &
        -5.3294445E-3 -3.999995968 68.00000346 0.0

PROP-DATA NRTL-1
    IN-UNITS ENG
    PROP-LIST NRTL
    BPVAL METHANOL WATER -2.626000000 1491.096768 .3000000000  &
        0.0 0.0 0.0 76.98200338 370.9400010
    BPVAL WATER METHANOL 4.824100000 -2393.178281 .3000000000  &
```

0.0 0.0 0.0 76.98200338 370.9400010

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 HYDRO-01 (H+ CL-) 1.00000000E-3

PPVAL (H+ CL-) HYDRO-01 -1.0000000E-3

PPVAL WATER (H+ CL-) 41.67400000

PPVAL (H+ CL-) WATER -22.15400000

PPVAL WATER (H+ OH-) 8.045000000

PPVAL (H+ OH-) WATER -4.072000000

PROP-DATA GMELCD-1

IN-UNITS ENG

PROP-LIST GMELCD

PPVAL WATER (H+ CL-) 9581.579923

PPVAL (H+ CL-) WATER -3967.379968

PROP-DATA GMELCE-1

IN-UNITS ENG

PROP-LIST GMELCE

PPVAL WATER (H+ CL-) -5.404000000

PPVAL (H+ CL-) WATER 5.188000000

```
PROP-DATA GMELCN-1
   IN-UNITS ENG
   PROP-LIST GMELCN
   PPVAL WATER ( H+ CL- ) .0283500000

STREAM 1
   SUBSTREAM MIXED TEMP=77. PRES=14.7
   MOLE-FLOW METHANOL 158.13 / HYDRO-01 163.13

BLOCK B1 MIXER

BLOCK B9 MIXER

BLOCK B8 FSPLIT
   FRAC 9 0.36

BLOCK B2 HEATER
   PARAM TEMP=675. PRES=14.7

BLOCK B4 HEATER
   PARAM TEMP=140. PRES=14.7

BLOCK B10 HEATER
   PARAM TEMP=75. PRES=0.

BLOCK B11 HEATER
   PARAM TEMP=25. PRES=0.

BLOCK B6 FLASH2
```

```
  PARAM TEMP=25. PRES=14.7

BLOCK B5 RADFRAC
  PARAM NSTAGE=6 MAXOL=50
  COL-CONFIG CONDENSER=PARTIAL-V
  FEEDS 5 3
  PRODUCTS 14 1 V / 15 6 L
  P-SPEC 1 14.7
  COL-SPECS MOLE-B=171. MOLE-RR=0.85269708
  SPEC 1 TEMP 75. STAGE=1
  VARY 1 MOLE-B 100. 314.

BLOCK B7 RADFRAC
  PARAM NSTAGE=2 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD  &
    ABSORBER=NO MAXOL=100
  COL-CONFIG CONDENSER=NONE REBOILER=NONE
  RATESEP-ENAB CALC-MODE=EQUILIBRIUM
  FEEDS 14 2 ON-STAGE / 13 1
  PRODUCTS 6 1 V / 7 2 L
  P-SPEC 1 14.7
  COL-SPECS
  PROPERTIES ELECNRTL HENRY-COMPS=HC-1 CHEMISTRY=C-1  &
    FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=NO

BLOCK B3 RPLUG
  PARAM TYPE=T-SPEC LENGTH=12. DIAM=10. NPHASE=2  &
    INT-TOL=0.0005 IGN-CAT-VOL=NO CAT-PRESENT=YES  &
    BED-VOIDAGE=0.5 CAT-RHO=0.2857 <gm/cc>
  T-SPEC 0.0 675.
```

```
   COOLANT TOL=0.001
   BLOCK-OPTION FREE-WATER=NO
   REACTIONS RXN-IDS=R-1

DESIGN-SPEC DS-2
   DEFINE H2OOUT MOLE-FLOW STREAM=6 SUBSTREAM=MIXED  &
      COMPONENT=WATER
   SPEC "H2OOUT" TO "3"
   TOL-SPEC ".001"
   VARY BLOCK-VAR BLOCK=B8 SENTENCE=FRAC VARIABLE=FRAC ID1=9
   LIMITS ".01" ".99"

EO-CONV-OPTI

STREAM-REPOR MOLEFLOW MASSFLOW STDVOLFLOW MOLEFRAC MASSFRAC  &
      STDVOLFRAC

REACTIONS R-1 POWERLAW
   REAC-DATA 1 PHASE=V RBASIS=CAT-WT
   RATE-CON 1 PRE-EXP=18160000. ACT-ENERGY=19178. <cal/mol>  &
      TEMP-EXPONEN=0.
   STOIC 1 MIXED METHANOL -1. / HYDRO-01 -1. / METHY-01 1. / &
      WATER 1.
   POWLAW-EXP 1 MIXED METHANOL 1. / MIXED HYDRO-01 1.
```

INPUT FILE FOR OPTIMIZED CASE METHYL CHLORIDE PRODUCTION VIA METHANOL (OPTION 1)

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS OLD-DATABANK=YES

DATABANKS PURE22  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
      NOASPENPCD

PROP-SOURCES PURE22  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
   METHANOL CH4O /
   HYDRO-01 HCL /
   METHY-01 CH3CL /
   WATER H2O /
   SULFU-01 H2SO4 /
   H+ H+ /
   CL- CL- /
   OH- OH-

HENRY-COMPS HC-1 HYDRO-01

CHEMISTRY C-1
   STOIC 1 HYDRO-01 -1. / H+ 1. / CL- 1.
   STOIC 4 H+ -1. / OH- -1. / WATER 1.

FLOWSHEET
   BLOCK B1 IN=1 OUT=2
   BLOCK B2 IN=2 OUT=3
   BLOCK B3 IN=3 OUT=4
   BLOCK B4 IN=4 OUT=5
   BLOCK B5 IN=5 OUT=14 15
   BLOCK B7 IN=14 13 OUT=6 7
   BLOCK B8 IN=15 OUT=10 9
   BLOCK B6 IN=16 OUT=11 12
   BLOCK B10 IN=9 OUT=13
   BLOCK B11 IN=6 OUT=16
   BLOCK B9 IN=12 OUT=8

PROPERTIES NRTL-RK
   PROPERTIES ELECNRTL

PROP-DATA HENRY-1
   IN-UNITS ENG
```

```
   PROP-LIST HENRY
   BPVAL HYDRO-01 METHANOL -49.26816209 2958.840065 7.527300000  &
      0.0 35.78000371 93.56000325 0.0
   BPVAL HYDRO-01 WATER -49.78140336 2186.999983 8.370700000  &
      -5.3294445E-3 -3.999995968 68.00000346 0.0

PROP-DATA NRTL-1
   IN-UNITS ENG
   PROP-LIST NRTL
   BPVAL METHANOL WATER -2.626000000 1491.096768 .3000000000  &
      0.0 0.0 0.0 76.98200338 370.9400010
   BPVAL WATER METHANOL 4.824100000 -2393.178281 .3000000000  &
      0.0 0.0 0.0 76.98200338 370.9400010

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 HYDRO-01 ( H+ CL- ) 1.00000000E-3
   PPVAL ( H+ CL- ) HYDRO-01 -1.0000000E-3
   PPVAL WATER ( H+ CL- ) 41.67400000
   PPVAL ( H+ CL- ) WATER -22.15400000
   PPVAL WATER ( H+ OH- ) 8.045000000
   PPVAL ( H+ OH- ) WATER -4.072000000

PROP-DATA GMELCD-1
   IN-UNITS ENG
   PROP-LIST GMELCD
   PPVAL WATER ( H+ CL- ) 9581.579923
   PPVAL ( H+ CL- ) WATER -3967.379968

PROP-DATA GMELCE-1
   IN-UNITS ENG
   PROP-LIST GMELCE
   PPVAL WATER ( H+ CL- ) -5.404000000
   PPVAL ( H+ CL- ) WATER 5.188000000

PROP-DATA GMELCN-1
   IN-UNITS ENG
   PROP-LIST GMELCN
   PPVAL WATER ( H+ CL- ) .0283500000

STREAM 1
   SUBSTREAM MIXED TEMP=77. PRES=14.7
   MOLE-FLOW METHANOL 158.13 / HYDRO-01 163.13

BLOCK B1 MIXER
```

```
BLOCK B9 MIXER

BLOCK B8 FSPLIT
   FRAC 9 0.36

BLOCK B2 HEATER
   PARAM TEMP=675. PRES=14.7

BLOCK B4 HEATER
   PARAM TEMP=140. PRES=14.7

BLOCK B10 HEATER
   PARAM TEMP=75. PRES=0.

BLOCK B11 HEATER
   PARAM TEMP=25. PRES=0.

BLOCK B6 FLASH2
   PARAM TEMP=25. PRES=14.7

BLOCK B5 RADFRAC
   PARAM NSTAGE=6 MAXOL=50
   COL-CONFIG CONDENSER=PARTIAL-V
   FEEDS 5 3
   PRODUCTS 14 1 V / 15 6 L
   P-SPEC 1 14.7
   COL-SPECS MOLE-B=171. MOLE-RR=0.85269708
   SPEC 1 TEMP 75. STAGE=1
   VARY 1 MOLE-B 100. 314.

BLOCK B7 RADFRAC
   PARAM NSTAGE=2 ALGORITHM=NONIDEAL INIT-OPTION=STANDARD  &
      ABSORBER=NO MAXOL=100
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   RATESEP-ENAB CALC-MODE=EQUILIBRIUM
   FEEDS 14 2 ON-STAGE / 13 1
   PRODUCTS 6 1 V / 7 2 L
   P-SPEC 1 14.7
   COL-SPECS
   PROPERTIES ELECNRTL HENRY-COMPS=HC-1 CHEMISTRY=C-1  &
      FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=NO

BLOCK B3 RPLUG
   PARAM TYPE=T-SPEC LENGTH=12. DIAM=10. NPHASE=2  &
      INT-TOL=0.0005 IGN-CAT-VOL=NO CAT-PRESENT=YES  &
      BED-VOIDAGE=0.5 CAT-RHO=0.2857 <gm/cc>
   T-SPEC 0.0 675.
   COOLANT TOL=0.001
   BLOCK-OPTION FREE-WATER=NO
   REACTIONS RXN-IDS=R-1
```

```
DESIGN-SPEC DS-2
   DEFINE H2OOUT MOLE-FLOW STREAM=6 SUBSTREAM=MIXED  &
      COMPONENT=WATER
   SPEC "H2OOUT" TO "3"
   TOL-SPEC ".001"
   VARY BLOCK-VAR BLOCK=B8 SENTENCE=FRAC VARIABLE=FRAC ID1=9
   LIMITS ".01" ".99"

EO-CONV-OPTI

OPTIMIZATION O-1
   DEFINE MIN MASS-FLOW STREAM=3 SUBSTREAM=MIXED  &
      COMPONENT=METHANOL
   DEFINE MOUT MASS-FLOW STREAM=4 SUBSTREAM=MIXED  &
      COMPONENT=METHANOL
   DEFINE M1R MASS-FLOW STREAM=1 SUBSTREAM=MIXED  &
      COMPONENT=METHANOL
   DEFINE H1R MASS-FLOW STREAM=1 SUBSTREAM=MIXED  &
      COMPONENT=HYDRO-01
   DEFINE M11P MASS-FLOW STREAM=11 SUBSTREAM=MIXED  &
      COMPONENT=METHY-01
   DEFINE W10P MASS-FLOW STREAM=10 SUBSTREAM=MIXED  &
      COMPONENT=WATER
   DEFINE B3HD BLOCK-VAR BLOCK=B3 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE B4HD BLOCK-VAR BLOCK=B4 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE B5HDC BLOCK-VAR BLOCK=B5 VARIABLE=COND-DUTY  &
      SENTENCE=RESULTS
   DEFINE B10HD BLOCK-VAR BLOCK=B10 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE B11HD BLOCK-VAR BLOCK=B11 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE B6HD BLOCK-VAR BLOCK=B6 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE B2HD BLOCK-VAR BLOCK=B2 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE WS7 STREAM-VAR STREAM=7 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE WS12 STREAM-VAR STREAM=12 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE B5HDR BLOCK-VAR BLOCK=B5 VARIABLE=REB-DUTY  &
      SENTENCE=RESULTS
   DEFINE MCP11 MASS-FLOW STREAM=11 SUBSTREAM=MIXED  &
      COMPONENT=METHY-01
F    X=1-(MOUT/MIN)
F    M1RC=M1R*0.294*0.454
F    H1RC=H1R*0.09*0.454
F    M11PR= M11P*0.82*0.454
F    W10PR=W10P*0.00638*0.454
```

```
F    HD=-((B3HD+B4HD+B5HDC+B6HD+B10HD+B11HD)*.454/60)
F    HDC=(HD/3.84)*0.00638
F    NG=(B2HD+B5HDR)
F    NGC = (NG)*(0.00451/1030)
F    WSC=(WS7+WS12)*0.2*0.454
F    REV=M11PR+W10PR
F    RMC=M1RC+H1RC
F    HDTC=HDC+NGC
F    PROFIT=M11PR+W10PR-M1RC-H1RC-HDC-NGC-WSC
   MAXIMIZE "PROFIT"
   VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=METHANOL
   LIMITS "120" "400"
   VARY BLOCK-VAR BLOCK=B3 VARIABLE=LENGTH SENTENCE=PARAM
   LIMITS "8" "40"
   VARY BLOCK-VAR BLOCK=B3 VARIABLE=TEMP SENTENCE=T-SPEC ID1=1
   LIMITS "570" "730"

CONV-OPTIONS
   PARAM SPEC-LOOP=OUTSIDE USER-LOOP=INSIDE
   WEGSTEIN MAXIT=50
   DIRECT MAXIT=50
   SECANT MAXIT=50
   BROYDEN MAXIT=50

STREAM-REPOR MOLEFLOW MASSFLOW STDVOLFLOW MOLEFRAC MASSFRAC  &
      STDVOLFRAC

REACTIONS R-1 POWERLAW
   REAC-DATA 1 PHASE=V RBASIS=CAT-WT
   RATE-CON 1 PRE-EXP=18160000. ACT-ENERGY=19178. <cal/mol>  &
      TEMP-EXPONEN=0.
   STOIC 1 MIXED METHANOL -1. / HYDRO-01 -1. / METHY-01 1. / &
      WATER 1.
   POWLAW-EXP 1 MIXED METHANOL 1. / MIXED HYDRO-01 1.;
;
;
;
```

INPUT FILE FOR BASE CASE METHYL CHLORIDE PRODUCTION VIA METHANE (OPTION 2)

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS OLD-DATABANK=YES

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
   METHANE CH4 /
   CHLORINE CL2 /
   METHYLCH CH3CL /
   DICHLORO CH2CL2 /
   CHLOROFO CHCL3 /
   CARBONTE CCL4 /
   WATER H2O /
   HYDROGEN HCL /
   NITROGEN N2 /
   H3O+ H3O+ /
   HCLO HCLO /
   CLO- CLO- /
   OH- OH- /
   CL- CL- /
   NAOH NAOH /
   NA+ NA+ /
   "NACL(S)" NACL /
   "NAOH(S)" NAOH /
   H2SO4 H2SO4 /
   HSO4- HSO4- /
   SO4-- SO4-2
```

```
HENRY-COMPS GLOBAL HCLO HYDROGEN

CHEMISTRY GLOBAL
    DISS NAOH OH- 1 / NA+ 1
    STOIC 1 HYDROGEN -1 / WATER -1 / CL- 1 / H3O+ 1
    STOIC 2 WATER -1 / HSO4- -1 / H3O+ 1 / SO4-- 1
    STOIC 3 WATER -1 / H2SO4 -1 / H3O+ 1 / HSO4- 1
    STOIC 4 WATER -1 / HCLO -1 / CLO- 1 / H3O+ 1
    STOIC 5 WATER -2 / CHLORINE -1 / HCLO 1 / CL- 1 /  &
        H3O+ 1
    STOIC 6 WATER -2 / OH- 1 / H3O+ 1
    K-STOIC 4 A=-16.151899 B=-1602.869995 C=0 D=0
    K-STOIC 5 A=-11.37532 B=-1286.972046 C=0 D=0
    K-STOIC 6 A=132.89888 B=-13445.900391 C=-22.477301 D=0
    SALT "NAOH(S)" OH- 1 / NA+ 1
    SALT "NACL(S)" CL- 1 / NA+ 1
    K-SALT "NAOH(S)" A=433.324097 B=-21656.691406 C=-63.231094  &
        D=0
    K-SALT "NACL(S)" A=-203.587494 B=4381.175781 C=35.875179  &
        D=-0.067216

FLOWSHEET
    BLOCK M-301 IN=1 2 3 OUT=4
    BLOCK E-601 IN=4 OUT=5
    BLOCK E-602 IN=6 OUT=7
    BLOCK T-601 IN=7 10 OUT=8 9
    BLOCK T-602 IN=8 11 OUT=12 13
    BLOCK E-603 IN=12 OUT=14
    BLOCK T-603 IN=14 17 OUT=15 16
    BLOCK E-604 IN=18 OUT=20
    BLOCK C-601 IN=15 OUT=18
    BLOCK T-604 IN=20 OUT=19 21
    BLOCK T-605 IN=21 OUT=22 23
    BLOCK T-608 IN=22 OUT=25 24
    BLOCK T-607 IN=23 OUT=26 27
    BLOCK T-606 IN=27 OUT=28 29
    BLOCK B3 IN=25 19 OUT=30
    BLOCK B4 IN=30 OUT=31 32
    BLOCK C-602 IN=31 OUT=33
    BLOCK E-605 IN=33 OUT=3
    BLOCK B1 IN=32 9 36 38 OUT=34
    BLOCK B5 IN=16 OUT=35 36
    BLOCK B7 IN=13 OUT=37 38
    BLOCK B2 IN=5 OUT=6

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &
        TRUE-COMPS=NO

PROP-DATA HENRY-1
    IN-UNITS ENG TEMPERATURE=K
```

```
   PROP-LIST HENRY
   BPVAL HYDROGEN DICHLORO 89.37548041 -4274.799805  &
      -12.77600000 .0142190000 223.1500000 273.1500000 0.0
   BPVAL HCLO WATER -28.83851659 0.0 0.0 0.0 273.0000000  &
      400.0000000 0.0

PROP-DATA HENRY-1
   IN-UNITS ENG
   PROP-LIST HENRY
   BPVAL HYDROGEN CHLOROFO -89.89187628 -1110.402018  &
      18.38500000 -.0319155558 -57.99999554 59.00000353 0.0
   BPVAL HYDROGEN CARBONTE 99.36231378 -7905.239586  &
      -12.44300000 5.80000005E-4 -39.99999568 68.00000346 0.0
   BPVAL HYDROGEN WATER 49.61444341 -13973.09749 0.0 0.0  &
      31.73000375 260.3300019 0.0

PROP-DATA NRTL-1
   IN-UNITS ENG
   PROP-LIST NRTL
   BPVAL WATER HCLO 11.25094000 0.0 .3000000000 0.0 0.0 0.0  &
      32.00000374 212.0000023
   BPVAL HCLO WATER -7.175849000 0.0 .3000000000 0.0 0.0 0.0  &
      32.00000374 212.0000023

PROP-DATA VLCLK-1
   IN-UNITS ENG
   PROP-LIST VLCLK
   BPVAL H3O+ CL- .5534556926 .2140997389
   BPVAL NA+ OH- -.2209618885 1.168080771
   BPVAL NA+ CL- .2425544568 .4050617685
   BPVAL H3O+ HSO4- .8778750698 .3242692842
   BPVAL NA+ SO4-- .1389686121 1.974549536

PROP-DATA GMELCC-1
   IN-UNITS ENG
   PROP-LIST GMELCC
   PPVAL CHLORINE ( H3O+ CLO- ) 15.00000000
   PPVAL ( H3O+ CLO- ) CHLORINE -8.000000000
   PPVAL CHLORINE ( H3O+ OH- ) 15.00000000
   PPVAL ( H3O+ OH- ) CHLORINE -8.000000000
   PPVAL CHLORINE ( H3O+ CL- ) 15.00000000
   PPVAL ( H3O+ CL- ) CHLORINE -8.000000000
   PPVAL WATER ( H3O+ OH- ) 8.045000000
   PPVAL ( H3O+ OH- ) WATER -4.072000000
   PPVAL WATER ( H3O+ CL- ) 4.110129000
   PPVAL ( H3O+ CL- ) WATER -3.344103000
   PPVAL HYDROGEN ( H3O+ CLO- ) 15.00000000
   PPVAL ( H3O+ CLO- ) HYDROGEN -8.000000000
   PPVAL HYDROGEN ( H3O+ OH- ) 15.00000000
   PPVAL ( H3O+ OH- ) HYDROGEN -8.000000000
   PPVAL HYDROGEN ( H3O+ CL- ) 12.00000000
```

PPVAL (H3O+ CL-) HYDROGEN -1.0000000E-3
PPVAL HCLO (H3O+ CLO-) 15.00000000
PPVAL (H3O+ CLO-) HCLO -8.000000000
PPVAL HCLO (H3O+ OH-) 15.00000000
PPVAL (H3O+ OH-) HCLO -8.000000000
PPVAL HCLO (H3O+ CL-) 15.00000000
PPVAL (H3O+ CL-) HCLO -8.000000000
PPVAL CHLORINE (NA+ CLO-) 15.00000000
PPVAL (NA+ CLO-) CHLORINE -8.000000000
PPVAL CHLORINE (NA+ OH-) 15.00000000
PPVAL (NA+ OH-) CHLORINE -8.000000000
PPVAL CHLORINE (NA+ CL-) 15.00000000
PPVAL (NA+ CL-) CHLORINE -8.000000000
PPVAL WATER (NA+ OH-) 6.737997000
PPVAL (NA+ OH-) WATER -3.771221000
PPVAL WATER (NA+ CL-) 5.980196000
PPVAL (NA+ CL-) WATER -3.789168000
PPVAL HYDROGEN (NA+ CLO-) 15.00000000
PPVAL (NA+ CLO-) HYDROGEN -8.000000000
PPVAL HYDROGEN (NA+ OH-) 15.00000000
PPVAL (NA+ OH-) HYDROGEN -8.000000000
PPVAL HYDROGEN (NA+ CL-) 15.00000000
PPVAL (NA+ CL-) HYDROGEN -8.000000000
PPVAL HCLO (NA+ CLO-) 15.00000000
PPVAL (NA+ CLO-) HCLO -8.000000000
PPVAL HCLO (NA+ OH-) 15.00000000
PPVAL (NA+ OH-) HCLO -8.000000000
PPVAL HCLO (NA+ CL-) 15.00000000
PPVAL (NA+ CL-) HCLO -8.000000000
PPVAL (NA+ OH-) (NA+ CL-) 8.407678000
PPVAL (NA+ CL-) (NA+ OH-) 1.950440000
PPVAL H2SO4 (H3O+ CL-) 10.00000000
PPVAL (H3O+ CL-) H2SO4 -2.000000000
PPVAL WATER (H3O+ HSO4-) 6.362000000
PPVAL (H3O+ HSO4-) WATER -3.749000000
PPVAL WATER (H3O+ SO4--) 8.000000000
PPVAL (H3O+ SO4--) WATER -4.000000000
PPVAL WATER (NA+ HSO4-) 7.663000000
PPVAL (NA+ HSO4-) WATER -3.944000000
PPVAL WATER (NA+ SO4--) 7.689221000
PPVAL (NA+ SO4--) WATER -4.284786000
PPVAL HYDROGEN (H3O+ HSO4-) 10.00000000
PPVAL (H3O+ HSO4-) HYDROGEN -2.000000000
PPVAL HYDROGEN (H3O+ SO4--) 15.00000000
PPVAL (H3O+ SO4--) HYDROGEN -8.000000000
PPVAL H2SO4 (H3O+ HSO4-) 12.99200000
PPVAL (H3O+ HSO4-) H2SO4 -2.981000000
PPVAL H2SO4 (H3O+ SO4--) 8.000000000
PPVAL (H3O+ SO4--) H2SO4 -4.000000000
PPVAL (H3O+ CL-) (H3O+ HSO4-) .9536271000
PPVAL (H3O+ HSO4-) (H3O+ CL-) 0.0

```
   PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 3.147792000
   PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -.5387706000
   PPVAL ( NA+ CL- ) ( NA+ SO4-- ) -11.44869000
   PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -.2697454000

PROP-DATA GMELCD-1
   IN-UNITS ENG
   PROP-LIST GMELCD
   PPVAL CHLORINE ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) CHLORINE 0.0
   PPVAL CHLORINE ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) CHLORINE 0.0
   PPVAL CHLORINE ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) CHLORINE 0.0
   PPVAL WATER ( H3O+ CL- ) 4151.955567
   PPVAL ( H3O+ CL- ) WATER -1176.370371
   PPVAL HYDROGEN ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) HYDROGEN 0.0
   PPVAL HCLO ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) HCLO 0.0
   PPVAL HCLO ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) HCLO 0.0
   PPVAL HCLO ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) HCLO 0.0
   PPVAL CHLORINE ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) CHLORINE 0.0
   PPVAL CHLORINE ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) CHLORINE 0.0
   PPVAL CHLORINE ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) CHLORINE 0.0
   PPVAL WATER ( NA+ OH- ) 2556.435580
   PPVAL ( NA+ OH- ) WATER -849.2763532
   PPVAL WATER ( NA+ CL- ) 1514.732568
   PPVAL ( NA+ CL- ) WATER -389.4562769
   PPVAL HYDROGEN ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) HYDROGEN 0.0
   PPVAL HCLO ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) HCLO 0.0
   PPVAL HCLO ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) HCLO 0.0
   PPVAL HCLO ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) HCLO 0.0
   PPVAL ( NA+ OH- ) ( NA+ CL- ) -324.8080174
```

```
   PPVAL ( NA+ CL- ) ( NA+ OH- ) -1491.716328
   PPVAL WATER ( H3O+ HSO4- ) 3524.759972
   PPVAL ( H3O+ HSO4- ) WATER -1049.759992
   PPVAL WATER ( H3O+ SO4-- ) 0.0
   PPVAL ( H3O+ SO4-- ) WATER 0.0
   PPVAL WATER ( NA+ SO4-- ) 1018.076932
   PPVAL ( NA+ SO4-- ) WATER -102.3078232
   PPVAL HYDROGEN ( H3O+ HSO4- ) 0.0
   PPVAL ( H3O+ HSO4- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( H3O+ SO4-- ) 0.0
   PPVAL ( H3O+ SO4-- ) HYDROGEN 0.0
   PPVAL H2SO4 ( H3O+ HSO4- ) -3119.219975
   PPVAL ( H3O+ HSO4- ) H2SO4 -292.1399977
   PPVAL H2SO4 ( H3O+ SO4-- ) 0.0
   PPVAL ( H3O+ SO4-- ) H2SO4 0.0
   PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) -363.1438771
   PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0
   PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 1408.793749
   PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -170.8229686
   PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 6763.469346
   PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -240.5010581

PROP-DATA GMELCE-1
   IN-UNITS ENG
   PROP-LIST GMELCE
   PPVAL CHLORINE ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) CHLORINE 0.0
   PPVAL CHLORINE ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) CHLORINE 0.0
   PPVAL CHLORINE ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) CHLORINE 0.0
   PPVAL WATER ( H3O+ CL- ) .3417959000
   PPVAL ( H3O+ CL- ) WATER 2.121453000
   PPVAL HYDROGEN ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) HYDROGEN 0.0
   PPVAL HCLO ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) HCLO 0.0
   PPVAL HCLO ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) HCLO 0.0
   PPVAL HCLO ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) HCLO 0.0
   PPVAL CHLORINE ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) CHLORINE 0.0
   PPVAL CHLORINE ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) CHLORINE 0.0
   PPVAL CHLORINE ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) CHLORINE 0.0
```

```
    PPVAL WATER ( NA+ OH- ) 3.013932000
    PPVAL ( NA+ OH- ) WATER 2.136557000
    PPVAL WATER ( NA+ CL- ) 7.433500000
    PPVAL ( NA+ CL- ) WATER -1.100418000
    PPVAL HYDROGEN ( NA+ CLO- ) 0.0
    PPVAL ( NA+ CLO- ) HYDROGEN 0.0
    PPVAL HYDROGEN ( NA+ OH- ) 0.0
    PPVAL ( NA+ OH- ) HYDROGEN 0.0
    PPVAL HYDROGEN ( NA+ CL- ) 0.0
    PPVAL ( NA+ CL- ) HYDROGEN 0.0
    PPVAL HCLO ( NA+ CLO- ) 0.0
    PPVAL ( NA+ CLO- ) HCLO 0.0
    PPVAL HCLO ( NA+ OH- ) 0.0
    PPVAL ( NA+ OH- ) HCLO 0.0
    PPVAL HCLO ( NA+ CL- ) 0.0
    PPVAL ( NA+ CL- ) HCLO 0.0
    PPVAL ( NA+ OH- ) ( NA+ CL- ) 100.0000000
    PPVAL ( NA+ CL- ) ( NA+ OH- ) 6.619543000
    PPVAL WATER ( H3O+ HSO4- ) -4.599000000
    PPVAL ( H3O+ HSO4- ) WATER 4.472000000
    PPVAL WATER ( NA+ SO4-- ) -14.08276000
    PPVAL ( NA+ SO4-- ) WATER 8.547499000
    PPVAL HYDROGEN ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) HYDROGEN 0.0
    PPVAL H2SO4 ( H3O+ HSO4- ) -30.12600000
    PPVAL ( H3O+ HSO4- ) H2SO4 .8060000000
    PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 43.39265000
    PPVAL ( NA+ SO4-- ) ( NA+ OH- ) 4.518955000
    PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 60.25378000
    PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -4.302999000

PROP-DATA GMELCN-1
    IN-UNITS ENG
    PROP-LIST GMELCN
    PPVAL CHLORINE ( H3O+ CLO- ) .1000000000
    PPVAL CHLORINE ( H3O+ OH- ) .1000000000
    PPVAL CHLORINE ( H3O+ CL- ) .1000000000
    PPVAL HYDROGEN ( H3O+ CLO- ) .1000000000
    PPVAL HYDROGEN ( H3O+ OH- ) .1000000000
    PPVAL HCLO ( H3O+ CLO- ) .1000000000
    PPVAL HCLO ( H3O+ OH- ) .1000000000
    PPVAL HCLO ( H3O+ CL- ) .1000000000
    PPVAL CHLORINE ( NA+ CLO- ) .1000000000
    PPVAL CHLORINE ( NA+ OH- ) .1000000000
    PPVAL CHLORINE ( NA+ CL- ) .1000000000
    PPVAL WATER ( NA+ OH- ) .2000000000
    PPVAL WATER ( NA+ CL- ) .2000000000
    PPVAL HYDROGEN ( NA+ CLO- ) .1000000000
    PPVAL HYDROGEN ( NA+ OH- ) .1000000000
    PPVAL HYDROGEN ( NA+ CL- ) .1000000000
    PPVAL HCLO ( NA+ CLO- ) .1000000000
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```
    PPVAL HCLO ( NA+ OH- ) .1000000000
    PPVAL HCLO ( NA+ CL- ) .1000000000
    PPVAL WATER ( H3O+ HSO4- ) .2000000000
    PPVAL WATER ( NA+ SO4-- ) .2000000000
    PPVAL HYDROGEN ( H3O+ SO4-- ) .1000000000
    PPVAL H2SO4 ( H3O+ HSO4- ) .2000000000

STREAM 1
    SUBSTREAM MIXED TEMP=77. PRES=14.7 MOLE-FLOW=323.
    MOLE-FRAC METHANE 0.98 / NITROGEN 0.02

STREAM 2
    SUBSTREAM MIXED TEMP=77. PRES=14.7 MOLE-FLOW=323.
    MOLE-FRAC CHLORINE 1.

STREAM 3
    SUBSTREAM MIXED TEMP=77 PRES=14.7 MOLE-FLOW=783.732252
    MOLE-FRAC METHANE 0.901053277 / METHYLCH 0.0270128601 /  &
        DICHLORO 0.00024133163 / CHLOROFO 2.066234E-005 /  &
        CARBONTE 1.339088E-006 / WATER 2.144660E-007 /  &
        NITROGEN 0.0716703158 / H2SO4 2.003709E-016

STREAM 10
    SUBSTREAM MIXED TEMP=86. PRES=14.7 MOLE-FLOW=2025.
    MOLE-FRAC WATER 1.

STREAM 11
    SUBSTREAM MIXED TEMP=86. PRES=14.7 MOLE-FLOW=200.
    MOLE-FRAC NAOH 1.

STREAM 17
    SUBSTREAM MIXED TEMP=90. PRES=14.7 MASS-FLOW=13551. <kg/hr>
    MOLE-FRAC H2SO4 1.

BLOCK B1 MIXER

BLOCK B3 MIXER

BLOCK M-301 MIXER
    PARAM PRES=14.7 NPHASE=1 PHASE=V T-EST=77.
    BLOCK-OPTION FREE-WATER=NO

BLOCK B4 FSPLIT
    FRAC 32 0.1

BLOCK B5 SEP2
    FRAC STREAM=35 SUBSTREAM=MIXED COMPS=METHANE CHLORINE  &
        METHYLCH DICHLORO CHLOROFO CARBONTE WATER HYDROGEN  &
        NITROGEN H3O+ HCLO CLO- OH- CL- NAOH NA+ "NACL(S)"  &
        "NAOH(S)" H2SO4 HSO4- SO4-- FRACS=0. 0. 0. 0. 0. 0.  &
        0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 1. 0. 0.
```

```
BLOCK B7 SEP2
   FRAC STREAM=37 SUBSTREAM=MIXED COMPS=METHANE CHLORINE  &
      METHYLCH DICHLORO CHLOROFO CARBONTE WATER HYDROGEN  &
      NITROGEN H3O+ HCLO CLO- OH- CL- NAOH NA+ "NACL(S)"  &
      "NAOH(S)" H2SO4 HSO4- SO4-- FRACS=0. 0. 0. 0. 0. 0.  &
      0. 0. 0. 0. 0. 0. 0. 0. 1. 0. 0. 0. 0. 0. 0.

BLOCK E-601 HEATER
   PARAM TEMP=572. PRES=14.7 NPHASE=1 PHASE=V
   BLOCK-OPTION FREE-WATER=NO

BLOCK E-602 HEATER
   PARAM TEMP=100. PRES=14.7 NPHASE=1 PHASE=V
   BLOCK-OPTION FREE-WATER=NO

BLOCK E-603 HEATER
   PARAM TEMP=100. PRES=14.7 NPHASE=1 PHASE=V
   BLOCK-OPTION FREE-WATER=NO

BLOCK E-604 HEATER
   PARAM TEMP=-58. PRES=115. NPHASE=2
   BLOCK-OPTION FREE-WATER=NO

BLOCK E-605 HEATER
   PARAM TEMP=77. PRES=14.7

BLOCK T-604 FLASH2
   PARAM PRES=115. DUTY=0.

BLOCK T-608 FLASH2
   PARAM TEMP=-100. PRES=15.

BLOCK T-606 DSTWU
   PARAM LIGHTKEY=CHLOROFO RECOVL=0.999 HEAVYKEY=CARBONTE  &
      RECOVH=0.001 PTOP=14.7 PBOT=14.7 NSTAGE=10

BLOCK T-601 RADFRAC
   PARAM NSTAGE=2
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   FEEDS 7 2 ON-STAGE / 10 1 ON-STAGE
   PRODUCTS 8 1 V / 9 2 L
   P-SPEC 1 14.7
   COL-SPECS

BLOCK T-602 RADFRAC
   PARAM NSTAGE=5 MAXOL=30
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   FEEDS 8 5 ON-STAGE / 11 1 ON-STAGE
   PRODUCTS 12 1 V / 13 5 L
   P-SPEC 1 14.7
```

```
    COL-SPECS
    T-EST 1 299.3 / 2 306.3
    X-EST 1 NAOH 0.89192 / 1 WATER 0.1068
    Y-EST 1 WATER 0.21598

BLOCK T-603 RADFRAC
    PARAM NSTAGE=2
    COL-CONFIG CONDENSER=NONE REBOILER=NONE
    FEEDS 14 2 ON-STAGE / 17 1
    PRODUCTS 15 1 V / 16 2 L
    P-SPEC 1 14.7
    COL-SPECS

BLOCK T-605 RADFRAC
    PARAM NSTAGE=12
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 21 6 ON-STAGE
    PRODUCTS 22 1 V / 23 12 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RR=1.2
    SPEC 1 MOLE-RECOV 0.995 COMPS=METHYLCH STREAMS=22  &
        BASE-STREAMS=21
    VARY 1 D:F 0.001 0.999

BLOCK T-607 RADFRAC
    PARAM NSTAGE=20
    COL-CONFIG CONDENSER=TOTAL REBOILER=KETTLE
    RATESEP-ENAB CALC-MODE=EQUILIBRIUM
    FEEDS 23 10
    PRODUCTS 26 1 L / 27 20 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RR=1.5
    SPEC 1 MOLE-RECOV 0.999 COMPS=DICHLORO STREAMS=26  &
        BASE-STREAMS=23
    VARY 1 D:F 0.001 0.999

BLOCK B2 RCSTR
    PARAM VOL=1600. TEMP=525. <C> PRES=14.7
    REACTIONS RXN-IDS=R-1

BLOCK C-602 COMPR
    PARAM TYPE=ASME-POLYTROP DELP=45. <psia>

BLOCK C-601 MCOMPR
    PARAM NSTAGE=2 TYPE=ASME-POLYTROPIC PRES=115. COMPR-NPHASE=1  &
        COOLER-NPHAS=1
    FEEDS 15 1
    PRODUCTS 18 2
    COOLER-SPECS 2 TEMP=275. / 1 TEMP=844.

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
   REAC-DATA 4 PHASE=V
   RATE-CON 1 PRE-EXP=256000000. ACT-ENERGY=35260.
   RATE-CON 2 PRE-EXP=62800000. ACT-ENERGY=30580.
   RATE-CON 3 PRE-EXP=256000000. ACT-ENERGY=35260.
   RATE-CON 4 PRE-EXP=293000000. ACT-ENERGY=37490.
   STOIC 1 MIXED METHANE -1. / CHLORINE -1. / METHYLCH 1. / &
      HYDROGEN 1.
   STOIC 2 MIXED METHYLCH -1. / CHLORINE -1. / DICHLORO 1. / &
      HYDROGEN 1.
   STOIC 3 MIXED DICHLORO -1. / CHLORINE -1. / CHLOROFO 1. / &
      HYDROGEN 1.
   STOIC 4 MIXED CHLOROFO -1. / CHLORINE -1. / CARBONTE 1. / &
      HYDROGEN 1.
   POWLAW-EXP 1 MIXED METHANE 1. / MIXED CHLORINE 1.
   POWLAW-EXP 2 MIXED METHYLCH 1. / MIXED CHLORINE 1.
   POWLAW-EXP 3 MIXED DICHLORO 1. / MIXED CHLORINE 1.
   POWLAW-EXP 4 MIXED CHLOROFO 1. / MIXED CHLORINE 1.
;
;
;
;
;
```

INPUT FILE FOR OPTIMIZED CASE OF METHYL CHLORIDE VIA METHANE (OPTION 2)

```
DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS OLD-DATABANK=YES

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
   METHANE CH4 /
   CHLORINE CL2 /
   METHYLCH CH3CL /
   DICHLORO CH2CL2 /
   CHLOROFO CHCL3 /
   CARBONTE CCL4 /
   WATER H2O /
   HYDROGEN HCL /
   NITROGEN N2 /
   H3O+ H3O+ /
   HCLO HCLO /
   CLO- CLO- /
   OH- OH- /
   CL- CL- /
   NAOH NAOH /
   NA+ NA+ /
   "NACL(S)" NACL /
   "NAOH(S)" NAOH /
   H2SO4 H2SO4 /
   HSO4- HSO4- /
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```
   SO4-- SO4-2

HENRY-COMPS GLOBAL HCLO HYDROGEN

CHEMISTRY GLOBAL
   DISS NAOH OH- 1 / NA+ 1
   STOIC 1 HYDROGEN -1 / WATER -1 / CL- 1 / H3O+ 1
   STOIC 2 WATER -1 / HSO4- -1 / H3O+ 1 / SO4-- 1
   STOIC 3 WATER -1 / H2SO4 -1 / H3O+ 1 / HSO4- 1
   STOIC 4 WATER -1 / HCLO -1 / CLO- 1 / H3O+ 1
   STOIC 5 WATER -2 / CHLORINE -1 / HCLO 1 / CL- 1 /  &
      H3O+ 1
   STOIC 6 WATER -2 / OH- 1 / H3O+ 1
   K-STOIC 4 A=-16.151899 B=-1602.869995 C=0 D=0
   K-STOIC 5 A=-11.37532 B=-1286.972046 C=0 D=0
   K-STOIC 6 A=132.89888 B=-13445.900391 C=-22.477301 D=0
   SALT "NAOH(S)" OH- 1 / NA+ 1
   SALT "NACL(S)" CL- 1 / NA+ 1
   K-SALT "NAOH(S)" A=433.324097 B=-21656.691406 C=-63.231094  &
      D=0
   K-SALT "NACL(S)" A=-203.587494 B=4381.175781 C=35.875179  &
      D=-0.067216

FLOWSHEET
   BLOCK M-301 IN=1 2 3 OUT=4
   BLOCK E-601 IN=4 OUT=5
   BLOCK E-602 IN=6 OUT=7
   BLOCK T-601 IN=7 10 OUT=8 9
   BLOCK T-602 IN=8 11 OUT=12 13
   BLOCK E-603 IN=12 OUT=14
   BLOCK T-603 IN=14 17 OUT=15 16
   BLOCK E-604 IN=18 OUT=20
   BLOCK C-601 IN=15 OUT=18
   BLOCK T-604 IN=20 OUT=19 21
   BLOCK T-605 IN=21 OUT=22 23
   BLOCK T-608 IN=22 OUT=25 24
   BLOCK T-607 IN=23 OUT=26 27
   BLOCK T-606 IN=27 OUT=28 29
   BLOCK B3 IN=25 19 OUT=30
   BLOCK B4 IN=30 OUT=31 32
   BLOCK C-602 IN=31 OUT=33
   BLOCK E-605 IN=33 OUT=3
   BLOCK B1 IN=32 9 36 38 OUT=34
   BLOCK B5 IN=16 OUT=35 36
   BLOCK B7 IN=13 OUT=37 38
   BLOCK B2 IN=5 OUT=6

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &
      TRUE-COMPS=NO

PROP-DATA HENRY-1
```

```
    IN-UNITS ENG TEMPERATURE=K
    PROP-LIST HENRY
    BPVAL HYDROGEN DICHLORO 89.37548041 -4274.799805  &
        -12.77600000 .0142190000 223.1500000 273.1500000 0.0
    BPVAL HCLO WATER -28.83851659 0.0 0.0 0.0 273.0000000  &
        400.0000000 0.0

PROP-DATA HENRY-1
    IN-UNITS ENG
    PROP-LIST HENRY
    BPVAL HYDROGEN CHLOROFO -89.89187628 -1110.402018  &
        18.38500000 -.0319155558 -57.99999554 59.00000353 0.0
    BPVAL HYDROGEN CARBONTE 99.36231378 -7905.239586  &
        -12.44300000 5.80000005E-4 -39.99999568 68.00000346 0.0
    BPVAL HYDROGEN WATER 49.61444341 -13973.09749 0.0 0.0  &
        31.73000375 260.3300019 0.0

PROP-DATA NRTL-1
    IN-UNITS ENG
    PROP-LIST NRTL
    BPVAL WATER HCLO 11.25094000 0.0 .3000000000 0.0 0.0 0.0  &
        32.00000374 212.0000023
    BPVAL HCLO WATER -7.175849000 0.0 .3000000000 0.0 0.0 0.0  &
        32.00000374 212.0000023

PROP-DATA VLCLK-1
    IN-UNITS ENG
    PROP-LIST VLCLK
    BPVAL H3O+ CL- .5534556926 .2140997389
    BPVAL NA+ OH- -.2209618885 1.168080771
    BPVAL NA+ CL- .2425544568 .4050617685
    BPVAL H3O+ HSO4- .8778750698 .3242692842
    BPVAL NA+ SO4-- .1389686121 1.974549536

PROP-DATA GMELCC-1
    IN-UNITS ENG
    PROP-LIST GMELCC
    PPVAL CHLORINE ( H3O+ CLO- ) 15.00000000
    PPVAL ( H3O+ CLO- ) CHLORINE -8.000000000
    PPVAL CHLORINE ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) CHLORINE -8.000000000
    PPVAL CHLORINE ( H3O+ CL- ) 15.00000000
    PPVAL ( H3O+ CL- ) CHLORINE -8.000000000
    PPVAL WATER ( H3O+ OH- ) 8.045000000
    PPVAL ( H3O+ OH- ) WATER -4.072000000
    PPVAL WATER ( H3O+ CL- ) 4.110129000
    PPVAL ( H3O+ CL- ) WATER -3.344103000
    PPVAL HYDROGEN ( H3O+ CLO- ) 15.00000000
    PPVAL ( H3O+ CLO- ) HYDROGEN -8.000000000
    PPVAL HYDROGEN ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) HYDROGEN -8.000000000
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PPVAL HYDROGEN ( H3O+ CL- ) 12.00000000
PPVAL ( H3O+ CL- ) HYDROGEN -1.0000000E-3
PPVAL HCLO ( H3O+ CLO- ) 15.00000000
PPVAL ( H3O+ CLO- ) HCLO -8.000000000
PPVAL HCLO ( H3O+ OH- ) 15.00000000
PPVAL ( H3O+ OH- ) HCLO -8.000000000
PPVAL HCLO ( H3O+ CL- ) 15.00000000
PPVAL ( H3O+ CL- ) HCLO -8.000000000
PPVAL CHLORINE ( NA+ CLO- ) 15.00000000
PPVAL ( NA+ CLO- ) CHLORINE -8.000000000
PPVAL CHLORINE ( NA+ OH- ) 15.00000000
PPVAL ( NA+ OH- ) CHLORINE -8.000000000
PPVAL CHLORINE ( NA+ CL- ) 15.00000000
PPVAL ( NA+ CL- ) CHLORINE -8.000000000
PPVAL WATER ( NA+ OH- ) 6.737997000
PPVAL ( NA+ OH- ) WATER -3.771221000
PPVAL WATER ( NA+ CL- ) 5.980196000
PPVAL ( NA+ CL- ) WATER -3.789168000
PPVAL HYDROGEN ( NA+ CLO- ) 15.00000000
PPVAL ( NA+ CLO- ) HYDROGEN -8.000000000
PPVAL HYDROGEN ( NA+ OH- ) 15.00000000
PPVAL ( NA+ OH- ) HYDROGEN -8.000000000
PPVAL HYDROGEN ( NA+ CL- ) 15.00000000
PPVAL ( NA+ CL- ) HYDROGEN -8.000000000
PPVAL HCLO ( NA+ CLO- ) 15.00000000
PPVAL ( NA+ CLO- ) HCLO -8.000000000
PPVAL HCLO ( NA+ OH- ) 15.00000000
PPVAL ( NA+ OH- ) HCLO -8.000000000
PPVAL HCLO ( NA+ CL- ) 15.00000000
PPVAL ( NA+ CL- ) HCLO -8.000000000
PPVAL ( NA+ OH- ) ( NA+ CL- ) 8.407678000
PPVAL ( NA+ CL- ) ( NA+ OH- ) 1.950440000
PPVAL H2SO4 ( H3O+ CL- ) 10.00000000
PPVAL ( H3O+ CL- ) H2SO4 -2.000000000
PPVAL WATER ( H3O+ HSO4- ) 6.362000000
PPVAL ( H3O+ HSO4- ) WATER -3.749000000
PPVAL WATER ( H3O+ SO4-- ) 8.000000000
PPVAL ( H3O+ SO4-- ) WATER -4.000000000
PPVAL WATER ( NA+ HSO4- ) 7.663000000
PPVAL ( NA+ HSO4- ) WATER -3.944000000
PPVAL WATER ( NA+ SO4-- ) 7.689221000
PPVAL ( NA+ SO4-- ) WATER -4.284786000
PPVAL HYDROGEN ( H3O+ HSO4- ) 10.00000000
PPVAL ( H3O+ HSO4- ) HYDROGEN -2.000000000
PPVAL HYDROGEN ( H3O+ SO4-- ) 15.00000000
PPVAL ( H3O+ SO4-- ) HYDROGEN -8.000000000
PPVAL H2SO4 ( H3O+ HSO4- ) 12.99200000
PPVAL ( H3O+ HSO4- ) H2SO4 -2.981000000
PPVAL H2SO4 ( H3O+ SO4-- ) 8.000000000
PPVAL ( H3O+ SO4-- ) H2SO4 -4.000000000
PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) .9536271000
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```
   PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0
   PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 3.147792000
   PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -.5387706000
   PPVAL ( NA+ CL- ) ( NA+ SO4-- ) -11.44869000
   PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -.2697454000

PROP-DATA GMELCD-1
   IN-UNITS ENG
   PROP-LIST GMELCD
   PPVAL CHLORINE ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) CHLORINE 0.0
   PPVAL CHLORINE ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) CHLORINE 0.0
   PPVAL CHLORINE ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) CHLORINE 0.0
   PPVAL WATER ( H3O+ CL- ) 4151.955567
   PPVAL ( H3O+ CL- ) WATER -1176.370371
   PPVAL HYDROGEN ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) HYDROGEN 0.0
   PPVAL HCLO ( H3O+ CLO- ) 0.0
   PPVAL ( H3O+ CLO- ) HCLO 0.0
   PPVAL HCLO ( H3O+ OH- ) 0.0
   PPVAL ( H3O+ OH- ) HCLO 0.0
   PPVAL HCLO ( H3O+ CL- ) 0.0
   PPVAL ( H3O+ CL- ) HCLO 0.0
   PPVAL CHLORINE ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) CHLORINE 0.0
   PPVAL CHLORINE ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) CHLORINE 0.0
   PPVAL CHLORINE ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) CHLORINE 0.0
   PPVAL WATER ( NA+ OH- ) 2556.435580
   PPVAL ( NA+ OH- ) WATER -849.2763532
   PPVAL WATER ( NA+ CL- ) 1514.732568
   PPVAL ( NA+ CL- ) WATER -389.4562769
   PPVAL HYDROGEN ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) HYDROGEN 0.0
   PPVAL HCLO ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) HCLO 0.0
   PPVAL HCLO ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) HCLO 0.0
   PPVAL HCLO ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) HCLO 0.0
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PPVAL ( NA+ OH- ) ( NA+ CL- ) -324.8080174
PPVAL ( NA+ CL- ) ( NA+ OH- ) -1491.716328
PPVAL WATER ( H3O+ HSO4- ) 3524.759972
PPVAL ( H3O+ HSO4- ) WATER -1049.759992
PPVAL WATER ( H3O+ SO4-- ) 0.0
PPVAL ( H3O+ SO4-- ) WATER 0.0
PPVAL WATER ( NA+ SO4-- ) 1018.076932
PPVAL ( NA+ SO4-- ) WATER -102.3078232
PPVAL HYDROGEN ( H3O+ HSO4- ) 0.0
PPVAL ( H3O+ HSO4- ) HYDROGEN 0.0
PPVAL HYDROGEN ( H3O+ SO4-- ) 0.0
PPVAL ( H3O+ SO4-- ) HYDROGEN 0.0
PPVAL H2SO4 ( H3O+ HSO4- ) -3119.219975
PPVAL ( H3O+ HSO4- ) H2SO4 -292.1399977
PPVAL H2SO4 ( H3O+ SO4-- ) 0.0
PPVAL ( H3O+ SO4-- ) H2SO4 0.0
PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) -363.1438771
PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0
PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 1408.793749
PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -170.8229686
PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 6763.469346
PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -240.5010581

PROP-DATA GMELCE-1
IN-UNITS ENG
PROP-LIST GMELCE
PPVAL CHLORINE ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) CHLORINE 0.0
PPVAL CHLORINE ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) CHLORINE 0.0
PPVAL CHLORINE ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) CHLORINE 0.0
PPVAL WATER ( H3O+ CL- ) .3417959000
PPVAL ( H3O+ CL- ) WATER 2.121453000
PPVAL HYDROGEN ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) HYDROGEN 0.0
PPVAL HYDROGEN ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) HYDROGEN 0.0
PPVAL HYDROGEN ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) HYDROGEN 0.0
PPVAL HCLO ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) HCLO 0.0
PPVAL HCLO ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) HCLO 0.0
PPVAL HCLO ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) HCLO 0.0
PPVAL CHLORINE ( NA+ CLO- ) 0.0
PPVAL ( NA+ CLO- ) CHLORINE 0.0
PPVAL CHLORINE ( NA+ OH- ) 0.0
PPVAL ( NA+ OH- ) CHLORINE 0.0
PPVAL CHLORINE ( NA+ CL- ) 0.0
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   PPVAL ( NA+ CL- ) CHLORINE 0.0
   PPVAL WATER ( NA+ OH- ) 3.013932000
   PPVAL ( NA+ OH- ) WATER 2.136557000
   PPVAL WATER ( NA+ CL- ) 7.433500000
   PPVAL ( NA+ CL- ) WATER -1.100418000
   PPVAL HYDROGEN ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) HYDROGEN 0.0
   PPVAL HYDROGEN ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) HYDROGEN 0.0
   PPVAL HCLO ( NA+ CLO- ) 0.0
   PPVAL ( NA+ CLO- ) HCLO 0.0
   PPVAL HCLO ( NA+ OH- ) 0.0
   PPVAL ( NA+ OH- ) HCLO 0.0
   PPVAL HCLO ( NA+ CL- ) 0.0
   PPVAL ( NA+ CL- ) HCLO 0.0
   PPVAL ( NA+ OH- ) ( NA+ CL- ) 100.0000000
   PPVAL ( NA+ CL- ) ( NA+ OH- ) 6.619543000
   PPVAL WATER ( H3O+ HSO4- ) -4.599000000
   PPVAL ( H3O+ HSO4- ) WATER 4.472000000
   PPVAL WATER ( NA+ SO4-- ) -14.08276000
   PPVAL ( NA+ SO4-- ) WATER 8.547499000
   PPVAL HYDROGEN ( H3O+ SO4-- ) 0.0
   PPVAL ( H3O+ SO4-- ) HYDROGEN 0.0
   PPVAL H2SO4 ( H3O+ HSO4- ) -30.12600000
   PPVAL ( H3O+ HSO4- ) H2SO4 .8060000000
   PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 43.39265000
   PPVAL ( NA+ SO4-- ) ( NA+ OH- ) 4.518955000
   PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 60.25378000
   PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -4.302999000

PROP-DATA GMELCN-1
   IN-UNITS ENG
   PROP-LIST GMELCN
   PPVAL CHLORINE ( H3O+ CLO- ) .1000000000
   PPVAL CHLORINE ( H3O+ OH- ) .1000000000
   PPVAL CHLORINE ( H3O+ CL- ) .1000000000
   PPVAL HYDROGEN ( H3O+ CLO- ) .1000000000
   PPVAL HYDROGEN ( H3O+ OH- ) .1000000000
   PPVAL HCLO ( H3O+ CLO- ) .1000000000
   PPVAL HCLO ( H3O+ OH- ) .1000000000
   PPVAL HCLO ( H3O+ CL- ) .1000000000
   PPVAL CHLORINE ( NA+ CLO- ) .1000000000
   PPVAL CHLORINE ( NA+ OH- ) .1000000000
   PPVAL CHLORINE ( NA+ CL- ) .1000000000
   PPVAL WATER ( NA+ OH- ) .2000000000
   PPVAL WATER ( NA+ CL- ) .2000000000
   PPVAL HYDROGEN ( NA+ CLO- ) .1000000000
   PPVAL HYDROGEN ( NA+ OH- ) .1000000000
   PPVAL HYDROGEN ( NA+ CL- ) .1000000000
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    PPVAL HCLO ( NA+ CLO- ) .1000000000
    PPVAL HCLO ( NA+ OH- ) .1000000000
    PPVAL HCLO ( NA+ CL- ) .1000000000
    PPVAL WATER ( H3O+ HSO4- ) .2000000000
    PPVAL WATER ( NA+ SO4-- ) .2000000000
    PPVAL HYDROGEN ( H3O+ SO4-- ) .1000000000
    PPVAL H2SO4 ( H3O+ HSO4- ) .2000000000

STREAM 1
    SUBSTREAM MIXED TEMP=77. PRES=14.7 MOLE-FLOW=323.
    MOLE-FRAC METHANE 0.98 / NITROGEN 0.02

STREAM 2
    SUBSTREAM MIXED TEMP=77. PRES=14.7 MOLE-FLOW=323.
    MOLE-FRAC CHLORINE 1.

STREAM 3
    SUBSTREAM MIXED TEMP=77 PRES=14.7 MOLE-FLOW=783.732252
    MOLE-FRAC METHANE 0.901053277 / METHYLCH 0.0270128601 /  &
        DICHLORO 0.00024133163 / CHLOROFO 2.066234E-005 /  &
        CARBONTE 1.339088E-006 / WATER 2.144660E-007 /  &
        NITROGEN 0.0716703158 / H2SO4 2.003709E-016

STREAM 10
    SUBSTREAM MIXED TEMP=86. PRES=14.7 MOLE-FLOW=2025.
    MOLE-FRAC WATER 1.

STREAM 11
    SUBSTREAM MIXED TEMP=86. PRES=14.7 MOLE-FLOW=200.
    MOLE-FRAC NAOH 1.

STREAM 17
    SUBSTREAM MIXED TEMP=90. PRES=14.7 MASS-FLOW=13551. <kg/hr>
    MOLE-FRAC H2SO4 1.

BLOCK B1 MIXER

BLOCK B3 MIXER

BLOCK M-301 MIXER
    PARAM PRES=14.7 NPHASE=1 PHASE=V T-EST=77.
    BLOCK-OPTION FREE-WATER=NO

BLOCK B4 FSPLIT
    FRAC 32 0.1

BLOCK B5 SEP2
    FRAC STREAM=35 SUBSTREAM=MIXED COMPS=METHANE CHLORINE  &
        METHYLCH DICHLORO CHLOROFO CARBONTE WATER HYDROGEN  &
        NITROGEN H3O+ HCLO CLO- OH- CL- NAOH NA+ "NACL(S)"  &
        "NAOH(S)" H2SO4 HSO4- SO4-- FRACS=0. 0. 0. 0. 0. 0.  &
```

```
    0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 1. 0. 0.

BLOCK B7 SEP2
  FRAC STREAM=37 SUBSTREAM=MIXED COMPS=METHANE CHLORINE  &
    METHYLCH DICHLORO CHLOROFO CARBONTE WATER HYDROGEN  &
    NITROGEN H3O+ HCLO CLO- OH- CL- NAOH NA+ "NACL(S)"  &
    "NAOH(S)" H2SO4 HSO4- SO4-- FRACS=0. 0. 0. 0. 0. 0.  &
    0. 0. 0. 0. 0. 0. 0. 0. 1. 0. 0. 0. 0. 0. 0.

BLOCK E-601 HEATER
  PARAM TEMP=572. PRES=14.7 NPHASE=1 PHASE=V
  BLOCK-OPTION FREE-WATER=NO

BLOCK E-602 HEATER
  PARAM TEMP=100. PRES=14.7 NPHASE=1 PHASE=V
  BLOCK-OPTION FREE-WATER=NO

BLOCK E-603 HEATER
  PARAM TEMP=100. PRES=14.7 NPHASE=1 PHASE=V
  BLOCK-OPTION FREE-WATER=NO

BLOCK E-604 HEATER
  PARAM TEMP=-58. PRES=115. NPHASE=2
  BLOCK-OPTION FREE-WATER=NO

BLOCK E-605 HEATER
  PARAM TEMP=77. PRES=14.7

BLOCK T-604 FLASH2
  PARAM PRES=115. DUTY=0.

BLOCK T-608 FLASH2
  PARAM TEMP=-100. PRES=15.

BLOCK T-606 DSTWU
  PARAM LIGHTKEY=CHLOROFO RECOVL=0.999 HEAVYKEY=CARBONTE  &
    RECOVH=0.001 PTOP=14.7 PBOT=14.7 NSTAGE=10

BLOCK T-601 RADFRAC
  PARAM NSTAGE=2
  COL-CONFIG CONDENSER=NONE REBOILER=NONE
  FEEDS 7 2 ON-STAGE / 10 1 ON-STAGE
  PRODUCTS 8 1 V / 9 2 L
  P-SPEC 1 14.7
  COL-SPECS

BLOCK T-602 RADFRAC
  PARAM NSTAGE=5 MAXOL=30
  COL-CONFIG CONDENSER=NONE REBOILER=NONE
  FEEDS 8 5 ON-STAGE / 11 1 ON-STAGE
  PRODUCTS 12 1 V / 13 5 L
```

```
    P-SPEC 1 14.7
    COL-SPECS
    T-EST 1 299.3 / 2 306.3
    X-EST 1 NAOH 0.89192 / 1 WATER 0.1068
    Y-EST 1 WATER 0.21598

BLOCK T-603 RADFRAC
    PARAM NSTAGE=2
    COL-CONFIG CONDENSER=NONE REBOILER=NONE
    FEEDS 14 2 ON-STAGE / 17 1
    PRODUCTS 15 1 V / 16 2 L
    P-SPEC 1 14.7
    COL-SPECS

BLOCK T-605 RADFRAC
    PARAM NSTAGE=12
    COL-CONFIG CONDENSER=PARTIAL-V
    FEEDS 21 6 ON-STAGE
    PRODUCTS 22 1 V / 23 12 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RR=1.2
    SPEC 1 MOLE-RECOV 0.995 COMPS=METHYLCH STREAMS=22  &
       BASE-STREAMS=21
    VARY 1 D:F 0.001 0.999

BLOCK T-607 RADFRAC
    PARAM NSTAGE=20
    COL-CONFIG CONDENSER=TOTAL REBOILER=KETTLE
    RATESEP-ENAB CALC-MODE=EQUILIBRIUM
    FEEDS 23 10
    PRODUCTS 26 1 L / 27 20 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RR=1.5
    SPEC 1 MOLE-RECOV 0.999 COMPS=DICHLORO STREAMS=26  &
       BASE-STREAMS=23
    VARY 1 D:F 0.001 0.999

BLOCK B2 RCSTR
    PARAM TEMP=525. <C> PRES=14.7 RES-TIME=0.002
    REACTIONS RXN-IDS=R-1

BLOCK C-602 COMPR
    PARAM TYPE=ASME-POLYTROP DELP=45. <psia>

BLOCK C-601 MCOMPR
    PARAM NSTAGE=2 TYPE=ASME-POLYTROPIC PRES=115. COMPR-NPHASE=1  &
       COOLER-NPHAS=1
    FEEDS 15 1
    PRODUCTS 18 2
    COOLER-SPECS 2 TEMP=275. / 1 TEMP=844.
```

```
DESIGN-SPEC DS-1
    DEFINE H20 MOLE-FRAC STREAM=15 SUBSTREAM=MIXED  &
        COMPONENT=WATER
    SPEC "H20" TO ".01"
    TOL-SPEC ".002"
    VARY MOLE-FLOW STREAM=17 SUBSTREAM=MIXED COMPONENT=H2SO4
    LIMITS "100" "750"

EO-CONV-OPTI

OPTIMIZATION O-1
    DEFINE MIN MASS-FLOW STREAM=5 SUBSTREAM=MIXED  &
        COMPONENT=CHLORINE
    DEFINE MOUT MASS-FLOW STREAM=6 SUBSTREAM=MIXED  &
        COMPONENT=CHLORINE
    DEFINE M1R MASS-FLOW STREAM=1 SUBSTREAM=MIXED  &
        COMPONENT=METHANE
    DEFINE C2R MASS-FLOW STREAM=2 SUBSTREAM=MIXED  &
        COMPONENT=CHLORINE
    DEFINE W10R MASS-FLOW STREAM=10 SUBSTREAM=MIXED  &
        COMPONENT=WATER
    DEFINE S11R MASS-FLOW STREAM=11 SUBSTREAM=MIXED  &
        COMPONENT=NAOH
    DEFINE SH17R MASS-FLOW STREAM=17 SUBSTREAM=MIXED  &
        COMPONENT=H2SO4
    DEFINE MC24P MASS-FLOW STREAM=24 SUBSTREAM=MIXED  &
        COMPONENT=METHYLCH
    DEFINE DC26P MASS-FLOW STREAM=26 SUBSTREAM=MIXED  &
        COMPONENT=DICHLORO
    DEFINE CH28P MASS-FLOW STREAM=28 SUBSTREAM=MIXED  &
        COMPONENT=CHLOROFO
    DEFINE CT29P MASS-FLOW STREAM=29 SUBSTREAM=MIXED  &
        COMPONENT=CARBONTE
    DEFINE WS34 STREAM-VAR STREAM=34 SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE E601HD BLOCK-VAR BLOCK=E-601 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE R601HD BLOCK-VAR BLOCK=B2 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE E602HD BLOCK-VAR BLOCK=E-602 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE E603HD BLOCK-VAR BLOCK=E-603 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE C601HD BLOCK-VAR BLOCK=C-601 VARIABLE=NET-WORK  &
        SENTENCE=RESULTS
    DEFINE E604HD BLOCK-VAR BLOCK=E-604 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE T605HD BLOCK-VAR BLOCK=T-605 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE T607HD BLOCK-VAR BLOCK=T-607 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
```

```
   DEFINE T606RH BLOCK-VAR BLOCK=T-606 VARIABLE=REB-DUTY  &
      SENTENCE=RESULTS
   DEFINE T606CH BLOCK-VAR BLOCK=T-606 VARIABLE=COND-DUTY  &
      SENTENCE=RESULTS
   DEFINE T608HD BLOCK-VAR BLOCK=T-608 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE C602HD BLOCK-VAR BLOCK=C-602 VARIABLE=NET-WORK  &
      SENTENCE=RESULTS
   DEFINE E605HD BLOCK-VAR BLOCK=E-605 VARIABLE=QCALC  &
      SENTENCE=PARAM
   DEFINE SH35P MASS-FLOW STREAM=35 SUBSTREAM=MIXED  &
      COMPONENT=H2SO4
   DEFINE S37P MASS-FLOW STREAM=37 SUBSTREAM=MIXED  &
      COMPONENT="NAOH(S)"
   DEFINE MCP24 MASS-FLOW STREAM=24 SUBSTREAM=MIXED  &
      COMPONENT=METHYLCH
   DEFINE DCMP26 MASS-FLOW STREAM=26 SUBSTREAM=MIXED  &
      COMPONENT=DICHLORO
   DEFINE CFP28 MASS-FLOW STREAM=28 SUBSTREAM=MIXED  &
      COMPONENT=CHLOROFO
   DEFINE CTP29 MASS-FLOW STREAM=29 SUBSTREAM=MIXED  &
      COMPONENT=CARBONTE
F    X = 1-(MOUT/MIN)
F    M1RC = M1R*0.21*0.454
F    C2RC = C2R*0.21*0.454
F    W10RC = W10R*0.00638*0.454
F    S11RC = S11R*0.441*0.454
F    SH17RC = SH17R*0.081*0.454
F    MC24PR = MC24P*0.82*0.454
F    DC26PR = DC26P*1.2*0.454
F    CH28PR = CH28P*1.014*0.454
F    CT29PR = CT29P*1.03*0.454
F    SH35PR = SH35P*.081*.454
F    S37PR=S37P*0.441*0.454
F    WS34C = WS34*0.0025*0.454
F
HD=R601HD+E602HD+E603HD+E604HD+T605HD+T607HD+T606CHD+T608HD+E605HD
F    HDC=-((HD*0.454/60)/3.84)*0.00638
F    NG=((E601HD+T606RHD))
F    NGC=(NG)*0.00451/1030
F    CHDC=(C601HD+C602HD)*0.746*0.0677
F    REV=MC24PR+DC26PR+CH28PR+CT29PR+SH35PR+S37PR
F    RMC=M1RC+C2RC+W10RC+S11RC+SH17RC
F    HDTC=HDC+NGC+CHDC
F    PROFIT=REV-RMC-HDTC-WS33C
   MAXIMIZE "PROFIT"
   VARY BLOCK-VAR BLOCK=B2 VARIABLE=RES-TIME SENTENCE=PARAM
   LIMITS "0.003" "0.5"
   VARY MASS-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=METHANE
   LIMITS "3200" "32000"
   VARY BLOCK-VAR BLOCK=B2 VARIABLE=TEMP SENTENCE=PARAM
```

```
    LIMITS "900" "1000"

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
    REAC-DATA 4 PHASE=V
    RATE-CON 1 PRE-EXP=256000000. ACT-ENERGY=35260.
    RATE-CON 2 PRE-EXP=62800000. ACT-ENERGY=30580.
    RATE-CON 3 PRE-EXP=256000000. ACT-ENERGY=35260.
    RATE-CON 4 PRE-EXP=293000000. ACT-ENERGY=37490.
    STOIC 1 MIXED METHANE -1. / CHLORINE -1. / METHYLCH 1. / &
        HYDROGEN 1.
    STOIC 2 MIXED METHYLCH -1. / CHLORINE -1. / DICHLORO 1. / &
        HYDROGEN 1.
    STOIC 3 MIXED DICHLORO -1. / CHLORINE -1. / CHLOROFO 1. / &
        HYDROGEN 1.
    STOIC 4 MIXED CHLOROFO -1. / CHLORINE -1. / CARBONTE 1. / &
        HYDROGEN 1.
    POWLAW-EXP 1 MIXED METHANE 1. / MIXED CHLORINE 1.
    POWLAW-EXP 2 MIXED METHYLCH 1. / MIXED CHLORINE 1.
    POWLAW-EXP 3 MIXED DICHLORO 1. / MIXED CHLORINE 1.
    POWLAW-EXP 4 MIXED CHLOROFO 1. / MIXED CHLORINE 1.
;
;
;
;
;
```

FORTRAN CODES FOR METHYL CHLORIDE PRODUCTION VIA METHANOL (OPTION 1)

Table A1: FORTRAN code for the base case methyl chloride via methanol sensitivity analysis and the optimization. The description of each calculation is included in the first column.

Line 1: conversion	X=1-(MOUT/MIN)
Line 2: methanol raw material cost	M1RC=M1R*0.294*0.454
Line 3: hydrogen chloride raw material cost	H1RC=H1R*0.09*0.454
Line 4: methyl chloride product revenue	M11PR= M11P*0.82*0.454
Line 5: water revenue	W10PR=W10P*0.00638*0.454
Line 6: heat duties	HD= -(B3HD+B4HD+B5HDC+B6HD+B10HD+B11HD)*.454/60)
Line 7: heat duties cost	HDC=(HD/3.84)*0.00638
Line 8: natural gas	NG=(B2HD+B5HDR)
Line 9: natural gas cost	NGC = (NG)*(0.00451/1030)
Line 10: waste treatment cost	WSC=(WS7+WS12)*0.2*0.454
Line 11: total revenue	REV=M11PR+W10PR
Line 12: total raw material cost	RMC=M1RC+H1RC
Line 13: total energy cost	HDTC=HDC+NGC
Line 14: profit	PROFIT=M11PR+W10PR-M1RC-H1RC-HDC-NGC-WSC

FORTRAN CODES FOR METHYL CHLORIDE PRODUCTION VIA METHANE
(OPTION 2)

Table A2: FORTRAN code for the base case methyl chloride via methane sensitivity analysis and optimization. The description of each calculation is included in the first column

Line 1: chlorine conversion	X=1-(MOUT/MIN)
Line 2: methane raw material cost	M1RC = M1R*0.21*0.454
Line 3: chlorine raw material cost	C2RC = C2R*0.21*0.454
Line 4: sodium hydroxide raw material cost	S11RC = S11R*0.441*0.454
Line 5: water raw material cost	W10RC = W10R*0.00638*0.454
Line 6: sulfuric acid raw material cost	SH17RC = SH17R*0.081*0.454
Line 7: methyl chloride product revenue	MC24PR = MC24P*0.82*0.454
Line 8: dichloromethane product revenue	DC26PR = DC26P*1.2*0.454
Line 9: chloroform product revenue	CH28PR = CH28P*1.014*0.454
Line 10: carbon tetrachloride product revenue	CT29PR = CT29P*1.03*0.454
Line 11: sulfuric acid product revenue	SH35PR = SH35P*.081*.454
Line 12: sodium hydroxide product revenue	S37PR=S37P*0.441*0.454
Line 13: waste treatment cost	WS34C = WS34*0.0025*0.454
Line 14: heat duty	HD = R601HD+E602HD+E603HD+E604HD+T605HD +T607HD+T606CHD+T608HD+E605HD
Line 15: heat duty cost	HDC=-((HD*0.454/60)/3.84)*0.00638
Line 16: total natural gas	NG=((E601HD+T606RHD))
Line 17: Natural gas cost	NGC=(NG)*0.00451/1030
Line 18: compressor heat duty cost	CHDC=(C601HD+C602HD)*0.746*0.0677
Line 19: total product revenue	REV=MC24PR+DC26PR+CH28PR +CT29PR+SH35PR+S37PR
Line 20: total raw material cost	RMC=M1RC+C2RC+W10RC+S11RC+SH17RC
Line 21: total heat duty cost	HDTC=HDC+NGC+CHDC
Line 22: total profit	PROFIT=REV-RMC-HDTC-WS33C

APPENDIX B: STREAM SUMMARIES, BLOCK FLOW DIAGRAM, AND SCHEMATICS FOR METHYL CHLORIDE PRODUCTION VIA METHANOL (OPTION 1) AND METHYL CHLORIDE PRODUCTION VIA METHANE (OPTION 2)

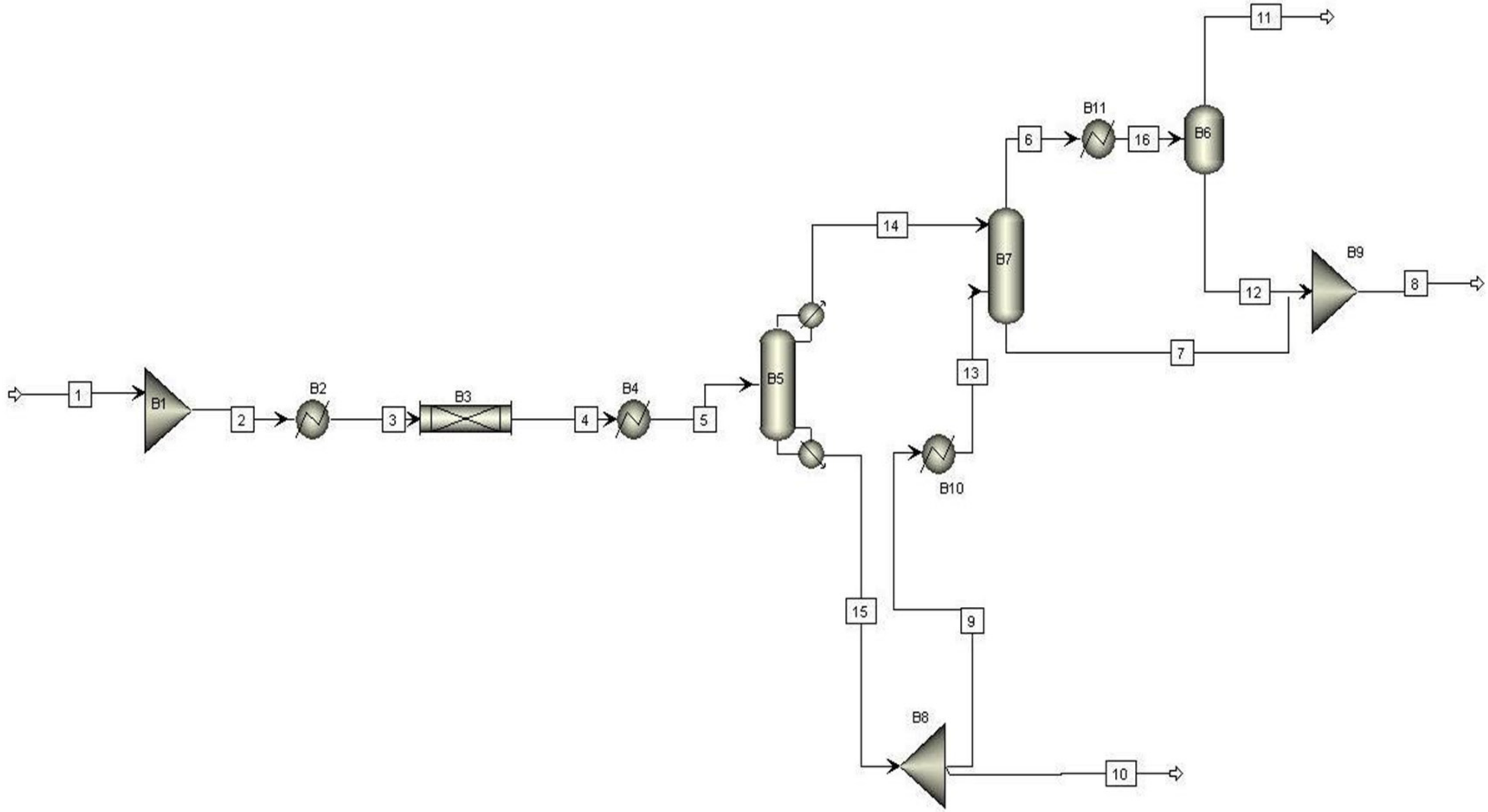
Stream Summary: Base Case Methyl Chloride via Methanol (Option 1)

Stream No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Mass Flow lb/hr								
METHANOL	5,066.83	5,066.83	5,066.83	17.31	17.31	17.21	0.03	8.54
HYDRO-01	5,947.82	5,947.82	5,947.82	202.00	202.00	11.39	190.61	190.63
METHY-01	0.00	0.00	0.00	7,956.32	7,956.32	7,955.20	1.09	126.44
WATER	0.00	0.00	0.00	2,839.03	2,839.03	54.04	163.75	211.36
SULFU-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow lb/hr	11,014.65	11,014.65	11,014.65	11,014.65	11,014.65	8,037.84	355.49	536.98
Temperature F	77.00	77.01	675.00	675.00	140.00	122.46	123.97	-60.60
Pressure psia	14.70	14.70	14.70	15.00	14.70	14.70	14.70	14.70
Vapor Frac	0.60	0.60	1.00	1.00	0.59	1.00	0.00	0.08
Enthalpy Btu/lb	-2,016.18	-2,016.18	-1,649.85	-1,834.92	-2,209.45	-728.50	-3,889.75	-3,442.34
Enthalpy Btu/hr	-22,208,000	-22,208,000	-18,173,000	-20,211,000	-24,336,000	-5,855,600	-1,382,700	-1,848,500
Stream No.	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Mass Flow lb/hr								
METHANOL	0.00	0.06	8.70	8.51	0.00	17.24	0.07	17.21
HYDRO-01	0.00	0.00	11.37	0.02	0.00	202.00	0.00	11.39
METHY-01	0.00	0.03	7,829.85	125.35	0.00	7,956.29	0.03	7,955.20
WATER	145.69	2,621.24	6.43	47.61	145.69	72.10	2,766.92	54.04
SULFU-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow lbmol/hr	8.09	145.50	156.03	5.39	8.09	167.67	153.59	161.42
Total Flow lb/hr	145.69	2,621.33	7,856.35	181.49	145.69	8,247.63	2,767.02	8,037.84
Temperature F	212.00	212.00	25.00	25.00	75.00	75.00	212.00	25.00
Pressure psia	14.70	14.70	14.70	14.70	14.70	14.70	14.70	14.70
Vapor Frac	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.97
Enthalpy Btu/lb	-6,685.13	-6,685.13	-715.52	-2,566.01	-6,819.34	-757.17	-6,685.13	-757.30
Enthalpy Btu/hr	-973,970	-17,524,000	-5,621,400	-465,700	-993,520	-6,244,800	-18,497,905	-6,087,074

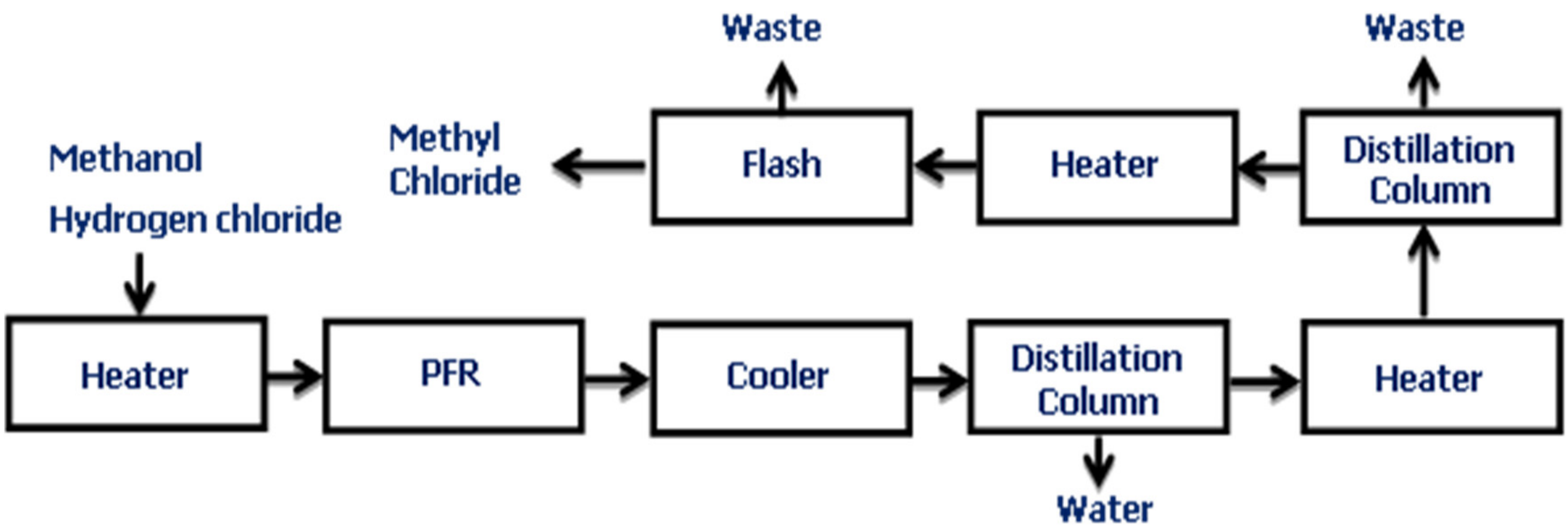
Stream Summary: Optimized Case Methyl Chloride via Methanol (Option 1)

Stream No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Mass Flow lb/hr								
METHANOL	5,256.11	5,256.11	5,256.11	63.19	63.19	62.86	0.05	35.69
HYDRO-01	5,947.82	5,947.82	5,947.82	38.82	38.82	0.55	38.28	0.00
METHY-01	0.00	0.00	0.00	8,182.27	8,182.27	8,181.93	0.30	167.73
WATER	0.00	0.00	0.00	2,919.65	2,919.65	54.05	47.08	48.84
SULFU-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow lb/hr	11,203.93	11,203.93	11,203.93	11,203.93	11,203.93	8,299.39	85.71	252.27
Temperature F	77.00	77.00	675.00	703.17	140.00	93.53	104.44	25.00
Pressure psia	14.70	14.70	14.70	14.70	14.70	14.70	14.70	14.70
Vapor Frac	0.58	0.58	1.00	1.00	0.58	1.00	0.00	0.00
Enthalpy Btu/lb	-2,036.32	-2,036.32	-1,663.26	-1,840.49	-2,231.13	-743.61	-4,409.79	-2,380.38
Enthalpy Btu/hr	-22,815,000	-22,815,000	-18,635,000	-20,621,000	-24,997,000	-6,171,500	-377,940	-600,490
Stream No.	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Mass Flow lb/hr								
METHANOL	0.00	0.28	27.17	35.69	0.00	62.90	0.28	62.86
HYDRO-01	0.00	0.00	0.54	0.00	0.00	38.82	0.00	0.55
METHY-01	0.00	0.04	8,014.20	167.73	0.00	8,182.23	0.04	8,181.93
WATER	32.07	2,818.52	5.20	48.84	32.07	69.06	2,850.59	54.05
SULFU-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow lb/hr	32.07	2,818.84	8,047.12	252.27	32.07	8,353.02	2,850.91	8,299.39
Temperature F	211.99	211.99	25.00	25.00	75.00	75.00	211.99	25.00
Pressure psia	14.70	14.70	14.70	14.70	14.70	14.70	14.70	14.70
Vapor Frac	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.96
Enthalpy Btu/lb	-6,684.87	-6,684.87	-718.66	-2,380.38	-6,819.06	-757.89	-6,684.87	-769.17
Enthalpy Btu/hr	-214,420	-18,844,000	-5,783,100	-600,490	-218,720	-6,330,700	-19,057,997	-6,383,629

SCHEMATIC FOR METHYL CHLORIDE PRODUCTION VIA METHANOL (OPTION 1)



BLOCK FLOW DIAGRAM FOR METHYL CHLORIDE PRODUCTION VIA METHANOL (OPTION 1)



Stream Summary: Base Case Methyl Chloride via Methane (Option 2)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Temperature F	77.0	77.0	77.0	76.8	572.0	977.0	100.0	161.4	157.3	86.0	86.0
Pressure psia	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Frac	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.0	0.0	0.0
Mole Flow lbmol/hr	323.0	323.0	779.2	1425.2	1425.2	1425.2	1425.2	1455.4	1994.8	2025.0	200.0
Mass Flow lb/hr	5259.1	22902.4	13908.0	42069.6	42069.6	42069.6	42069.6	35963.5	42587.1	36480.9	7999.4
Volume Flow cuft/hr	126315.8	125087.1	304694.4	556238.8	1073120.0	1494810.0	580129.4	657472.5	613.6	586.9	60.2
Enthalpy MMBtu/hr	-10.2	0.0	-23.4	-33.6	-26.7	-33.4	-47.3	-70.8	-225.2	-248.7	-36.6
Mass Flow lb/hr											
METHANE	5078.2		11254.0	16332.1	16332.1	12628.0	12628.0	12599.8	28.2		
CHLORINE		22902.4		22902.4	22902.4	458.5	458.5	440.3	18.2		
METHYLCH			1045.4	1045.4	1045.4	9264.5	9264.5	9096.1	168.4		
DICHLORO			15.5	15.5	15.5	4483.8	4483.8	4011.5	472.3		
CHLOROFO			1.9	1.9	1.9	1604.0	1604.0	1279.2	324.8		
CARBONTE			0.2	0.2	0.2	317.7	317.7	217.1	100.7		
WATER			0.0	0.0	0.0	0.0	0.0	6461.9	30019.1	36480.9	
HYDROGEN						11541.0	11541.0	86.0	11455.1		
NITROGEN	181.0		1591.1	1772.0	1772.0	1772.0	1772.0	1771.7	0.3		
NAOH											7999.4
NA+											
NACL(S)											
NAOH(S)											
H2SO4			trace	trace	trace	trace	trace				

Stream Summary: Base Case Methyl Chloride via Methane (Option 2) Continued

	12	13	14	15	16	17	18	19	20	21	22
Temperature F	300.4	307.1	100.0	332.9	371.4	90.0	275.0	-58.0	-58.0	-58.0	-23.7
Pressure psia	14.7	14.7	14.7	14.7	14.7	14.7	115.0	115.0	115.0	115.0	14.7
Vapor Frac	1.0	0.0	1.0	1.0	0.0	0.0	1.0	1.0	0.7	0.0	1.0
Mole Flow lbmol/hr	1384.8	270.6	1384.8	1098.0	749.1	462.4	1098.0	813.0	1098.0	285.0	213.5
Mass Flow lb/hr	34277.8	9685.1	34277.8	29102.6	50523.8	45348.6	29102.6	14468.3	29102.6	14634.2	8907.3
Volume Flow cuft/hr	766902.5	99.5	563086.6	634695.0	507.0	403.5	74473.9	29311.5	29537.8	226.1	66826.9
Enthalpy MMBtu/hr	-62.5	-44.9	-65.1	-33.1	-194.8	-162.8	-33.8	-25.3	-39.8	-14.5	-7.8
Mass Flow lb/hr											
METHANE	12597.8	2.0	12597.8	12593.9	3.9		12593.9	11741.4	12593.9	852.6	852.6
CHLORINE	trace	440.3	trace								
METHYLCH	9077.7	18.4	9077.7	9030.8	47.0		9030.8	989.8	9030.8	8040.9	8000.7
DICHLORO	3989.4	22.1	3989.4	3946.4	43.0		3946.4	17.3	3946.4	3929.1	< 0.001
CHLOROFO	1267.9	11.3	1267.9	1247.4	20.6		1247.4	2.1	1247.4	1245.3	trace
CARBONTE	214.2	2.9	214.2	209.1	5.1		209.1	0.2	209.1	208.9	trace
WATER	5359.1	1102.8	5359.1	210.1	5148.9		210.1	0.0	210.1	210.1	trace
HYDROGEN	trace	86.0	trace								
NITROGEN	1771.7	0.0	1771.7	1771.6	0.1		1771.6	1717.6	1771.6	54.0	54.0
CL-											
NAOH	trace	7999.4	trace								
NA+											
NACL(S)											
NAOH(S)											
H2SO4				93.3	45255.3	45348.6	93.3	trace	93.3	93.3	trace

Stream Summary: Base Case Methyl Chloride via Methane (Option 2) Continued

	23	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**
Temperature F	113.0	-100.0	-100.0	99.2	150.6	141.8	198.5	-70.1	-70.1	-70.1	157.8
Pressure psia	14.7	15.0	15.0	14.7	14.7	14.7	14.7	15.0	15.0	15.0	60.0
Vapor Frac	0.0	0.0	1.0	0.0	0.0	0.0	0.0	1.0	1.0	1.0	1.0
Mole Flow lbmol/hr	71.5	160.8	52.8	48.8	22.7	8.7	14.0	865.8	779.2	86.6	779.2
Mass Flow lb/hr	5726.9	7922.3	985.0	4178.8	1548.1	1035.2	512.9	15453.4	13908.0	1545.3	13908.0
Volume Flow cuft/hr	69.9	120.6	13469.3	51.6	18.2	11.7	6.5	240011.6	216010.5	24001.2	85651.5
Enthalpy MMBtu/hr	-4.9	-7.7	-1.7	-2.6	-2.3	-0.5	-1.8	-27.0	-24.3	-2.7	-22.8
Mass Flow lb/hr											
METHANE	trace	89.5	763.0	trace	trace			12504.4	11254.0	1250.4	11254.0
CHLORINE											
METHYLCH	40.2	7829.0	171.7	40.2	trace	trace	trace	1161.6	1045.4	116.2	1045.4
DICHLORO	3929.1	< 0.001	trace	3925.2	3.9	3.9	trace	17.3	15.5	1.7	15.5
CHLOROFO	1245.3	trace	trace	213.1	1032.1	1031.1	1.0	2.1	1.9	0.2	1.9
CARBONTE	208.9	trace	trace	0.3	208.6	0.2	208.4	0.2	0.2	0.0	0.2
WATER	210.1			trace	210.1		210.1	0.0	0.0	0.0	0.0
HYDROGEN											
NITROGEN	trace	3.8	50.3					1767.9	1591.1	176.8	1591.1
H3O+											
CL-											
NAOH											
NA+											
NACL(S)											
NAOH(S)											
H2SO4	93.3			trace	93.3		93.3	trace	trace	trace	trace

Stream Summary: Base Case Methyl Chloride via Methane (Option 2) Continued

	34	35	36	37	38
Temperature F	211.8	371.4	371.4	307.1	307.1
Pressure psia	14.7	14.7	14.7	14.7	14.7
Vapor Frac	0.2	0.0	1.0	0.0	1.0
Mole Flow lbmol/hr	2439.7	461.4	287.7	200.0	70.6
Mass Flow lb/hr	51086.6	45255.3	5268.5	7999.4	1685.7
Volume Flow cuft/hr	178871.7	452.3	173851.2	60.2	39353.8
Enthalpy MMBtu/hr	-263.4	-157.8	-29.1	-35.7	-6.4
Mass Flow lb/hr					
METHANE	1284.6		3.9		2.0
CHLORINE	458.5				440.3
METHYLCH	349.9		47.0		18.4
DICHLORO	539.1		43.0		22.1
CHLOROFO	356.9		20.6		11.3
CARBONTE	108.6		5.1		2.9
WATER	36270.8		5148.9		1102.8
HYDROGEN	11541.0				86.0
NITROGEN	177.2		0.1		0.0
CL-					
NAOH				7999.4	
NA+					
NACL(S)					
NAOH(S)					
H2SO4	trace	45255.3			

Stream Summary: Optimized Case Methyl Chloride via Methane (Option 2)

	1	2	3	4	5	6	7	8	9	10	11
Temperature F	77.0	77.0	77.0	76.8	572.0	907.9	100.0	161.9	154.3	86.0	86.0
Pressure psia	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Frac	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.0	0.0	0.0
Mole Flow lbmol/hr	334.0	323.0	840.2	1497.2	1497.2	1497.2	1497.2	1530.2	1992.0	2025.0	200.0
Mass Flow lb/hr	5436.1	22902.4	14939.3	43277.9	43277.9	43277.9	43277.9	37153.7	42605.1	36480.9	7999.4
Enthalpy MMBtu/hr	-10.6	0.0	-25.3	-35.9	-28.6	-36.6	-49.9	-73.9	-224.7	-248.7	-36.6
Mass Flow lb/hr											
METHANE	5255.2		12207.2	17462.4	17462.4	13690.3	13690.3	13660.4	29.9		
CHLORINE		22902.4		22902.4	22902.4	1.8	1.8	1.7	0.1		
METHYLCH			1118.9	1118.9	1118.9	9421.9	9421.9	9255.6	166.3		
DICHLORO			17.5	17.5	17.5	4719.4	4719.4	4233.5	485.9		
CHLOROFO			2.0	2.0	2.0	1606.8	1606.8	1289.5	317.3		
CARBONTE			0.2	0.2	0.2	287.4	287.4	198.8	88.6		
WATER			0.0	0.0	0.0	0.0	0.0	6595.6	29885.3	36480.9	
HYDROGEN						11775.9	11775.9	144.4	11631.4		
NITROGEN	181.0		1593.4	1774.4	1774.4	1774.4	1774.4	1774.1	0.3		
NAOH											7999.4
NA+											
NACL(S)											
NAOH(S)											
H2SO4			trace	trace	trace	trace	trace				
HSO4-											
SO4--											

Stream Summary: Optimized Case Methyl Chloride via Methane (Option 2) Continued

	12	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
Temperature F	291.1	285.0	100.0	327.4	365.2	90.0	275.0	-58.0	-58.0	-58.0	-23.8
Pressure psia	14.7	14.7	14.7	14.7	14.7	14.7	115.0	115.0	115.0	115.0	14.7
Vapor Frac	1.0	0.0	1.0	1.0	0.0	0.0	1.0	1.0	0.8	0.0	1.0
Mole Flow lbmol/hr	1447.7	282.5	1447.7	1168.4	729.1	449.7	1168.4	879.9	1168.4	288.5	216.1
Mass Flow lb/hr	35553.7	9599.4	35553.7	30509.5	49155.3	44111.1	30509.5	15598.7	30509.5	14910.9	9005.6
Enthalpy MMBtu/hr	-63.9	-46.6	-66.5	-35.2	-189.7	-158.4	-35.9	-27.5	-42.1	-14.6	-7.9
Mass Flow lb/hr											
METHANE	13658.3	2.1	13658.3	13654.3	4.0		13654.3	12785.0	13654.3	869.3	869.3
CHLORINE	trace	1.7	trace								
METHYLCH	9239.8	15.8	9239.8	9194.7	45.1		9194.7	1068.5	9194.7	8126.2	8085.5
DICHLORO	4210.8	22.7	4210.8	4167.2	43.6		4167.2	19.5	4167.2	4147.7	< 0.001
CHLOROFO	1278.2	11.3	1278.2	1258.2	20.0		1258.2	2.3	1258.2	1255.9	trace
CARBONTE	196.2	2.6	196.2	191.7	4.5		191.7	0.2	191.7	191.5	trace
WATER	5196.3	1399.3	5196.3	181.9	5014.5		181.9	0.0	181.9	181.9	trace
HYDROGEN	trace	144.4	trace								
NITROGEN	1774.1	0.0	1774.1	1774.0	0.1		1774.0	1723.2	1774.0	50.8	50.8
NAOH	trace	7999.4	trace								
NA+											
NACL(S)											
NAOH(S)											
H2SO4				87.6	44023.5	44111.1	87.6	trace	87.6	87.6	trace
HSO4-											
SO4--											

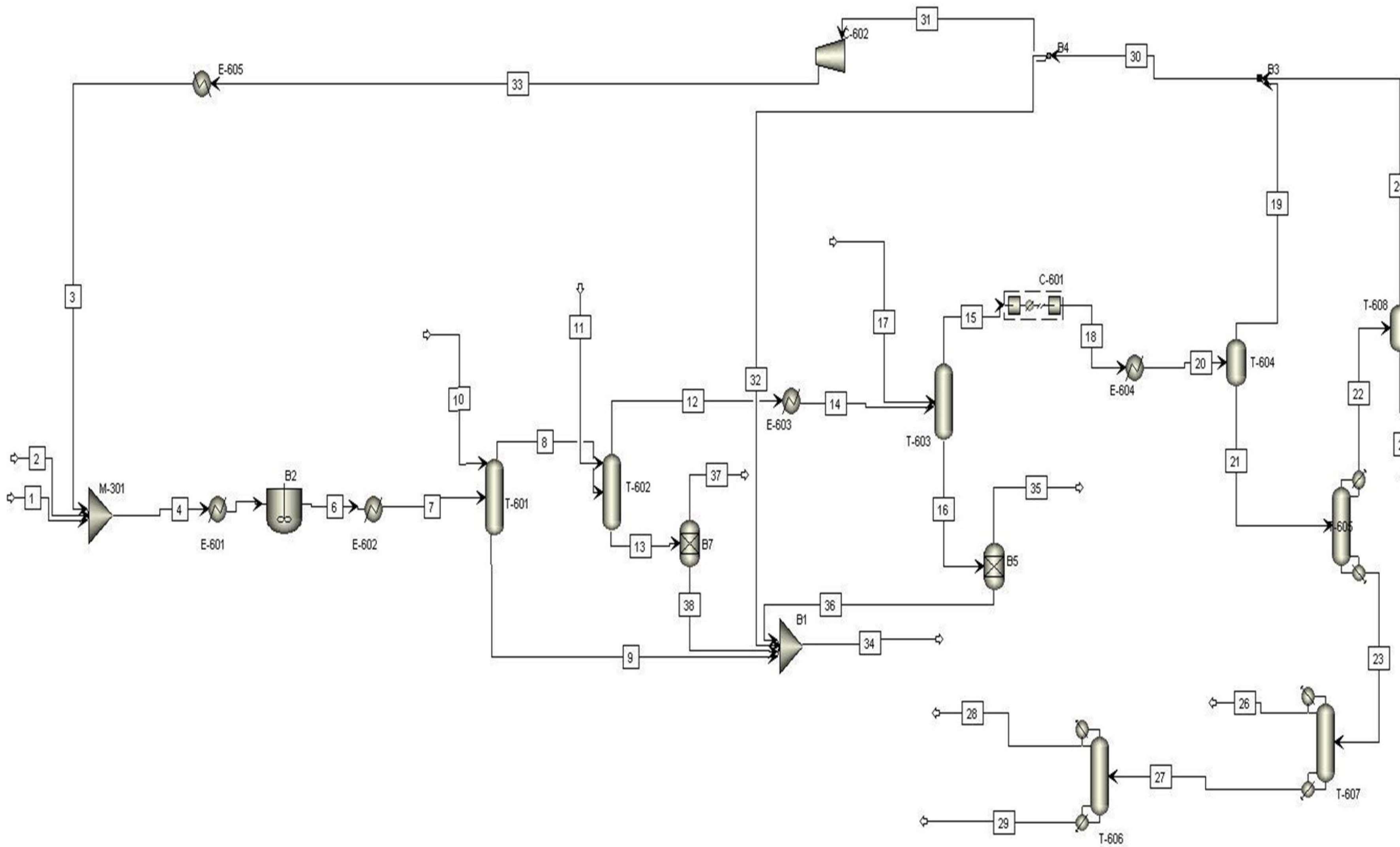
Stream Summary: Optimized Case Methyl Chloride via Methane (Option 2) Continued

	23	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**
Temperature F	112.1	-100.0	-100.0	99.3	147.5	141.8	196.7	-70.0	-70.0	-70.0	157.7
Pressure psia	14.7	15.0	15.0	14.7	14.7	14.7	14.7	15.0	15.0	15.0	60.0
Vapor Frac	0.0	0.0	1.0	0.0	0.0	0.0	0.0	1.0	1.0	1.0	1.0
Mole Flow lbmol/hr	72.4	162.5	53.7	51.3	21.1	8.9	12.2	933.5	840.2	93.4	840.2
Mass Flow lb/hr	5905.3	8005.0	1000.6	4384.7	1520.5	1058.9	461.6	16599.2	14939.3	1659.9	14939.3
Enthalpy MMBtu/hr	-4.8	-7.8	-1.8	-2.7	-2.1	-0.5	-1.6	-29.3	-26.3	-2.9	-24.8
Mass Flow lb/hr											
METHANE	trace	90.7	778.6	trace	trace			13563.6	12207.2	1356.4	12207.2
CHLORINE											
METHYLCH	40.6	7910.8	174.7	40.6	trace	trace	trace	1243.3	1118.9	124.3	1118.9
DICHLORO	4147.7	< 0.001	trace	4143.6	4.1	4.1	trace	19.5	17.5	1.9	17.5
CHLOROFO	1255.9	trace	trace	200.3	1055.6	1054.6	1.1	2.3	2.0	0.2	2.0
CARBONTE	191.5	trace	trace	0.2	191.3	0.2	191.1	0.2	0.2	0.0	0.2
WATER	181.9			trace	181.9	< 0.001	181.9	0.0	0.0	0.0	0.0
HYDROGEN											
NITROGEN	trace	3.5	47.3					1770.5	1593.5	177.1	1593.5
NAOH											
NA+											
NACL(S)											
NAOH(S)											
H2SO4	87.6			trace	87.6	< 0.001	87.6	trace	trace	trace	trace
HSO4-											
SO4--											

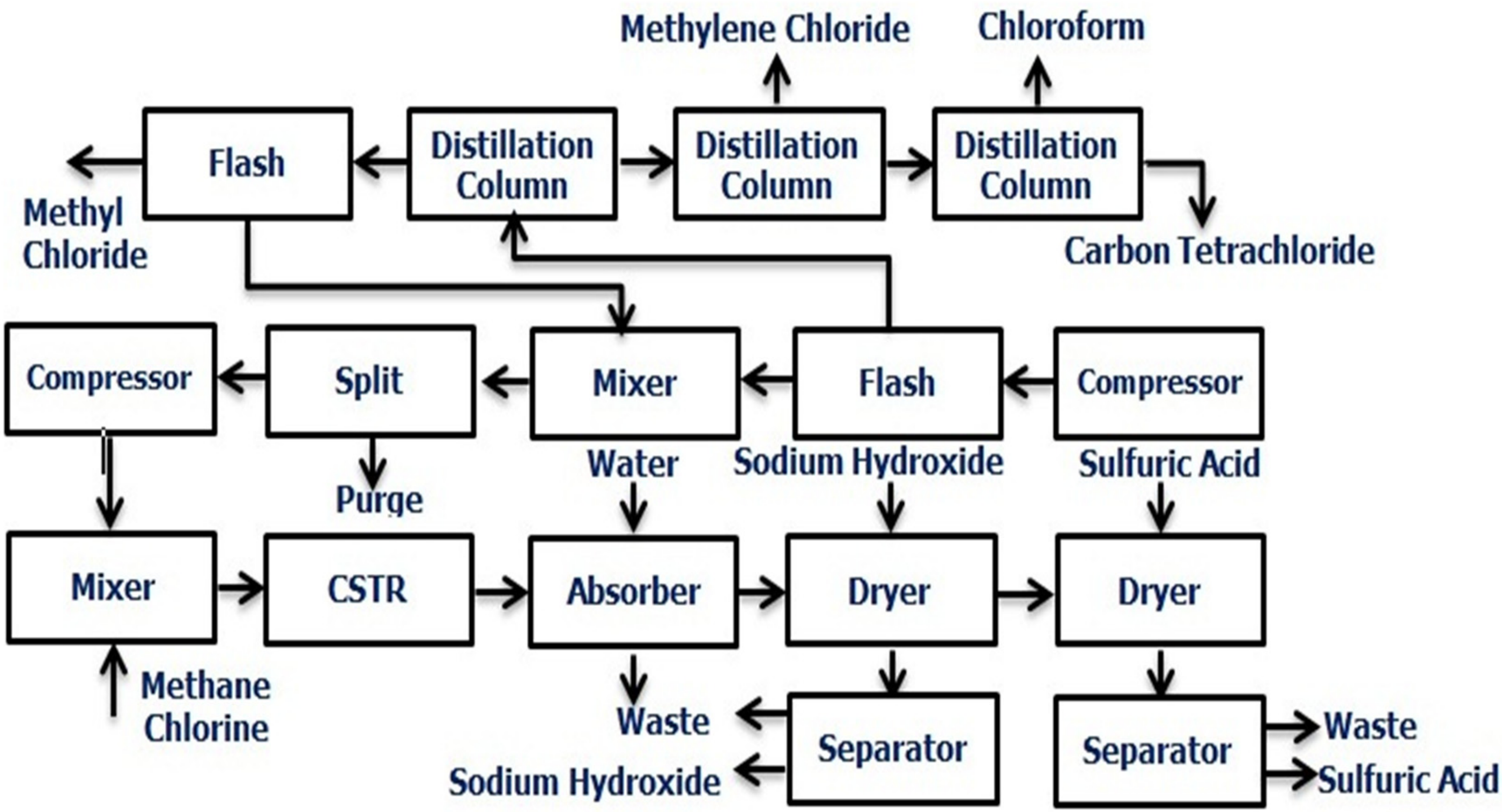
Stream Summary: Optimized Case Methyl Chloride via Methane (Option 2) Continued

	34	**35**	**36**	**37**	**38**
Temperature F	211.7	365.2	365.2	285.0	285.0
Pressure psia	14.7	14.7	14.7	14.7	14.7
Vapor Frac	0.2	0.0	1.0	0.0	1.0
Mole Flow lbmol/hr	2448.1	448.9	280.2	200.0	82.5
Mass Flow lb/hr	50996.9	44023.5	5131.8	7999.4	1600.0
Enthalpy MMBtu/hr	-264.1	-153.6	-28.4	-35.7	-8.1
Mass Flow lb/hr					
METHANE	1392.4		4.0		2.1
CHLORINE	1.8				1.7
METHYLCH	351.6		45.1		15.8
DICHLORO	554.1		43.6		22.7
CHLOROFO	348.9		20.0		11.3
CARBONTE	95.8		4.5		2.6
WATER	36299.1		5014.5		1399.3
HYDROGEN	11775.9				144.4
NITROGEN	177.5		0.1		0.0
NAOH				7999.4	
NA+					
NACL(S)					
NAOH(S)					
H2SO4	trace	44023.5			
HSO4-					
SO4--					

SCHEMATIC FOR METHYL CHLORIDE PRODUCTION VIA METHANE (OPTION 2)



BLOCK FLOW DIAGRAM FOR METHYL CHLORIDE PRODUCTION VIA METHANE (OPTION 2)


Methylene Chloride
Chloroform
Flash
Distillation Column
Distillation Column
Distillation Column
Methyl Chloride
Carbon Tetrachloride
Compressor
Split
Mixer
Flash
Compressor
Purge
Water
Sodium Hydroxide
Sulfuric Acid
Mixer
CSTR
Absorber
Dryer
Dryer
Methane
Chlorine
Waste
Separator
Separator
Sodium Hydroxide
Waste
Sulfuric Acid

VITA

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Industrial intern at the R&D Center for Saudi Arabian Oil Company (Saudi Aramco) Downstream Division in summer 2005; bioengineering researcher in the Molecular Bioengineering Lab at Oklahoma State University from Fall 2006 to Spring 2008; bioengineering intern at the National Centre for Biomedical Engineering Sciences at National University of Ireland-Galway in summer 2008; graduate research and teaching assistant in the School of Chemical Engineering at Oklahoma State University from Fall 2009 to Spring 2011.

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Institution: Oklahoma State University Location: Stillwater, Oklahoma

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Pages in Study: 123 Candidate for the Degree of Master of Science

Major Field: Chemical Engineering

Scope and Method of Study: Increasing concerns over global climate change due to greater amounts of greenhouse gases in the atmosphere or ozone depletion etc. are leading engineers to address ‘environmental' impacts of industrial processes. Additionally, the impact on ecosystems on which people depend and consequently the health of people is another growing concern. Furthermore, the ‘economics' of the industrial processes were dictated as the main constraint in the design of chemical process plants. However, recently health, safety, and public welfare or in other words the ‘social’ concern is included as another important constraint. Addressing environmental, social, and economic concerns falls under the evaluation of sustainability of industrial processes. With all these concerns, engineers are developing novel methods for chemical process design.

Findings and Conclusions: A methodology for evaluating the sustainability of processes was demonstrated using the SUSTAINABILITY EVALUATOR (SE) in conjunction with Aspen Plus process simulator. The SE is a Microsoft Excel based tool that requires mass and energy flows from Aspen Plus as inputs to the tool. The outputs from the tool include the economic, environmental, social, and overall sustainability impacts. The goal of using this tool is to assist decision makers or processes designers in quantifying the sustainability of processes and providing them with the ability to improve the process’ sustainability. The methodology includes simulating a process in Aspen Plus, evaluating the sustainability using the SE, conducting a sensitivity analysis and subsequently optimizing the process in Aspen Plus, and finally re-evaluating the sustainability of the process using the SE. This methodology was demonstrated on a case study involving two different chemistries to produce methyl chloride; hydrochlorination of methanol and thermal chlorination of methane. The different chemistries were chosen to assist a process engineer in making a decision regarding the sustainability of a process e.g. whether one process is more sustainable than another. The SE tool addresses sustainability concerns and quantifies them in order to measure changes in sustainability of a process. The study found the process with the hydrochlorination of methanol chemistry to have a lower overall sustainability impact than the process with the thermal chlorination of methane chemistry. The lower the overall sustainability impact, the more sustainable is the process.

ADVISER’S APPROVAL: Dr. Karen High