AN ECONOMIC CASE STUDY OF PROCESS MODIFICATION FOR THE ALLYL CHLORIDE PROCESS

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NOMENCLATURE

Abbreviations

12DCP	1,2-dichloropropane
13DCP	1,3-dichloropropene
CAAA	Clean Air Act Amendments
Cl_2	Chlorine
COMP	ASPEN PLUS™ module for compressors
CPI	Chemical Processing Industry
CSTR	Continuous Stirred Tank Reactor
DIPPR	Design Institute of Physical Property Research
DSTWU	ASPEN PLUS™ module for shortcut distillation
EPA	Environmental Protection Agency
HCl	Hydrogen chloride
HEATER	ASPEN PLUS™ module for simple heaters
HON	Hazardous Organic NESHAPS
MACT	Maximum Achievable Control Technology
MGal	1000 gallons
MMBTU	1 million BTUs
NESHAPS	National Emissions Standards for Hazardous Air Pollutants
ORD	EPA's Office of Research and Development
PFR	Plug Flow Reactor
PPA	Pollution Prevention Act
RADFRAC	ASPEN PLUS™ module for rigorous distillation

RCSTR	ASPEN PLUS™ module for CSTR
RPLUG	ASPEN PLUS™ module for PFR
SEP	ASPEN PLUS™ module for separation of components
SRV	Source Reduction Variable
VOCs	Volatile Organic Compounds
WRO	Waste Reduction Option

Equation Nomenclature

AT	Averaging time, days·year
BW	Body weight, kg
C	Concentration at exposure point, mg/m^3
CDI	Chronic daily intake, mg/kg·day
ED	Exposure duration, years
EF	Exposure frequency, days
HI	Hazard Index
RfD	Reference dose, mg/kg·day

CHAPTER I

INTRODUCTION

Society's increasing environmental awareness has forced the government to pass more stringent environmental laws. These laws have put both economic and societal pressure on companies to cleanup chemical processes. Such current and anticipated future regulations regarding environmental pollution have created the need to significantly change the manufacturing philosophy in this country. The major impact of these regulations is the requirement that companies must re-analyze their current schemes for chemical waste reduction and develop new strategies for minimizing the production of waste and hazardous chemicals.

There are many benefits in developing new strategies for waste minimization. As a member of society, one wants to leave a clean environment for the generations that will follow. In addition, a more efficient process with less waste is an economic incentive. For a company, there are also intangible benefits: improved corporate image and reduced environmental liability. Regardless of the reason, companies are changing the way they view pollution.

The promulgation of the Pollution Prevention Act (PPA) of 1990 exhibits the trend of American governmental policy. Although this legislation is not enforceable, it symbolizes the attitude of society and its views on the preservation of the environment. The PPA indicates the importance of preventing pollution, whether through waste treatment, source reduction, or recycling.

Reduction of waste at the source is one such strategy that is replacing the more traditional method of end-of-pipe waste treatment. The Environmental Protection Agency

(EPA) prefers source reduction over waste treatment for waste minimization because it eliminates the waste before it occurs. Source reduction reflects a new long-term philosophy that advocates anticipation of a problem (waste) before it happens (is generated). Many companies find this strategy difficult, since it means incurring a capital cost which may be larger than a current annual cost for waste treatment. Thus, this work shows how new waste minimization strategies, like source reduction, can be implemented cost effectively. The objective of this work is to develop a waste minimization methodology by applying source reduction techniques to the allyl chloride (3-chloropropene) process.

This research is designed to develop a strategy for minimizing waste by the source reduction technique of process modification. Examples of process modifications can be adjustment of reactor conditions and types, feed ratios, and general operating parameters. Although process modifications might entail capital costs, they can provide an environmental cost savings by reducing waste treatment costs. In addition, less waste means a more efficient process and a reduction in the risk to human health and the environment.

Currently, the waste limits imposed on companies for processes are technology based standards. In other words, the technology used in a process must perform so that process effluents do not exceed designated waste levels. However, in the future, the EPA will emphasize risk based regulations of waste. Most companies are knowledgeable on technology based standards but lack expertise on the application of regulatory risk to process design or debottlenecking. To account for these inadequacies, this work shows how regulatory risk analysis could be incorporated as an economical optimization constraint.

The allyl chloride process is an ideal vehicle for applying process modification. Allyl chloride is a colorless, mobile liquid that is only slightly soluble in water (Kneupper and Saathoff 1993). The allyl chloride process provides an opportunity for reducing the effluents of several toxic pollutants regulated by the EPA. The product, allyl chloride, has been labeled as a very volatile hazardous air pollutant (vvhap) (Norman and others 1992). Two of the primary byproducts, 1,2-dichloropropane (12DCP) and 1,3-dichloropropene (13DCP) are less hazardous and therefore listed under the title of volatile organic hazardous air pollutants (vohap) (Norman and others 1992). Both of these byproducts are also on the Clean Water Act's list of priority pollutants (Kovalic 1987). In addition, all three chemicals are regulated under the recent Hazardous Organic National Emission Standards for Hazardous Air Pollutants (Hazardous Organic NESHAPs or HON) (1994b) implemented by the Clean Air Act.

Allyl chloride is usually produced from high temperature (570-1100°F) chlorination of propylene (propene). Although many byproducts are formed by this reaction, the primary byproducts are 12DCP and 13DCP. The reaction products leaving the reactor are cooled and fed to a prefractionator, where the overhead products are primarily hydrogen chloride and unreacted propylene; the bottom products are chlorinated hydrocarbons. The hydrogen chloride is removed from the distillate product via absorption with water, forming commercial grade aqueous hydrogen chloride. The propylene is then washed with caustic soda to remove the remaining hydrogen chloride. After compression and condensation to remove water, the propylene is recycled to the reactor. Three distillation columns are used to separate the bottoms product of the prefractionator into allyl chloride and the dichloride byproducts. The process modification techniques were developed to reduce the waste byproducts, 12DCP and 13DCP.

The general methodology followed a three step approach. First, the process was modeled using ASPEN PLUS™. This software package provided a versatile array of unit operations, an optimization routine, sensitivity analyses, and case study capabilities. The process variables, including the kinetic data and approximate temperatures and pressures obtained from the literature (Biegler and Hughes 1983; Hopper and others 1992) yielded a process model that produced good results (similar to published results).

The next phase was the determination of source reduction variables (SRVs). For example, if modifying the reactor temperature directs the reaction selectivity away from byproduct formation, then reaction temperature is a SRV. By doing a sensitivity analysis via the process model, the (SRVs) were found to be: reactor feed temperature, feed ratio, reactor pressure, reactor type (plug flow, or PFR, and continuous-flow stirred-tank, or CSTR), and reactor operation (adiabatic or isothermal). In addition, this procedure was also used to determine the range of each SRV. However, because some SRVs were discontinuous and could not be varied in a single simulation, four simulations were generated to accommodate all the SRVs.

In the final stage, the waste minimization options were found by varying the SRVs in the simulated process. Often, an alternative that minimizes the waste is evaluated by comparison to a base case. Since an actual operating base case was not available for the allyl chloride process, waste minimization options were compared at a constant allyl chloride product flow rate. Altering the SRVs affected other parameters besides the byproduct formation (utility use, product formation, and raw material consumption), therefore economic evaluations were used to put all parts of the model on the same basis. The optimization was performed with an economic objective function in terms of the preliminary profit which includes: the revenue from the products, the cost of the raw materials, cost of treating the waste, and the cost of the utilities. The aspect of the objective function that should be noted is the inclusion of the waste costs. Instead of assigning waste costs to the overhead costs, this method penalizes the objective function and deals with the source of the waste (the process).

In contrast to the work done by Hopper (Hopper and others 1992) on non economic waste minimization with the allyl chloride process, this research approaches waste minimization by optimizing a preliminary economic model. Thus, waste reduction is no longer based on the least possible waste, but instead is based on the least economically feasible waste. When each variable is optimized separately (as done by Hopper), the local rather than the global optimum is determined. Through the use of optimization, this methodology finds the global optimum by simultaneously varying several SRVs.

From the optimization of the four cases (adiabatic PFR, isothermal PFR, adiabatic CSTR, and isothermal CSTR), it was found that the adiabatic plug flow reactor produced the highest preliminary profit. Due to the anticipated increase in the environmental regulations, this research also evaluated the effects of increasing the waste costs. The preliminary profit decreased because of lower optimum production levels, when the waste costs were increased in 20% increments up to 80% (of the original waste costs) and the simulation was re-optimized. This lower production level was optimum, because with higher waste costs, it was no longer feasible to produce as much waste. In addition to these flowrate changes, the operating temperature of the reactor increases which directs the kinetics toward a lower production rate of the waste products.

The general methodology developed in this research also has the flexibility to incorporate regulatory risk. The intent of incorporating risk into this process modification based waste minimization strategy was to determine a maximum production level that will not pose a risk to the plant's environment. This maximum production level of a byproduct can then be used as a constraint in the optimization routine. Since information concerning location of the plant and its potential damage to its environment is not available, only a partial quantitative risk analysis was performed.

In summary, the objective of this work was to develop a strategy for selecting process modification options that minimize the waste in chemical processes while remaining economical. Through the study of the allyl chloride process, a general methodology was developed and applied that includes: process modeling, selection of source reduction variables and ranges, and economic optimization. In addition, the methodology was successfully applied to determine the most economically and environmentally feasible operating parameters for the allyl chloride process. This report discusses the details of this research and is broken into the following sections:

1) Background on environmental regulations, process motivation, ASPEN PLUS™ simulator, economic analysis, optimization, and regulatory risk analysis.
2) Description of the allyl chloride process
3) Proposed methodology
4) Application of the methodology to the allyl chloride process
    a. Process modeling
    b. Selection of source reduction variables and ranges
    c. Economic optimization and application of regulatory risk
5) Conclusions and recommendations of this research.

CHAPTER II

BACKGROUND

This chapter provides the background for this research which minimizes waste by process modification. It is broken down into six sections: Environmental Background, Process Motivation, ASPEN PLUS™ Modeling, Economic Analysis, Optimization, and Regulatory Risk Analysis.

Environmental Background

The primary motivation for this research stems from the increased regulation of the chemical processing industry (CPI) and the changes in processing methodology that these regulations have introduced. Due to the recent promulgation of more stringent environmental laws, companies are being pressured into changing their environmental policies. It is no longer acceptable to just treat waste at the end-of-the-pipe. The government expects companies to search for methods to minimize the waste (often referred to as pollution prevention). In a reflection of these goals, the EPA's Office of Research and Development (ORD) initiated the Waste Minimization Research Program in 1987. Whether for design or retrofit, waste minimization is now a high priority for chemical and petroleum companies.

The term waste minimization is defined by the Environmental Protection Agency (EPA) as (1986):

> The reduction, to the extent feasible, of hazardous waste that is generated or subsequently treated, stored, or disposed of. It includes any source reduction or recycling activity undertaken by a generator that results in either (1) the reduction of total volume or quantity of hazardous waste, or (2) the reduction of toxicity of hazardous waste, or both, so long as the reduction is consistent with the goal of minimizing present and future threats to human health and the environment.

This definition lists three techniques by which waste can be minimized: source reduction, recycling, or waste treatment.

Several researchers have explored waste minimization with respect to process design and retrofit. It was found that the Douglas hierarchical decision procedure could be used to determine design alternatives that do not lead to pollution problems (Douglas 1992). In a related paper, Fonyo and others (1994) concluded that the Douglas hierarchical decision procedure could also be applied to the retrofitting problem. In addition, Manousiouthakis and Allen (1994) suggest that waste minimization is a process synthesis activity. Through these researchers work, methodologies were developed for the application of waste minimization to design or retrofit processes.

In 1990 the US Congress showed its support of waste minimization by passing the Pollution Prevention Act of 1990 which outlines the following waste management hierarchy:

- pollution should be prevented or reduced at the source wherever feasible;
- pollution that cannot be prevented should be recycled in an environmentally safe manner whenever feasible;
- pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and
- disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner.

In the past ten years many companies have actively pursued pollution prevention programs. Several of the industrial accomplishments are listed in Table 1 (Freeman and others 1992). However, despite extensive interest in the concept of waste minimization, pollution prevention initiatives are rare in most companies (Freeman and others 1992). Even though pollution prevention seems to work (Table 1), companies are still not buying into the concept. Corporate management holds the same resistance to waste reduction as was formally put up against total quality management. Similarly, it needs to be thought of as just 'a good way to do business' (Shanley 1993).

TABLE 1: COMPANY-WIDE POLLUTION PREVENTION PROGRAMS

Company	Accomplishments
Amoco Waste Minimization Program (1983)	Between 1983 and 1988, Amoco reduced its hazardous waste by 86%, saving the company about $50 million.
Chevron Save Money and Reduce Toxics Program (SMART, 1987)	From 1987 to 1990, Chevron reduced hazardous waste by 60% and saved more than $10 million in disposal costs. Case Study: Chevron used to dispose of tank bottoms in landfills. It now uses a centrifuge to separate oil from waster; it reuses the oil and treats the waster, leaving only a small amount of solid to be landfilled (less than 5% of the original sludge).
Dow Waste Reduction Always Pays (WRAP, 1986)	SARA 313 overall releases are down from 12,252 tons in 1987 to 9,659 tons in 1989, a 21% reduction. Offsite transfers are down from 2,855 tons (1987) to 2,422 tons (1989), a reduction of 15%. Air emissions for 1989 showed a 54% decrease from 1984.
General Dynamics Zero Discharge (1985)	Nearly 40 million lbs. of hazardous waste discharge eliminated from 1984 to 1988 (approx. 72%). Sales increased from $7.3 to 9.35 billion over the same period.
IBM	Hazardous waste generation was reduced 38% from 1984 to 88; 84% of IBM's hazardous waste was recycled in 1988; 28% of all solid waste from IBM United States operations was recycled in 1988; IBM U.S. emissions were reduced 20% from 1987 to 1988; and, IBM U.S. had a decrease of 25% in its CFC emissions between 1987 and 1988.
Monsanto Priority One (TRI wastes)	From 1987 to 1990, Monsanto achieved a 39% reduction in hazardous air emissions.

Source: Freeman, 1992

As mentioned earlier, the Pollution Prevention Act clearly states that the preferred method of waste minimization is source reduction. The EPA states that source reduction is (1986):

> The reduction or elimination of waste generation at the source, usually within a process. Source reduction measures can include some types of treatment processes, but they also include process modifications, feedstock substitutions or improvements in feedstock purity, various housekeeping and management practices, increases in the efficiency of machinery, and even recycling within the process. Source reduction implies any action that reduces the amount of waste exiting from a process.

As Figure 1 shows (Freeman 1990), source reduction can be broken down into source control and product substitution. The three categories of source control are: good housekeeping practices, input material modification, and technology modification.

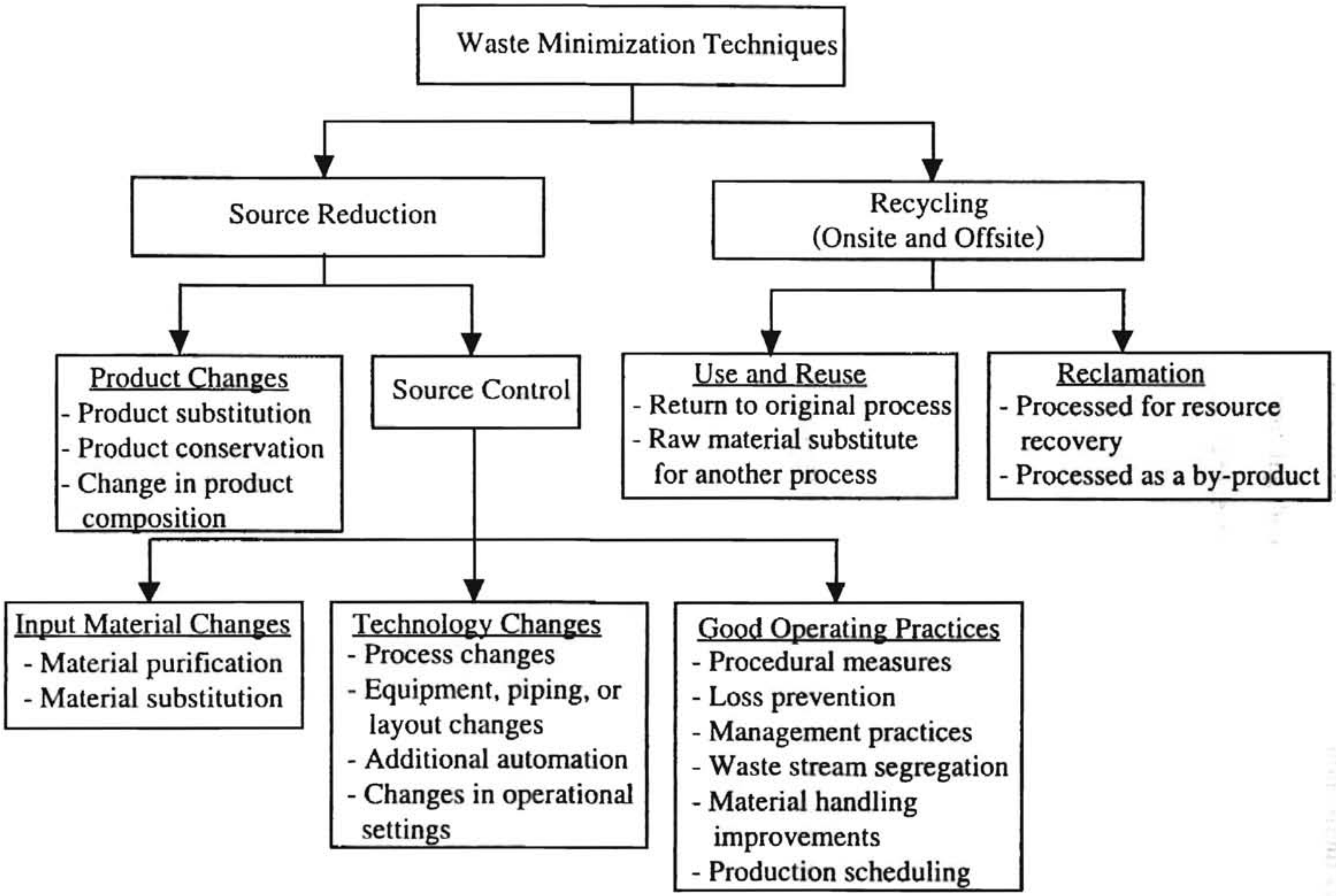


Figure 1: Waste Minimization Techniques (Source: Freeman, 1990)

Initially source reduction programs focused on good housekeeping practices such as inventory control and spill/leak prevention. Although these methods significantly reduced the waste, they are rapidly reaching their limits. The second generation of source control is aimed at reducing wastes through technology modifications (Freeman and others 1992), which include:

1) Improved Controls
2) Process Modifications
3) Equipment Changes
4) Energy Conservation
5) Water Conservation

The work presented herein is primarily concerned with process modification as the source reduction technique.

In this work, a general definition is used for process modification which incorporates changes in both process parameters and the type of equipment. For example, a change in a process parameter would be increasing the feed temperature to the reactor, whereas a change in the equipment would be using a continuous-flow stirred-tank reactor (CSTR) instead of a plug flow reactor (PFR). Both cases are considered process modifications.

Process Motivation

Because the allyl chloride process has three chemicals (allyl chloride, 1,2-dichloropropane, and 1,3-dichloropropene) regulated by the EPA, it supplies an ideal challenge for process modification. This process also provided a variety of equipment with which a general methodology could be developed. In addition, a sizable amount of information exists for the allyl chloride process including its chemistry and kinetics (Biegler and Hughes 1983; Fairbairn and others 1947; Groll and Hearne 1939; Hopper and others 1992; Kneupper and Saathoff 1993; Krahling and others 1985; Porter and Rust 1956;

Yabroff and Anderson 1951). This section explains the environmental incentives for choosing the allyl chloride process.

All sources of volatile organic compounds (VOCs) are being regulated due to the concern for health effects. Originally, the VOCs, allyl chloride, 1,2-dichloropropane (12DCP), and 1,3-dichloropropene (13DCP) were regulated under the Maximum Achievable Control Technology (MACT) standards implemented by the 1990 Clean Air Act Amendments (CAAA) of 1990 (Norman and others 1992). However, on April 22, 1994 the Hazardous Organic National Emission Standards for Hazardous Air Pollutants (Hazardous Organic NESHAPS or HON) Rule were published (1994b), replacing the MACT standards.

The HON Rule, promulgated under the 1990 CAAA, states that any facility that satisfies all three of the following criteria is covered by the rule (Jagiella and Kickman 1994):

1) Manufactures as a primary product any of the 385 synthetic organic chemicals listed in Table 1 at the end of Subpart F
2) Uses as a reactant, or manufactures as a product, byproduct, or coproduct one or more of the HAPs listed in Table 2 at the end of Subpart F
3) Is a major source (as per Section 112 of the CAAA).

Allyl chloride, 12DCP, and 13DCP fulfill all three requirements and thus are regulated under HON Rule.

Most research that has used allyl chloride process explores novel optimization techniques (Biegler and Hughes 1983; Ciric and Jia 1994). However, significant research in applying waste minimization by process modification was done with the allyl chloride process by Hopper (Hopper and others 1992). The reactor, both PFR and CSTR, and separation equipment were modeled from basic principles. The goal in their work was to select the reactor and separation design parameters that reduced the waste generation. The drawbacks in their research are:

- They did not model or evaluate the entire process (recycle, absorption, etc.),
- They optimized the parts of the process individually leading to local optimums instead of global optimums,
- Optimal operating parameters were not based on economics.

Therefore there is space and interest (regulations) for exploration of waste minimization by process modification for the allyl chloride process.

ASPEN PLUS™ Modeling

Modeling often utilizes process simulators such as the steady state simulation package ASPEN PLUS™. This software is commercially available from Aspen Technology, Boston, Massachusetts. It provides a variety of preprogrammed unit operations, several thermodynamic equations of state and activity coefficient models, and a number of databases. In addition, it can be linked with the graphical interface, ModelManager™, which allows the user to set up the unit operations graphically and to input the information in series of menu driven screens. It also has optimization, sensitivity, and case study capabilities. For more information concerning other features of this simulator please consult ASPEN PLUS™ Users Guide (Aspen Technology 1988).

Economic Analysis

A process modification can not be implemented unless it is justified economically. Therefore, potential profitability is evaluated by developing a cost model. This cost model can then be used as an objective function for optimization. The result is economically optimum process parameters.

The cost model is developed by associating costs and revenues with the process model. This allows the efficiency of the process to be evaluated based on current market conditions. Some of the basic economic data needed to construct such a model include: product, raw material, and utility prices and environmental costs.

The environmental costs associated with a waste minimization program play a significant role in the economic analysis. Environmental costs are often simply disposal costs, however Freeman (1990) suggests a four tier approach. The first tier, Tier 0 involves the usual costs (process equipment, process materials, direct labor). At this stage, if the project looks to be cost-beneficial then the analysis should be broadened to include Tiers 1-3. Tier 1 includes Tier 0 and adds avoided regulatory costs called hidden costs (monitoring, paperwork, permit requirements). In the third tier, future liabilities costs (remedial action, personal injury, property damage), fines or failures are avoided. Finally, the last tier consists of a more subjective framework in evaluating the less tangible costs (consumer responses, employee relations, corporate image). As the analysis moves from Tier 0 to 3 the certainty of the cost occurrence and the precision of the estimates decreases. However, this method does provide a thorough procedure for environmental cost estimation.

Optimization

In both design and retrofit calculations there are many choices and many decisions to be made. Optimization provides the engineer with an efficient tool that hopefully finds the 'best' option. Ultimately, of course, decision making is still up to the individual's 'engineering judgment.'

Once a problem is defined, mathematics is usually used to find the quantitative solution of the optimization problem. Most optimization problems contain three essential categories (Edgar and Himmelblau 1988):

1) At least one objective function to be optimized (profit function, cost function, etc.)
2) Equality constraints (equations)
3) Inequality constraints (inequalities)

Category 1 is often called the economic model whereas 2 and 3 are usually the model of the process equipment.

A set of values of the variables that satisfies categories 2 and 3 to a specified precision is termed a feasible solution of the optimization problem. A feasible solution that provides the optimal value for the function in category 1 is called the optimal solution.

Optimization is performed on models which generally fall into two categories (Edgar and Himmelblau 1988): those based on physical theory and those based on strictly empirical descriptions (black-box models). Models based on mass and energy balances, thermodynamics, chemical reaction kinetics are in the first category. On the other hand, empirical models are developed from correlations or patterns found in the input and output data of a process.

Optimization provides a powerful tool for selecting a waste minimization strategy. A waste reduction option may typically include several process modifications. Optimization of these source reduction variables will give the optimum operating conditions for the process, and based on the objective function, a cleaner, more economical process.

Regulatory Risk Analysis

Currently, the waste limits imposed on companies for processes are technology based standards. In other words, the technology used in a process must perform so that process effluents do not exceed designated waste levels. However, in the future the EPA will emphasize risk based regulations of waste. Thus, it is imperative that any waste minimization strategy involve regulatory risk analysis. The method by which it could be accomplished and its effect on the waste minimization methodology are described in this section.

Risk is defined as the possibility of suffering harm from a hazard (Cohrssen and Covello 1989). Risk is created by a hazard, however a toxic substance that is hazard to human health is not considered a risk unless humans are exposed to it. A risk agent is a biological organism, chemical substance, radioactive material, or other potentially hazardous substance or activity.

Usually the goal of risk assessment is to determine the risk of a leak or spill on the environment surrounding the plant. It follows a four stage process created by the U.S. Academy of Sciences that includes: hazard identification, exposure assessment, toxicity assessment, and risk characterization (Freeman 1990). In contrast, the intent for incorporating risk into a process modification based waste minimization strategy is to determine a maximum production level that will not pose a risk to the plant's environment. This maximum production level of a byproduct can then be used as a constraint in the optimization routine.

The risk analysis methodology proposed for this research modifies the traditional four stage process to include source reduction. It is broken into a qualitative section and a quantitative section as follows:

Qualitative

1) Hazard identification - which chemicals are important,
2) Exposure assessment - where do the chemicals go, who might be exposed, and how,
3) Toxicity assessment - determining numerical indices of toxicity for computing risk,

Quantitative

4) Risk level determination - maximum acceptable risk,
5) Maximum concentration evaluation - calculate the delivered concentration that causes the risk,
6) Exposure assessment - calculate what original concentration caused the delivered concentration.

In the first section, the traditional risk assessment steps are qualitatively followed in the designated order. Next, the methodology quantitatively follows these same steps in reverse order to back-calculate the maximum allowable waste level. It seeks to determine what quantity of waste produces the minimum acceptable risk as opposed to a risk assessment which calculates the risk caused by a certain amount of waste.

Hazard Identification The purpose of the hazard identification step is to determine which byproducts or unreacted reactants are considered risks to the plant's environment. In addition, all data concerning air, ground water, surface water, and soils and sediments for the contaminants must be collected. Selection of chemicals for assessment is based on the risk they pose, for example (LaGrega and others 1994):

- The most toxic, persistent, and mobile
- The most prevalent in terms of spatial distribution and concentration
- Those involved in the more significant exposures.

Qualitative Exposure Assessment The next qualitative step is to determine who or what (the receptor) might be affected by the contaminants identified in the previous step. It is also important to find out how (exposure route) they will be affected. Some possible exposure routes are: ingestion, dermal contact, and inhalation.

Toxicity Assessment Once the hazardous chemical has been identified and the exposure route to the receptor determined, the toxicity can be defined. The toxicity of a chemical depends on two factors the receptor and the exposure route. It is a mathematical constant that is determined scientifically by (in order of decreasing uncertainty) experimental or clinical human studies, human epidemiological studies, *in vivo* animal bioassays, *in vitro* cell and tissue culture tests, or structure activity relationship analyses (computer modeling). In order to quantify human health risks chemicals are characterized as carcinogenic (those that can cause cancer), non-carcinogenic, or both. Based on this characterization, toxicity values are called either slope factors (SFs for carcinogens) or reference doses (RfDs for non-carcinogens).

Risk Level Determination At this stage, one must determine what level of risk is acceptable. This is often difficult choice since it involves the personal concept of "acceptability". The U.S. EPA uses a range 10^{-4} to 10^{-6} excess lifetime cancer risk for carcinogens and hazard index (HI) of less than 1.0 for non-carcinogens. However, the decision ultimately falls on the shoulders of the public that is affected by the risk.

Maximum Concentration Evaluation The maximum acceptable concentration uses the equations for risk characterization (from the traditional risk assessment method) and back-calculates the chronic daily intake or CDI. Computations are as follows:

for carcinogens

$$CDI = {}^{Risk}\!/_{SF} \tag{1}$$

and for non-carcinogens

$$CDI = HI \times RfD \tag{2}$$

The CDI is also called the administered dose which is concentration that is actually absorbed into the body and causes the risk.

Quantitative Exposure Assessment In this final stage, the chronic daily intake (the concentration that causes risk) must be used to back-calculate the maximum production level of this chemical or chemicals. The first step of this stage is to determine the concentration of the chemical at the exposure point from the administered dose. The generic equation for this calculation is:

$$C = \frac{CDI \times BW \times AT}{CR \times EF \times ED} \tag{3}$$

where

C = concentration at exposure point

BW = body weight

AT = averaging time

CR = contact rate

EF = frequency

ED = exposure duration

Next, the exposure pathway must be used to trace the exposure concentration back to the plant. This often involves the meteorological and/or ground water modeling to determine how the chemical got to the receptor and how that process affected its concentration. This release concentration is then followed back into the plant where maximum waste production level is back-calculated from the mode of disposal or release (e.g. an incinerator efficiency).

Although the preceding description is fairly simple, risk analysis is usually a complicated process involving several iterations. In addition, it contains inherent uncertainty in the toxicity values. However, if the data exists this methodology provides a useful technique for incorporating risk analysis into a waste minimization strategy.

In summary, more stringent environmental laws are pressuring companies to change their environmental policies. Instead of end-of-the-pipe type waste treatment industrial emphasis is now on solutions such as process modification. Due to a current increase in regulatory pressure and an abundance of process information, the allyl chloride process provides an ideal case to illustrate how process modification can be utilized in a waste minimization strategy. Several tools will be used to develop the methodology: ASPEN PLUS™ Modeling, economic analysis, process optimization. In addition, the incorporation of regulatory risk analysis is also explored. Thus, this research demonstrates how a process modification methodology that includes process modeling, selection of source reduction variables, and economic optimization can be used on the allyl chloride process to minimize the waste.

The following chapters are dedicated to a detailed description of the allyl chloride process, the general process modification methodology, and the results and conclusions from applying this methodology.

CHAPTER III

PROCESS DESCRIPTION

Allyl chloride is a colorless liquid with a disagreeable, pungent odor that is only slightly soluble in water. Most allyl chloride is used to produce epichlorohydrin, which is then consumed as the raw material for epoxy resins and glycerol. Shell Development Company discovered the first efficient and economical synthesis method of allyl chloride in the late 1930s (Groll and Hearne 1939). Although World War II delayed the commercialization of this chemistry, the years since 1945 have shown a substantial increase in allyl chloride production. The global production as of 1989-1990 was 500,000 - 600,000 tons/yr with the major producers thought to be Dow Chemical Company (Freeport, TX and Stade, Germany) and Shell Chemical Company (Pernis, Holland and Norca, LA) (Kneupper and Saathoff 1993). As of October 1994 the price of allyl chloride was \$0.78/lb (Chemical Marketing Reporter 1994).

Process Chemistry

Although other methods exist for producing allyl chloride the primary commercial route is by substitutive chlorination of propylene.

$$\underset{\text{propylene}}{CH_2 = CH - CH_3} + Cl_2 \rightarrow \underset{\text{allyl chloride}}{CH_2 = CH - CH_2Cl} + HCl \qquad (4)$$

The reaction occurs at high temperature (570-1100°F) by a free-radical mechanism in which the substitution of an allylic hydrogen is favored over the addition of chlorine to the double bond.

Several byproducts are formed even at optimal reactor conditions. Below 390°F the most significant reaction is the addition of chlorine across the double bond of propylene giving 1,2-dichloropropane (12DCP).

$$\underset{\text{propylene}}{CH_2 = CH - CH_3} + Cl_2 \rightarrow \underset{\text{1,2 - dichloropropane}}{CH_2Cl - CHCl - CH_3} \tag{5}$$

However, above 570°F 12DCP is merely a byproduct and allyl chloride predominates as the product. The byproducts *cis-* and *trans-* 1,3-dichloropropene (13DCP) are produced in the secondary chlorination reaction of allyl chloride.

$$\underset{\text{allyl chloride}}{CH_2 = CH - CH_2Cl} + Cl_2 \rightarrow \underset{\text{1,3 - dichloropropene}}{CHCl = CH - CH_2Cl} + HCl \tag{6}$$

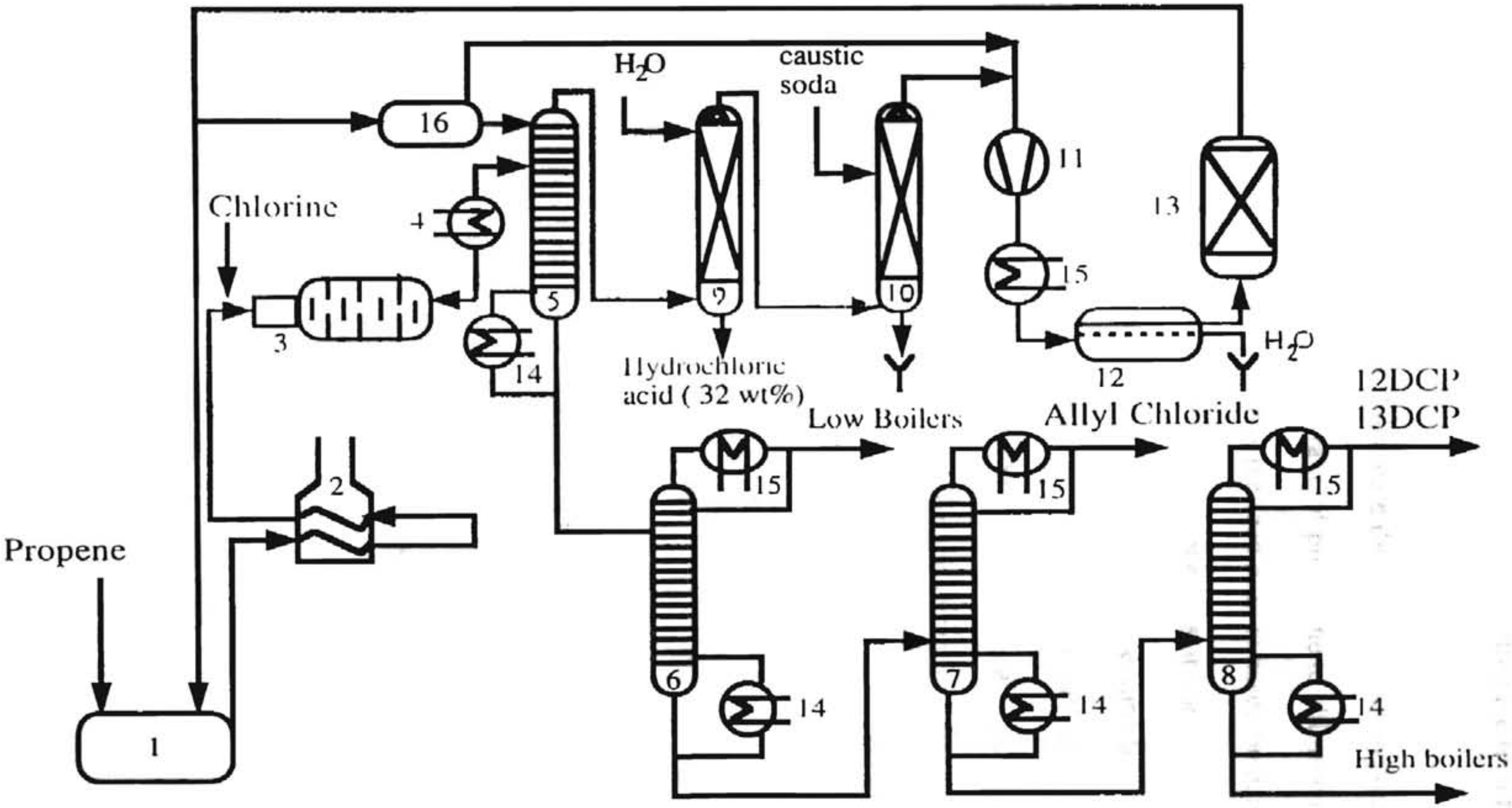
Several other chlorination products are also formed, but because they occur in small amounts they were not considered in this work.

Production Process

The following is a brief description of the allyl chloride process shown in Figure 2. The process can be divided into three steps, synthesis, purification, and recycle. In the synthesis step, allyl chloride and the byproducts are produced in the reactor. These products are then separated into the light ends, allyl chloride, and the heavy ends in the purification section. Finally, the unused propylene is purified and recycled back to the reactor.

Synthesis The most important reaction variables are temperature and propylene/chlorine feed ratio (Krahling and others 1985). Pressure and residence time have relatively little effect on the allyl chloride yield (Fairbairn and others 1947) and the reaction selectivity. However, too long a residence time leads to thermal decomposition of the allyl chloride.

The mixing temperature of the feed must be kept above 480-570°F to avoid the addition reaction (Equation 2). All the reactions are highly exothermic thus most reactors are adiabatic. Industrial reactors show the best yield at a maximum reaction temperature of 930-950°F (Fairbairn and others 1947). Above this temperature spontaneous pyrolysis



1) Storage vessel for liquid propene 2) Evaporator and superheater for propene 3) Reactor 4) Cooler 5) Prefractionator 6) Light-ends column 7) Allyl chloride purification column 8) Dichloropropene column 9) Hydrogen chloride absorber 10) Gas washer 11) Compressor 12) Decanter for removing water 13) Propene dryer 14) Evaporator 15) Condenser 16) Cold propene storage vessel

Figure 2: PFD for Allyl Chloride Process

occurs, causing the formation of soot and high boiling tars (Porter and Rust 1956). The maximum reactor temperature can be obtained by adjusting the feed ratio and the feed temperature of the reactants.

An excess of propylene will decrease the formation of byproducts by acting as a diluent and heat sink. Yet as the feed ratio of propylene to chlorine increases, so does the cost of processing the propylene. Thus the feed ratio is based on economic considerations including the salability of the byproducts. Researchers at Shell Chemical Company have reported that the best feed ratio is 6:1 (Yabroff and Anderson 1951).

Typically, industrial reactors are operated adiabatically, even though higher yield would be possible by isothermal operation. Due to the high reaction velocity and exothermic characteristic of the reaction, the cooling required for isothermal operation would be enormous. Thus, the high costs of cooling usually prohibit the reactor from being operated isothermally.

Even at optimal conditions, small amounts of carbon are produced in the reactor, catalyzing the reaction. Because of a vitreous layer of carbon containing highly chlorinated materials deposits in the reactor, the reactor walls must be cleaned at 4 to 8 week intervals. Usually, this requires the use of two parallel reactor chains.

<u>Purification</u> The reaction products leaving the reactor are then cooled and fed to a prefractionator. The overhead products are primarily hydrogen chloride and unreacted propylene, and the bottom products are chlorinated hydrocarbons.

The bottoms product contains 80% allyl chloride, 3% low boilers, 16% dichlorides (mainly 12DCP and 13DCP), and 1% trichlorides and other heavy boilers (Krahling and others 1985). It is separated with three distillation columns. The first column removes the low boilers in an overhead product, the second produces allyl chloride in the distillate product, and the third separates the dichlorides from the high boilers. Commercial grade allyl chloride is typically available in the United States in purities of about 99.5% (Kneupper and Saathoff 1993).

Recycle The hydrogen chloride is removed from the prefractionator distillate product via absorption with water, forming aqueous commercial grade hydrogen chloride. The propylene leaves the absorber in the vapor stream and is washed with caustic soda to remove hydrogen chloride. It is then compressed to 175 psia and liquefied in a condenser. In the final step, the propylene is dried in an adsorber and recycled back to the propylene feed storage tank.

The following chapters describe the general methodology, the results from the application of this methodology, and the conclusions and recommendations developed through this research.

CHAPTER IV

GENERAL METHODOLOGY

This process modification for waste minimization research follows a three step approach. First, the allyl chloride process was modeled with the simulation software, ASPEN PLUS™. The next phase involved identification of source reduction variables (SRVs) that would yield possible waste reduction options (WROs). In addition, the acceptable range for these variables was also determined, creating an 'experimental grid' for optimization. In the last step, economics were associated with the process model so that the optimal values of the source reduction variables in the grid could be calculated by ASPEN PLUS™.

Process Model

The process model is the first step in implementing waste minimization strategies. In order to determine which process modifications are feasible (technically economically, or environmentally), one must evaluate the options on a model of the process. Although this can be accomplished through small scale laboratory experimentation or pilot plant operation, simulation of the model is safer and less expensive. Simulation of the process model also allows one to explore the feasibility of any process modification.

The first phase in the modeling process was to set up a skeleton of the process diagram on ModelManager™. First, the feed streams, heaters/coolers, reactor, and separation equipment were modeled. Initially, simple models and shortcut methods were used to avoid problems and make the simulation easy to debug. Complex models require more information, which at the initial modeling phase was not available. Use of rigorous models means several parameters must be guessed or estimated, which leads to numerous time consuming iterations to achieve convergence. However, simple models tend to converge easier since they are usually set-up for design purposes in which little information is required.

When all the syntax errors had been removed from the initial simulation, more units were added to the simulation. At this stage, the recycle section and the user specified blocks were modeled. Furthermore, the shortcut methods were replaced with rigorous techniques believed to yield more robust results.

Once a stable model (converged without problems) was established, the model's sensitivity was tested. One way to examine the model's accuracy is to alter variables and note if the results display similar trends as published results. For instance, if it is known that above a certain temperature one reaction dominates, increase the reactor temperature and monitor the trend in product formation. Once confidence was established in the model, the second stage of the research was pursued.

Determination of Source Reduction Variables and Ranges

The objective is to generate a comprehensive list of source reduction variables (SRVs) that offer a real potential for eliminating or minimizing wastes and reducing costs. However, since this process is simulated the possible feasibility of these variables is not a big concern. A SRV is a variable, that if changed is believed to reduce the waste. These variables include but are not restricted to: process variables (reactor temperature), operational variables (adiabatic vs isothermal), or equipment substitution (PFR vs CSTR). Although possible source reduction variables can be identified in the literature, this portion of the work often requires engineering creativity.

A waste reduction option (WRO) is the resulting process once these modifications have been incorporated into the process model. The main steps in generating WROs are as follows (Shyamkumar 1994):

1) Search the literature for process variables known to affect the process
2) Analyze simulation for sensitivity to process variables

3) Target the significant process variables

4) Develop waste reduction options based on these significant variables

5) Incorporate into the process model additional constraints corresponding to the alternatives.

For each process variable deemed feasible a source reduction variables, a range was determined from the sensitivity study. If the calculations showed potential for waste reduction outside this range, then the range was extended. From this range of variables an 'experimental' grid was developed to explore the waste reduction potential of several of the variables simultaneously.

Economic Optimization

Although the SRVs could be optimized to find a WRO that produces the lowest waste, this operating scheme might not always be economical. For instance, an WRO might reduce the waste, but require that the company operate with a negative cash flow. Since this is clearly unacceptable, economics must be linked with the objective function that optimizes the simulation.

An objective function in terms of preliminary profit was developed which incorporates both the revenues and costs of the process.

$$\begin{matrix} \textit{Preliminary} \\ \textit{Profit} \end{matrix} = \begin{matrix} \textit{Product} \\ \textit{Revenue} \end{matrix} - \begin{matrix} \textit{Raw Material} \\ \textit{Costs} \end{matrix} - \begin{matrix} \textit{Utility} \\ \textit{Costs} \end{matrix} - \begin{matrix} \textit{Waste Treatment} \\ \textit{Costs} \end{matrix} \tag{7}$$

The revenues and costs in Equation (7) can be further broken down as follows:

$$\textit{Product Revenue} = \textit{Allyl Chloride} + \textit{HCl} \tag{8}$$

$$\textit{Raw Material Cost} = \textit{Propylene} + \textit{Chlorine} \tag{9}$$

$$\textit{Utility Cost} = \textit{Fuel} + \textit{Electricity} + \textit{Cooling Water} \tag{10}$$

$$\textit{Waste Treatment Cost} = \textit{12DCP} + \textit{13DCP} + \textit{Unused Chlorine} \tag{11}$$

The fixed costs that any economic analysis will have such as labor, maintenance, etc. were not included in the objective function since they will not be significantly changed by the process modifications. Since this research was done in the design mode (as opposed to the retrofit mode), no base case process existed and thus the capital costs were also not considered.

The basis for comparison of each optimized case was a constant allyl chloride product flowrate. For each grid analyzed, ASPEN PLUS™ was used to find the maximum value (maximum profit) of the objective function. In other words, the simulator's optimization routine changed the SRVs to find the optimal value of the SRVs that yield the highest profit.

CHAPTER V

PROCESS MODEL

A process model provides an economical method to evaluate waste minimization through process modification of the base case. Optimization of this model can give insight into the SRVs for an actual full scale facility. This chapter describes the process model developed for the production of allyl chloride from propylene.

Process Characterization

In the first phase, a skeleton of the process diagram with a plug flow reactor (PFR) was developed on ModelManager™ by modeling the feed streams, heaters/coolers, reactor, and separation equipment. The propylene feed was determined by back-calculation from actual estimated production values (Kneupper and Saathoff 1993). The heaters and coolers were modeled as HEATER blocks, which only required outlet temperature specifications.

Initially, the reactor was specified as a PFR (RPLUG block) in order to validate the kinetic data provided by (Biegler and Hughes 1983). The activation energy and pre-exponential factor were based on partial pressure concentrations; however, ASPEN PLUS™ requires that these kinetic data be in terms of mass concentration. Thus, the kinetic data were replotted in terms of mass concentration, and a new activation energy and pre-exponential factor were determined (Smith 1981).

To avoid problems and to make the simulation easy to debug, shortcut distillation blocks (DSTWU) were used for the distillation columns. The DSTWU block uses Winn's method to estimate the minimum number of stages, Underwood's method to estimate the minimum reflux ratio, and Gilliland's correlation to estimate the required reflux ratio for specified number of stages or the required number of stages for a specified reflux ratio.

Once all the errors had been removed from the initial simulation, more units were added to complete the simulation. The results from the shortcut distillation blocks, number of stages and reflux ratio, were used in a more rigorous distillation model (RADFRAC). When first implemented the RADFRAC blocks did not converge. This problem was alleviated by altering the reflux ratio and distillate vapor fraction. The process flow diagram for the complete simulation is shown in Figure 3, and unit operations and their corresponding ASPEN PLUS™ models is shown in Table 2.

TABLE 2: UNIT OPERATIONS AND THEIR ASPEN PLUS™ MODELS

Unit Operation	ASPEN PLUS™ Model
Reactors - plug flow	RPLUG
continuous-flow stirred-tank	RCSTR
Prefractionator	RADFRAC
Allyl Chloride Purification Column	RADFRAC
Absorber	RADFRAC
Propylene Feed Preheater	HEATER
Product Cooler	HEATER
Dryer	SEP
Compressor	COMP

When process modifications are performed on the process model they will cause changes in the composition and flow through the distillation columns. To ensure that the columns operated correctly, SPEC statements within the RADFRAC blocks were used to vary the distillate/feed ratio to give 99% product recovery in the prefractionator and 99.5% purity in the allyl chloride purification column (Kneupper and Saathoff 1993).

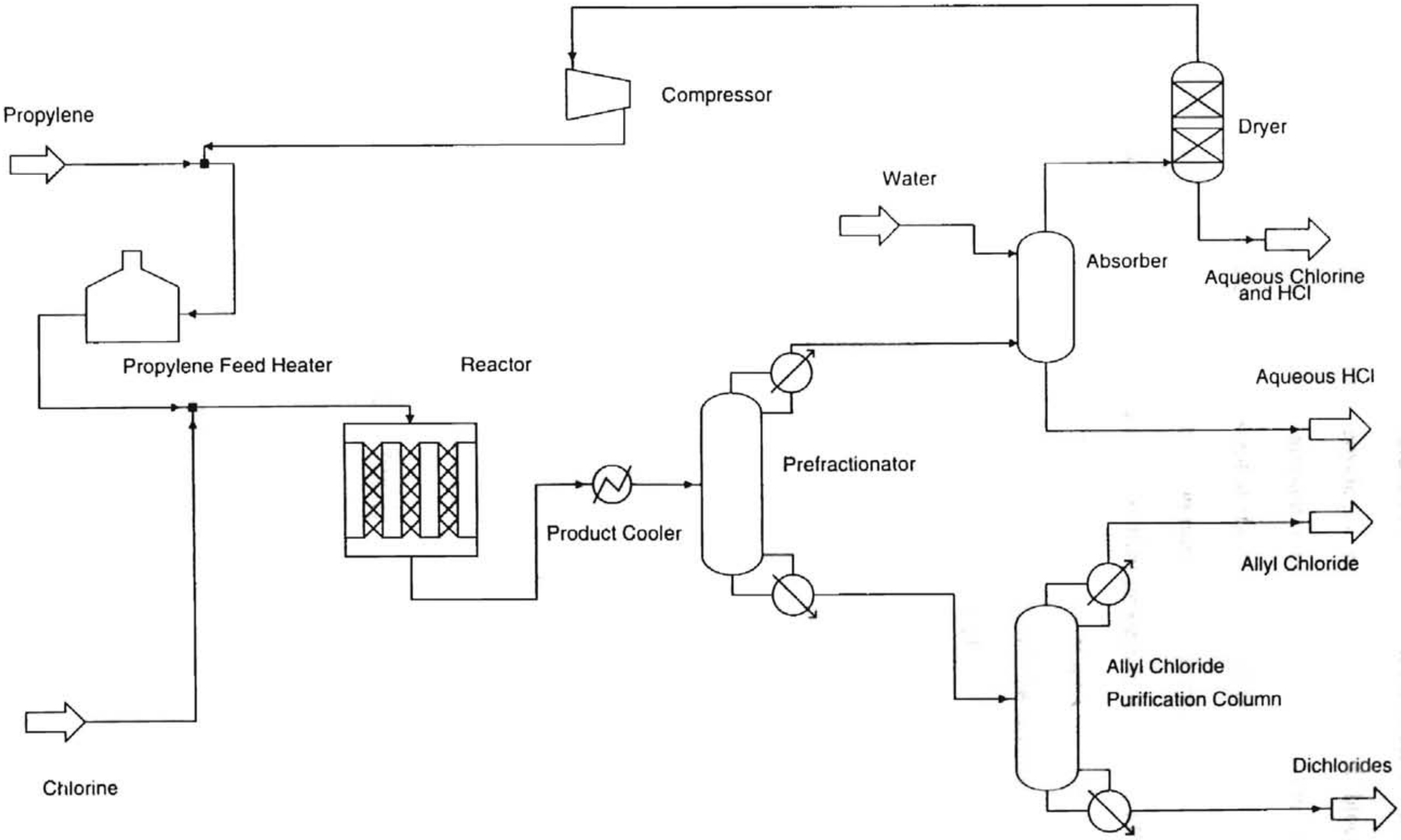


Figure 3: ASPEN PLUS Flowsheet of the Allyl Chloride Process

The second phase of modeling also included the incorporation of the compressor and recycle portion of the process. For the recycle section, a DESIGN-SPEC block was used to vary the propylene feed based on the amount of recycled propylene. This addition to the model kept the feed to the reactor constant at 1000 lbmol/hr of propylene.

Since it was also necessary to evaluate a continuous-flow stirred-tank reactor (CSTR), a new input file was created. It had the identical process units as the PFR simulation with the exception of the RCSTR block used to model the CSTR. In addition, the DESIGN-SPEC used to keep the residence time constant had to be slightly altered to accommodate the available access variables for the RCSTR block.

For comparison purposes, four cases (adiabatic PFR, isothermal PFR, adiabatic CSTR, and isothermal CSTR) were run with a constant propylene to chlorine feed ratio of 6, constant reactor temperature of 950°F, and a constant reactor pressure of 45 psia. From the results in Table 3 it can be seen that the adiabatic PFR produces the highest amount of allyl chloride. However, it also has a production rate of 12DCP that is nearly four times higher than the other three cases and a production rate of 13DCP that is lower than the other three cases. These results were used to provide an understanding of how the reactor type and reactor operation affected the product and byproduct flowrates.

TABLE 3: PRODUCT FLOWRATES AT CONSTANT FEED RATIO, REACTOR TEMPERATURE, AND REACTOR PRESSURE

Variable	Adiabatic PFR	Isothermal PFR	Adiabatic CSTR	Isothermal CSTR
Allyl chloride (lb/hr)	5772	5054	3778	3745
Aq. hydrogen chloride (lb/hr)	16292	18024	17922	17915
1,2-dichloropropane (lb/hr)	2692	987	906	907
1,3-dichloropropene (lb/hr)	3717	5044	5959	5956
Unused Chlorine (lb/hr)	2.71×10^{-3}	0.00	108	112

Sensitivity Analyses

To determine the validity of the model, sensitivity analyses were performed with ASPEN PLUS™ using the SENSITIVITY block. The purpose of these studies was to determine if the model was affected by changes in variables in similar manner as the actual process cited in the literature.

Reactor Feed Temperature Similar to the literature (Krahling and others 1985), the model predicts that below 400°F propylene reacts with chlorine mainly by the addition reaction to form the byproduct 12DCP. It also gives the highest yields of allyl chloride at around 950°F, which is typical for industrial reactors.

Reactor Feed Ratio As expected the formation of byproducts decreases with increasing excess of propylene. In agreement with Hopper and others (1992) this model was found to produce a minimum amount of byproduct at a feed ratio of propylene to chlorine of approximately 6.

Reactor Pressure The sensitivity studies also showed that the feed pressure could be varied between approximately 25-50 psia. The reactor produced slightly higher yields at 30 psia.

Residence Time In agreement with the literature in which complete conversion occurred in 1-4 seconds (Kneupper and Saathoff 1993; Krahling and others 1985), the simulated models residence time was kept constant at 4 seconds. Complete conversion was achieved with unreacted chlorine flowrate of 1×10^{-2} mol/hr.

Process Modeling Tool

The allyl chloride process was modeled using the steady state simulation package ASPEN PLUS™ version 8.5-4. It provides a variety of preprogrammed unit operations, several thermodynamic equations of state and activity coefficient models, and a number of databases. In addition, it can be linked with the graphical interface, ModelManager™, which allows the user to set up the unit operations graphically and to input the information in series of menu driven screens. For evaluation purposes, ASPEN PLUS™ has optimization, sensitivity, and case study blocks. These blocks allow the user to evaluate the model numerous times during one simulation run.

The main database used for the simulations in this research was the Design Institute of Physical Property Research (DIPPR) database. However, 1,3-dichloropropene (13DCP) is not in the database, so many of its properties were estimated by ASPEN PLUS™. Since the literature (Hopper and others 1992) provided the boiling point and ideal gas enthalpies, they were not estimated. ASPEN PLUS™ estimated the properties of 13DCP by using a user provided structure and the boiling point.

CHAPTER VI

SOURCE REDUCTION VARIABLES

A SRV is a variable, that if changed, is believed to reduce the waste. The objective is to generate a comprehensive list of options that offer a real potential for eliminating or minimizing wastes and reducing costs. Probable process modification variables can be found in the literature or through sensitivity analyses. This chapter presents the source reduction variables used and the ranges over which they were applied.

SRVs from Literature

Several sources were found in the literature (Kneupper and Saathoff 1993; Krahling and others 1985) that provided an abundance of information describing the effects of different variables on the process. Table 4 lists the source reduction variables used in this work.

TABLE 4: SOURCE REDUCTION VARIABLES AND RANGES

Source Reduction Options	Range
Propylene/chlorine feed ratio	1 to 12
Reactor feed temperature	400 to 800 °F
Reactor pressure	25 to 50 psia
Reactor classification	PFR and CSTR
Reactor operation	Adiabatic and Isothermal

The two variables that had the most effect on the amount of byproduct formed are the reactor feed temperature and propylene chlorine feed ratio. Reactor pressure was added to the list of source reduction variables, even though in previous studies reactor pressure had not significantly affected the byproduct formation.

SRVs' Ranges

For each SRV, a range was determined from the sensitivity study. If the calculations showed potential for waste reduction outside this range, then the range was extended. The ranges for each SRV are shown in Table 4. From this range of variables an 'experimental' grid was developed to explore the waste reduction potential of several of the variables.

A grid was developed that varied the feed ratio, feed temperature, and reactor pressure for each reactor classification and operation. Thus there were four grids evaluated: Adiabatic PFR, Isothermal PFR, Adiabatic CSTR, and Isothermal CSTR.

The ranges for each of the four grids varied according to the results of the sensitivity studies. For some grids a reactor pressure of 25 psia caused calculation errors and for others it would not. Despite these differences the ranges did not extend outside those listed in Table 4.

CHAPTER VII

OPTIMIZATION AND ECONOMICS

Optimization provides a useful tool for evaluating a multiple variable problem that leads to several alternatives. Although the process variables could be optimized to find a waste reduction option that produces the lowest waste output, that solution might not always be economical. Thus, economic objective function must be linked with the simulation. This chapter details the economics that were applied to the allyl chloride process to develop the objective function and the optimization of this objective function with ASPEN PLUS™.

Economic Data

The economics that were associated with the process parameters to develop the objective function were gathered from many sources. The quoted industrial utility rates given by Oklahoma Natural Gas (fuel gas) and the City of Stillwater (water and electricity) are listed in Table 5. The cost of the fuel gas and the electricity were converted from \$/1000 scf to \$/MMBTU (heating value of gas 1000 BTU/scf) and \$/KW-hr to \$/hp-hr, respectively because the heat and power required in the simulation results were listed in BTU and hp, respectively.

All the heating in the process was assumed to be provided by fuel gas, and all the cooling was assumed to be done with cooling water. These assumptions avoided the problem of heat integration. Considering this model is not based on an actual working process, it is very difficult to determine the availability of outside cooling and heating sources within the plant. Further, the utility costs are simplified because only one type of cooling and heating medium are used. This assumption is valid since the goal of the optimization is to obtain a rough sketch of the efficiency and profitability of the process modifications.

TABLE 5: UTILITY COSTS

Utility	Cost As Quoted
Fuel Gas	\$3.399/1000 scf
Water	First 15 Mgal - \$2.25/Mgal. 15 to 300 Mgal - \$1.85/Mgal Above 300 Mgal - \$1.65/Mgal.
Electricity	\$0.0714/KW-hr

Mgal = 1000 gallons

The quoted raw material costs and product prices shown in Table 6, were found in the Chemical Marketing Reporter (1994). Hydrogen chloride is considered a product, since the allyl chloride process is known to produce it in aqueous, 32 wt%, commercial grade quantities.

TABLE 6: CHEMICAL PRICES

Chemical	Price As Quoted
Raw Materials	
Chlorine	\$225/short ton
Propylene	\$0.165/lb
Products	
Allyl chloride	\$0.78/lb
Hydrogen chloride	\$300/ton

Source: Chemical Marketing Reporter - October 17, 1994

The wastes produced in the allyl chloride process are the 1,2-dichloropropane (12DCP), 1,3-dichloropropane (13DCP), and the unused chlorine. The costs for waste treatment company to dispose of the chlorinated hydrocarbons by fuel blending and reclamation of the chlorine are shown in Table 7 (Fox 1994). The 1,3-dichloropropene could be considered a product due to its use as a fertilizer. However, since the sale price was not readily available, it was considered a waste. This assumption gives this study a more conservative approach by penalizing the objective function for an undesired byproduct and forcing it toward the desired product, allyl chloride.

TABLE 7: WASTE TREATMENT COSTS

Waste	Cost As Quoted	Cost ($/lb)
1,2-dichloropropane	$145/drum	0.33
1,3-dichloropropene	$145/drum	0.33
Chlorine	$400/drum	0.68

Source: Personal communication Greg Fox

Economic Optimization

For each of the four cases (adiabatic PFR, isothermal PFR, adiabatic CSTR, and isothermal CSTR), the propylene feed temperature, feed ratio, and reactor pressure were varied. The optimal values (those that yield the highest preliminary profit) for each case are listed in Table 8. Each case was evaluated based on a constant reactor residence time of 4 seconds and a constant production rate of allyl chloride.

The largest value of preliminary profit is obtained by operating the reactor as an adiabatic plug flow reactor. These results agree with industry in that most reactors are usually adiabatic plug flow reactors. The amount of cooling required to operate isothermally is often difficult to achieve due to the high reaction velocity.

Optimal operation of both the adiabatic and isothermal continuous-flow stirred-tank reactors supplied a lower preliminary profit than the adiabatic PFR. This lower profit was mainly due higher yield of the 13DCP waste product.

TABLE 8: ECONOMIC OPTIMIZATION RESULTS

Variable	Adiabatic PFR	Isothermal PFR	Adiabatic CSTR	Isothermal CSTR
Source Reduction Variables				
Propylene Feed Temperature (°F)	709	788	588	500
Reactant Feed Ratio (C_3H_6/Cl_2)	7.5	4.1	8.3	7.8
Reactor Pressure (psia)	39.8	46.1	50	50
Products & Byproducts				
Allyl chloride (lb/hr)	5219	5219	5219	5219
Aq. hydrogen chloride (lb/hr)	12966	13478	14186	14624
1,2-dichloropropane (lb/hr)	2115	2965	2100	2164
1,3-dichloropropene (lb/hr)	2509	2720	3102	3277
Unused chlorine (lb/hr)	0.00	0.00	1.00	1.00
Economics				
Revenue ($/hr)	6014	6090	6196	6261
Waste material costs ($/hr)	1522	1871	1713	1792
Raw material costs ($/hr)	1857	2026	2015	2070
Utilities costs ($/hr)	239	154	258	255
Optimal Preliminary Profit ($/hr)	2394	2037	2210	2144

The utilities costs for each of the four cases did not have much effect on the preliminary profit. They remained fairly constant at around $250/hr except for the isothermal PFR. In a more rigorous approach to the economics, the utility costs would have a greater impact on the profit since they would include all the utilities consumed at the facility including instrument air, electricity and additional utilities of auxiliary equipment.

The waste treatment costs for the adiabatic PFR were significantly lower than they were for the other three cases. These higher waste costs give the isothermal PFR the lowest ratio of revenue to waste costs (3.25). Even though the two CSTR cases have a high revenue, they have a lower revenue to waste cost ratio (3.62 and 3.50) than the adiabatic PFR (3.95). Evaluating the revenue to waste cost ratio provides useful insight into the degree that wastes were penalized in the objective function. However, it is not a valid method to choose which way to operate the process since the objective function was based on maximizing preliminary profit.

Reactor Pressure Optimal reactor pressures differed based on reactor type. Both CSTRs produced the highest profit at 50 psia. In contrast, the optimal pressure for the PFRs were less than 50 psia, varying from 40 psia for the adiabatic case to 46 psia for the isothermal case. Sensitivity analysis showed that the pressure had little effect on the yield or distribution of the products. Normally, this pressure is set by the pressure drop of the propylene circulation system of the plant.

Reactant Feed Ratio For each case, the propylene feed was kept constant at 1000 lbmol/hr while the chlorine was varied between 83.3 and 1000 lbmol/hr (feed ratio 12 to 1). Table 8 shows that the reactant feed ratio of propylene to chlorine varied from 4 to almost 9. As one would expect, there exists a direct correlation between the feed ratio and the product formation. As the feed ratio decreases (more chlorine is reacted), more products and byproducts are formed.

Reactor Temperature With the exception of the isothermal PFR, the reactors have similar average/operating temperatures (see Table 9). The maximum reactor temperature for the adiabatic PFR was close to the temperature suggested for industrial reactors (Krahling and others 1985).

Therefore, if allyl chloride was being produced with an adiabatic plug flow reactor, the economically optimal waste minimization strategy would be to adjust the propylene feed temperature to the reactor to 682°F to achieve a maximum outlet or ultimate temperature of 920°F reactor.

TABLE 9: REACTOR TEMPERATURES

Reactor Temperature	Adiabatic PFR	Isothermal PFR	Adiabatic CSTR	Isothermal CSTR
Inlet (°F)	682	737	568	481
Outlet (°F)	920	737	792	791
Average or Operating (°F)	801	737	792	791

Sensitivity of Waste Costs

In the near future, more stringent environmental regulations will cause waste treatment and disposal costs to rise. For this reason, this research pursued the effects that increasing the waste treatment costs will have on the optimal operating parameters. In other words, the waste costs in the objective function were increased and new optimal operating parameters were determined.

The isothermal plug flow reactor was used to study the changes that occurred in the preliminary profit, propylene feed temperature, propylene to chlorine feed ratio, and the reactor pressure when the waste costs were increased by 20%, 40%, 60%, and 80% of the original waste costs. In addition, the variation of the optimal reactant, and waste material flowrates were determined with respect to the increasing waste costs.

As would be expected and can be seen in Figure 4, the preliminary profit decreases with increased waste costs. From an initial point of \$2037/hr, it drops down linearly to \$1652/hr when the waste costs are increased by 80%. The lower preliminary profit is also a result of optimally lower use of the reactants (see Figure 5) which, in turn, produces less waste products, 12DCP and 13DCP (see Figure 6). Since less chlorine is being used and the actual propylene (recycled propylene + fresh propylene) fed to the reactor is constant, feed ratio increases (see Figure 7).

To keep a constant reactor temperature with decreasing feed ratio ordinarily means that the propylene feed temperature would have to decrease. However, as Figure 8 shows,

Figure 4: Preliminary Profit versus Increased Waste Costs

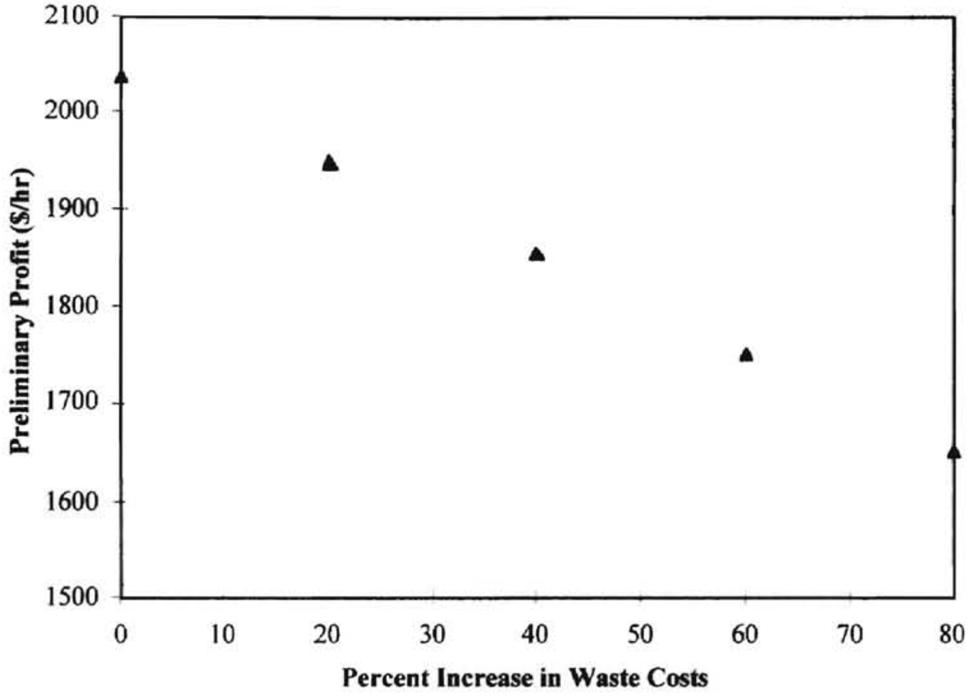


Figure 5: Optimal Reactant Flowrate versus Increased Waste Costs

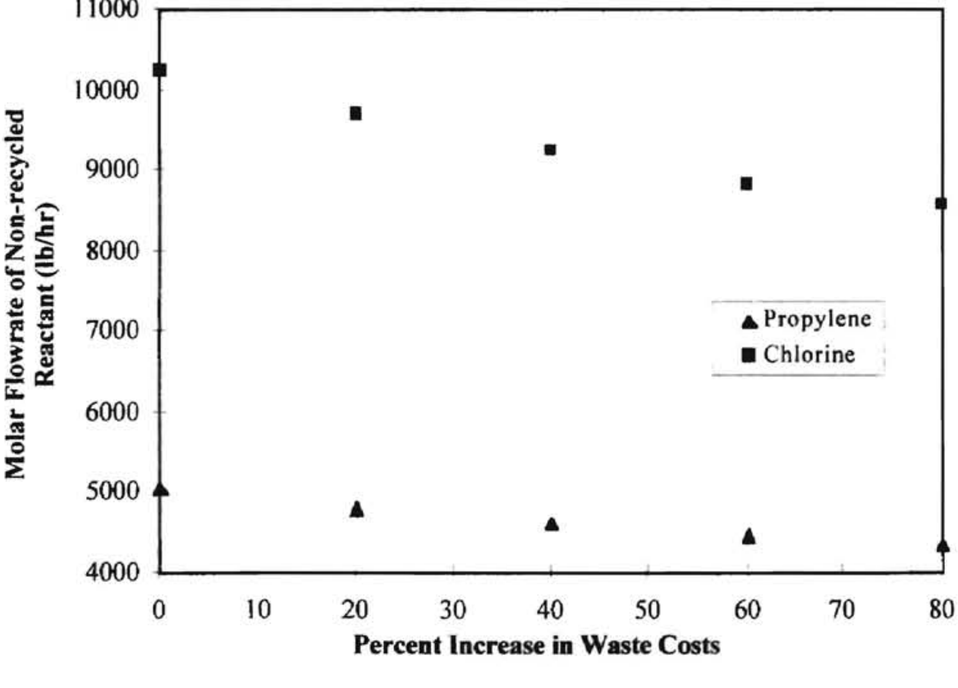


Figure 6: Waste Production Rate versus Increased Waste Costs

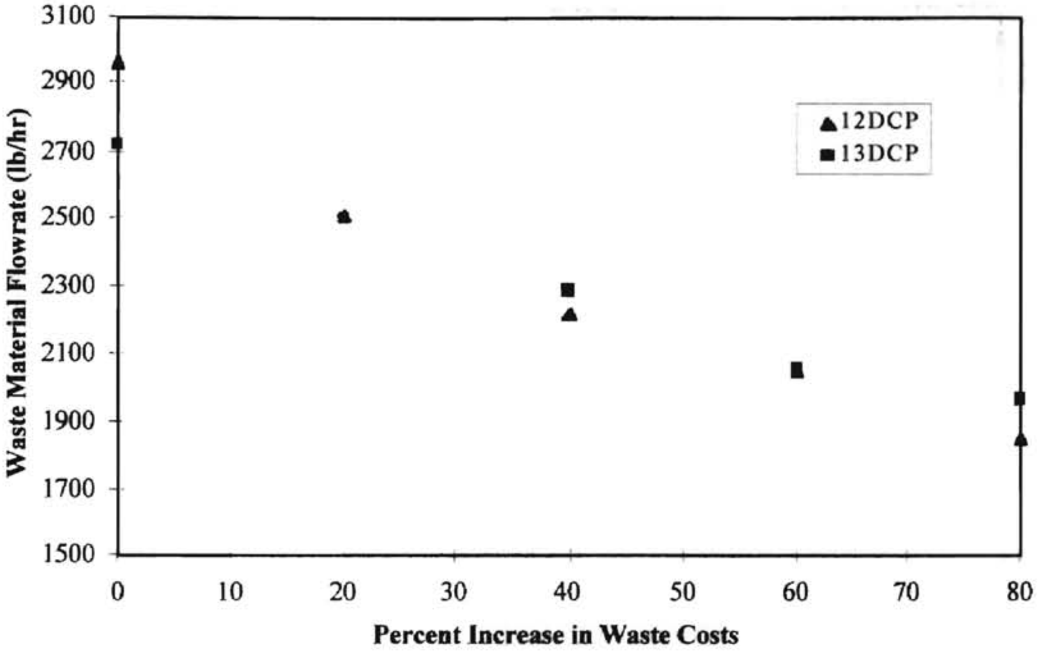


Figure 7: Feed Ratio versus Increased Waste Costs

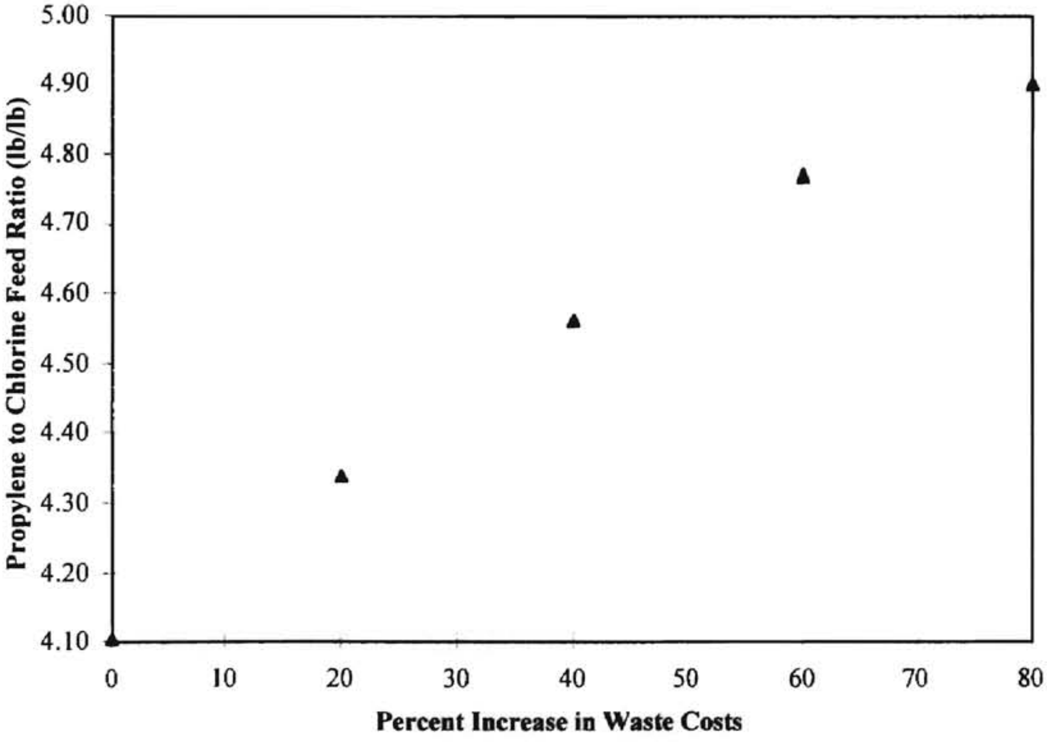
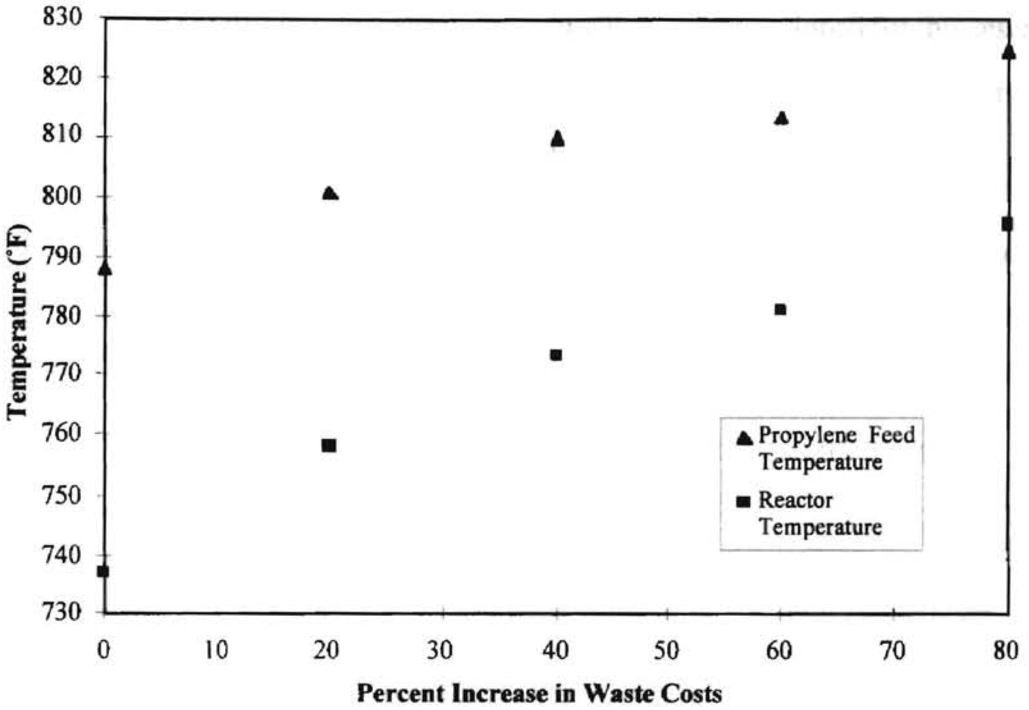


Figure 8: Propylene Feed and Reactor Temperature versus Increased Waste Costs



the reactor temperature is increasing and thus the propylene feed temperature must also increase (see Figure 9 for PFD).

The optimal reactor pressure was not found to exhibit any trends related to the increased waste costs. The reactor pressure remained in the range of 46-50 psia for all five cases. Lack of effect of reactor pressure on the optimum is in accordance with the previous sensitivity studies and published literature.

Regulatory Risk Analysis

In the future, risk based regulations will likely replace the current technology based standards. Thus, it is imperative that any waste minimization strategy involve regulatory risk analysis. Since information concerning location of the plant and its potential damage to its environment is not available, a complete quantitative risk analysis could not be performed. However, the methodology was partially quantitatively applied to show how risk analysis can be incorporated into process modification based waste minimization strategy to determine a maximum waste production level.

As described earlier in Chapter 2, the methodology developed for this research uses a six step approach that is broken into a qualitative section and a quantitative section. The second section was addressed quantitatively due to the limited information.

Hazard Identification The two byproducts, 1,2-dichloropropane and 1,3-dichloropropene, are the wastes that pose the most significant risk. Since they are the waste products, they will have to be disposed of either at the plant or somewhere else. If one assumes the chemicals are disposed of by incineration at the plant site, the possibility of a risk is posed to the plant's environment.

Qualitative Exposure Assessment At this stage the source, transport mechanism, and exposure route must be determined. The source is the incinerator, which through combustion of the chlorinated hydrocarbons releases hydrogen chloride (HCl) and chlorine (Cl_2). The hazardous chemicals are then transported via the air to the population (the receptors) that live near the facility. The obvious exposure route is inhalation. However, the receptors can also be exposed by ingestion (faucet water) or dermal contact (shower water) if the released hazard gets into a drinking water supply, such as a lake.

Toxicity Assessment In defining the toxicity of the chemicals, one must determine the numerical indices of toxicity. First the hazardous chemicals must be classified in terms of carcinogenicity. Neither HCl nor Cl_2 has been classified as a carcinogen. Several sources exist for toxicity data but perhaps the most used is U.S. EPA's Integrated Risk Information Systems (IRIS). The toxicity data for chlorine and hydrogen chloride is shown in Table 10.

Risk Level Determination As mentioned earlier, the departure point set for the hazard index (HI) by the EPA for non-carcinogens is 1.0. Although this is a good number to start the quantitative analysis, selection of an acceptable risk level depends on public opinion and as such will involve much discussion through public meetings, poles, and interviews.

TABLE 10: TOXICITY DATA

Chemical	Oral RfD (mg/kg·day)	Inhalation RfD (mg/kg·day)
Chlorine	no data	pending
Hydrogen chloride	no data	2.00×10^{-3}

Maximum Concentration Evaluation Given the hazard index and inhalation RfD for HCl determined in the previous two steps, the chronic daily intake is calculated using Equation (2).

$$CDI = HI \times RfD = 1 \times 2.00 \times 10^{-3} = 2.00 \times 10^{-3} \text{ mg / kg} \cdot \text{day} \qquad (12)$$

This number provides a measure of the administered dose or the dose that is inhaled.

Quantitative Exposure Assessment Based on the chronic daily intake of a non-carcinogen for an adult the following values for Equation (3) will be used:

CDI = 2.00×10^{-3} mg/kg·day

BW = 70 kg (average body weight for an adult)

ED = 30 years (chronic exposure to non carcinogens)

CR = 0.83 m3/hour x 24 hours/day = 19.92 m3·day (based on the average breathing rate for adult males)

EF = 365 days

AT = 30 years x 365 days = 10,950 days·years

These values are then used to calculate the exposure point concentration.

$$C = \frac{CDI \times BW \times AT}{CR \times EF \times ED} = \frac{(2 \times 10^{-3}) \times 70 \times 10,950}{19.92 \times 365 \times 30} = 7.03 \times 10^{-3} \text{ mg / m}^3 \qquad (13)$$

Unfortunately, the last few steps can not be completed quantitatively due to the lack of data on the plant location, meteorology, and vicinity of possible exposed population. These last two steps are

- Tracing the exposure pathway back to the source, which means determining the weather patterns, the hazardous chemicals dissipation in the air, and the distance and direction of the receptor from the source.
- Follow the release concentration back into the plant to back-calculate the maximum byproduct production rate through the use of the incinerator efficiency.

Although the preceding description is fairly simple, risk analysis is usually a complicated process involving several iterations. In addition, it contains inherent uncertainty in the toxicity values. However, if the data exists this methodology provides a useful straight-forward technique for incorporating risk analysis into a waste minimization strategy.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

The objective of this research was to show that source reduction through process modification is a viable technique to minimize process waste. To accomplish this goal, the allyl chloride process was studied. The approach involved three steps: process modeling, selection of source reduction variables and their ranges, and optimization of an economic objective function. Through this work a general methodology was developed for the application of source reduction to process modeling. The following is a list of conclusions determined through this research.

1) The process simulator ASPEN PLUS™ was successfully used to develop a working model of the allyl chloride process that produced good results (similar to published results).
2) ASPEN PLUS™ was found to be a flexible tool through the use of sensitivity analyses and optimization studies.
3) Through the sensitivity analysis of the model it was concluded that the SRVs were: reactor feed temperature, feed ratio, reactor pressure, reactor type (PFR or CSTR), and reactor operation (adiabatic or isothermal).
4) The adiabatic plug flow reactor produces the highest value of preliminary profit and thus can be considered the most environmentally and economically feasible mode of operation.
5) The ratio of revenue to waste costs is the highest for the adiabatic PFR and the lowest for the isothermal PFR.

6) The preliminary profit decreases with increasing waste costs due to decrease in raw material use and product and byproduct formation.

7) Lower raw material use causes increase in the optimal feed ratio with increasing waste costs.

8) When the waste treatment costs are increased the optimal operating temperature of the reactor increases which directs the kinetics toward a lower production rate of the waste products.

9) The general methodology has the flexibility to incorporate regulatory risk as optimization constraint for the maximum production level of a byproduct.

10) The general methodology of process modeling, selection of SRVs and ranges, and optimization of the SRVs was successfully implemented to determine process modifications that yielded a environmentally and economically sound operating parameters for the allyl chloride process. The methodology provided a flexible tool that can provide structure for process modification based waste minimization strategies.

11) In contrast to the work done by Hopper and others (1992) on waste minimization with the allyl chloride process, this research uses a process modification based waste minimization strategy that finds a optimum for a preliminary economic model. Thus waste reduction is no longer based on the least possible waste, but instead is based on the least possible economically feasible waste.

The primary recommendations for future work are:

1) Implement other process modification variables
    a. Reactor Schemes
        i. Fluidized bed reactor
        ii. Cascade reactors
            - Chlorine distributed among several reactors

        - Charge only first reactor with preheated propylene and chlorine; add liquid propene and gaseous chlorine to other reactors
    b. Alternative chemistries
        i. Catalytic chlorination - use tellurium containing catalysts, main byproduct is isopropyl chloride
        ii. Dehydrochlorination 12DCP - main byproduct monochloropropenes
        iii. Oxychlorination - uses catalyst to convert hydrogen chloride and propylene or propane to allyl chloride
2) Improvements in the process model
    a. Get actual process information from an industrial producer of allyl chloride
    b. Incorporate heat integration
3) Develop a more complete costing model with the addition of:
    a. Fixed costs
    b. Capital costs
    c. More complex approach to waste costs
        i. hidden costs (monitoring, paperwork, permit requirements)
        ii. future liabilities costs (remedial action, personal injury, property damage)
        iii. less tangible costs (consumer responses, employee relations, corporate image)
4) Gather information on actual operating allyl chloride plant that can be used to quantitatively complete the application of regulatory risk in this methodology
5) Perform more sensitivity studies
    a. Waste costs for the adiabatic plug flow reactor
    b. Chemical prices
    c. Utilities costs

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APPENDICES

APPENDIX A

ASPEN PLUS™ INPUT FILES

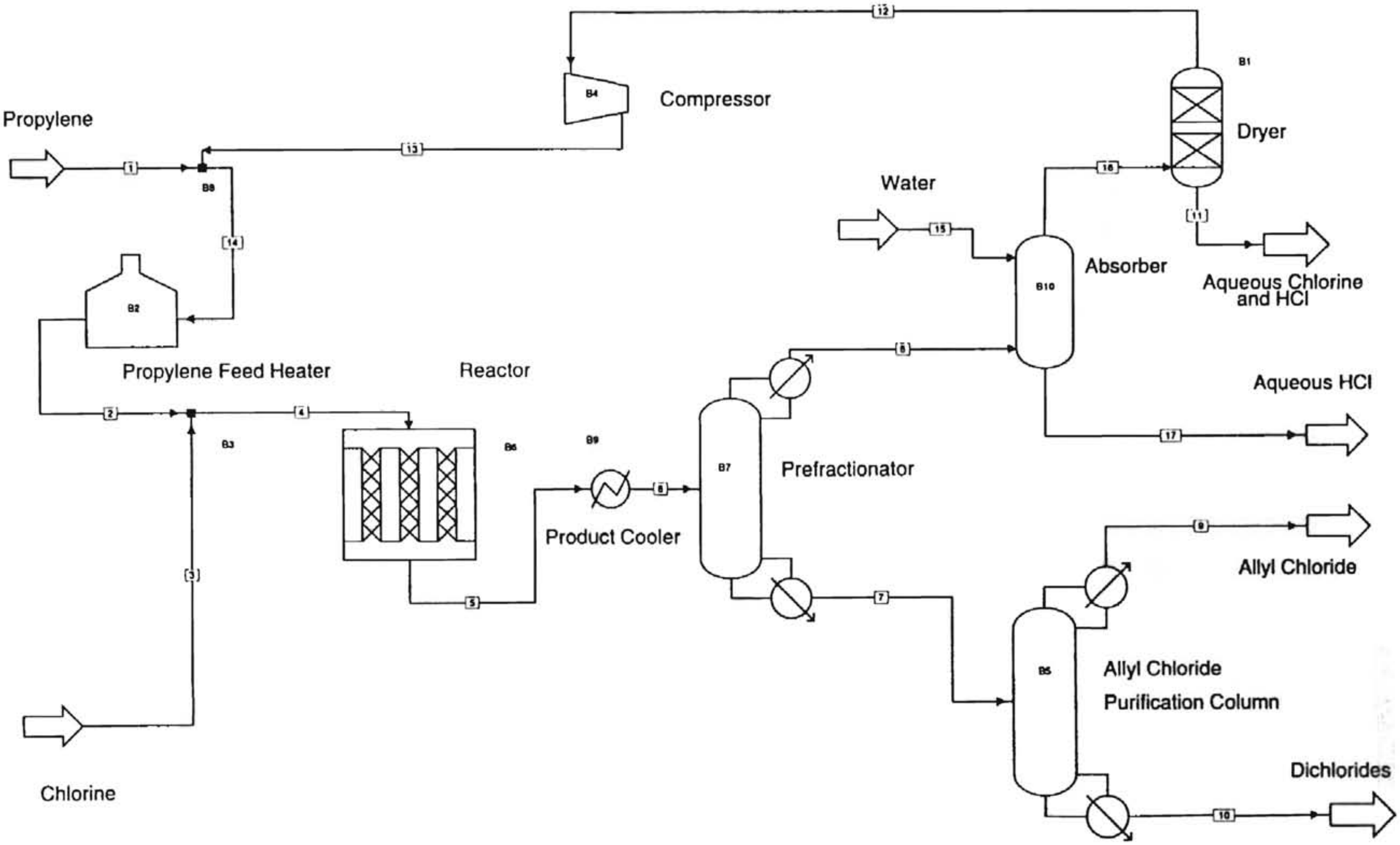

Figure 9: PFD of the Allyl Chloride Process with Stream and Block Labels

INPUT FILE FOR ADIABATIC PLUG FLOW REACTOR

```
TITLE "PRODUCTION OF ALLYL CHLORIDE FROM PROPYLENE "

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=1.000E+05 MAX-ERRORS=500

DESCRIPTION "ECONOMICALLY OPTIMAL ADIABATIC PLUG FLOW REACTOR"

DATABANKS AQUEOUS / DIPPRPCD / ASPENPCD

PROP-SOURCES AQUEOUS / DIPPRPCD / ASPENPCD

COMPONENTS
    H2O H2O H2O /
    HCL HCL HCL /
    C3H6 C3H6-2 C3H6 /
    CL2 CL2 CL2 /
    AC C3H5CL AC /
    12DCP C3H6CL2 12DCP /
    13DCP * 13DCP /
    H+ H+ H+ /
    CL- CL- CL-

HENRY-COMPS ALL HCL C3H6 CL2

CHEMISTRY HCL
    STOIC 1 HCL -1.0 / H+ 1.0 / CL- 1.0

FLOWSHEET
    BLOCK B2 IN=14 OUT=2
    BLOCK B3 IN=2 3 OUT=4
    BLOCK B6 IN=4 OUT=5
    BLOCK B9 IN=5 OUT=6
    BLOCK B1 IN=16 OUT=12 11
    BLOCK B8 IN=1 13 OUT=14
    BLOCK B4 IN=12 OUT=13
    BLOCK B5 IN=7 OUT=9 10
    BLOCK B7 IN=6 OUT=8 7
    BLOCK B11 IN=8 OUT=18 19
    BLOCK B10 IN=18 15 OUT=16 17

PROPERTIES SYSOP11
    PROPERTIES SYSOP15

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST TB
    PVAL 13DCP 377.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST CPIG
    PVAL 13DCP 11750.0 322.20 -.26390 8.9830E-05
```

```
PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST HENRY
    BPVAL HCL H2O 58.452960 -7762.8320 .0 .0 .0 1000.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST GMELCC
    PPVAL H2O ( H+ CL- ) 41.6740
    PPVAL ( H+ CL- ) H2O -22.1540
    PPVAL HCL ( H+ CL- ) .0010
    PPVAL ( H+ CL- ) HCL -.0010

PROP-DATA DATA3
    IN-UNITS SI
    PROP-LIST GMELCD
    PPVAL H2O ( H+ CL- ) 5323.10
    PPVAL ( H+ CL- ) H2O -2204.10

PROP-DATA DATA4
    IN-UNITS SI
    PROP-LIST GMELCE
    PPVAL H2O ( H+ CL- ) -5.4040
    PPVAL ( H+ CL- ) H2O 5.1880

PROP-DATA DATA5
    IN-UNITS SI
    PROP-LIST GMELCN
    PPVAL H2O ( H+ CL- ) .028350
    PPVAL ( H+ CL- ) H2O .028350

ESTIMATE ALL

STRUCTURES
    STRUCTURES 13DCP CL1 C2 S / C2 C3 D / C3 C4 S / C4   &
        CL5 S

PCES-PROP-DA
    GAMINF 13DCP H2O 68.0 1360.0 * * / 86.0 1430.0 * * /  &
        104.0 1460.0 * *
    GAMINF 12DCP H2O 68.0 2340.0 * * / 86.0 2310.0 * * /  &
        104.0 2090.0 * *

STREAM 1
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW HCL .0 / C3H6 1000.0 / CL2 .0 / AC .0 /  &
        12DCP .0

STREAM 15
    SUBSTREAM MIXED TEMP=70.0 PRES=14.70
    MOLE-FLOW H2O 1200.0

STREAM 3
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW CL2 133

BLOCK B3 MIXER
```

```
BLOCK B8 MIXER

BLOCK B1 SEP
    FRAC STREAM=12 SUBSTREAM=MIXED COMPS=H2O HCL C3H6 CL2  &
        AC 12DCP 13DCP FRACS=.0 .0 1.0 .0 .0 .0 .0

BLOCK B11 SEP
    FRAC STREAM=18 SUBSTREAM=MIXED COMPS=H2O HCL C3H6 CL2  &
        AC 12DCP 13DCP H+ CL- FRACS=1.0 1.0 1.0 1.0 .0 .0  &
        .0 1.0 1.0

BLOCK B2 HEATER
    DESCRIPTION "PREHEATER"
    PARAM TEMP=730 PRES=74.70

BLOCK B9 HEATER
    DESCRIPTION "COOLER"
    PARAM TEMP=70.0 PRES=74.70

BLOCK B10 RADFRAC
    PARAM NSTAGE=10 ALGORITHM=NONIDEAL MAXOL=100 MAXIL=50
    FEEDS 18 10 ON-STAGE / 15 1 ON-STAGE
    PRODUCTS 16 1 V / 17 10 L
    P-SPEC 1 14.70
    COL-SPECS Q1=.0 QN=.0 MOLE-RDV=1.0
    T-EST 1 110.0 / 10 68.0
    PROPERTIES SYSOP15 HENRY-COMPS=ALL TRUE-COMPS=NO  &
        CHEMISTRY=HCL

BLOCK B5 RADFRAC
    PARAM NSTAGE=15
    FEEDS 7 6
    PRODUCTS 9 1 V / 10 15 L
    P-SPEC 1 16.0 / 15 25.0
    COL-SPECS D:F=.5390380 MOLE-RDV=1.0 MOLE-RR=4.025540
    SPEC 1 MOLE-RECOV .9950 COMPS=AC STREAMS=9 BASE-STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B7 RADFRAC
    PARAM NSTAGE=15
    FEEDS 6 7
    PRODUCTS 8 1 V / 7 15 L
    P-SPEC 1 20.0 / 15 27.0
    COL-SPECS D:F=.8930390 MOLE-RDV=1.0 MOLE-RR=.50
    SPEC 1 MOLE-RECOV .99990 COMPS=AC STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B6 RPLUG
    PARAM TYPE=ADIABATIC LENGTH=20.0 DIAM=6.0 PRES=40
    STOIC 1 MIXED C3H6 -1.0 / CL2 -1.0 / AC 1.0 / HCL  &
        1.0
    STOIC 2 MIXED C3H6 -1.0 / CL2 -1.0 / 12DCP 1.0
    STOIC 3 MIXED AC -1.0 / CL2 -1.0 / 13DCP 1.0 / HCL  &
        1.0
    RATE-CON 1 4.040E+07 7.430E+07 <J/KMOL>
    RATE-CON 2 2300.0 2.730E+07 <J/KMOL>
    RATE-CON 3 9.030E+10 1.100E+08 <J/KMOL>
```

```
    POWLAW-EXP 1 C3H6 1.0 / CL2 1.0
    POWLAW-EXP 2 C3H6 1.0 / CL2 1.0
    POWLAW-EXP 3 AC 1.0 / CL2 1.0

BLOCK B4 COMPR
    PARAM TYPE=RIG-POLYTROP PRES=90.0

DESIGN-SPEC FEED
    DEFINE S19C3 MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    SPEC "S19C3" TO "1000"
    TOL-SPEC "0.1"
    VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=C3H6
    LIMITS "50" "1000"

DESIGN-SPEC RESTM
    DEFINE RESTM BLOCK-VAR BLOCK=B6 VARIABLE=RES-TIME  &
        SENTENCE=PARAM
    SPEC "RESTM" TO "1.11E-3"
    TOL-SPEC "0.0001"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=LENGTH SENTENCE=PARAM
    LIMITS "1" "200"

OPTIMIZATION MAXPROFT
    DEFINE AC9 MOLE-FLOW STREAM=9 SUBSTREAM=MIXED COMPONENT=AC
    DEFINE HCL17 MOLE-FLOW STREAM=17 SUBSTREAM=MIXED  &
        COMPONENT=HCL
    DEFINE D12C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
        COMPONENT=12DCP
    DEFINE D13C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
        COMPONENT=13DCP
    DEFINE CL8 MOLE-FLOW STREAM=8 SUBSTREAM=MIXED COMPONENT=CL2
    DEFINE CL3 MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
    DEFINE PROP1 MOLE-FLOW STREAM=1 SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    DEFINE H2O15 MASS-FLOW STREAM=15 SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE FDHTR BLOCK-VAR BLOCK=B2 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE REB1 BLOCK-VAR BLOCK=B7 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE REB2 BLOCK-VAR BLOCK=B5 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE COMP BLOCK-VAR BLOCK=B4 VARIABLE=BRAKE-POWER  &
        SENTENCE=RESULTS
    DEFINE COOLER BLOCK-VAR BLOCK=B9 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE COND1 BLOCK-VAR BLOCK=B7 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE COND2 BLOCK-VAR BLOCK=B5 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE PROFIT PARAMETER 1
F        REVAC=59.69
F        REVHCL=0.15
F        CSTCL2=7.98
F        CSTPRP=7.27
F        WCST2D=37.17
F        WCST3D=36.51
```

```
F         WCSTCL=47.96
F         AQHCL=(HCL17*36.46)/0.32
F         REVNUE=REVAC*AC9+REVHCL*AQHCL
F         RAWCST=CSTCL2*CL3+CSTPRP*PROP1
F         WSTCST=WCST2D*D12C10+WCST3D*D13C10+WCSTCL*CL8
F         TOTGAS=REB1+REB2+FDHTR
F         GASCST=(TOTGAS)*(3.399/1.0E6)
F         ELECST=0.0532*COMP
F         H2OBTU=-(COOLER+COND1+COND2)
F         FLWH2O=((H2OBTU/50)+H2O15)/8.345
F         H2OCST=0.835+(FLWH2O-446.4)*0.00165
F         UTLCST=GASCST+ELECST+H2OCST
F         PROFIT=REVNUE-RAWCST-WSTCST-UTLCST
    MAXIMIZE "PROFIT"
    VARY BLOCK-VAR BLOCK=B2 VARIABLE=TEMP SENTENCE=PARAM
    LIMITS "200" "1000"
    VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
    LIMITS "130" "1000"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=PRES SENTENCE=PARAM
    LIMITS "25" "50"

CONV-OPTIONS
    SQP MAXIT=100 MAXPASS=1000
```

INPUT FILE FOR ISOTHERMAL PLUG FLOW REACTOR

```
TITLE "PRODUCTION OF ALLYL CHLORIDE FROM PROPYLENE"

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=1.000E+05 MAX-ERRORS=500

DESCRIPTION "ECONOMICALLY OPTIMAL ISOTHERMAL PLUG FLOW REACTOR "

DATABANKS AQUEOUS / DIPPRPCD / ASPENPCD

PROP-SOURCES AQUEOUS / DIPPRPCD / ASPENPCD

COMPONENTS
    H2O H2O H2O /
    HCL HCL HCL /
    C3H6 C3H6-2 C3H6 /
    CL2 CL2 CL2 /
    AC C3H5CL AC /
    12DCP C3H6CL2 12DCP /
    13DCP * 13DCP /
    H+ H+ H+ /
    CL- CL- CL-

HENRY-COMPS ALL HCL C3H6 CL2

CHEMISTRY HCL
    STOIC 1 HCL -1.0 / H+ 1.0 / CL- 1.0

FLOWSHEET
    BLOCK B2 IN=14 OUT=2
    BLOCK B3 IN=2 3 OUT=4
    BLOCK B6 IN=4 OUT=5
    BLOCK B9 IN=5 OUT=6
    BLOCK B1 IN=16 OUT=12 11
    BLOCK B8 IN=1 13 OUT=14
    BLOCK B4 IN=12 OUT=13
    BLOCK B5 IN=7 OUT=9 10
    BLOCK B7 IN=6 OUT=8 7
    BLOCK B11 IN=8 OUT=18 19
    BLOCK B10 IN=18 15 OUT=16 17

PROPERTIES SYSOP11
    PROPERTIES SYSOP15

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST TB
    PVAL 13DCP 377.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST CPIG
    PVAL 13DCP 11750.0 322.20 -.26390 8.9830E-05
```

```
PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST HENRY
    BPVAL HCL H2O 58.452960 -7762.8320 .0 .0 .0 1000.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST GMELCC
    PPVAL H2O ( H+ CL- ) 41.6740
    PPVAL ( H+ CL- ) H2O -22.1540
    PPVAL HCL ( H+ CL- ) .0010
    PPVAL ( H+ CL- ) HCL -.0010

PROP-DATA DATA3
    IN-UNITS SI
    PROP-LIST GMELCD
    PPVAL H2O ( H+ CL- ) 5323.10
    PPVAL ( H+ CL- ) H2O -2204.10

PROP-DATA DATA4
    IN-UNITS SI
    PROP-LIST GMELCE
    PPVAL H2O ( H+ CL- ) -5.4040
    PPVAL ( H+ CL- ) H2O 5.1880

PROP-DATA DATA5
    IN-UNITS SI
    PROP-LIST GMELCN
    PPVAL H2O ( H+ CL- ) .028350
    PPVAL ( H+ CL- ) H2O .028350

ESTIMATE ALL

STRUCTURES
    STRUCTURES 13DCP CL1 C2 S / C2 C3 D / C3 C4 S / C4  &
        CL5 S

PCES-PROP-DA
    GAMINF 13DCP H2O 68.0 1360.0 * * / 86.0 1430.0 * * /  &
        104.0 1460.0 * *
    GAMINF 12DCP H2O 68.0 2340.0 * * / 86.0 2310.0 * * /  &
        104.0 2090.0 * *

STREAM 1
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW HCL .0 / C3H6 1000.0 / CL2 .0 / AC .0 /  &
        12DCP .0

STREAM 15
    SUBSTREAM MIXED TEMP=70.0 PRES=14.70
    MOLE-FLOW H2O 1200.0

STREAM 3
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW CL2 200.0

BLOCK B3 MIXER
```

```
BLOCK B8 MIXER

BLOCK B1 SEP
    FRAC STREAM=12 SUBSTREAM=MIXED COMPS=H2O HCL C3H6 CL2  &
        AC 12DCP 13DCP FRACS=.0 .0 1.0 .0 .0 .0 .0

BLOCK B11 SEP
    FRAC STREAM=18 SUBSTREAM=MIXED COMPS=H2O HCL C3H6 CL2  &
        AC 12DCP 13DCP H+ CL- FRACS=1.0 1.0 1.0 1.0 .0 .0  &
        .0 1.0 1.0

BLOCK B2 HEATER
    DESCRIPTION "PREHEATER"
    PARAM TEMP=830.0 PRES=74.70

BLOCK B9 HEATER
    DESCRIPTION "COOLER"
    PARAM TEMP=70.0 PRES=74.70

BLOCK B10 RADFRAC
    PARAM NSTAGE=10 ALGORITHM=NONIDEAL MAXOL=50 MAXIL=25
    FEEDS 18 10 ON-STAGE / 15 1 ON-STAGE
    PRODUCTS 16 1 V / 17 10 L
    P-SPEC 1 14.70
    COL-SPECS Q1=.0 QN=.0 MOLE-RDV=1.0
    T-EST 1 110.0 / 10 68.0
    PROPERTIES SYSOP15 HENRY-COMPS=ALL TRUE-COMPS=NO  &
        CHEMISTRY=HCL

BLOCK B5 RADFRAC
    PARAM NSTAGE=15
    FEEDS 7 6
    PRODUCTS 9 1 V / 10 15 L
    P-SPEC 1 16.0 / 15 25.0
    COL-SPECS D:F=.5390380 MOLE-RDV=1.0 MOLE-RR=4.025540
    SPEC 1 MOLE-RECOV .9950 COMPS=AC STREAMS=9 BASE-STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B7 RADFRAC
    PARAM NSTAGE=15
    FEEDS 6 7
    PRODUCTS 8 1 V / 7 15 L
    P-SPEC 1 20.0 / 15 27.0
    COL-SPECS D:F=.8930390 MOLE-RDV=1.0 MOLE-RR=.50
    SPEC 1 MOLE-RECOV .990 COMPS=AC STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B6 RPLUG
    PARAM TYPE=T-SPEC LENGTH=20.0 DIAM=6.0 PRES=46
    STOIC 1 MIXED C3H6 -1.0 / CL2 -1.0 / AC 1.0 / HCL  &
        1.0
    STOIC 2 MIXED C3H6 -1.0 / CL2 -1.0 / 12DCP 1.0
    STOIC 3 MIXED AC -1.0 / CL2 -1.0 / 13DCP 1.0 / HCL  &
        1.0
    RATE-CON 1 4.040E+07 7.430E+07 <J/KMOL>
    RATE-CON 2 2300.0 2.730E+07 <J/KMOL>
    RATE-CON 3 9.030E+10 1.100E+08 <J/KMOL>
```

```
          POWLAW-EXP 1 C3H6 1.0 / CL2 1.0
          POWLAW-EXP 2 C3H6 1.0 / CL2 1.0
          POWLAW-EXP 3 AC 1.0 / CL2 1.0

      BLOCK B4 COMPR
          PARAM TYPE=RIG-POLYTROP PRES=90.0

      DESIGN-SPEC FEED
          DEFINE S19C3 MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
              COMPONENT=C3H6
          SPEC "S19C3" TO "1000"
          TOL-SPEC "0.1"
          VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=C3H6
          LIMITS "50" "1000"

      DESIGN-SPEC RESTM
          DEFINE RESTM BLOCK-VAR BLOCK=B6 VARIABLE=RES-TIME  &
              SENTENCE=PARAM
          SPEC "RESTM" TO "1.11E-3"
          TOL-SPEC "0.0001"
          VARY BLOCK-VAR BLOCK=B6 VARIABLE=LENGTH SENTENCE=PARAM
          LIMITS "1" "200"

      OPTIMIZATION MAXPROFT
          DEFINE AC9 MOLE-FLOW STREAM=9 SUBSTREAM=MIXED COMPONENT=AC
          DEFINE HCL17 MOLE-FLOW STREAM=17 SUBSTREAM=MIXED  &
              COMPONENT=HCL
          DEFINE D12C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
              COMPONENT=12DCP
          DEFINE D13C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
              COMPONENT=13DCP
          DEFINE CL8 MOLE-FLOW STREAM=8 SUBSTREAM=MIXED COMPONENT=CL2
          DEFINE CL3 MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
          DEFINE PROP1 MOLE-FLOW STREAM=1 SUBSTREAM=MIXED  &
              COMPONENT=C3H6
          DEFINE H2O15 MASS-FLOW STREAM=15 SUBSTREAM=MIXED  &
              COMPONENT=H2O
          DEFINE FDHTR BLOCK-VAR BLOCK=B2 VARIABLE=QCALC  &
              SENTENCE=PARAM
          DEFINE REB1 BLOCK-VAR BLOCK=B7 VARIABLE=REB-DUTY  &
              SENTENCE=RESULTS
          DEFINE REB2 BLOCK-VAR BLOCK=B5 VARIABLE=REB-DUTY  &
              SENTENCE=RESULTS
          DEFINE COMP BLOCK-VAR BLOCK=B4 VARIABLE=BRAKE-POWER  &
              SENTENCE=RESULTS
          DEFINE COOLER BLOCK-VAR BLOCK=B9 VARIABLE=QCALC  &
              SENTENCE=PARAM
          DEFINE COND1 BLOCK-VAR BLOCK=B7 VARIABLE=COND-DUTY  &
              SENTENCE=RESULTS
          DEFINE COND2 BLOCK-VAR BLOCK=B5 VARIABLE=COND-DUTY  &
              SENTENCE=RESULTS
          DEFINE RDUTY BLOCK-VAR BLOCK=B6 VARIABLE=QCALC  &
              SENTENCE=PARAM
          DEFINE PROFIT PARAMETER 1
      F         REVAC=59.69
      F         REVHCL=0.15
      F         CSTCL2=7.98
      F         CSTPRP=7.27
```

```
F         WCST2D=37.17
F         WCST3D=36.51
F         WCSTCL=47.96
F         AQHCL=(HCL17*36.46)/0.32
F         REVNUE=REVAC*AC9+REVHCL*AQHCL
F         RAWCST=CSTCL2*CL3+CSTPRP*PROP1
F         WSTCST=WCST2D*D12C10+WCST3D*D13C10+WCSTCL*CL8
F         IF (RDUTY.GT.0) TOTGAS=REB1+REB2+FDHTR+RDUTY
F         TOTGAS=REB1+REB2+FDHTR
F         GASCST=(TOTGAS)*(3.399/1.0E6)
F         ELECST=0.0532*COMP
F         IF (RDUTY.LT.0D0) H2OBTU=-(COOLER+COND1+COND2+RDUTY)
F         H2OBTU=-(COOLER+COND1+COND2)
F         FLWH2O=((H2OBTU/50)+H2O15)/8.345
F         H2OCST=0.835+(FLWH2O-446.4)*0.00165
F         UTLCST=GASCST+ELECST+H2OCST
F         PROFIT=REVNUE-RAWCST-WSTCST-UTLCST
    MAXIMIZE "PROFIT"
    VARY BLOCK-VAR BLOCK=B2 VARIABLE=TEMP SENTENCE=PARAM
    LIMITS "200" "1000"
    VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
    LIMITS "125" "1000"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=PRES SENTENCE=PARAM
    LIMITS "25" "50"

CONV-OPTIONS
    SQP MAXIT=100 MAXPASS=1000
```

INPUT FILE FOR ADIABATIC CONTINUOUS-FLOW STIRRED-TANK REACTOR

```
TITLE "PRODUCTION OF ALLYL CHLORIDE FROM PROPYLENE"

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=1.000E+05 MAX-ERRORS=500

DESCRIPTION "ECONOMICALLY OPTIMAL ADIABATIC CSTR"

DATABANKS AQUEOUS / DIPPRPCD / ASPENPCD

PROP-SOURCES AQUEOUS / DIPPRPCD / ASPENPCD

COMPONENTS
    H2O H2O H2O /
    HCL HCL HCL /
    C3H6 C3H6-2 C3H6 /
    CL2 CL2 CL2 /
    AC C3H5CL AC /
    12DCP C3H6CL2 12DCP /
    13DCP * 13DCP /
    H+ H+ H+ /
    CL- CL- CL-

HENRY-COMPS ALL HCL C3H6 CL2

CHEMISTRY HCL
    STOIC 1 HCL -1.0 / H+ 1.0 / CL- 1.0

FLOWSHEET
    BLOCK B2 IN=14 OUT=2
    BLOCK B3 IN=2 3 OUT=4
    BLOCK B6 IN=4 OUT=5
    BLOCK B9 IN=5 OUT=6
    BLOCK B1 IN=16 OUT=12 11
    BLOCK B8 IN=1 13 OUT=14
    BLOCK B4 IN=12 OUT=13
    BLOCK B5 IN=7 OUT=9 10
    BLOCK B7 IN=6 OUT=8 7
    BLOCK B11 IN=8 OUT=18 19
    BLOCK B10 IN=18 15 OUT=16 17

PROPERTIES SYSOP11
    PROPERTIES SYSOP15

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST TB
    PVAL 13DCP 377.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST CPIG
    PVAL 13DCP 11750.0 322.20 -.26390 8.9830E-05
```

```
PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST HENRY
    BPVAL HCL H2O 58.452960 -7762.8320 .0 .0 .0 1000.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST GMELCC
    PPVAL H2O ( H+ CL- ) 41.6740
    PPVAL ( H+ CL- ) H2O -22.1540
    PPVAL HCL ( H+ CL- ) .0010
    PPVAL ( H+ CL- ) HCL -.0010

PROP-DATA DATA3
    IN-UNITS SI
    PROP-LIST GMELCD
    PPVAL H2O ( H+ CL- ) 5323.10
    PPVAL ( H+ CL- ) H2O -2204.10

PROP-DATA DATA4
    IN-UNITS SI
    PROP-LIST GMELCE
    PPVAL H2O ( H+ CL- ) -5.4040
    PPVAL ( H+ CL- ) H2O 5.1880

PROP-DATA DATA5
    IN-UNITS SI
    PROP-LIST GMELCN
    PPVAL H2O ( H+ CL- ) .028350
    PPVAL ( H+ CL- ) H2O .028350

ESTIMATE ALL

STRUCTURES
    STRUCTURES 13DCP CL1 C2 S / C2 C3 D / C3 C4 S / C4  &
        CL5 S

PCES-PROP-DA
    GAMINF 13DCP H2O 68.0 1360.0 * * / 86.0 1430.0 * * /  &
        104.0 1460.0 * *
    GAMINF 12DCP H2O 68.0 2340.0 * * / 86.0 2310.0 * * /  &
        104.0 2090.0 * *

STREAM 1
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW HCL .0 / C3H6 1000.0 / CL2 .0 / AC .0 /  &
        12DCP .0

STREAM 15
    SUBSTREAM MIXED TEMP=70.0 PRES=14.70
    MOLE-FLOW H2O 1200.0

STREAM 3
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW CL2 145.0

BLOCK B3 MIXER
```

```
BLOCK B8 MIXER

BLOCK B1 SEP
    FRAC STREAM=12 SUBSTREAM=MIXED COMPS=H2O HCL C3H6 CL2  &
        AC 12DCP 13DCP FRACS=.0 .0 1.0 .0 .0 .0 .0

BLOCK B11 SEP
    FRAC STREAM=18 SUBSTREAM=MIXED COMPS=H2O HCL C3H6 CL2  &
        AC 12DCP 13DCP H+ CL- FRACS=1.0 1.0 1.0 1.0 .0 .0  &
        .0 1.0 1.0

BLOCK B2 HEATER
    DESCRIPTION "PREHEATER"
    PARAM TEMP=510 PRES=74.70

BLOCK B9 HEATER
    DESCRIPTION "COOLER"
    PARAM TEMP=70.0 PRES=74.70

BLOCK B10 RADFRAC
    PARAM NSTAGE=10 ALGORITHM=NONIDEAL MAXOL=50 MAXIL=25
    FEEDS 18 10 ON-STAGE / 15 1 ON-STAGE
    PRODUCTS 16 1 V / 17 10 L
    P-SPEC 1 14.70
    COL-SPECS Q1=.0 QN=.0 MOLE-RDV=1.0
    T-EST 1 110.0 / 10 68.0
    PROPERTIES SYSOP15 HENRY-COMPS=ALL TRUE-COMPS=NO  &
        CHEMISTRY=HCL

BLOCK B5 RADFRAC
    PARAM NSTAGE=15
    FEEDS 7 6
    PRODUCTS 9 1 V / 10 15 L
    P-SPEC 1 16.0 / 15 25.0
    COL-SPECS D:F=.5390380 MOLE-RDV=1.0 MOLE-RR=4.025540
    SPEC 1 MOLE-RECOV .995 COMPS=AC STREAMS=9 BASE-STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B7 RADFRAC
    PARAM NSTAGE=15
    FEEDS 6 7
    PRODUCTS 8 1 V / 7 15 L
    P-SPEC 1 20.0 / 15 27.0
    COL-SPECS D:F=.8930390 MOLE-RDV=1.0 MOLE-RR=.50
    SPEC 1 MOLE-RECOV .9990 COMPS=AC STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B6 RCSTR
    PARAM VOL=3000.0 PRES=42 DUTY=0 TEST=700
    STOIC 1 MIXED C3H6 -1.0 / CL2 -1.0 / AC 1.0 / HCL  &
        1.0
    STOIC 2 MIXED C3H6 -1.0 / CL2 -1.0 / 12DCP 1.0
    STOIC 3 MIXED AC -1.0 / CL2 -1.0 / 13DCP 1.0 / HCL  &
        1.0
    RATE-CON 1 4.040E+07 7.430E+07 <J/KMOL>
    RATE-CON 2 2300.0 2.730E+07 <J/KMOL>
    RATE-CON 3 9.030E+10 1.100E+08 <J/KMOL>
```

```
    POWLAW-EXP 1 C3H6 1.0 / CL2 1.0
    POWLAW-EXP 2 C3H6 1.0 / CL2 1.0
    POWLAW-EXP 3 AC 1.0 / CL2 1.0

BLOCK B4 COMPR
    PARAM TYPE=RIG-POLYTROP PRES=90.0

DESIGN-SPEC FEED
    DEFINE S19C3 MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    SPEC "S19C3" TO "1000"
    TOL-SPEC "0.1"
    VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=C3H6
    LIMITS "50" "1000"

DESIGN-SPEC RESTM
    DEFINE VOL BLOCK-VAR BLOCK=B6 VARIABLE=VOL SENTENCE=PARAM
    DEFINE MASSFL STREAM-VAR STREAM=5 SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE DENSTY STREAM-VAR STREAM=5 SUBSTREAM=MIXED  &
        VARIABLE=MASS-DENSITY
F        VOLFLW=MASSFL/DENSTY
F        RESTM=VOL/VOLFLW
    SPEC "RESTM" TO "1.11E-3"
    TOL-SPEC "0.0001"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=VOL SENTENCE=PARAM
    LIMITS "50" "5000"

OPTIMIZATION MAXPROFT
    DEFINE AC9 MOLE-FLOW STREAM=9 SUBSTREAM=MIXED COMPONENT=AC
    DEFINE HCL17 MOLE-FLOW STREAM=17 SUBSTREAM=MIXED  &
        COMPONENT=HCL
    DEFINE D12C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
        COMPONENT=12DCP
    DEFINE D13C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
        COMPONENT=13DCP
    DEFINE CL8 MOLE-FLOW STREAM=8 SUBSTREAM=MIXED COMPONENT=CL2
    DEFINE CL3 MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
    DEFINE PROP1 MOLE-FLOW STREAM=1 SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    DEFINE H2O15 MASS-FLOW STREAM=15 SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE FDHTR BLOCK-VAR BLOCK=B2 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE REB1 BLOCK-VAR BLOCK=B7 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE REB2 BLOCK-VAR BLOCK=B5 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE COMP BLOCK-VAR BLOCK=B4 VARIABLE=BRAKE-POWER  &
        SENTENCE=RESULTS
    DEFINE COOLER BLOCK-VAR BLOCK=B9 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE COND1 BLOCK-VAR BLOCK=B7 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE COND2 BLOCK-VAR BLOCK=B5 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE PROFIT PARAMETER 1
F        REVAC=59.69
```

```
F         REVHCL=0.15
F         CSTCL2=7.98
F         CSTPRP=7.27
F         WCST2D=37.17
F         WCST3D=36.51
F         WCSTCL=47.96
F         AQHCL=(HCL17*36.46)/0.32
F         REVNUE=REVAC*AC9+REVHCL*AQHCL
F         RAWCST=CSTCL2*CL3+CSTPRP*PROP1
F         WSTCST=WCST2D*D12C10+WCST3D*D13C10+WCSTCL*CL8
F         TOTGAS=REB1+REB2+FDHTR
F         GASCST=(TOTGAS)*(3.399/1.0E6)
F         ELECST=0.0532*COMP
F         H2OBTU=-(COOLER+COND1+COND2)
F         FLWH2O=((H2OBTU/50)+H2O15)/8.345
F         H2OCST=0.835+(FLWH2O-446.4)*0.00165
F         UTLCST=GASCST+ELECST+H2OCST
F         PROFIT=REVNUE-RAWCST-WSTCST-UTLCST
    MAXIMIZE "PROFIT"
    VARY BLOCK-VAR BLOCK=B2 VARIABLE=TEMP SENTENCE=PARAM
    LIMITS "500" "1000"
    VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
    LIMITS "100" "1000"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=PRES SENTENCE=PARAM
    LIMITS "20" "50"

CONV-OPTIONS
    SQP MAXIT=100 MAXPASS=1000
```

INPUT FILE FOR ISOTHERMAL CONTINUOUS-FlOW STIRRED-TANK REACTOR

```
TITLE "PRODUCTION OF ALLYL CHLORIDE FROM PROPYLENE"

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=1.000E+05 MAX-ERRORS=1000

DESCRIPTION "ECONOMICALLY OPTIMAL ISOTHERMAL CSTR"

DATABANKS AQUEOUS / DIPPRPCD / ASPENPCD

PROP-SOURCES AQUEOUS / DIPPRPCD / ASPENPCD

COMPONENTS
    H2O H2O H2O /
    HCL HCL HCL /
    C3H6 C3H6-2 C3H6 /
    CL2 CL2 CL2 /
    AC C3H5CL AC /
    12DCP C3H6CL2 12DCP /
    13DCP * 13DCP /
    H+ H+ H+ /
    CL- CL- CL-

HENRY-COMPS ALL HCL C3H6 CL2

CHEMISTRY HCL
    STOIC 1 HCL -1.0 / H+ 1.0 / CL- 1.0

FLOWSHEET
    BLOCK B2 IN=14 OUT=2
    BLOCK B3 IN=2 3 OUT=4
    BLOCK B6 IN=4 OUT=5
    BLOCK B9 IN=5 OUT=6
    BLOCK B1 IN=16 OUT=12 11
    BLOCK B8 IN=1 13 OUT=14
    BLOCK B4 IN=12 OUT=13
    BLOCK B5 IN=7 OUT=9 10
    BLOCK B7 IN=6 OUT=8 7
    BLOCK B11 IN=8 OUT=18 19
    BLOCK B10 IN=18 15 OUT=16 17

PROPERTIES SYSOP11
    PROPERTIES SYSOP15

PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST TB
    PVAL 13DCP 377.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST CPIG
    PVAL 13DCP 11750.0 322.20 -.26390 8.9830E-05
```

```
PROP-DATA DATA1
    IN-UNITS SI
    PROP-LIST HENRY
    BPVAL HCL H2O 58.452960 -7762.8320 .0 .0 .0 1000.0

PROP-DATA DATA2
    IN-UNITS SI
    PROP-LIST GMELCC
    PPVAL H2O ( H+ CL- ) 41.6740
    PPVAL ( H+ CL- ) H2O -22.1540
    PPVAL HCL ( H+ CL- ) .0010
    PPVAL ( H+ CL- ) HCL -.0010

PROP-DATA DATA3
    IN-UNITS SI
    PROP-LIST GMELCD
    PPVAL H2O ( H+ CL- ) 5323.10
    PPVAL ( H+ CL- ) H2O -2204.10

PROP-DATA DATA4
    IN-UNITS SI
    PROP-LIST GMELCE
    PPVAL H2O ( H+ CL- ) -5.4040
    PPVAL ( H+ CL- ) H2O 5.1880

PROP-DATA DATA5
    IN-UNITS SI
    PROP-LIST GMELCN
    PPVAL H2O ( H+ CL- ) .028350
    PPVAL ( H+ CL- ) H2O .028350

ESTIMATE ALL

STRUCTURES
    STRUCTURES 13DCP CL1 C2 S / C2 C3 D / C3 C4 S / C4  &
        CL5 S

PCES-PROP-DA
    GAMINF 13DCP H2O 68.0 1360.0 * * / 86.0 1430.0 * * /  &
        104.0 1460.0 * *
    GAMINF 12DCP H2O 68.0 2340.0 * * / 86.0 2310.0 * * /  &
        104.0 2090.0 * *

STREAM 1
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW C3H6 1000.0 / CL2 .0 / HCL .0 / AC .0 /  &
        12DCP .0

STREAM 15
    SUBSTREAM MIXED TEMP=70.0 PRES=14.70
    MOLE-FLOW H2O 1200.0

STREAM 3
    SUBSTREAM MIXED TEMP=80.0 PRES=74.70
    MOLE-FLOW CL2 120.0

BLOCK B3 MIXER
```

```
BLOCK B8 MIXER

BLOCK B1 SEP
    FRAC STREAM=12 SUBSTREAM=MIXED COMPS=C3H6 CL2 HCL AC  &
        12DCP H2O 13DCP FRACS=1.0 .0 .0 .0 .0 .0 .0

BLOCK B11 SEP
    FRAC STREAM=18 SUBSTREAM=MIXED COMPS=H2O HCL C3H6 CL2  &
        AC 12DCP 13DCP H+ CL- FRACS=1.0 1.0 1.0 1.0 .0 .0  &
        .0 1.0 1.0

BLOCK B2 HEATER
    DESCRIPTION "PREHEATER"
    PARAM TEMP=550.0 PRES=74.70

BLOCK B9 HEATER
    DESCRIPTION "COOLER"
    PARAM TEMP=70.0 PRES=74.70

BLOCK B10 RADFRAC
    PARAM NSTAGE=10 ALGORITHM=NONIDEAL MAXOL=50 MAXIL=25
    FEEDS 18 10 ON-STAGE / 15 1 ON-STAGE
    PRODUCTS 16 1 V / 17 10 L
    P-SPEC 1 14.70
    COL-SPECS Q1=.0 QN=.0 MOLE-RDV=1.0
    T-EST 1 110.0 / 10 68.0
    PROPERTIES SYSOP15 HENRY-COMPS=ALL TRUE-COMPS=NO  &
        CHEMISTRY=HCL

BLOCK B5 RADFRAC
    PARAM NSTAGE=15
    FEEDS 7 6
    PRODUCTS 9 1 V / 10 15 L
    P-SPEC 1 16.0 / 15 25.0
    COL-SPECS D:F=.5390380 MOLE-RDV=1.0 MOLE-RR=4.025540
    SPEC 1 MOLE-RECOV .9950 COMPS=AC STREAMS=9 BASE-STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B7 RADFRAC
    PARAM NSTAGE=15
    FEEDS 6 7
    PRODUCTS 8 1 V / 7 15 L
    P-SPEC 1 20.0 / 15 27.0
    COL-SPECS D:F=.8930390 MOLE-RDV=1.0 MOLE-RR=.50
    SPEC 1 MOLE-RECOV .990 COMPS=AC STREAMS=7
    VARY 1 D:F 1.000E-03 .9990

BLOCK B6 RCSTR
    PARAM VOL=3000.0 TEMP=900.0 PRES=30.0
    STOIC 1 MIXED C3H6 -1.0 / CL2 -1.0 / AC 1.0 / HCL  &
        1.0
    STOIC 2 MIXED C3H6 -1.0 / CL2 -1.0 / 12DCP 1.0
    STOIC 3 MIXED AC -1.0 / CL2 -1.0 / 13DCP 1.0 / HCL  &
        1.0
    RATE-CON 1 4.040E+07 7.430E+07 <J/KMOL>
    RATE-CON 2 2300.0 2.730E+07 <J/KMOL>
    RATE-CON 3 9.030E+10 1.100E+08 <J/KMOL>
```

```
    POWLAW-EXP 1 C3H6 1.0 / CL2 1.0
    POWLAW-EXP 2 C3H6 1.0 / CL2 1.0
    POWLAW-EXP 3 AC 1.0 / CL2 1.0

BLOCK B4 COMPR
    PARAM TYPE=RIG-POLYTROP PRES=90.0

DESIGN-SPEC FEED
    DEFINE S19C3 MOLE-FLOW STREAM=14 SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    SPEC "S19C3" TO "1000"
    TOL-SPEC "0.1"
    VARY MOLE-FLOW STREAM=1 SUBSTREAM=MIXED COMPONENT=C3H6
    LIMITS "50" "1000"

DESIGN-SPEC RESTM
    DEFINE VOL BLOCK-VAR BLOCK=B6 VARIABLE=VOL SENTENCE=PARAM
    DEFINE MASSFL STREAM-VAR STREAM=5 SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW
    DEFINE DENSTY STREAM-VAR STREAM=5 SUBSTREAM=MIXED  &
        VARIABLE=MASS-DENSITY
F        VOLFLW=MASSFL/DENSTY
F        RESTM=VOL/VOLFLW
    SPEC "RESTM" TO "1.11E-3"
    TOL-SPEC "0.0001"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=VOL SENTENCE=PARAM
    LIMITS "50" "5000"

OPTIMIZATION MAXPROFT
    DEFINE AC9 MOLE-FLOW STREAM=9 SUBSTREAM=MIXED COMPONENT=AC
    DEFINE HCL17 MOLE-FLOW STREAM=17 SUBSTREAM=MIXED  &
        COMPONENT=HCL
    DEFINE D12C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
        COMPONENT=12DCP
    DEFINE D13C10 MOLE-FLOW STREAM=10 SUBSTREAM=MIXED  &
        COMPONENT=13DCP
    DEFINE CL8 MOLE-FLOW STREAM=8 SUBSTREAM=MIXED COMPONENT=CL2
    DEFINE CL3 MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
    DEFINE PROP1 MOLE-FLOW STREAM=1 SUBSTREAM=MIXED  &
        COMPONENT=C3H6
    DEFINE H2O15 MASS-FLOW STREAM=15 SUBSTREAM=MIXED  &
        COMPONENT=H2O
    DEFINE FDHTR BLOCK-VAR BLOCK=B2 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE REB1 BLOCK-VAR BLOCK=B7 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE REB2 BLOCK-VAR BLOCK=B5 VARIABLE=REB-DUTY  &
        SENTENCE=RESULTS
    DEFINE COMP BLOCK-VAR BLOCK=B4 VARIABLE=BRAKE-POWER  &
        SENTENCE=RESULTS
    DEFINE COOLER BLOCK-VAR BLOCK=B9 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE COND1 BLOCK-VAR BLOCK=B7 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE COND2 BLOCK-VAR BLOCK=B5 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE RDUTY BLOCK-VAR BLOCK=B6 VARIABLE=QCALC  &
        SENTENCE=PARAM
```

```
    DEFINE PROFIT PARAMETER 1
F        REVAC=59.69
F        REVHCL=0.15
F        CSTCL2=7.98
F        CSTPRP=7.27
F        WCST2D=37.17
F        WCST3D=36.51
F        WCSTCL=47.96
F        AQHCL=(HCL17*36.46)/0.32
F        REVNUE=REVAC*AC9+REVHCL*AQHCL
F        RAWCST=CSTCL2*CL3+CSTPRP*PROP1
F        WSTCST=WCST2D*D12C10+WCST3D*D13C10+WCSTCL*CL8
F        IF (RDUTY.GT.0) TOTGAS=REB1+REB2+FDHTR+RDUTY
F        TOTGAS=REB1+REB2+FDHTR
F        GASCST=(TOTGAS)*(3.399/1.0E6)
F        ELECST=0.0532*COMP
F        IF (RDUTY.LT.0D0) H2OBTU=-(COOLER+COND1+COND2+RDUTY)
F        H2OBTU=-(COOLER+COND1+COND2)
F        FLWH2O=((H2OBTU/50)+H2O15)/8.345
F        H2OCST=0.835+(FLWH2O-446.4)*0.00165
F        UTLCST=GASCST+ELECST+H2OCST
F        PROFIT=REVNUE-RAWCST-WSTCST-UTLCST
    MAXIMIZE "PROFIT"
    VARY BLOCK-VAR BLOCK=B2 VARIABLE=TEMP SENTENCE=PARAM
    LIMITS "500" "950"
    VARY MOLE-FLOW STREAM=3 SUBSTREAM=MIXED COMPONENT=CL2
    LIMITS "115" "1000"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=PRES SENTENCE=PARAM
    LIMITS "30" "50"
    VARY BLOCK-VAR BLOCK=B6 VARIABLE=TEMP SENTENCE=PARAM
    LIMITS "500" "950"

CONV-OPTIONS
    SQP MAXIT=100 MAXPASS=1000
```

APPENDIX B

ASPEN PLUS™ OUTPUT FILES

OUTPUT FILE FOR ADIABATIC PLUG FLOW REACTOR

```
OPTIMIZATION: MAXPROFT
----------------------------------------------------------------
! ITER- ! OBJECT-  ! LAGRANG- ! VARY    1 ! VARY    2 ! VARY    3 !
! ATION ! IVE      ! IAN      ! B2        ! 3         ! B6        !
! NO    ! FUNCTION ! FUNCTION ! PARAM     ! MIXED     ! PARAM     !
!       !          !          ! TEMP      ! CL2 MOLE  ! PRES      !
!       !          !          !           ! FLOW      !           !
!       !          !          ! F         ! LBMOL/HR  ! PSI       !
!       !          !          !           !           !           !
!=======!==========!==========!==========!==========!==========!
!   0   !  2386.19 !  MISSING !    730.00 !    133.00 !     40.00 !
!   1   !  2396.31 !  2396.09 !    709.10 !    132.88 !     39.60 !
!   2   !  2396.33 !  2396.28 !    708.82 !    132.52 !     39.77 !
----------------------------------------------------------------


BLOCK:  B1        MODEL: SEP
---------------------------
  INLET STREAM:           16
  OUTLET STREAMS:         12          11
  PROPERTY OPTION SET:    SYSOP11    UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
 COMPONENT = H2O
   STREAM      SUBSTREAM    SPLIT FRACTION
   11          MIXED                 1.00000

 COMPONENT = C3H6
   STREAM      SUBSTREAM    SPLIT FRACTION
   12          MIXED                 1.00000


BLOCK:  B10       MODEL: RADFRAC
-------------------------------
   INLETS    - 18        STAGE  10
               15        STAGE   1
   OUTLETS   - 16        STAGE   1
               17        STAGE  10
  PROP. OPT. SET:   SYSOP15   ELECTROLYTE NRTL / REDLICH-KWONG-SOAVE
  HENRY-COMPS ID:       ALL
  CHEMISTRY ID:         HCL       - APPARENT COMPONENTS

                          *******************
                          ****  RESULTS  ****
                          *******************
   TOP STAGE TEMPERATURE          F                          89.9238
   BOTTOM STAGE TEMPERATURE       F                          114.153
   TOP STAGE LIQUID FLOW          LBMOL/HR                  1,215.75
   BOTTOM STAGE LIQUID FLOW       LBMOL/HR                  1,268.97
   TOP STAGE VAPOR FLOW           LBMOL/HR                   934.921
   BOTTOM STAGE VAPOR FLOW        LBMOL/HR                   956.317
   CONDENSER DUTY (W/O SUBCOOL)   BTU/HR                       0.0
   REBOILER DUTY                  BTU/HR                       0.0
```

```
BLOCK:  B11       MODEL: SEP
---------------------------
  INLET STREAM:            8
  OUTLET STREAMS:          18         19
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG

                            ***  RESULTS  ***
 COMPONENT = HCL
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = C3H6
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = AC
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000

 COMPONENT = 12DCP
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000

 COMPONENT = 13DCP
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000


BLOCK:  B2        MODEL: HEATER
-----------------------------
PREHEATER
  INLET STREAM:            14
  OUTLET STREAM:           2
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG

                            ***  RESULTS  ***
  OUTLET TEMPERATURE      F                                      708.82
  OUTLET PRESSURE         PSI                                    74.700
  HEAT DUTY               BTU/HR                                 .10661E+08
  VAPOR FRACTION                                                 1.0000


BLOCK:  B3        MODEL: MIXER
-----------------------------
  INLET STREAMS:           2          3
  OUTLET STREAM:           4
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG


BLOCK:  B4        MODEL: COMPR
-----------------------------
  INLET STREAM:            12
  OUTLET STREAM:           13
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG



                            ***  RESULTS  ***
```

```
   INDICATED  HORSEPOWER REQUIREMENT  HP                          1,092.65
   BRAKE      HORSEPOWER REQUIREMENT  HP                          1,092.65
   NET WORK, HP                                                  -1,092.65
   CALCULATED OUTLET TEMP  F                                        273.004
   OUTLET VAPOR FRACTION                                              1.00000


BLOCK:  B5       MODEL: RADFRAC
-----------------------------
   INLETS   - 7         STAGE  6
   OUTLETS  - 9         STAGE  1
              10        STAGE 15
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                         *******************
                         ****  RESULTS  ****
                         *******************
   TOP STAGE TEMPERATURE          F                                 118.524
   BOTTOM STAGE TEMPERATURE       F                                 244.936
   TOP STAGE LIQUID FLOW          LBMOL/HR                          274.535
   BOTTOM STAGE LIQUID FLOW       LBMOL/HR                           41.6948
   TOP STAGE VAPOR FLOW           LBMOL/HR                           68.1983
   BOTTOM STAGE VAPOR FLOW        LBMOL/HR                          284.206
   MOLAR REFLUX RATIO                                                 4.02554
   MOLAR BOILUP RATIO                                                 6.81635
   CONDENSER DUTY (W/O SUBCOOL)   BTU/HR                     -3,093,420.
   REBOILER DUTY                  BTU/HR                      3,857,390.

  ****   MANIPULATED VARIABLES    ****
   DISTILLATE TO FEED RATIO                                           0.62059

  ****    DESIGN SPECIFICATIONS    ****
NO  SPEC-TYPE    UNIT   SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV           .99500             .99500           -.93840E-11


BLOCK:  B6       MODEL: RPLUG
-----------------------------
  INLET STREAM:           4
  OUTLET STREAM:          5
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                          ***  RESULTS  ***
   REACTOR DUTY                BTU/HR                                 -.37856
   RESIDENCE TIME              HR                                      .10723E-02
   REACTOR MINIMUM TEMPERATURE F                                      681.80
   REACTOR MAXIMUM TEMPERATURE F                                      919.79




          *** RESULTS PROFILE (PROCESS STREAM) ***
      LENGTH        PRESSURE      TEMPERATURE   VAPOR FRAC     RES-TIME
```

```
   FT            PSI          F                                HR
  .00000E+00    40.015       681.80         1.0000          .00000E+00
  1.5482        40.015       915.95         1.0000          .11446E-03
  3.0964        40.015       919.77         1.0000          .22092E-03
  4.6447        40.015       919.77         1.0000          .32734E-03
  6.1929        40.015       919.77         1.0000          .43377E-03
  7.7411        40.015       919.77         1.0000          .54019E-03
  9.2893        40.015       919.77         1.0000          .64662E-03
  10.838        40.015       919.77         1.0000          .75304E-03
  12.386        40.015       919.77         1.0000          .85946E-03
  13.934        40.015       919.77         1.0000          .96589E-03
  15.482        40.015       919.77         1.0000          .10723E-02

       ***  TOTAL MOLE FRACTION PROFILE (PROCESS STREAM) ***
   LENGTH        HCL          C3H6           CL2             AC
   FT
  .00000E+00   .00000E+00    .88299         .11701          .00000E+00
  1.5482       .10019        .80039         .20722E-02      .61086E-01
  3.0964       .10217        .79916         .00000E+00      .61544E-01
  4.6447       .10217        .79916         .00000E+00      .61544E-01
  6.1929       .10216        .79916         .73283E-06      .61543E-01
  7.7411       .10216        .79916         .78103E-06      .61543E-01
  9.2893       .10216        .79916         .35400E-06      .61543E-01
  10.838       .10217        .79916         .00000E+00      .61544E-01
  12.386       .10217        .79916         .00000E+00      .61544E-01
  13.934       .10217        .79916         .00000E+00      .61544E-01
  15.482       .10217        .79916         .00000E+00      .61544E-01

       ***  TOTAL MOLE FRACTION PROFILE (PROCESS STREAM) ***
   LENGTH        12DCP         13DCP
   FT
    .00000E+00    .00000E+00    .00000E+00
    1.5482        .16704E-01    .19553E-01
    3.0964        .16817E-01    .20311E-01
    4.6447        .16817E-01    .20311E-01
    6.1929        .16817E-01    .20311E-01
    7.7411        .16817E-01    .20311E-01
    9.2893        .16817E-01    .20311E-01
    10.838        .16817E-01    .20311E-01
    12.386        .16817E-01    .20311E-01
    13.934        .16817E-01    .20311E-01
    15.482        .16817E-01    .20311E-01


BLOCK:  B7        MODEL: RADFRAC
-------------------------------
   INLETS   - 6         STAGE   7
   OUTLETS  - 8         STAGE   1
              7         STAGE  15
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG




                             *******************
                             ****  RESULTS  ****
                             *******************
```

```
   TOP STAGE TEMPERATURE            F                            -45.1322
   BOTTOM STAGE TEMPERATURE         F                            174.331
   TOP STAGE LIQUID FLOW            LBMOL/HR                     501.951
   BOTTOM STAGE LIQUID FLOW         LBMOL/HR                     109.893
   TOP STAGE VAPOR FLOW             LBMOL/HR                   1,003.90
   BOTTOM STAGE VAPOR FLOW          LBMOL/HR                     264.491
   MOLAR REFLUX RATIO                                              0.50000
   MOLAR BOILUP RATIO                                              2.40680
   CONDENSER DUTY (W/O SUBCOOL)    BTU/HR                 -3,959,790.
   REBOILER DUTY                    BTU/HR                  3,089,190.

  ****   MANIPULATED VARIABLES    ****
   DISTILLATE TO FEED RATIO                                        0.90133

  ****    DESIGN SPECIFICATIONS    ****
NO  SPEC-TYPE   UNIT  SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV          .99990              .99990          -.54401E-14


BLOCK:  B8       MODEL: MIXER
-----------------------------
  INLET STREAMS:          1           13
  OUTLET STREAM:          14
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG


BLOCK:  B9       MODEL: HEATER
------------------------------
COOLER
  INLET STREAM:           5
  OUTLET STREAM:          6
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
  OUTLET TEMPERATURE    F                                           70.000
  OUTLET PRESSURE       PSI                                         74.700
  HEAT DUTY             BTU/HR                                    -.22671E+08
  VAPOR FRACTION                                                    .85497
```

```
                              STREAM SECTION

1 10 11 12 13
-------------
STREAM ID                1         10         11         12         13
FROM :                  ----       B5         B1         B1         B4
TO   :                  B8         ----       ----       B4         B8
SUBSTREAM: MIXED
PHASE:                  VAPOR      LIQUID     LIQUID     VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                     0.0        0.0       44.91       0.0        0.0
  HCL                     0.0      2.05-26      0.0        0.0        0.0
  C3H6                  109.99     1.58-19      0.0      890.01     890.01
  CL2                     0.0        0.0        0.0        0.0        0.0
  AC                      0.0        0.34       0.0        0.0        0.0
  12DCP                   0.0       18.73       0.0        0.0        0.0
  13DCP                   0.0       22.62       0.0        0.0        0.0
TOTAL FLOW:
  LBMOL/HR              109.99      41.69      44.91     890.01     890.01
  LB/HR                4628.28    4652.84     809.02    3.75+04    3.75+04
  CUFT/HR              7934.09      77.68      13.14    3.53+05    7.51+04
STATE VARIABLES:
  TEMP    F              80.00     244.94      89.92      89.92     273.00
  PRES    PSI            74.70      25.00      14.70      14.70      90.00
  VFRAC                   1.00       0.0        0.0        1.00       1.00
  LFRAC                   0.0        1.00       1.00       0.0        0.0
  SFRAC                   0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL            8312.67 -5.04+04 -1.23+05    8637.63    1.18+04
  BTU/LB                197.54   -451.84 -6805.71     205.26     279.50
  BTU/HR               9.14+05 -2.10+06 -5.51+06    7.69+06    1.05+07
ENTROPY:
  BTU/LBMOL-R           -37.39     -72.17     -38.47     -33.67     -32.31
  BTU/LB-R               -0.89      -0.65      -2.14      -0.80      -0.77
DENSITY:
  LBMOL/CUFT           1.39-02       0.54       3.42    2.52-03    1.18-02
  LB/CUFT                 0.58      59.89      61.59       0.11       0.50
AVG MW                   42.08     111.59      18.02      42.08      42.08
```

```
14 15 16 17 18
--------------
STREAM ID              14        15        16        17        18
FROM :                 B8        ----      B10       B10       B11
TO   :                 B2        B10       B1        ----      B10
SUBSTREAM: MIXED
PHASE:                 VAPOR     LIQUID    VAPOR     LIQUID     VAPOR
COMPONENTS: LBMOL/HR
  H2O                    0.0     1200.00     44.91   1155.09      0.0
  HCL                    0.0        0.0       0.0     113.79    113.79
  C3H6                1000.00       0.0     890.01   9.09-02    890.10
  CL2                    0.0        0.0       0.0       0.0       0.0
  AC                     0.0        0.0       0.0       0.0       0.0
  12DCP                  0.0        0.0       0.0       0.0       0.0
  13DCP                  0.0        0.0       0.0       0.0       0.0
TOTAL FLOW:
  LBMOL/HR            1000.00   1200.00    934.92   1268.97   1003.90
  LB/HR               4.21+04   2.16+04   3.83+04   2.50+04   4.16+04
  CUFT/HR             9.92+04    346.95   3.75+05    336.87   2.16+05
STATE VARIABLES:
  TEMP   F             252.34     70.00     89.92    114.15    -45.13
  PRES   PSI            74.70     14.70     14.70     14.70     20.00
  VFRAC                  1.00      0.0       1.00      0.0       1.00
  LFRAC                  0.0       1.00      0.0       1.00      0.0
  SFRAC                  0.0       0.0       0.0       0.0       0.0
ENTHALPY:
  BTU/LBMOL           1.14+04 -1.23+05   3269.97 -1.18+05   1314.61
  BTU/LB               270.48 -6827.94     79.90 -5982.92     31.72
  BTU/HR              1.14+07 -1.48+08   3.06+06 -1.49+08   1.32+06
ENTROPY:
  BTU/LBMOL-R          -32.48    -39.20    -32.13    -37.18    -33.32
  BTU/LB-R              -0.77     -2.18     -0.79     -1.89     -0.80
DENSITY:
  LBMOL/CUFT          1.01-02      3.46   2.49-03      3.77   4.65-03
  LB/CUFT                0.42     62.31      0.10     74.10      0.19
AVG MW                  42.08     18.02     40.92     19.67     41.44
```

```
19 2 3 4 5
----------
STREAM ID                 19         2          3          4          5
FROM :                    B11        B2         ----       B3         B6
TO   :                    ----       B3         B3         B6         B9
SUBSTREAM: MIXED
PHASE:                    LIQUID     VAPOR      VAPOR      VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                       0.0        0.0        0.0        0.0        0.0
  HCL                       0.0        0.0        0.0        0.0      113.79
  C3H6                      0.0     1000.00       0.0     1000.00     890.11
  CL2                       0.0        0.0      132.52     132.52       0.0
  AC                      6.85-03      0.0        0.0        0.0       68.55
  12DCP                   3.10-11      0.0        0.0        0.0       18.73
  13DCP                   3.28-11      0.0        0.0        0.0       22.62
TOTAL FLOW:
  LBMOL/HR                6.85-03   1000.00     132.52    1132.53    1113.80
  LB/HR                     0.52    4.21+04    9396.57    5.15+04    5.15+04
  CUFT/HR                 8.38-03   1.67+05    9656.29    1.85+05    4.11+05
STATE VARIABLES:
  TEMP    F               -45.13     708.82      80.00     682.82     919.77
  PRES    PSI              20.00      74.70      74.70      74.70      40.02
  VFRAC                     0.0        1.00       1.00       1.00       1.00
  LFRAC                     1.00       0.0        0.0        0.0        0.0
  SFRAC                     0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL              -1.51+04   2.20+04    -151.16    1.94+04    1.98+04
  BTU/LB                 -197.95     523.82      -2.13     427.81     427.81
  BTU/HR                 -103.84    2.20+07   -2.00+04    2.20+07    2.20+07
ENTROPY:
  BTU/LBMOL-R             -62.41     -21.06      -3.39     -18.05     -12.00
  BTU/LB-R                 -0.82      -0.50   -4.78-02      -0.40      -0.26
DENSITY:
  LBMOL/CUFT                0.82    5.99-03    1.37-02    6.13-03    2.71-03
  LB/CUFT                  62.56       0.25       0.97       0.28       0.13
AVG MW                     76.53      42.08      70.91      45.45      46.22
```

```
6 7 8 9
-------
STREAM ID                  6          7          8          9
FROM :                     B9         B7         B7         B5
TO   :                     B7         B5         B11        ----
SUBSTREAM: MIXED
PHASE:                     MIXED      LIQUID     VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                      0.0        0.0        0.0        0.0
  HCL                    113.79     2.13-11    113.79     2.13-11
  C3H6                   890.11     1.72-07    890.10     1.73-07
  CL2                      0.0        0.0        0.0        0.0
  AC                      68.55      68.54     6.85-03     68.20
  12DCP                   18.73      18.73     3.10-11    5.91-04
  13DCP                   22.62      22.62     3.28-11    1.74-04
TOTAL FLOW:
  LBMOL/HR              1113.80     109.89    1003.90      68.20
  LB/HR                 5.15+04    9871.77    4.16+04    5218.93
  CUFT/HR               6.76+04     171.58    2.16+05    2.57+04
STATE VARIABLES:
  TEMP    F               70.00     174.33     -45.13     118.52
  PRES    PSI             74.70      27.00      20.00      16.00
  VFRAC                    0.85       0.0        1.00       1.00
  LFRAC                    0.15       1.00       0.0        0.0
  SFRAC                    0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL             -582.25   -2.58+04    1314.58     403.67
  BTU/LB                 -12.60    -287.57      31.72       5.27
  BTU/HR               -6.49+05   -2.84+06    1.32+06    2.75+04
ENTROPY:
  BTU/LBMOL-R            -36.11     -59.28     -33.32     -34.33
  BTU/LB-R                -0.78      -0.66      -0.80      -0.45
DENSITY:
  LBMOL/CUFT            1.65-02       0.64    4.65-03    2.66-03
  LB/CUFT                  0.76      57.53       0.19       0.20
AVG MW                    46.22      89.83      41.44      76.53
```

OUTPUT FILE FOR ISOTHERMAL PLUG FLOW REACTOR

```
OPTIMIZATION: MAXPROFT
----------------------------------------------------------------
! ITER- ! OBJECT-  ! LAGRANG- ! VARY    1 ! VARY    2 ! VARY    3 !
! ATION ! IVE      ! IAN      ! B2        ! 3         ! B6        !
! NO.   ! FUNCTION ! FUNCTION ! PARAM     ! MIXED     ! PARAM     !
!       !          !          ! TEMP      ! CL2 MOLE  ! PRES      !
!       !          !          !           ! FLOW      !           !
!       !          !          ! F         ! LBMOL/HR  ! PSI       !
!       !          !          !           !           !           !
!=======!==========!==========!==========!==========!==========!
!   0   !  3285.89 !  MISSING !   830.00 !   200.00 !     46.00 !
!   1   !  3362.04 !  3361.88 !   773.30 !   272.00 !     45.97 !
!   2   !  3367.76 !  3367.73 !   779.83 !   282.21 !     45.97 !
!   3   !  3417.51 !  3417.45 !   788.11 !   242.10 !     46.06 !
!   4   !  3417.55 !  3417.45 !   788.11 !   242.10 !     46.06 !
----------------------------------------------------------------
```

```
BLOCK:  B1       MODEL: SEP
---------------------------
  INLET STREAM:            16
  OUTLET STREAMS:          12         11
  PROPERTY OPTION SET:     SYSOP11    UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
 COMPONENT = H2O
   STREAM      SUBSTREAM    SPLIT FRACTION
   11          MIXED                 1.00000

 COMPONENT = C3H6
   STREAM      SUBSTREAM    SPLIT FRACTION
   12          MIXED                 1.00000
```

```
BLOCK:  B10      MODEL: RADFRAC
-------------------------------
   INLETS    - 18        STAGE  10
               15        STAGE   1
   OUTLETS   - 16        STAGE   1
               17        STAGE  10
  PROP. OPT. SET:    SYSOP15   ELECTROLYTE NRTL / REDLICH-KWONG-SOAVE
  HENRY-COMPS ID:          ALL
  CHEMISTRY ID:            HCL       - APPARENT COMPONENTS

                          *******************
                          ****  RESULTS  ****
                          *******************
   TOP STAGE TEMPERATURE            F                        122.581
   BOTTOM STAGE TEMPERATURE         F                        140.565
   TOP STAGE LIQUID FLOW            LBMOL/HR               1,251.95
   BOTTOM STAGE LIQUID FLOW         LBMOL/HR               1,284.21
   TOP STAGE VAPOR FLOW             LBMOL/HR                 912.887
   BOTTOM STAGE VAPOR FLOW          LBMOL/HR                 933.815
   CONDENSER DUTY (W/O SUBCOOL)     BTU/HR                     0.0
   REBOILER DUTY                    BTU/HR                     0.0
```

```
BLOCK:  B11       MODEL: SEP
---------------------------
  INLET STREAM:            8
  OUTLET STREAMS:          18          19
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG

                            ***  RESULTS  ***
 COMPONENT = HCL
   STREAM     SUBSTREAM    SPLIT FRACTION
   18         MIXED                 1.00000

 COMPONENT = C3H6
   STREAM     SUBSTREAM    SPLIT FRACTION
   18         MIXED                 1.00000

 COMPONENT = AC
   STREAM     SUBSTREAM    SPLIT FRACTION
   19         MIXED                 1.00000

 COMPONENT = 12DCP
   STREAM     SUBSTREAM    SPLIT FRACTION
   19         MIXED                 1.00000

 COMPONENT = 13DCP
   STREAM     SUBSTREAM    SPLIT FRACTION
   19         MIXED                 1.00000


BLOCK:  B2        MODEL: HEATER
------------------------------
PREHEATER
  INLET STREAM:            14
  OUTLET STREAM:           2
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG

                            ***  RESULTS  ***
  OUTLET TEMPERATURE      F                                     788.11
  OUTLET PRESSURE         PSI                                   74.700
  HEAT DUTY               BTU/HR                                .12605E+08
  VAPOR FRACTION                                                1.0000


BLOCK:  B3        MODEL: MIXER
-----------------------------
  INLET STREAMS:           2           3
  OUTLET STREAM:           4
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG


BLOCK:  B4        MODEL: COMPR
-----------------------------
  INLET STREAM:            12
  OUTLET STREAM:           13
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG



                            ***  RESULTS  ***
```

```
   INDICATED  HORSEPOWER REQUIREMENT  HP                1,035.87
   BRAKE      HORSEPOWER REQUIREMENT  HP                1,035.87
   NET WORK, HP                                        -1,035.87
   CALCULATED OUTLET TEMP  F                              307.943
   OUTLET VAPOR FRACTION                                    1.00000


BLOCK:  B5       MODEL: RADFRAC
-------------------------------
   INLETS   - 7        STAGE   6
   OUTLETS  - 9        STAGE   1
              10       STAGE  15
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                         *******************
                         ****  RESULTS  ****
                         *******************
   TOP STAGE TEMPERATURE          F                       118.525
   BOTTOM STAGE TEMPERATURE       F                       244.235
   TOP STAGE LIQUID FLOW          LBMOL/HR                459.838
   BOTTOM STAGE LIQUID FLOW       LBMOL/HR                 85.6306
   TOP STAGE VAPOR FLOW           LBMOL/HR                114.230
   BOTTOM STAGE VAPOR FLOW        LBMOL/HR                477.987
   MOLAR REFLUX RATIO                                       4.02554
   MOLAR BOILUP RATIO                                       5.58196
   CONDENSER DUTY (W/O SUBCOOL)   BTU/HR           -5,181,470.
   REBOILER DUTY                  BTU/HR            6,476,130.

  ****   MANIPULATED VARIABLES   ****
   DISTILLATE TO FEED RATIO                                 0.57155

  ****    DESIGN SPECIFICATIONS   ****
NO  SPEC-TYPE   UNIT   SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV           .99500            .99500           .41123E-10


BLOCK:  B6       MODEL: RPLUG
-----------------------------
  INLET STREAM:          4
  OUTLET STREAM:         5
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                          ***  RESULTS  ***
   REACTOR DUTY               BTU/HR                        -.13195E+08
   RESIDENCE TIME             HR                             .10889E-02
   REACTOR MINIMUM TEMPERATURE F                            737.28
   REACTOR MAXIMUM TEMPERATURE F                            737.28




          *** RESULTS PROFILE (PROCESS STREAM) ***
      LENGTH        PRESSURE      TEMPERATURE   VAPOR FRAC    RES-TIME
```

```
  FT             PSI            F                              HR
 .00000E+00     46.064        737.28        1.0000         .00000E+00
 1.3296         46.064        737.28        1.0000         .10889E-03
 2.6592         46.064        737.28        1.0000         .21779E-03
 3.9889         46.064        737.28        1.0000         .32668E-03
 5.3185         46.064        737.28        1.0000         .43558E-03
 6.6481         46.064        737.28        1.0000         .54447E-03
 7.9777         46.064        737.28        1.0000         .65337E-03
 9.3073         46.064        737.28        1.0000         .76226E-03
 10.637         46.064        737.28        1.0000         .87116E-03
 11.967         46.064        737.28        1.0000         .98005E-03
 13.296         46.064        737.28        1.0000         .10889E-02

     ***  TOTAL MOLE FRACTION PROFILE (PROCESS STREAM) ***
  LENGTH         HCL            C3H6          CL2            AC
  FT
 .00000E+00     .00000E+00    .80509        .19491         .00000E+00
 1.3296         .12810        .69382        .43018E-01     .82913E-01
 2.6592         .15802        .67205        .84444E-02     .94296E-01
 3.9889         .16393        .66787        .16366E-02     .96311E-01
 5.3185         .16508        .66706        .31809E-03     .96695E-01
 6.6481         .16530        .66691        .67712E-04     .96767E-01
 7.9777         .16534        .66687        .15742E-04     .96782E-01
 9.3073         .16535        .66687        .61953E-05     .96785E-01
 10.637         .16535        .66687        .42104E-05     .96786E-01
 11.967         .16536        .66686        .00000E+00     .96787E-01
 13.296         .16536        .66686        .00000E+00     .96788E-01

     ***  TOTAL MOLE FRACTION PROFILE (PROCESS STREAM) ***
  LENGTH         12DCP          13DCP
  FT
  .00000E+00      .00000E+00     .00000E+00
  1.3296          .29548E-01     .22595E-01
  2.6592          .35331E-01     .31862E-01
  3.9889          .36442E-01     .33811E-01
  5.3185          .36656E-01     .34192E-01
  6.6481          .36697E-01     .34265E-01
  7.9777          .36705E-01     .34280E-01
  9.3073          .36707E-01     .34283E-01
  10.637          .36707E-01     .34283E-01
  11.967          .36708E-01     .34285E-01
  13.296          .36708E-01     .34286E-01


BLOCK:  B7        MODEL: RADFRAC
-------------------------------
   INLETS    - 6         STAGE   7
   OUTLETS   - 8         STAGE   1
               7         STAGE  15
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG



                             *******************
                             ****  RESULTS  ****
                             *******************
```

```
   TOP STAGE TEMPERATURE              F                           -44.1471
   BOTTOM STAGE TEMPERATURE           F                           178.284
   TOP STAGE LIQUID FLOW              LBMOL/HR                    499.131
   BOTTOM STAGE LIQUID FLOW           LBMOL/HR                    199.861
   TOP STAGE VAPOR FLOW               LBMOL/HR                    998.262
   BOTTOM STAGE VAPOR FLOW            LBMOL/HR                    414.608
   MOLAR REFLUX RATIO                                               0.50000
   MOLAR BOILUP RATIO                                               2.07448
   CONDENSER DUTY (W/O SUBCOOL)       BTU/HR                 -4,925,390.
   REBOILER DUTY                      BTU/HR                  4,904,070.

  ****   MANIPULATED VARIABLES       ****
   DISTILLATE TO FEED RATIO                                         0.83319

  ****    DESIGN SPECIFICATIONS    ****
NO  SPEC-TYPE   UNIT   SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV          .99000               .99000          -.49738E-13


BLOCK:  B8       MODEL: MIXER
-----------------------------
  INLET STREAMS:          1            13
  OUTLET STREAM:          14
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG


BLOCK:  B9       MODEL: HEATER
------------------------------
COOLER
  INLET STREAM:           5
  OUTLET STREAM:          6
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
  OUTLET TEMPERATURE    F                                          70.000
  OUTLET PRESSURE       PSI                                        74.700
  HEAT DUTY             BTU/HR                                   -.19550E+08
  VAPOR FRACTION                                                   .73180
```

```
                              STREAM SECTION

1 10 11 12 13
-------------
STREAM ID              1         10        11        12        13
FROM :                 ----      B5        B1        B1        B4
TO   :                 B8        ----      ----      B4        B8
SUBSTREAM: MIXED
PHASE:                 VAPOR     LIQUID    LIQUID    VAPOR     VAPOR
COMPONENTS: LBMOL/HR
  H2O                    0.0       0.0     114.01      0.0       0.0
  HCL                    0.0    1.37-25      0.0       0.0       0.0
  C3H6                 201.12   4.52-19      0.0     798.88    798.88
  CL2                    0.0       0.0       0.0       0.0       0.0
  AC                     0.0       0.57      0.0       0.0       0.0
  12DCP                  0.0      43.98      0.0       0.0       0.0
  13DCP                  0.0      41.08      0.0       0.0       0.0
TOTAL FLOW:
  LBMOL/HR             201.12     85.63    114.01    798.88    798.88
  LB/HR               8463.16   9571.34   2053.84   3.36+04   3.36+04
  CUFT/HR             1.45+04    159.39     33.96   3.36+05   7.10+04
STATE VARIABLES:
  TEMP    F             80.00    244.24    122.58    122.58    307.94
  PRES    PSI           74.70     25.00     14.70     14.70     90.00
  VFRAC                  1.00      0.0       0.0       1.00      1.00
  LFRAC                  0.0       1.00      1.00      0.0       0.0
  SFRAC                  0.0       0.0       0.0       0.0       0.0
ENTHALPY:
  BTU/LBMOL           8312.67  -5.39+04  -1.22+05   9166.49   1.25+04
  BTU/LB               197.54   -482.64  -6774.88    217.83    296.23
  BTU/HR              1.67+06  -4.62+06  -1.39+07   7.32+06   9.96+06
ENTROPY:
  BTU/LBMOL-R          -37.39    -72.89    -37.49    -32.74    -31.37
  BTU/LB-R              -0.89     -0.65     -2.08     -0.78     -0.75
DENSITY:
  LBMOL/CUFT          1.39-02      0.54      3.36   2.38-03   1.13-02
  LB/CUFT                0.58     60.05     60.48      0.10      0.47
AVG MW                  42.08    111.77     18.02     42.08     42.08
```

```
14 15 16 17 18
--------------
STREAM ID              14         15         16         17         18
FROM :                 B8         ----       B10        B10        B11
TO   :                 B2         B10        B1         ----       B10
SUBSTREAM: MIXED
PHASE:                 VAPOR      LIQUID     VAPOR      LIQUID     VAPOR
COMPONENTS: LBMOL/HR
  H2O                    0.0     1200.00     114.01    1085.99       0.0
  HCL                    0.0        0.0        0.0      198.12     198.12
  C3H6                1000.00       0.0      798.88   9.74-02     798.98
  CL2                    0.0        0.0        0.0        0.0        0.0
  AC                     0.0        0.0        0.0        0.0        0.0
  12DCP                  0.0        0.0        0.0        0.0        0.0
  13DCP                  0.0        0.0        0.0        0.0        0.0
TOTAL FLOW:
  LBMOL/HR            1000.00    1200.00     912.89    1284.21     997.10
  LB/HR               4.21+04    2.16+04    3.57+04    2.68+04    4.08+04
  CUFT/HR             1.01+05     346.95    3.88+05     326.55    2.15+05
STATE VARIABLES:
  TEMP    F            265.06      70.00     122.58     140.56     -44.15
  PRES    PSI           74.70      14.70      14.70      14.70      20.00
  VFRAC                  1.00       0.0        1.00       0.0        1.00
  LFRAC                  0.0        1.00       0.0        1.00       0.0
  SFRAC                  0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL           1.16+04 -1.23+05 -4885.64 -1.14+05 -2704.59
  BTU/LB               276.38 -6827.94   -125.03 -5443.55     -66.02
  BTU/HR              1.16+07 -1.48+08 -4.46+06 -1.46+08 -2.70+06
ENTROPY:
  BTU/LBMOL-R          -32.13     -39.20     -29.11     -36.36     -29.73
  BTU/LB-R              -0.76      -2.18      -0.74      -1.74      -0.73
DENSITY:
  LBMOL/CUFT          9.89-03       3.46    2.35-03       3.93    4.63-03
  LB/CUFT                0.42      62.31    9.19-02      82.05       0.19
AVG MW                  42.08      18.02      39.08      20.86      40.96
```

```
19 2 3 4 5
----------
STREAM ID              19         2          3          4          5
FROM :                 B11        B2         ----       B3         B6
TO   :                 ----       B3         B3         B6         B9
SUBSTREAM: MIXED
PHASE:                 LIQUID     VAPOR      VAPOR      VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                    0.0        0.0        0.0        0.0        0.0
  HCL                    0.0        0.0        0.0        0.0      198.12
  C3H6                   0.0     1000.00       0.0     1000.00     798.98
  CL2                    0.0        0.0      242.10     242.10       0.0
  AC                     1.16       0.0        0.0        0.0      115.96
  12DCP              2.93-08        0.0        0.0        0.0       43.98
  13DCP              1.31-08        0.0        0.0        0.0       41.08
TOTAL FLOW:
  LBMOL/HR              1.16    1000.00     242.10    1242.10    1198.12
  LB/HR                88.74    4.21+04    1.72+04    5.92+04    5.92+04
  CUFT/HR               1.42    1.78+05    1.76+04    2.13+05    3.33+05
STATE VARIABLES:
  TEMP    F           -44.15     788.11      80.00     738.07     737.28
  PRES    PSI          20.00      74.70      74.70      74.70      46.07
  VFRAC                  0.0       1.00       1.00       1.00       1.00
  LFRAC                 1.00        0.0        0.0        0.0        0.0
  SFRAC                  0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL         -1.51+04    2.42+04    -151.16    1.95+04    9184.30
  BTU/LB             -197.64     575.93      -2.13     408.44     185.73
  BTU/HR            -1.75+04    2.42+07  -3.66+04    2.42+07    1.10+07
ENTROPY:
  BTU/LBMOL-R         -62.35     -19.25      -3.39     -14.74     -14.61
  BTU/LB-R             -0.81      -0.46  -4.78-02      -0.31      -0.30
DENSITY:
  LBMOL/CUFT            0.82    5.60-03    1.37-02    5.84-03    3.60-03
  LB/CUFT              62.53       0.24       0.97       0.28       0.18
AVG MW                 76.53      42.08      70.91      47.70      49.45
```

```
6 7 8 9
-------
STREAM ID                 6           7           8           9
FROM :                    B9          B7          B7          B5
TO   :                    B7          B5          B11         ----
SUBSTREAM: MIXED
PHASE:                    MIXED       LIQUID      VAPOR       VAPOR
COMPONENTS: LBMOL/HR
  H2O                     0.0         0.0         0.0         0.0
  HCL                     198.12      9.87-11     198.12      9.87-11
  C3H6                    798.98      3.74-07     798.98      3.74-07
  CL2                     0.0         0.0         0.0         0.0
  AC                      115.96      114.80      1.16        114.23
  12DCP                   43.98       43.98       2.93-08     1.45-03
  13DCP                   41.08       41.08       1.31-08     3.29-04
TOTAL FLOW:
  LBMOL/HR                1198.12     199.86      998.26      114.23
  LB/HR                   5.92+04     1.83+04     4.09+04     8741.57
  CUFT/HR                 6.28+04     316.11      2.16+05     4.30+04
STATE VARIABLES:
  TEMP    F               70.00       178.28      -44.15      118.52
  PRES    PSI             74.70       27.00       20.00       16.00
  VFRAC                   0.73        0.0         1.00        1.00
  LFRAC                   0.27        1.00        0.0         0.0
  SFRAC                   0.0         0.0         0.0         0.0
ENTHALPY:
  BTU/LBMOL               -7133.18    -2.94+04    -2704.30    403.40
  BTU/LB                  -144.25     -320.44     -65.95      5.27
  BTU/HR                  -8.55+06    -5.87+06    -2.70+06    4.61+04
ENTROPY:
  BTU/LBMOL-R             -36.31      -60.57      -29.73      -34.33
  BTU/LB-R                -0.73       -0.66       -0.72       -0.45
DENSITY:
  LBMOL/CUFT              1.91-02     0.63        4.63-03     2.66-03
  LB/CUFT                 0.94        57.93       0.19        0.20
AVG MW                    49.45       91.63       41.01       76.53
```

OUTPUT FILE FOR ADIABATIC CONTINUOUS-FLOW STIRRED-TANK REACTOR

```
OPTIMIZATION: MAXPROFT
-----------------------------------------------------------------
! ITER- ! OBJECT-  ! LAGRANG- ! VARY    1 ! VARY    2 ! VARY    3 !
! ATION ! IVE      ! IAN      ! B2        ! 3         ! B6        !
! NO.   ! FUNCTION ! FUNCTION ! PARAM     ! MIXED     ! PARAM     !
!       !          !          ! TEMP      ! CL2 MOLE  ! PRES      !
!       !          !          !           ! FLOW      !           !
!       !          !          ! F         ! LBMOL/HR  ! PSI       !
!       !          !          !           !           !           !
!=======!==========!==========!==========!==========!==========!
!   0   !  1537.05 !  MISSING !    510.00 !    145.00 !     42.00 !
!   1   !  1561.31 !  1561.26 !    514.51 !    152.86 !     42.07 !
!   2   !  1589.33 !  1589.33 !    553.32 !    137.00 !     44.45 !
!   3   !  1644.16 !  1644.16 !    592.70 !    120.42 !     50.00 !
!   4   !  1649.00 !  1648.96 !    581.27 !    123.66 !     50.00 !
!-------+----------+----------+----------+----------+----------!
!   5   !  1649.36 !  1649.32 !    588.39 !    121.16 !     50.00 !
-----------------------------------------------------------------


BLOCK:  B1        MODEL: SEP
---------------------------
  INLET STREAM:            16
  OUTLET STREAMS:          12         11
  PROPERTY OPTION SET:     SYSOP11    UNIQUAC / REDLICH-KWONG

                            ***  RESULTS  ***
 COMPONENT = H2O
   STREAM      SUBSTREAM    SPLIT FRACTION
   11          MIXED                 1.00000

 COMPONENT = C3H6
   STREAM      SUBSTREAM    SPLIT FRACTION
   12          MIXED                 1.00000

 COMPONENT = CL2
   STREAM      SUBSTREAM    SPLIT FRACTION
   11          MIXED                 1.00000


BLOCK:  B10       MODEL: RADFRAC
-------------------------------
   INLETS    - 18        STAGE  10
               15        STAGE   1
   OUTLETS   - 16        STAGE   1
               17        STAGE  10
  PROP. OPT. SET:   SYSOP15   ELECTROLYTE NRTL / REDLICH-KWONG-SOAVE
  HENRY-COMPS ID:          ALL
  CHEMISTRY ID:            HCL       - APPARENT COMPONENTS
```

```
                              *******************
                              ****  RESULTS  ****
                              *******************
  TOP STAGE TEMPERATURE           F                                  84.9526
  BOTTOM STAGE TEMPERATURE        F                                  105.862
  TOP STAGE LIQUID FLOW           LBMOL/HR                          1,211.23
  BOTTOM STAGE LIQUID FLOW        LBMOL/HR                          1,263.47
  TOP STAGE VAPOR FLOW            LBMOL/HR                           947.821
  BOTTOM STAGE VAPOR FLOW         LBMOL/HR                           964.439
  CONDENSER DUTY (W/O SUBCOOL)    BTU/HR                               0.0
  REBOILER DUTY                   BTU/HR                               0.0

BLOCK:  B11       MODEL: SEP
---------------------------
 INLET STREAM:            8
 OUTLET STREAMS:          18         19
 PROPERTY OPTION SET:     SYSOP11    UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
 COMPONENT = HCL
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = C3H6
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = CL2
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = AC
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000

 COMPONENT = 13DCP
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000

BLOCK:  B2        MODEL: HEATER
------------------------------
PREHEATER
 INLET STREAM:            14
 OUTLET STREAM:           2
 PROPERTY OPTION SET:     SYSOP11    UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
 OUTLET TEMPERATURE     F                                          588.39
 OUTLET PRESSURE        PSI                                        74.700
 HEAT DUTY              BTU/HR                                     .75551E+07
 VAPOR FRACTION                                                    1.0000



BLOCK:  B3        MODEL: MIXER
```

```
-----------------------------
  INLET STREAMS:         2           3
  OUTLET STREAM:         4
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

BLOCK:  B4       MODEL: COMPR
-----------------------------
  INLET STREAM:          12
  OUTLET STREAM:         13
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                          ***  RESULTS  ***
   INDICATED  HORSEPOWER REQUIREMENT  HP                1,101.90
   BRAKE      HORSEPOWER REQUIREMENT  HP                1,101.90
   NET WORK, HP                                        -1,101.90
   CALCULATED OUTLET TEMP  F                              267.685
   OUTLET VAPOR FRACTION                                    1.00000

BLOCK:  B5       MODEL: RADFRAC
-------------------------------
   INLETS    - 7        STAGE   6
   OUTLETS   - 9        STAGE   1
             10        STAGE  15
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                         *******************
                         ****  RESULTS  ****
                         *******************
   TOP STAGE TEMPERATURE          F                       118.524
   BOTTOM STAGE TEMPERATURE       F                       245.930
   TOP STAGE LIQUID FLOW          LBMOL/HR                225.562
   BOTTOM STAGE LIQUID FLOW       LBMOL/HR                 38.5450
   TOP STAGE VAPOR FLOW           LBMOL/HR                 56.0327
   BOTTOM STAGE VAPOR FLOW        LBMOL/HR                233.735
   MOLAR REFLUX RATIO                                         4.02554
   MOLAR BOILUP RATIO                                         6.06395
   CONDENSER DUTY (W/O SUBCOOL)   BTU/HR           -2,541,610.
   REBOILER DUTY                  BTU/HR            3,174,250.

  ****   MANIPULATED VARIABLES   ****
   DISTILLATE TO FEED RATIO                                   0.59245

  ****    DESIGN SPECIFICATIONS   ****
NO  SPEC-TYPE   UNIT   SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV          .99500             .99500          .59799E-10

BLOCK:  B6       MODEL: RCSTR
-----------------------------
  INLET STREAM:          4
  OUTLET STREAM:         5
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                          ***  RESULTS  ***
   REACTOR TEMPERATURE  F                                    792.26
```

```
BLOCK:  B7        MODEL: RADFRAC
-------------------------------
   INLETS    - 6         STAGE   7
   OUTLETS   - 8         STAGE   1
               7         STAGE  15
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                           *******************
                           ****  RESULTS  ****
                           *******************
   TOP STAGE TEMPERATURE            F                          -44.5626
   BOTTOM STAGE TEMPERATURE         F                          176.755
   TOP STAGE LIQUID FLOW            LBMOL/HR                   505.649
   BOTTOM STAGE LIQUID FLOW         LBMOL/HR                    94.5777
   TOP STAGE VAPOR FLOW             LBMOL/HR                 1,011.30
   BOTTOM STAGE VAPOR FLOW          LBMOL/HR                   255.869
   MOLAR REFLUX RATIO                                            0.50000
   MOLAR BOILUP RATIO                                            2.70539
   CONDENSER DUTY (W/O SUBCOOL)     BTU/HR              -3,982,220.
   REBOILER DUTY                    BTU/HR               3,008,200.

  ****   MANIPULATED VARIABLES    ****
   DISTILLATE TO FEED RATIO                                      0.91448

  ****    DESIGN SPECIFICATIONS    ****
NO  SPEC-TYPE   UNIT   SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV           .99900              .99996         -.95625E-03


BLOCK:  B8        MODEL: MIXER
-----------------------------
  INLET STREAMS:          1           13
  OUTLET STREAM:          14
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

BLOCK:  B9        MODEL: HEATER
------------------------------
COOLER
  INLET STREAM:           5
  OUTLET STREAM:          6
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                            ***  RESULTS  ***
  OUTLET TEMPERATURE     F                                      70.000
  OUTLET PRESSURE        PSI                                    74.700
  HEAT DUTY              BTU/HR                                -.18451E+08
  VAPOR FRACTION                                                .87652
```

```
                              STREAM SECTION

1 10 11 12 13
-------------

STREAM ID                 1          10         11         12         13
FROM :                    ----       B5         B1         B1         B4
TO   :                    B8         ----       ----       B4         B8
SUBSTREAM: MIXED
PHASE:                    VAPOR      LIQUID     MIXED      VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                       0.0        0.0      38.91        0.0        0.0
  HCL                       0.0     1.30-26       0.0        0.0        0.0
  C3H6                    94.68     1.09-19       0.0     905.32     905.32
  CL2                       0.0     3.21-20      3.59        0.0        0.0
  AC                        0.0        0.28       0.0        0.0        0.0
  12DCP                     0.0       15.28       0.0        0.0        0.0
  13DCP                     0.0       22.98       0.0        0.0        0.0
TOTAL FLOW:
  LBMOL/HR                94.68       38.55     42.50     905.32     905.32
  LB/HR                 3984.22     4298.46    955.62    3.81+04    3.81+04
  CUFT/HR               6830.00       71.92    366.25    3.55+05    7.58+04
STATE VARIABLES:
  TEMP    F               80.00      245.93     84.95      84.95     267.69
  PRES    PSI             74.70       25.00     14.70      14.70      90.00
  VFRAC                    1.00         0.0   2.11-02       1.00       1.00
  LFRAC                     0.0        1.00      0.98        0.0        0.0
  SFRAC                     0.0         0.0       0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL             8312.67   -4.76+04  -1.13+05    8559.11    1.17+04
  BTU/LB                 197.54    -426.45  -5017.26     203.40     276.99
  BTU/HR                7.87+05   -1.83+06  -4.79+06    7.75+06    1.06+07
ENTROPY:
  BTU/LBMOL-R            -37.39     -71.65    -36.12     -33.82     -32.45
  BTU/LB-R                -0.89      -0.64     -1.61      -0.80      -0.77
DENSITY:
  LBMOL/CUFT            1.39-02       0.54      0.12    2.55-03    1.19-02
  LB/CUFT                  0.58      59.76      2.61       0.11       0.50
AVG MW                    42.08     111.52     22.48      42.08      42.08
```

```
14 15 16 17 18
--------------

STREAM ID                 14          15          16          17          18
FROM :                    B8          ----        B10         B10         B11
TO   :                    B2          B10         B1          ----        B10
SUBSTREAM: MIXED
PHASE:                    VAPOR       LIQUID      VAPOR       LIQUID      VAPOR
COMPONENTS: LBMOL/HR
  H2O                        0.0      1200.00       38.91     1161.09        0.0
  HCL                        0.0         0.0         0.0       102.28      102.28
  C3H6                    1000.00        0.0       905.32    9.71-02      905.42
  CL2                        0.0         0.0         3.59    6.15-03        3.60
  AC                         0.0         0.0         0.0         0.0         0.0
  12DCP                      0.0         0.0         0.0         0.0         0.0
  13DCP                      0.0         0.0         0.0         0.0         0.0
TOTAL FLOW:
  LBMOL/HR                1000.00     1200.00      947.82     1263.47     1011.30
  LB/HR                   4.21+04     2.16+04     3.91+04     2.47+04     4.21+04
  CUFT/HR                 9.88+04      346.95     3.77+05      337.95     2.18+05
STATE VARIABLES:
  TEMP    F                250.14       70.00       84.95      105.86      -44.56
  PRES    PSI               74.70       14.70       14.70       14.70       20.00
  VFRAC                      1.00        0.0         1.00        0.0         1.00
  LFRAC                      0.0         1.00        0.0         1.00        0.0
  SFRAC                      0.0         0.0         0.0         0.0         0.0
ENTHALPY:
  BTU/LBMOL               1.13+04    -1.23+05     3946.76    -1.18+05     1871.00
  BTU/LB                   269.47    -6827.94       95.79    -6062.90       44.96
  BTU/HR                  1.13+07    -1.48+08     3.74+06    -1.49+08     1.89+06
ENTROPY:
  BTU/LBMOL-R              -32.54      -39.20      -32.30      -37.46      -33.65
  BTU/LB-R                  -0.77       -2.18       -0.78       -1.92       -0.81
DENSITY:
  LBMOL/CUFT              1.01-02        3.46     2.52-03        3.74     4.65-03
  LB/CUFT                    0.43       62.31        0.10       72.94        0.19
AVG MW                      42.08       18.02       41.20       19.51       41.61
```

```
19 2 3 4 5
----------
STREAM ID                19         2          3          4          5
FROM :                   B11        B2         ----       B3         B6
TO   :                   ----       B3         B3         B6         B9
SUBSTREAM: MIXED
PHASE:                   LIQUID     VAPOR      VAPOR      VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                      0.0        0.0        0.0        0.0        0.0
  HCL                      0.0        0.0        0.0        0.0      102.23
  C3H6                     0.0     1000.00       0.0     1000.00     905.44
  CL2                      0.0        0.0      121.16     121.16       3.64
  AC                    2.46-03       0.0        0.0        0.0       56.31
  12DCP                    0.0        0.0        0.0        0.0       15.28
  13DCP                 1.07-11       0.0        0.0        0.0       22.96
TOTAL FLOW:
  LBMOL/HR              2.46-03   1000.00     121.16    1121.16    1105.87
  LB/HR                    0.19   4.21+04    8590.98    5.07+04    5.07+04
  CUFT/HR               3.01-03   1.49+05    8828.43    1.64+05    2.98+05
STATE VARIABLES:
  TEMP    F              -44.56    588.39      80.00     567.80     792.26
  PRES    PSI             20.00     74.70      74.70      74.70      49.70
  VFRAC                    0.0       1.00       1.00       1.00       1.00
  LFRAC                    1.00      0.0        0.0        0.0        0.0
  SFRAC                    0.0       0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL            -1.51+04   1.89+04    -151.16    1.68+04    1.71+04
  BTU/LB                -197.77    449.02      -2.13     372.54     372.54
  BTU/HR                 -37.29   1.89+07   -1.83+04    1.89+07    1.89+07
ENTROPY:
  BTU/LBMOL-R            -62.38    -23.90      -3.39     -20.84     -15.26
  BTU/LB-R                -0.82     -0.57   -4.78-02      -0.46      -0.33
DENSITY:
  LBMOL/CUFT               0.82   6.70-03    1.37-02    6.84-03    3.71-03
  LB/CUFT                 62.54      0.28       0.97       0.31       0.17
AVG MW                    76.53     42.08      70.91      45.20      45.82
```

```
6 7 8 9
-------

STREAM ID                6          7          8          9
FROM :                   B9         B7         B7         B5
TO   :                   B7         B5         B11        ----
SUBSTREAM: MIXED
PHASE:                 MIXED      LIQUID      VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                    0.0        0.0        0.0        0.0
  HCL                 102.23   1.12-11     102.28    1.12-11
  C3H6                905.44   1.02-07     905.42    1.02-07
  CL2                   3.64   6.12-09       3.60    6.12-09
  AC                   56.31     56.31    2.46-03      56.03
  12DCP                15.28     15.28    6.64-12    4.92-04
  13DCP                22.96     22.98    1.07-11    1.80-04
TOTAL FLOW:
  LBMOL/HR           1105.87     94.58    1011.30      56.03
  LB/HR             5.07+04    8586.41    4.21+04    4287.95
  CUFT/HR           6.88+04     148.86    2.18+05    2.11+04
STATE VARIABLES:
  TEMP    F            70.00    176.76     -44.56     118.52
  PRES    PSI          74.70     27.00      20.00      16.00
  VFRAC                 0.88       0.0       1.00       1.00
  LFRAC                 0.12      1.00        0.0        0.0
  SFRAC                  0.0       0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL           385.03  -2.58+04    1870.99     403.65
  BTU/LB                8.40   -284.53      44.96       5.27
  BTU/HR            4.26+05  -2.44+06    1.89+06    2.26+04
ENTROPY:
  BTU/LBMOL-R         -35.97    -59.64     -33.65     -34.33
  BTU/LB-R             -0.78     -0.66      -0.81      -0.45
DENSITY:
  LBMOL/CUFT        1.61-02       0.64    4.65-03    2.66-03
  LB/CUFT               0.74     57.68       0.19       0.20
AVG MW                 45.82     90.79      41.61      76.53
```

OUTPUT FILE FOR ISOTHERMAL CONTINUOUS-FLOW STIRRED-TANK REACTOR

```
OPTIMIZATION: MAXPROFT
-----------------------------------------------------------------------
! ITER- ! OBJECT-  ! LAGRANG- ! VARY   1! VARY   2! VARY   3! VARY   4!
! ATION ! IVE      ! IAN      ! B2      ! 3       ! B6      ! B6      !
! NO.   ! FUNCTION ! FUNCTION ! PARAM   ! MIXED   ! PARAM   ! PARAM   !
!       !          !          ! TEMP    ! CL2 MOLE! PRES    ! TEMP    !
!       !          !          !         ! FLOW    !         !         !
!       !          !          ! F       ! LBMOL/HR! PSI     ! F       !
!       !          !          !         !         !         !         !

!=======!==========!==========!=========!=========!=========!=========!
!   0   !  1321.77 !  MISSING !  550.00 !  120.00 !   32.00 !  900.00 !
!   1   !  1503.59 !  1503.59 !  535.00 !  118.50 !   37.04 !  780.00 !
!   2   !  1593.58 !  1593.58 !  500.00 !  115.00 !   50.00 !  789.63 !
!   3   !  1610.01 !  1610.00 !  500.00 !  150.12 !   50.00 !  794.95 !
!   4   !  1631.06 !  1630.73 !  500.00 !  127.57 !   50.00 !  791.31 !
!-------+----------+----------+---------+---------+---------!---------!
!   5   !  1631.23 !  1630.73 !  500.00 !  127.57 !   50.00 !  791.31 !
-----------------------------------------------------------------------


BLOCK:  B1        MODEL: SEP
---------------------------
  INLET STREAM:            16
  OUTLET STREAMS:          12         11
  PROPERTY OPTION SET:     SYSOP11   UNIQUAC / REDLICH-KWONG

                            ***  RESULTS  ***
 COMPONENT = H2O
   STREAM      SUBSTREAM    SPLIT FRACTION
   11          MIXED                 1.00000

 COMPONENT = C3H6
   STREAM      SUBSTREAM    SPLIT FRACTION
   12          MIXED                 1.00000

 COMPONENT = CL2
   STREAM      SUBSTREAM    SPLIT FRACTION
   11          MIXED                 1.00000


BLOCK:  B10       MODEL: RADFRAC
-------------------------------
   INLETS    - 18        STAGE  10
               15        STAGE   1
   OUTLETS   - 16        STAGE   1
               17        STAGE  10
  PROP. OPT. SET:    SYSOP15   ELECTROLYTE NRTL / REDLICH-KWONG-SOAVE
  HENRY-COMPS ID:          ALL
  CHEMISTRY ID:            HCL      - APPARENT COMPONENTS
```

```
                           *******************
                           ****  RESULTS  ****
                           *******************
   TOP STAGE TEMPERATURE          F                            87.5648
   BOTTOM STAGE TEMPERATURE       F                            110.116
   TOP STAGE LIQUID FLOW          LBMOL/HR                    1,213.56
   BOTTOM STAGE LIQUID FLOW       LBMOL/HR                    1,265.61
   TOP STAGE VAPOR FLOW           LBMOL/HR                     946.878
   BOTTOM STAGE VAPOR FLOW        LBMOL/HR                     965.985
   CONDENSER DUTY (W/O SUBCOOL)   BTU/HR                         0.0
   REBOILER DUTY                  BTU/HR                         0.0


BLOCK:  B11      MODEL: SEP
---------------------------
  INLET STREAM:           8
  OUTLET STREAMS:         18        19
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
 COMPONENT = HCL
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = C3H6
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = CL2
   STREAM      SUBSTREAM    SPLIT FRACTION
   18          MIXED                 1.00000

 COMPONENT = AC
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000

 COMPONENT = 12DCP
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000

 COMPONENT = 13DCP
   STREAM      SUBSTREAM    SPLIT FRACTION
   19          MIXED                 1.00000


BLOCK:  B2      MODEL: HEATER
------------------------------
PREHEATER
  INLET STREAM:           14
  OUTLET STREAM:          2
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                           ***  RESULTS  ***
  OUTLET TEMPERATURE    F                                        500.00
  OUTLET PRESSURE       PSI                                      74.700
  HEAT DUTY             BTU/HR                                   .53585E+07
  VAPOR FRACTION                                                 1.0000
```

```
BLOCK:  B3       MODEL: MIXER
-----------------------------
  INLET STREAMS:         2           3
  OUTLET STREAM:         4
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG


BLOCK:  B4       MODEL: COMPR
-----------------------------
  INLET STREAM:          12
  OUTLET STREAM:         13
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                          ***  RESULTS  ***
   INDICATED  HORSEPOWER REQUIREMENT  HP                  1,101.53
   BRAKE      HORSEPOWER REQUIREMENT  HP                  1,101.53
   NET WORK, HP                                          -1,101.53
   CALCULATED OUTLET TEMP  F                                270.480
   OUTLET VAPOR FRACTION                                      1.00000


BLOCK:  B5       MODEL: RADFRAC
-------------------------------
   INLETS   - 7        STAGE   6
   OUTLETS  - 9        STAGE   1
              10       STAGE  15
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                         *******************
                         ****  RESULTS  ****
                         *******************
   TOP STAGE TEMPERATURE           F                        118.524
   BOTTOM STAGE TEMPERATURE        F                        246.081
   TOP STAGE LIQUID FLOW           LBMOL/HR                 230.513
   BOTTOM STAGE LIQUID FLOW        LBMOL/HR                  41.1847
   TOP STAGE VAPOR FLOW            LBMOL/HR                  57.2626
   BOTTOM STAGE VAPOR FLOW         LBMOL/HR                 239.009
   MOLAR REFLUX RATIO                                         4.02554
   MOLAR BOILUP RATIO                                         5.80334
   CONDENSER DUTY (W/O SUBCOOL)    BTU/HR             -2,597,400.
   REBOILER DUTY                   BTU/HR              3,245,790.

  ****   MANIPULATED VARIABLES    ****
   DISTILLATE TO FEED RATIO                                   0.58166

  ****    DESIGN SPECIFICATIONS    ****
NO    SPEC-TYPE   UNIT   SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV           .99500             .99500           -.26803E-10


BLOCK:  B6       MODEL: RCSTR
-----------------------------
  INLET STREAM:          4
  OUTLET STREAM:         5
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG


                          ***  RESULTS  ***
   REACTOR DUTY         BTU/HR                                 .18357E+07
```

```
BLOCK:  B7       MODEL: RADFRAC
-------------------------------
   INLETS   - 6         STAGE  7
   OUTLETS  - 8         STAGE  1
              7         STAGE 15
  PROPERTY OPTION SET:   SYSOP11   UNIQUAC / REDLICH-KWONG

                         *******************
                         ****  RESULTS  ****
                         *******************
   TOP STAGE TEMPERATURE          F                        -42.8156
   BOTTOM STAGE TEMPERATURE       F                        177.683
   TOP STAGE LIQUID FLOW          LBMOL/HR                 506.536
   BOTTOM STAGE LIQUID FLOW       LBMOL/HR                  98.4473
   TOP STAGE VAPOR FLOW           LBMOL/HR               1,013.07
   BOTTOM STAGE VAPOR FLOW        LBMOL/HR                 313.601
   MOLAR REFLUX RATIO                                        0.50000
   MOLAR BOILUP RATIO                                        3.18547
   CONDENSER DUTY (W/O SUBCOOL)   BTU/HR              -4,595,650.
   REBOILER DUTY                  BTU/HR               3,694,750.

  ****  MANIPULATED VARIABLES   ****
   DISTILLATE TO FEED RATIO                                  0.91143

  ****   DESIGN SPECIFICATIONS   ****
NO  SPEC-TYPE   UNIT   SPECIFIED VALUE   CALCULATED VALUE   ABS. ERROR
 1  MOLE-RECOV             .99000             .99000         .31941E-12


BLOCK:  B8       MODEL: MIXER
-----------------------------
  INLET STREAMS:          1           13
  OUTLET STREAM:          14
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG


BLOCK:  B9       MODEL: HEATER
------------------------------
COOLER
  INLET STREAM:           5
  OUTLET STREAM:          6
  PROPERTY OPTION SET:    SYSOP11   UNIQUAC / REDLICH-KWONG

                          ***  RESULTS  ***
  OUTLET TEMPERATURE    F                                     70.000
  OUTLET PRESSURE       PSI                                   74.700
  HEAT DUTY             BTU/HR                               -.18558E+08
  VAPOR FRACTION                                              .86936
```

```
                              STREAM SECTION

1 10 11 12 13
-------------

STREAM ID                  1         10        11        12        13
FROM :                     ----      B5        B1        B1        B4
TO   :                     B8        ----      ----      B4        B8
SUBSTREAM: MIXED
PHASE:                     VAPOR     LIQUID    MIXED     VAPOR     VAPOR
COMPONENTS: LBMOL/HR
  H2O                        0.0       0.0      42.23      0.0       0.0
  HCL                        0.0     9.67-27     0.0       0.0       0.0
  C3H6                      99.14    7.50-20     0.0     900.92    900.92
  CL2                        0.0     2.24-20     3.73      0.0       0.0
  AC                         0.0       0.29      0.0       0.0       0.0
  12DCP                      0.0      16.09      0.0       0.0       0.0
  13DCP                      0.0      24.81      0.0       0.0       0.0
TOTAL FLOW:
  LBMOL/HR                  99.14     41.18     45.96    900.92    900.92
  LB/HR                   4171.71   4592.81   1025.16   3.79+04   3.79+04
  CUFT/HR                 7151.40     76.87    385.68   3.55+05   7.58+04
STATE VARIABLES:
  TEMP    F                 80.00    246.08     87.56     87.56    270.48
  PRES    PSI               74.70     25.00     14.70     14.70     90.00
  VFRAC                      1.00      0.0    2.05-02      1.00      1.00
  LFRAC                      0.0       1.00      0.98      0.0       0.0
  SFRAC                      0.0       0.0       0.0       0.0       0.0
ENTHALPY:
  BTU/LBMOL               8312.67  -4.72+04  -1.13+05   8600.30   1.17+04
  BTU/LB                   197.54   -423.67  -5073.23    204.38    278.31
  BTU/HR                  8.24+05  -1.95+06  -5.20+06   7.75+06   1.06+07
ENTROPY:
  BTU/LBMOL-R              -37.39    -71.59    -36.13    -33.74    -32.38
  BTU/LB-R                  -0.89     -0.64     -1.62     -0.80     -0.77
DENSITY:
  LBMOL/CUFT              1.39-02      0.54      0.12   2.54-03   1.19-02
  LB/CUFT                    0.58     59.75      2.66      0.11      0.50
AVG MW                      42.08    111.52     22.31     42.08     42.08
```

```
14 15 16 17 18
--------------

STREAM ID               14         15         16         17         18
FROM :                  B8         ----       B10        B10        B11
TO   :                  B2         B10        B1         ----       B10
SUBSTREAM: MIXED
PHASE:                  VAPOR      LIQUID     VAPOR      LIQUID     VAPOR
COMPONENTS: LBMOL/HR
  H2O                     0.0      1200.00      42.23    1157.77       0.0
  HCL                     0.0         0.0        0.0      107.75     107.75
  C3H6                 1000.05        0.0      900.92    9.33-02     901.01
  CL2                     0.0         0.0        3.73    6.11-03       3.73
  AC                      0.0         0.0        0.0        0.0        0.0
  12DCP                   0.0         0.0        0.0        0.0        0.0
  13DCP                   0.0         0.0        0.0        0.0        0.0
TOTAL FLOW:
  LBMOL/HR             1000.05    1200.00     946.88    1265.61    1012.49
  LB/HR                4.21+04    2.16+04    3.89+04    2.48+04    4.21+04
  CUFT/HR              9.91+04     346.95    3.78+05     337.31    2.19+05
STATE VARIABLES:
  TEMP    F             251.94      70.00      87.56     110.12     -42.82
  PRES    PSI            74.70      14.70      14.70      14.70      20.00
  VFRAC                   1.00       0.0        1.00       0.0        1.00
  LFRAC                   0.0        1.00       0.0        1.00       0.0
  SFRAC                   0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL            1.14+04   -1.23+05    3586.16   -1.18+05    1642.52
  BTU/LB                270.30   -6827.94      87.21   -6024.16      39.49
  BTU/HR               1.14+07   -1.48+08    3.40+06   -1.49+08    1.66+06
ENTROPY:
  BTU/LBMOL-R           -32.49     -39.20     -32.11     -37.32     -33.37
  BTU/LB-R               -0.77      -2.18      -0.78      -1.90      -0.80
DENSITY:
  LBMOL/CUFT           1.01-02       3.46    2.50-03       3.75    4.63-03
  LB/CUFT                 0.42      62.31       0.10      73.49       0.19
AVG MW                   42.08      18.02      41.12      19.59      41.59
```

```
19 2 3 4 5
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STREAM ID                19         2          3          4          5
FROM :                   B11        B2         ----       B3         B6
TO   :                   ----       B3         B3         B6         B9
SUBSTREAM: MIXED
PHASE:                   LIQUID     VAPOR      VAPOR      VAPOR      VAPOR
COMPONENTS: LBMOL/HR
  H2O                      0.0        0.0        0.0        0.0        0.0
  HCL                      0.0        0.0        0.0        0.0      107.75
  C3H6                     0.0     1000.04       0.0     1000.04     901.01
  CL2                      0.0        0.0      127.57     127.57       3.73
  AC                       0.58       0.0        0.0        0.0       58.13
  12DCP                  8.03-09      0.0        0.0        0.0       16.09
  13DCP                  6.72-09      0.0        0.0        0.0       24.80
TOTAL FLOW:
  LBMOL/HR                 0.58    1000.04     127.57    1127.61    1111.52
  LB/HR                   44.48    4.21+04    9045.50    5.11+04    5.11+04
  CUFT/HR                  0.71    1.36+05    9295.51    1.51+05    2.97+05
STATE VARIABLES:
  TEMP    F              -42.82     500.00      80.00     481.12     791.31
  PRES    PSI             20.00      74.70      74.70      74.70      50.00
  VFRAC                    0.0        1.00       1.00       1.00       1.00
  LFRAC                    1.00       0.0        0.0        0.0        0.0
  SFRAC                    0.0        0.0        0.0        0.0        0.0
ENTHALPY:
  BTU/LBMOL             -1.51+04    1.67+04   -151.16     1.48+04    1.67+04
  BTU/LB                -197.22     397.63      -2.13     326.91     362.81
  BTU/HR               -8773.11    1.67+07  -1.93+04    1.67+07    1.86+07
ENTROPY:
  BTU/LBMOL-R            -62.28     -26.06      -3.39     -22.66     -15.18
  BTU/LB-R                -0.81      -0.62   -4.78-02      -0.50      -0.33
DENSITY:
  LBMOL/CUFT               0.82    7.34-03    1.37-02    7.49-03    3.74-03
  LB/CUFT                 62.47       0.31       0.97       0.34       0.17
AVG MW                    76.53      42.08      70.91      45.34      46.00
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```
6 7 8 9
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STREAM ID                 6           7           8           9
FROM :                    B9          B7          B7          B5
TO   :                    B7          B5          B11         ----
SUBSTREAM: MIXED
PHASE:                    MIXED       LIQUID      VAPOR       VAPOR
COMPONENTS: LBMOL/HR
  H2O                       0.0         0.0         0.0         0.0
  HCL                     107.75      7.77-12     107.75      7.77-12
  C3H6                    901.01      6.65-08     901.01      6.65-08
  CL2                       3.73      4.11-09       3.73      4.11-09
  AC                       58.13       57.55        0.58       57.26
  12DCP                    16.09       16.09      8.03-09     5.23-04
  13DCP                    24.81       24.81      6.72-09     1.96-04
TOTAL FLOW:
  LBMOL/HR               1111.52       98.45     1013.07       57.26
  LB/HR                  5.11+04     8974.87     4.22+04     4382.07
  CUFT/HR                6.86+04      155.41     2.19+05     2.15+04
STATE VARIABLES:
  TEMP    F                70.00      177.68      -42.82      118.52
  PRES    PSI              74.70       27.00       20.00       16.00
  VFRAC                     0.87        0.0         1.00        1.00
  LFRAC                     0.13        1.00        0.0         0.0
  SFRAC                     0.0         0.0         0.0         0.0
ENTHALPY:
  BTU/LBMOL                -7.73    -2.61+04     1640.17      403.63
  BTU/LB                   -0.17     -286.48       39.42        5.27
  BTU/HR                -8596.89    -2.57+06     1.66+06     2.31+04
ENTROPY:
  BTU/LBMOL-R             -35.94      -59.83      -33.36      -34.33
  BTU/LB-R                 -0.78       -0.66       -0.80       -0.45
DENSITY:
  LBMOL/CUFT             1.62-02        0.63     4.63-03     2.66-03
  LB/CUFT                   0.75       57.75        0.19        0.20
AVG MW                     46.00       91.16       41.61       76.53
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VITA

Dick U. van der Helm

Candidate for the Degree of

Master of Science

Thesis: AN ECONOMIC CASE STUDY OF PROCESS MODIFICATION FOR THE ALLYL CHLORIDE PROCESS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Norman, Oklahoma, on October 21, 1970, the son of Dick and Louise van der Helm.

Education: Graduated from Norman High School, Norman, Oklahoma in May 1988; received Bachelor of Science degree in Chemical Engineering from Oklahoma State University, Stillwater, Oklahoma in December 1992. Completed the requirements for the Master of Science degree with a major in Chemical Engineering at Oklahoma State University in December, 1997.

Experience: Worked as a summer intern for Kerr-McGee Corporation at their Technical Center in Oklahoma City, Oklahoma during the summer of 1990, for Exxon Company in Houston, Texas during the summer of 1991, and for Amoco Production Company at their Research Center in Tulsa, Oklahoma during the summer of 1994. After defending my thesis (but before completing the changes to my thesis), employed as a process engineer by Koch Refining Company in Corpus Christi, Texas from March 1995 until January 1997. From February 1997 until October 1997, worked as an applications engineer for John Zink in Tulsa, Oklahoma. Currently employed with John Zink, but working in Luxembourg, Luxembourg.

Professional Memberships: American Institute of Chemical Engineers, Tau Beta Pi National Engineering Honor Society, Omega Chi Epsilon Chemical Engineering Honor Society.