

PROCESS ENHANCEMENT BY PROCESS
SIMULATION AND MULTIOBJECTIVE
OPTIMIZATION

By

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PROCESS ENHANCEMENT BY PROCESS
SYNTHESIS AND MULTIOBJECTIVE
OPTIMIZATION

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NOMENCLATURE

A	Pre-exponential Factor
a	Temperature Exponent
A_c	Additional costs (\$/yr.)
<i>alt</i>	process alternative
CAA	Clean Air Act
CF	Fixed capital cost
CFR	Code of Federal Regulations
CSTR	Continuous Stirred Tank Reactor
CWA	Clean Water Act
D	Diameter
D_f	Depreciation factor
E_a	Activation Energy
EPA	Environmental Protection Agency
F_{A0}	Inlet Mole Flow Rate.
FCC	Fixed Capital Cost
f_D	Discount factor
H	Height

I	Interest Rate
k	rate constant
K	Relative Volatility
MILP	Mixed Integer Linear Programming
MINLP	Mixed Integer Non Linear Programming
NLP	Non Linear Problem
M&S	Marshall and Swift Index
n	New process
NPV	Net Present Value
ny	Number of Years
O	Operating Costs
P	Profit
PFR	Plug Flow Reactor
Q_v	Plant or equipment capacity
r_A	Reaction Rate of Component A
R	Gas Constant
RCC	Reactor Capital Cost
RCSTR	Aspen PLUS™ Model For CSTR
RPFR	Aspen PLUS™ Model For PFR
Rw	Raw materials cost (\$/yr.)
SQP	Sequential Quadratic Programming
T	Tax rate

TRI	Toxics Release Inventory
UCWR	University Center for Water Research
V	Reactor Volume
W	Waste Costs (\$/yr.)
ψ	Exponent 0.6 - 0.7
X_A	Conversion of Propylene.
Y	Total Number of Units

CHAPTER 1

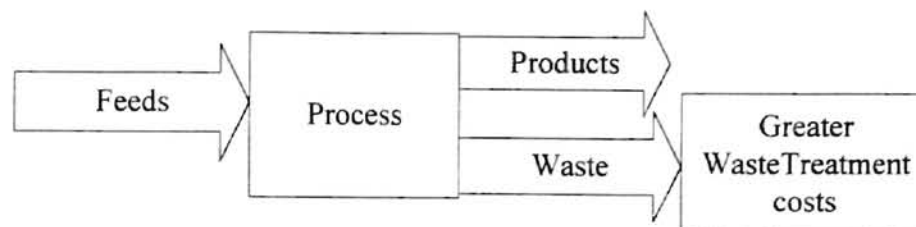
INTRODUCTION

Every sphere of life is now facing increasing pressure to minimize their impact on the environment. This is due to the fragile nature of today's environment resulting from man's destructive effect on it over the years. It has therefore become necessary to implement techniques that will prevent industrial pollution from causing a major ecological disaster. The Environmental Protection Agency (EPA) defines pollution prevention as "the use of materials, processes or practices that eliminate the creation of pollutants at the source. It includes practices that reduce the use of hazardous materials, energy, water or other resources and practices that protect natural resources through conservation or more efficient use" (Freeman, 1995). One of the benefits of pollution prevention is that it is often economical. It leads to increasing the savings in regulatory and compliance costs, improving the overall process effectiveness, minimizing uncertainty, and avoiding cross-media transfers. Pollution prevention has become the current industrial buzzword.

Pollution prevention can be achieved by utilizing waste minimization techniques. "The total cost for managing waste is rising at a rate of 20-30% per lb. per year" (Hollod, 1988). A waste minimization procedure lowers the operating costs, the process liability and the regulatory burden for the company. It also reduces the taxes and improves the

public attitude towards the company (Benforado, 1991). Figure 1.1 (Smith, 1991) illustrates the effect of waste minimization as a means of reducing waste treatment

Before Waste Minimization



After Waste Minimization

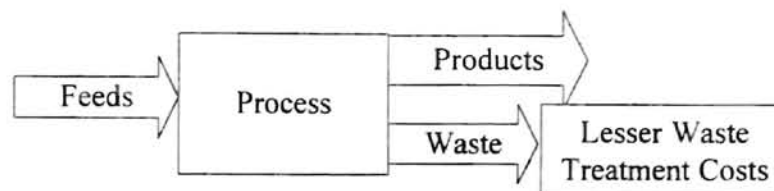


Figure 1.1: Effect of waste minimization in a chemical process.

costs and lowering raw material costs. The waste that is generated in a process can be dealt with by waste minimization or by waste treatment. The waste minimization techniques that are practiced in the industry can be broadly classified into source reduction and recycling techniques. Source reduction, as the name implies, deals with the reduction of waste at the source itself, thereby doing away with the need to incorporate pollution control techniques at a later stage. The EPA defines source reduction as the “elimination or reduction of waste generation at the source, usually within the process. Source reduction measures can include treatment processes, but they usually include process modifications, feed stock substitutions or improvements in feed stock purity,

various housekeeping and management practices, increases in efficiency of machinery and even recycling within a process. Source reduction implies any action that reduces the amount of waste exiting a process” (Freeman, 1993). Source reduction can be easily understood as the concept that “if you don’t generate waste you don’t have to treat it” (Hydrocarbon Processing, 1993). Source reduction can be achieved by incorporating product changes or source control. Product changes can be done by product substitution, product conservation or by changing the product composition. Source control deals with input material changes, improving the technology and employing good operating practices. Waste treatment or the “end of the pipe” treatment deals with managing and cleaning up the waste after it is created.

It is desirable that pollution abatement in one part does not affect another part of the environment. Source reduction would help reduce the necessity for pollution abatement at a later stage. Understandably, source reduction is preferred by the EPA rather than the “end of the pipe” treatment. An EPA policy statement clarified “pollution prevention as source reduction” (Freeman, 1995). The “end of the pipe treatment” or waste treatment is fast being replaced by source reduction in industries to diminish pollution. It should, however, be noted that the cleanest process might not be the least expensive process (Douglas, 1992). Emphasis should be placed on source reduction rather than end of pipe treatment as a more cost effective method of implementing waste minimization. Source reduction is being more widely accepted as the better treatment practice as this method reduces any negative impact on the human health and the environment. Another economic advantage of source reduction is that it

reduces or diminishes the burden on the later steps such as the waste treatment, regulatory compliance and liability costs (Fonyo, 1994).

Regulatory Risk Analysis

Risk can be defined as the probability of harm to human health and the environment. Assessing the risk that is caused to the environment is fast becoming an integral part of pollution prevention (Chiang, 1995). Risk is quantified on a scale of zero to one where zero depicts absolute safety and one denotes absolute harm. Risk analysis involves measures that are taken to ensure minimum risk to the environment. In 1992, the US EPA proposed risk based management of hazardous waste. The EPA has divided various known toxic and otherwise harmful chemicals into various categories and has set limits which industries are not supposed to exceed. Risk analysis is based on maintaining risk below these limits.

Objectives

The objectives of this research are:

1. To provide a general methodology that can be followed by other chemical processes for reducing waste and also generating profits simultaneously. This methodology uses the concepts of multiobjective optimization to provide a cost effective process. Manufacture of acrylonitrile is studied as an example for cost effective processing and simultaneous reduction of waste.

2. Apply waste minimization techniques in the methodology to enhance the chemical process.

Brief Description of the Methodology

The methodology followed can be broadly classified into four sections:

1. Development of base case model.
2. Identification of important process parameters.
3. Development of process alternatives.
4. Application of multiobjective optimization techniques.

Initially, a base case model of the acrylonitrile process was developed on ASPEN PLUS™. The release 9.2 version of ASPEN PLUS was used in this research. All reference in this thesis on ASPEN PLUS is to be considered as modeled on version 9.2. The base case process flow diagram, kinetics and the reaction conditions were obtained from literature (Hopper, 1992). The next step involved the analysis of the stream summaries and identification of product and waste streams. Process alternatives were then evaluated from the stream summaries. Using the concepts of multiobjective optimization, the superior alternative was identified. The net present value method of economic calculations was used to evaluate the savings.

Brief Description of the Acrylonitrile Process

Acrylonitrile is a colorless liquid with a slightly pungent odor. It is used in the manufacture of resins, nitrile elastomers and as an intermediate in the production of

adiponitrile and acrylamide. Acrylonitrile is mainly produced by the "Sohio" process. The Sohio process involves the ammoxidation of propylene in the presence of a catalyst at 662 °F - 1112 °F. The catalysts used are mixed metal oxides such as iron-antimony oxides, uranium-antimony oxides, bismuth-molybdenum oxide, etc. Propylene and ammonia are reacted along with oxygen in the presence of a catalyst. The reactor effluent consists of major products such as acrylonitrile and acetonitrile, waste gases and unconverted raw material. The reactor effluent is cooled by quenching with water and is neutralized using sulfuric acid to remove unconverted ammonia to produce ammonium sulfate which can be used as a fertilizer. The acrylonitrile and acetonitrile are then separated from the waste gases and purified in a cascade of separation columns.

The thesis is divided into the following sections:

- Background of research done at OSU and by other researchers.
- General methodology.
- Case study - The acrylonitrile process.
- Concepts of multiobjective optimization.
- Determination and selection of process alternatives.
- Results and conclusion.

In summary, this research develops a methodology that minimizes waste and also optimizes the earnings by using the concepts of multiobjective optimization. A brief description of the research and the methodologies developed done in and out of OSU will be dealt with in the next chapter.

CHAPTER 2

BACKGROUND

This chapter will deal with a background of the environmental regulations and the waste minimization methodologies that are existing today. A brief description of related work done at Oklahoma State University will also be discussed.

The necessity to safeguard our environment has been increasing ever since the industrial revolution, which heralded the beginning of new technological ventures that caused a lot of pollution. Advancement in technology caused environmental deterioration. If this deterioration continues unchecked, it will lead to the extinction of nature and mankind in the long run.

The society of today is very much aware of it's impact on the environment. Society's increasing desire to live in a cleaner environment has led the governments of many countries to set up measures to curb pollution as much as possible. In the United States, the Environmental Protection Agency (EPA) was set up by an Executive Order in December 1970. "The mission of the EPA is to protect the health and welfare of the American people by preventing, abating, and cleaning up pollution standards" (Focht, 1995). The Pollution Prevention Act of 1990 favored recycling wherever possible and source reduction techniques. The EPA initiated the 33/50 program that encouraged industries reporting toxic releases under the Toxics Release Inventory (TRI) to voluntarily reduce their net emission of 17 chemicals to 33% by 1992 and to 50 % by

1995 (Freeman, 1992). The 33/50 program was deemed as successful. Some other programs that have been initiated recently are the 'Environmental Leadership Program' which is an experiment into new approaches for dealing with current regulations. 'Project XL' is a new program that would be an experiment into letting regulated entities develop their own environmental management systems with freedom from current regulations (Embers, 1995). Table 2.1 gives a listing of some of the waste reduction projects that have been undertaken by industries.

Today's industries have to deal with the emission standards for factories that were built decades before these regulations were envisioned (Valenti, 1992). Some of the aspects that need to be addressed in order to achieve pollution prevention are plant configuration, research and development, process design and human resources. In industry, the separation techniques, process development, pollution reduction, by-product reuse, design concepts, process control and material substitution can all be used to reduce pollution (Freeman, 1992).

2.1 Existing Waste Minimization Methodologies

Two well known methodologies for tackling waste minimization problems are:

- (a) Hierarchical procedure, and
- (b) Pinch Analysis

TABLE 2.1
WASTE REDUCTION PROJECTS

Company	Accomplishments
<i>Amoco</i> Waste Minimization Program (1983)	Between 1983 and 1988, Amoco reduced its hazardous waste by 86%, saving the company about \$50 million.
<i>Chevron</i> 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.
<i>Dow</i> 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.
<i>General Dynamics</i> Zero Discharge (1985)	Nearly 40 mill. lb. of hazardous waste discharge eliminated from 1984 to 88 (approx. 72%). Sales increased from \$7.3 to 9.35 billion over the same period.
<i>IBM</i>	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 US operations was recycled in 1988; IBM US emissions were reduced 20% from 1987 to 88; and, IBM US had a decrease of 25% in its CFC emissions between 1987 and 88.
<i>Monsanto</i> Priority One (TRI wastes)	From 1987 to 1990, Monsanto achieved a 39% reduction in hazardous air emissions.
<i>Specialty Adhesives and Chemicals</i>	An analysis of an amine production process increased the conversion reducing the waste in 95 tons/yr. By considering the recycling of excess reactant an additional waste reduction of 70 tons/yr. and a decrease of 20% of manufacturing costs was obtained.

Source: Benforado and Ridlehoover (1991); Freeman (1992); Morris and Robertson (1993); Thayer (1992); Woodman (1989).

2.1.1 Hierarchical Procedure

The hierarchical procedure helps in identifying a chemical plant's pollution problems. This procedure is based on :

- Making the right decisions in order to design a cleaner process and
- Identifying problems that would occur if a different decision that changed the process alternatives were made.

The hierarchical procedure (Douglas, et al., 1992; Rossiter, et al., 1993; Fonyo, et al., 1994) is a standard procedure to develop process alternatives as shown in Table 2.2.

TABLE 2.2

METHODOLOGY FOR HIERARCHICAL PROCEDURE

Level 1: Input information: Design process flowsheet using process input information shown in Table 3.1.

Level 2: Input-output Structure: Description of all streams that enter and leave the process.

Level 3: Recycle Structure: Depending on the stream summary a decision is to be made as to how to carry out the recycling.

Level 4: Specification of the separation system: Deciding on which option could replace the present separation system depending on the phase of recovery.

Level 5: Energy Integration: Improvement of the process energy requirement depending on incorporation of heat integration techniques.

Level 6: Evaluation of Alternatives

Level 7: Flexibility and Control

Level 8: Safety

(b) Pinch Analysis

Pinch analysis is a procedure that evolved during the energy crisis of 1970, from a necessity to increase the energy savings, especially when using heat exchanger networks. It resulted in the optimization of heat integration. The scope of pinch analysis has now broadened to separation, waste-removal as well as non energy objectives such as capital cost, operability and emissions. Savings of nearly 25% of the overall utility operating cost have been obtained using pinch analysis (Linnhoff, 1986). The advantage of using pinch technology is that it provides a quantitative method of incorporating waste treatment within the process (Rossiter, 1991). Table 2.3 briefly explains the three main concepts involved in pinch analysis.

TABLE 2.3

METHODOLOGY FOR PINCH ANALYSIS

(a) Development of Composite Curves: The entire process is represented on a temperature enthalpy

diagram by composite curves which represent the cumulative heat sources and sinks within the process (Linhoff, 1988). These composite curves are arrived at from stream data derived from a process heat and material balance. These allow prediction of hot and cold targets ahead of design.

(b) Grid Diagram Development: This is a diagram which helps in developing heat recovery networking.

The hot streams run from left to right while cold streams run counter-current at the bottom.

(c) Pinch Identification: A grand composite curve is drawn which is composed of the composite curves for all the streams and the equipment are “appropriately placed”. Appropriate placement can be done for equipment that can be represented in terms of heat sources and sinks. This implies that this can be used for heat pumps, distillation columns, evaporators, heat engines, etc. From this grand composite curve, the pinch temperature can be determined (Linhoff, 1994).

2.2 Prior Research in Multiobjective Optimization

Multiobjective optimization is a method which helps in simultaneously maximizing the profits before waste treatment and minimizing the waste production. Haimes and Li (1988) have reviewed the solution methods for multiobjective optimization. Its engineering applications have been reviewed by Goicoechea (1980). Its chemical engineering applications have been reviewed by Sawaragi (1985). Previously, discrete alternatives were identified using an iterative procedure proposed by Zionts (1981). Optimization problems have been solved using branch and bound techniques (Marcotte, 1986) as well as using dynamic programming (Villareal, 1981). Solution methods for multiobjective integer linear problems (MOILP) have been done in Bitran (1977,1979), Klein (1982) and Esawaran (1989). Ciric and Jia (1993) have extensively researched multiobjective optimization and have presented a novel method of solving multiobjective optimization problems that is based on modification of the outer approximation method of solving multi integer non linear problems (MINLP).

2.3 Prior Research at Oklahoma State University

A one year research project funded by the OSU University Center for Water Research (UCWR) entitled "Reduction of Wastewater Through the Process Modification" was directed toward initiating modeling studies of the allyl chloride and methyl chloride processes. Both projects gave insight to process modeling and provided opportunities for reducing effluents of several toxic wastewater pollutants regulated by the Environmental Protection Agency.

The UCWR project served as a tool to quantify the advantages of applying waste minimization techniques instead of the end-of pipe treatment approach. The allyl chloride project done by Dicky Van der Helm involved three steps: process modeling, selection of source reduction variables and their ranges, and optimization of an economic objective function. The process simulator ASPEN PLUSTM was used to model and evaluate the process. Process operating conditions that have major effect on the process are known as source reduction variables. Source reduction variables were primarily located through the literature and sensitivity analysis. The reactor feed ratio, the feed temperature, the reactor pressure and the reactor type were the source reduction variables that were found. To find the best value of these process variables, optimization of an economic objective function was performed. Regulatory risk was successfully incorporated into the process modification waste minimization strategy through its use as a constraint in the objective function. It was found that the ratio of the revenue to waste cost was the maximum for the adiabatic plug flow reactor model for the modelled allyl chloride process.

The methyl chloride project conducted by Mauricio Dantus consisted of identifying the waste minimization options through a sensitivity analysis and possible flow sheet configurations through a hierarchical procedure. The alternatives identified were used to construct a superstructure, which was formulated as a mixed integer nonlinear programming (MINLP) problem. The superstructure was evaluated and optimized to select the best flow sheet configuration. The superstructure was optimized using an economic model based on the net present value method to incorporate both

manufacturing and capital costs. As a next step, the selected flow sheet was integrated to improve the energy efficiency by the formulation of a heat exchanger network superstructure. By using the methodology, the optimal process flowsheet to produce methyl chloride was found to be the hydrochlorination of methanol. Further, this process resulted in a 65% decrease in waste generated, a 67% increase in profit and a 95% decrease in utility requirements.

Presently, manufacture of glycerol via the allyl chloride process is being further researched and optimized by Kaushik Suchak by incorporation of pinch technology techniques. The project helps in minimizing fresh water consumption and reducing wastewater generation. The wastewater streams and the contaminant levels are identified. Pinch diagrams are then formulated which consists of plotting the concentration of contaminant in the inlet and the outlet flow of water versus the mass flow rate of the *contaminant*. This will be used to calculate the thermodynamic theoretical requirement of water. Based on this, alternate flow sheets are generated and economic optimization is carried out for the source reduction variables to generate a more efficient process.

2.4 Motivation

There is a need for development of a methodology that would help the society from an environmental point of view by reducing pollution as well as help industry from an economic point of view by increasing the industry's revenue earned. Multiobjective optimization helps in achieving a tradeoff that would help achieve both ends simultaneously. The multiobjective optimization has not been fully explored on a process

simulator, such as ASPEN PLUS™, for processes with both continuous and discrete variables. (Ciric, 1993) The methodology can help in making decisions regarding the tradeoffs that would be needed to make while designing new process or revamping existing processes. This approach eliminates the need to do optimization for every possible process alternative over the whole range of parametric variables. In contrast with single optimization approach, the multiobjective optimization strategy takes the waste generation and the profits earned simultaneously into consideration. While the single optimization approach would give the results for the maximum revenue earned and the minimum waste generation separately, it does not give an overall idea of the effect of the effect of the waste on the profits as multiobjective optimization does. The multiobjective optimization approach differs from the previous researchers at OSU in this area in the optimization strategy that is being followed.

The acrylonitrile manufacturing process presents an ideal process that can be studied and modified since it is one of the top 50 chemicals produced in the United States. Further, the acrylonitrile manufacturing process presents a challenge since it is a complicated process with five side reactions. Acrylonitrile is a raw material for the manufacture of nylon, ABS resins, moldings and fibers. Although the products and byproducts of the acrylonitrile process are used for making several day to day accessories, the process is not environmentally benign. Due to its high production and usefulness, it is desirable to check for alternative procedures which could lead to a better, more efficient process. This is a process in which many of the by-products such as hydrogen cyanide and carbon monoxide that are formed are toxic by nature and are

heavily regulated. Acrolein and acrylonitrile are the main products that themselves are classified by the EPA in the list of priority pollutants in section 307 of the Clean Water Act of 1987. Acrolein and acrylonitrile are also classified as class X (reportable quantity - 1lb) and class B (reportable quantity - 100 lbs) hazardous substances respectively in section 311 of the Clean Water Act. The acrylonitrile process also produces undesired wastes such as hydrogen cyanide and carbon monoxide which are classified as hazardous substances by the EPA. Therefore, the waste reduction potential for the acrylonitrile process is also high.

A general description of the proposed methodology to design enhanced processes will be discussed in the next chapter.

CHAPTER 3

METHODOLOGY

Due to increasing waste treatment costs and increased attention towards a healthier environment, a methodology that relates positively to the environment as well as the process economy is required to be incorporated in chemical plants. This chapter will present a general methodology that can be followed in retrofitting an existing process or while designing a new process.

The methodology that has been used in evaluating the acrylonitrile process can be used in other processes as well. It involves the following:

- Development of base case model.
- Identification of important process parameters
 - Stream analysis.
 - Sensitivity analysis.
- Development of process alternatives.
- Application of multiobjective optimization techniques.

The general methodology is shown in more detail in Figure 3.1. There are four stages in implementing a waste elimination scheme:

- Identification of the chemicals of concern in the waste.
- Establishment of the origin of the chemicals of concern.
- Selection of the technically feasible reduction or recovery techniques.

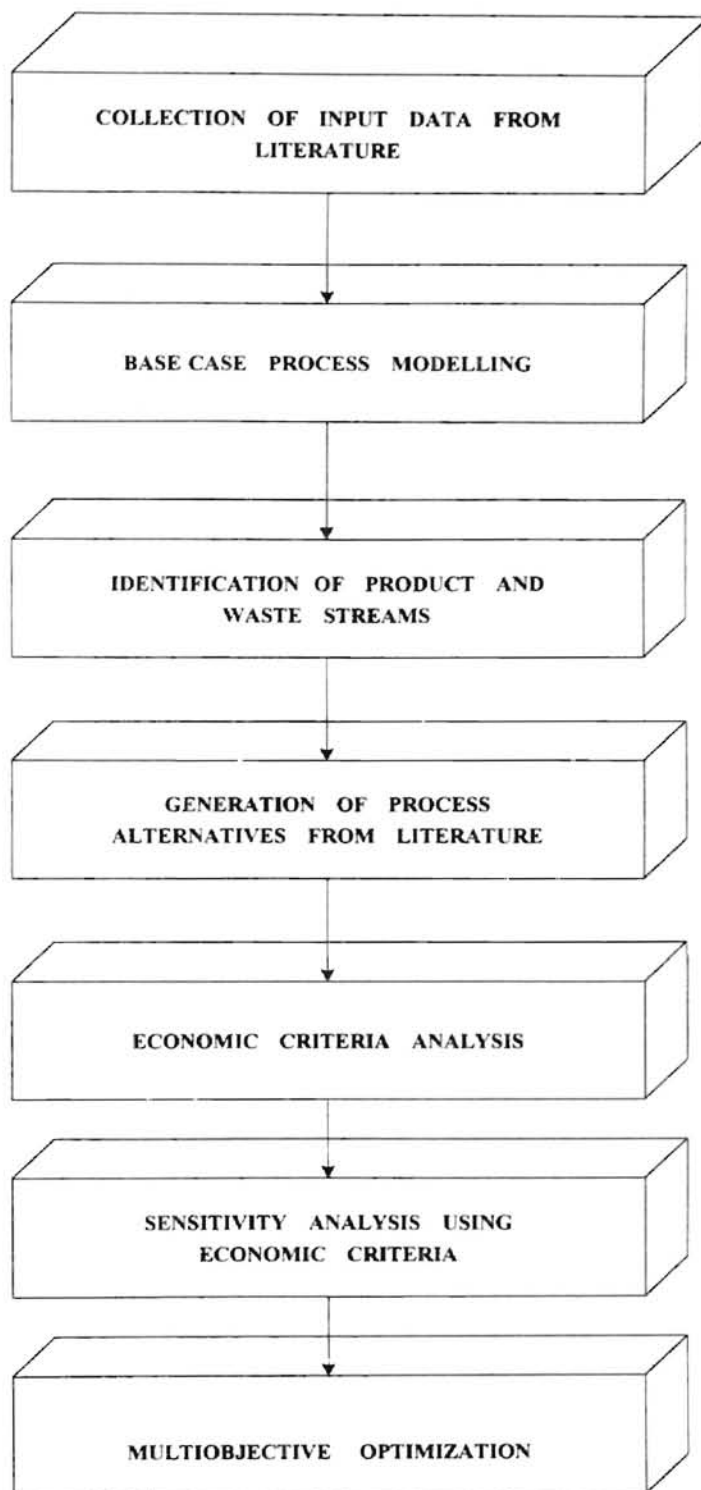


Figure 3.1: General Methodology for Incorporating Waste Minimization in Chemical Plants

- Economic comparison among waste elimination alternatives and among other approaches in the hierarchy for waste management (Smith, 1991).

3.1 Development of Base case Model

ASPEN PLUS™ was the simulator that was used to develop a base case model of the process. ASPEN PLUS™ has inbuilt thermodynamic models as well as an extensive database called PROPERTIES PLUS™ that prove to be very convenient when simulating large processes. Further, it is useful when convergence and iterations form an integral part of the calculations. Process simulation tools can be used to evaluate cost effective options (Sowa, 1994). The process flow diagram was created from a base case flow sheet (see Figure 4.1, pg 29). The base case of the process is modeled using the parameters given in Table 3.1.

TABLE 3.1

INPUT PARAMETERS FOR BASE CASE PROCESS MODELING

-
1. Feed streams.
 2. Thermodynamic model.
 3. Reaction system.
 4. Reaction kinetics.
 5. Other process equipment and their input specifications.
 6. Identification of waste streams.
 7. Identification of product streams.
 8. Formulation of the economic objective function.
-

The performance of the model in terms of economics as well as waste generation was noted in order to facilitate comparison with alternative processes at a later stage. Rigorous methods were not used initially for separation equipment due to lack of detailed data. Good estimates obtained using shortcut distillation methods were used to develop rigorous evaluation for the distillation columns. The DSTWU model of ASPEN PLUS™ 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 a specified number of stages or the required number of stages for a specified reflux ratio.

3.2 Stream Analysis

After a base case has been developed, the component flows in each stream were analyzed. After noting the different compounds present in effluents, perusal of the US Code of Federal Regulations (CFR) gave information regarding the hazardous compounds. This helps in identification of waste streams and the product streams. Then, the product and waste streams were analyzed to see if there is contamination of the product stream by any wastes or if there is considerable outflow of product in the waste streams.

3.3 Sensitivity Analysis

When it is desired to find the effect of variation of a particular variable on any other variable in the process (for example, the effect of increase in temperature on the

product flow rates), a sensitivity analysis is done. ASPEN PLUS™ has the capability to perform a sensitivity analysis on the varied parameters or the independent variables and can give the corresponding effects on the dependent variables. A sensitivity analysis helps in evaluating the process alternatives and can considerably help in improving the optimization by eliminating non sensitive parameters. In a process, potentially important parametric variables usually are the reactor variables such as the reaction temperature, reactor pressure etc., and in a separation sequence, are the parameters associated with distillation columns such as the number of stages and the reflux ratio. A sensitivity analysis was applied on the potentially important parametric variables and its effect on the product as well as on the waste distribution was found. A sensitivity analysis was carried out on all the variables that may affect the process. This shows which variables need to be varied and which variables need not be for the next stage. This helps determine which variables affect the process and, thereby, the development of process retrofit alternatives.

3.4 Process Alternatives/Modifications

Two classes of waste from chemical processes are the process waste and the utility waste. Figure 3.2 (Smith, 1991) depicts the two classes of wastes from chemical processes. Process waste, generated primarily from reactors and separation equipment, is defined as waste from products and purge streams. Utility waste is the waste generated mainly from heat exchanger networks and utilities. Examples of utility waste could be waste from fuel combustion, boiler feed water treatment etc. (Smith, 1991)

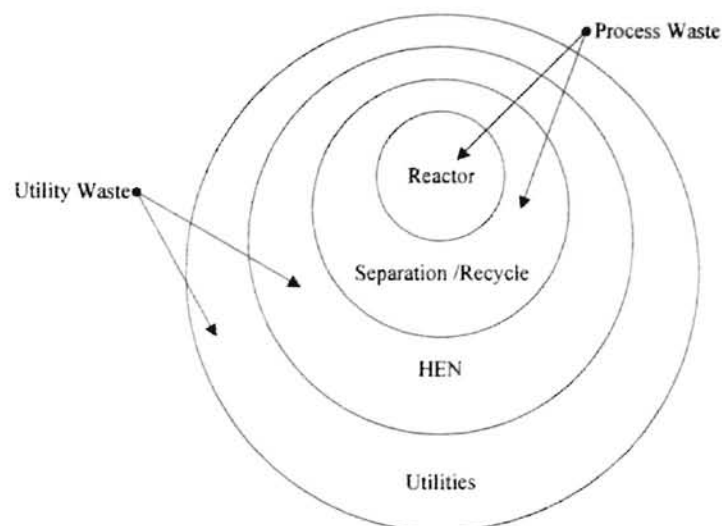


Figure 3.2: Hierarchy of wastes in chemical processes

Based on the stream analysis and the sensitivity analysis, process retrofit alternatives were developed. Some examples of process retrofit alternatives could be:

- Reduction in the flow rate of a purge stream by lowering the purge fraction.
- Addition of separation units to the recycle or purge stream.
- Reduction in the production of unwanted reaction by-products through (Ciric, 1992)
 - (a) using a different reaction path,
 - (b) changing the feed ratio,
 - (c) modifying the reactor operating conditions,
 - (d) recycling by-products so that they accumulate to equilibrium levels.

The load on the separation can be reduced by improving the conversion at the reaction step itself. For irreversible reactions, low conversion can be increased by increasing the residence time in the reactor, a higher reaction temperature or a higher reaction pressure. For continuous reactors, increasing the volume of the reactor or

reducing the inlet flow rate of feed are about the only ways to increase the residence time in the reactor (Smith, 1991). Increasing temperature and pressure reduces residence time in the reactor.

3.5 Economic Analysis

The effect of the process alternatives on its economy is imperative to the manufacturing company since the most efficient process in terms of least waste generation could turn out to be prohibitively expensive. A brief description of known profitability estimation methods is given in Table 3.2 (Peters, 1991).

Based on the methods discussed in Table 3.2, the net present worth or the net present value (NPV) method is presented as the most suitable method as it is more detailed and incorporated methods 1 and 2. Method 4 is ideal for a small system (e.g. an equipment's costing alone) within an overall process while payout period deals with time required and does not take care of the tax and the depreciation factors.

A cost analysis and evaluation of the economic parameters using the net present value method (Peters, 1991) was incorporated in the optimization of the process. Economic optimization deals with optimizing the net savings the investor will achieve if he does not invest an equal amount of money in a bank after taking care of the waste.

TABLE 3.2
PROFITABILITY EVALUATION METHODS

1. Rate of return on investment:

(Yearly Profit/Total Investment) * 100. Profit is defined here as the difference between income and expense.

2. Discounted cash flow based on full life performance:

Takes into account the time value of money and is based on the amount of investment that is not returned at the end of each year during the life of the project.

3. Net present worth:

This considers depreciation, time value of money, discount factors.

4. Capitalized costs:

This is useful for comparing alternatives which exist as possible investment choices within a single overall project.

5. Payout period:

This is the minimum time required to recover the original capital investment the form of cash flow to the project based on the total income minus all costs except depreciation

3.6 Multiobjective Optimization

It is no longer sufficient to maintain and deal with processes that have only a economic value. The environmental and waste aspects of the process need to be given equal importance too. Therefore, it is necessary to incorporate newer methodologies and practices that will yield appropriate objectives. Multiobjective optimization helps to do just that. In order to optimize the process such that it is viable both economically as well

as from an environmental point of view, optimization of both these factors have to be done simultaneously. In this work, optimization will be done separately using the Sequential Quadratic Programming (SQP) optimizer of ASPEN PLUS™ for maximizing the profit and minimizing the waste simultaneously using the procedure detailed in the section on multiobjective optimization.

The next chapter deals with the case study of the acrylonitrile process that has been used for researching this methodology.

CHAPTER 4

THE ACRYLONITRILE PROCESS

This chapter describes the acrylonitrile process that has been used as a case study for the proposed methodology. This chapter will also briefly describe the modeling of the base case.

Acrylonitrile is a clear, colorless liquid with a slightly pungent odor. Acrylonitrile was ranked 39th in the top 50 chemicals produced in the United States during 1994. The acrylonitrile production increased from 2146 million lb./year in 1984 to 3085 million lb./year in 1994, a 43.7 % increase in production (Kirschner, 1995). It is used extensively as a starting material for a wide range of chemical and polymer products. The annual increase from 1993 to 1994 was 24%. Approximately 4,000,000 metric tons of acrylonitrile is produced worldwide each year. Acrylonitrile is used in resins and nitrile elastomers and as an intermediate in the production of adiponitrile and acrylamide. Considering that acrylonitrile is produced in such huge amounts due to its varied uses and that it is a toxic chemical with stringent regulations on its environmental impacts, the process is viable for modification. Its physical properties are listed in Table 4.1.

TABLE 4.1
PHYSICAL PROPERTIES OF ACRYLONITRILE

Property	Value
Boiling Point (°F)	171.4
Freezing Point(°F)	-118.3
Solubility in water, 68°F, wt%	7.3
Viscosity, 77°F (cP)	0.34
pH	6.0 - 7.5

Modeling of the acrylonitrile process was carried out using ASPEN PLUS™ as the simulator. At present, acrylonitrile is commercially produced by the catalytic ammoxidation of propylene. Although acrylonitrile can be produced in various ways, the most efficient method that has been found is the ammoxidation of propylene. This process is called the Sohio process. The sohio process will form the basis of this research.

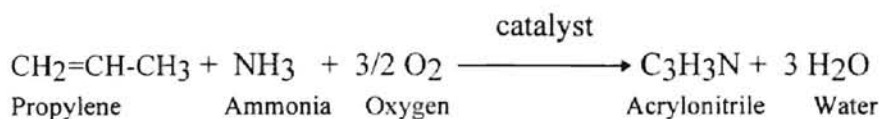
4.1 Description of the acrylonitrile process

Propylene and ammonia are reacted in the presence of air at almost stoichiometric quantities at 30 psia and a temperature of 662°F - 1112°F. The catalysts used in the process are mostly based on mixed metal oxides such as bismuth-molybdenum oxide, iron-antimony oxide, uranium-antimony oxide,

tellurium - molybdenum oxide etc. The reactor product is cooled by quenching with water and is neutralized using sulfuric acid to remove unconverted ammonia. Acrylonitrile is removed by extractive distillation, while crude acetonitrile and hydrogen cyanide are separated from the bottom products. Hydrogen cyanide is then removed by distillation. Some of the wastes that are generated from the process are processed as follows:

- Ammonium sulfate that is produced as the bottoms product from the neutralizer can be used as a fertilizer.
- Unconverted ammonia is vented to the atmosphere. Aqueous wastes containing cyanides, sulfates etc., are disposed of either incinerated, deep well injection or by biological treatment.

The main reactions and the side reactions of the process are given as follows:



Apart from the above main reaction there are the following side reactions:

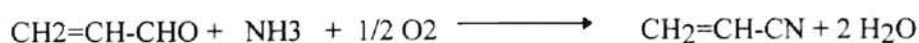
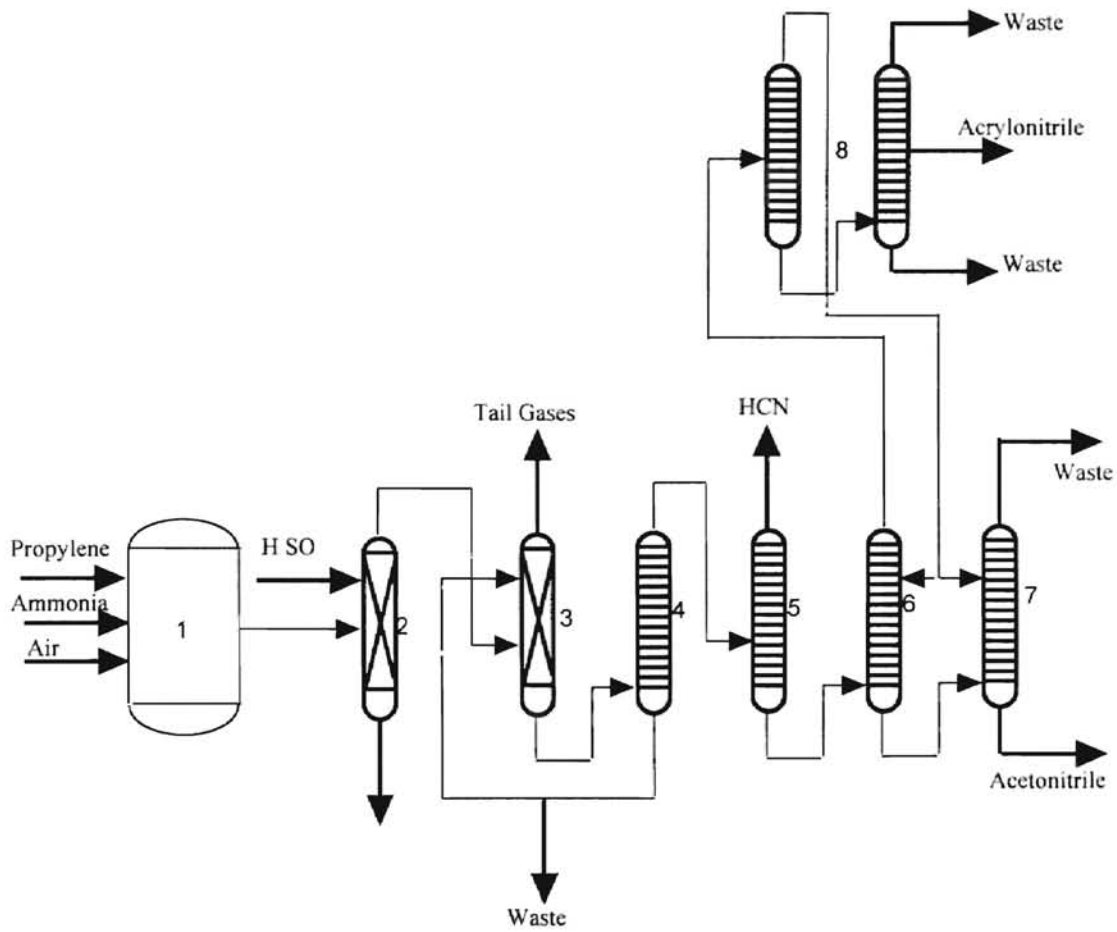


Figure 4.1 shows the process flow diagram of the acrylonitrile process that has been described.



- 1) Reactor
- 2) Neutralizer
- 3) Absorber
- 4) Stripper
- 5) HCN Column
- 6) Extractive Distillation Column
- 7) Acetonitrile Purification Column
- 8) Acrylonitrile Purification Columns

Figure 4.1: Process flow diagram of the acrylonitrile process

Kinetic data for the above reactions are given in Table 4.2 (Hopper, 1992).

TABLE 4.2
KINETIC DATA FOR THE ACRYLONITRILE PROCESS

Reaction Number	Activation Energy, E_i (cal/mol)	Rate Constant, k_i (sec^{-1}) at 662°F
1	19,000	0.40556
2	19,000	0.00973
3	7,000	0.01744
4	7,000	6.81341
5	19,800	0.16222
6	7,000	0.073

The rate equations for the acrylonitrile process are:

$$(-r_1) = k_1 C_{C_3H_6} \quad (4.1)$$

$$(-r_2) = k_2 C_{C_3H_6} \quad (4.2)$$

$$(-r_3) = k_3 C_{C_3H_6} \quad (4.3)$$

$$(-r_4) = k_4 C_{CH_2CHCHO} \quad (4.4)$$

$$(-r_5) = k_5 C_{CH_2CHCN} \quad (4.5)$$

$$(-r_6) = k_6 C_{CH_3CN} \quad (4.6)$$

The rate constants, expressed in k_i 's, are expressed in the Arrhenius form as

$$k_{i,t_1} = k_{i,t_2} \cdot e^{-(E/R)((1/t_1)-(1/t_2))} \quad (4.7)$$

where k = Rate constant,
 E = Activation energy,
 t_1 and t_2 = Temperatures.
 R = Gas constant.

On conversion of the above parameters (as shown in Appendix A), the equations become:

$$-r_1 = 1.57089E+05 e^{-19000/RT} \quad (4.8)$$

$$-r_2 = 3.768E+03 e^{-19000/RT} \quad (4.9)$$

$$-r_3 = 1.99 e^{-7000/RT} \quad (4.10)$$

$$-r_4 = 780.07 e^{-7000/RT} \quad (4.11)$$

$$-r_5 = 1.08015E+05 e^{-19800/RT} \quad (4.12)$$

$$-r_6 = 8.357 e^{-7000/RT} \quad (4.13)$$

4.2 Process Modeling using ASPEN PLUS™

ASPEN PLUS™, a product of Aspen Technology, Boston, is a steady state simulator that has a built-in variety of pre-programmed unit operations with a user friendly graphical interface- ModelManager™. It allows the chemical engineer to model a process or to estimate properties using a variety of thermodynamic equations of state and activity coefficient models. Rigorous rating calculations are available for column trays, heat exchangers, pressure relief systems. It has powerful model analysis tools such as sensitivity analysis, optimization, data fit and costing and economic analysis. Sensitivity analysis of ASPEN PLUS™ can be used to conveniently study the effect of variation of operating conditions. Optimization can be used to maximize or minimize a specified objective function. Sizing and costing of equipment and prediction of plant capital costs, labor and operating costs, cash flow and profitability can be done using the costing and economic analysis. Further, a complete set of physical property models based on both equation of state models and activity coefficient approaches are available.

It also has the capability to allow user kinetics and user models to perform desired unit operations. The flow sheet is usually developed using ModelManager™. Since ASPEN PLUS™ is known to perform a) sensitivity analysis b) optimization and c) unit

operations calculations for chemical processes satisfactorily, this simulator is an useful tool to perform research on multiobjective optimization.

4.3 Base case Process Modeling

A skeleton of the acrylonitrile process flow sheet was developed on ModelManager™ using the feed streams, reactor, separation units and product streams. Recommended literature input data are given in Table 4.3.

TABLE 4.3
RECOMMENDED INPUT DATA FOR THE ACRYLONITRILE PROCESS

Parameter	Value
Temperature Range	662-1112° F
Pressure	5 - 45 psia
Feed Ratio	
• Propylene / ammonia	1 - 2
• Oxygen / Propylene	0.5 - 3

TABLE 4.4
BASE CASE INPUT DATA FOR THE ACRYLONITRILE PROCESS

Parameter	Value
Reaction Temperature	842° F
Reaction Pressure	15 psia
Feed Ratio	
• Propylene / Ammonia	1.33
• Oxygen / Propylene	1.5

The acrylonitrile process mainly consists of two sections: the reaction section and the separation section. The reaction section for the base case was modeled using a CSTR (RCSTR block). The product recovery achieved using modeling agrees with the estimated product recovery given by Hopper (1992) as shown in Table 4.5.

TABLE 4.5
COMPARISON OF BASE CASE SIMULATION RESULTS WITH LITERATURE

Reactor Type	Residence Time (sec.)	Conversion of Propylene (%)	HCN/ACN ratio	ACE/ACN ratio
PFR				
Base case	2	20.11	0.04358	0.0975
Literature	2	19.97	0.04356	0.09767
Base case	10	68.91	0.28870	0.09526
Literature	10	66.88	0.26389	0.09565
CSTR				
Base case	2	18.89	0.08681	0.09715
Literature	2	19.29	0.08907	0.09728
Base case	10	52.06	0.40383	0.09490
Literature	10	54.43	0.44404	0.09491

Since the individual specifications for the separation equipment were not available, the K values were used to estimate the required separation within each equipment. The K values for each component in the incoming stream to the separation equipment is noted. The greater the K value, the lighter is that component for the incoming stream. The light key and the heavy key component for each distillation unit is

found and depending on the function of that particular distillation unit, the required recovery is inputted. This analysis was followed by modeling the separation equipment using shortcut distillation methods. Shortcut distillation models were used to estimate the unknown variables such as the feed stage location, the actual number of trays, the reflux ratio and bottoms vs. feed or the distillate vs. feed ratio. Using the K value data explained earlier, the data for recovery required is provided as input for the shortcut distillation units. Once the requirement of light key and heavy key component was specified, the number of stages, the feed stage location etc. are calculated. Since the components in the process have a wide range of K values due to very heavy compounds such as acrylonitrile, sulfuric acid and water and very light compounds such as carbon monoxide, carbon-di-oxide and oxygen, the ammonia is converted into ammonium sulfate and is removed early on in the process. The product consists of acrylonitrile and acetonitrile. The byproduct is ammonium sulfate and the waste consists of all the other waste gases that are emitted.

TABLE 4.6
ANALYSIS OF BASE CASE STREAM SUMMARY

Streams	Status	Major components
Acrylo	Product	87.58 % recovery Acrylonitrile
Acryl2	Product	4.62 % recovery Acrylonitrile
Aceto	Product	86.42 % recovery Acetonitrile
Acryl3	Product	4.66 % recovery Acrylonitrile
S-12Gas	Waste	CO, CO ₂ , Propylene, oxygen
S-16Was	Waste	Negligible quantity of waste
S-17HCN	Waste	93.9 % recovery HCN
Ammsul	By Product	86.35 % recovery Ammonium Sulfate

The percentage recovery specified is the recovery of the compound as the fraction of the outlet production immediately after the reaction step. The cost involved for the base case simulation was found using the FORTRAN block. Cost analysis of the process is based on the assumption that the process already exists. The net revenue for the process is calculated using equation 4.8 shown below.

$$\text{Profit} = \text{Product revenue} + \text{By-product revenue} - (\text{Raw material cost} + \text{Waste Treatment Cost} + \text{Utility cost}) \quad (4.8)$$

The acrylonitrile process was simulated on ASPEN PLUS™ and the results of the base case simulation is shown in Table 4.7.

TABLE 4.7
BASE CASE RESULTS

Variable	Value
Product flow rate	145 lbmole/hr.
Waste	6730 lb./hr.
Capital Costs (\$)	0
Manufacturing costs (\$/yr.)	26996410.
Net Present Value (\$)	6698307

The next chapter will discuss the theoretical concepts involved in multiobjective optimization approach.

CHAPTER 5

MULTIOBJECTIVE OPTIMIZATION

It is desired to have the maximum profit while generating the least amount of waste. However, it is usually not possible to achieve the maximum profit and the minimum waste generation at the same time. Multiobjective optimization is a strategy that helps achieve a tradeoff between the revenue and the waste generated in a process. The concepts involved in multiobjective optimization will be discussed in this chapter.

5.1 Overview of multiobjective optimization

The goal of multiobjective optimization is to simultaneously maximize profit while minimizing the waste produced.

$$\max. p ; \min. w \quad (5.1)$$

subject to

$$h(x) - Ay = 0 \quad (5.2)$$

$$g(x) - By \leq 0 \quad (5.3)$$

$$w = w(x,y) \quad (5.4)$$

where

x is the vector of continuous process variables.

y is the vector of integer variables, in other words, discrete alternatives.

w is the vector of waste streams.

h are the set of equality constraints for the process.

g is the set of inequality constraints for the process.

In order to optimize an objective function that has both the waste and the profit as its arguments, there needs to be a tradeoff. Fig. 5.1 shows the tendency of the net profit to be inversely related to the treatment cost in chemical plants. At low treatment costs, the net profit is usually high and when the treatment costs are high, the net profit is usually low.

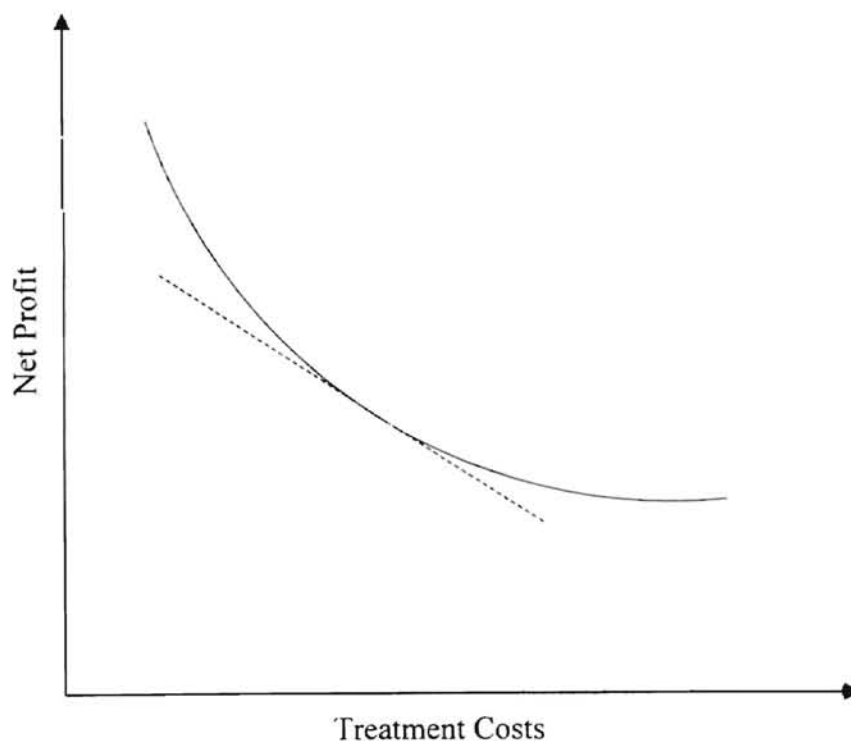


Figure 5.1: Plot of net profits versus treatment costs in a chemical engineering optimization problem.

The process alternatives that are generated can either be continuous or discrete or a combination of both. Continuous alternatives are those that can be varied using the same equipment but at different operating conditions. Examples of continuous variables are temperature, pressure, inlet feed flows etc. Discrete process alternatives are those for which there is either a variation in the process design or a variation in the process flowsheet. Examples of discrete process alternatives can be variation in equipment or variation in process flow structure. When discrete process alternatives are generated, then the multiobjective problem transforms into a multiobjective mixed integer linear programming problem (MINLP). The MINLP is based on giving an integer value of 0 to a discrete alternative if it is not chosen in the reaction scheme or a value of 1 if it is chosen in the reaction scheme for evaluating the process. More information on MINLP and the algorithm to solve it automatically on ASPEN PLUS™ can be obtained from Dantus (1995).

The non-inferior solution set can be defined as “the set of solutions where the profit cannot be increased without simultaneously increasing waste production. There exists a simple transform between the non-inferior set and the sensitivity curve” (Ciric, 1993). The multiobjective problem is to be solved for the non inferior discrete alternative solution set.

The multiobjective optimization approach follows a three step procedure:

- Identifying the discrete regions of the non inferior solution set using a solution algorithm.
- Finding the non inferior curve using successive quadratic programming and

- Using the basic relationship between sensitivity analysis and multiobjective optimization.

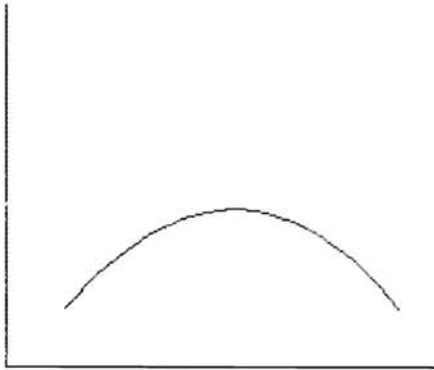


Figure 5.2(a): Concave Region

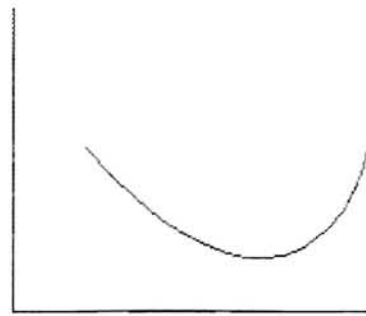


Figure 5.2(b): Convex Region

Figure 5.2(a) and 5.2(b) show the shape of the concave and convex regions.

It has been proven that :

“(1) The optimal solutions of the sensitivity problem would lie in the convex hull of the non-inferior curve.

(2) A simple transform exists between the non-inferior set and the sensitivity curve”

(Ciric, 1993).

The following properties helps in determining an efficient approach in multiobjective optimization.

“(a) The optimum solution of the sensitivity problem cannot lie at an inferior point of the multiobjective optimization problem.

(b) All solutions of the sensitivity problem lie at either an extreme point or a concave portion of the non inferior solution set.

(c) At the optimum solution $\delta P/\delta w = \alpha$ " (Ciric, 1993).

The net profit, $NP = p - \alpha w$

where

NP = Net Profit.

p = Profit before waste treatment.

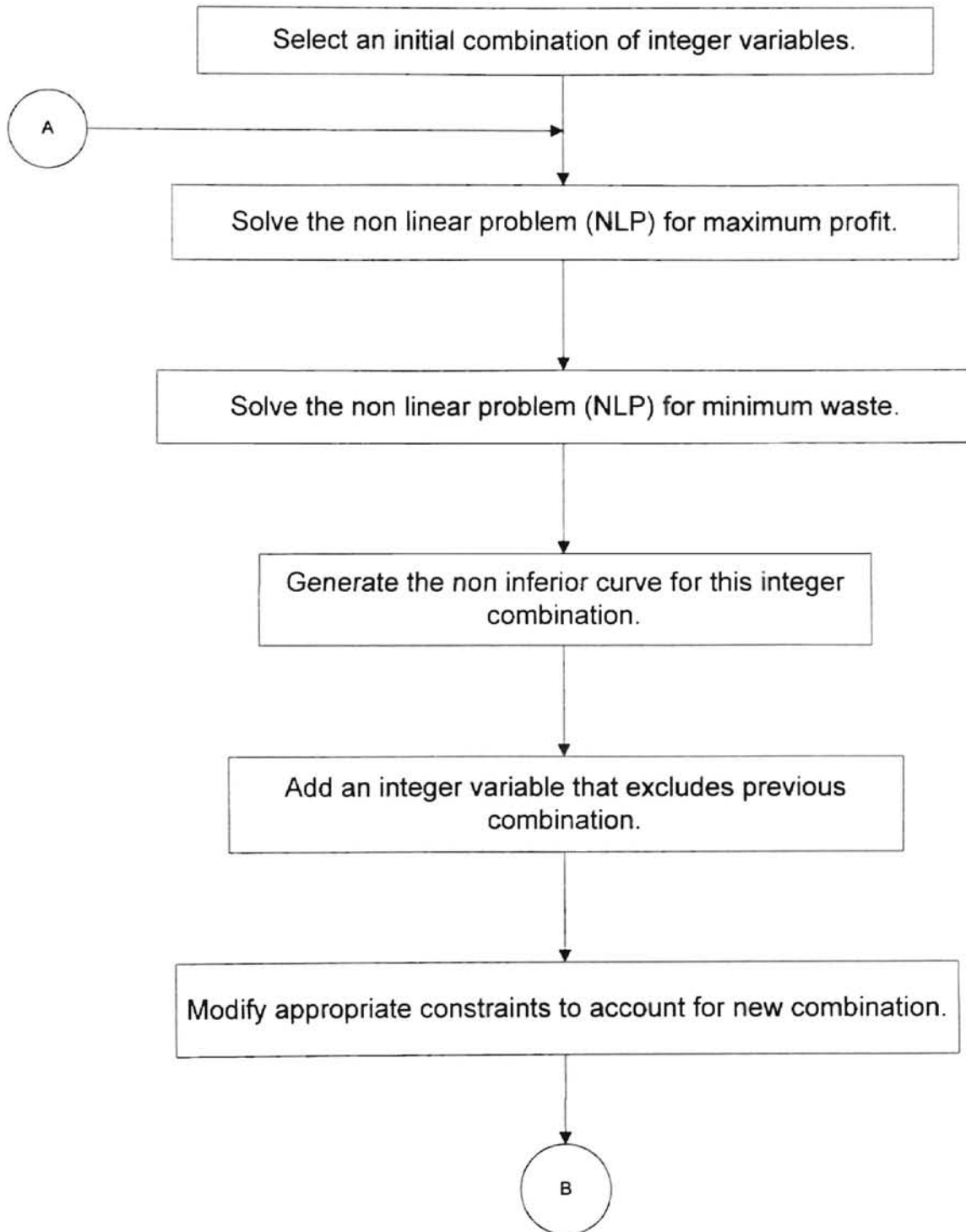
w = Waste flow rate and

α = Derivative of the net profit with respect to waste treatment costs.

In this problem, the objective function is defined either as the sum of the wastes or as the net revenue. Sensitivity analysis showed that only certain parameters affected the process and therefore these variables form the continuous variables in the process. The discrete variables are the individual combinations of models. The values of the profit versus the waste are then plotted for each discrete alternative. The non inferior discrete alternative curve can be inferred from this plot. This discrete alternative is the most optimum of all the alternatives. The slope of the line connecting the maximum revenue and the minimum waste is found and used as the weighing parameter for the waste produced. This is then used in the optimum set of discrete variables and optimized again.

This methodology for multiobjective optimization is based on discarding discrete alternatives based on their proximity to optimum values. Each discrete alternative is compared to every other alternative. Based on this comparison, the best alternative is selected and the further optimized while the others are not. This approach is advantageous since each discrete flow sheet is visited exactly once and the computational effort is focused where the slope is changing.

Figure 5.3 shows the algorithm that is followed to incorporate multiobjective optimization to achieve the final sensitivity curve.



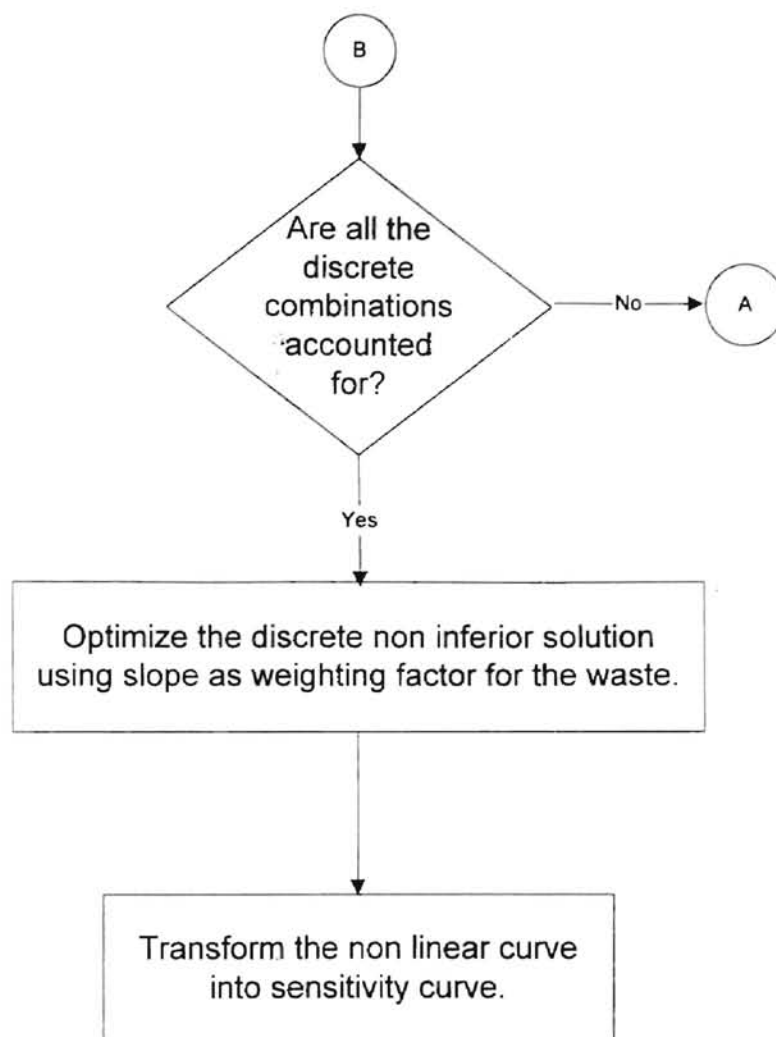


Figure 5.3: Solution Algorithm for Multiobjective optimization.

In a nutshell, the figure 5.3 can be explained as identification of the best non inferior solution followed by evaluation of the final sensitivity curve that depicts the tradeoffs necessary for that solution. Figure 5.4 depicts the range of discrete solutions on the profit-waste (p-w) plane.

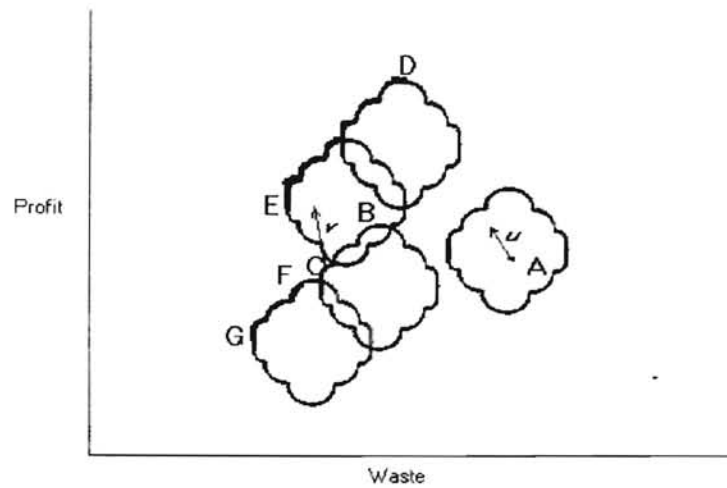


Figure 5.4: Non inferior solution sets for discrete feasible regions in optimization problems.

Each of the enclosed curves shown in figure 5.4 denote a separate alternative. Here, point A is an inferior solution to the optimization problem. This is because moving in direction u would lead to higher profits as well as lesser waste. So is the case with point C for which a better solution could be obtained if one moved in the direction v . Point B is also an inferior solution as change in a discrete alternative could lead to higher profits and lesser wastes. However F is a non inferior solution of the optimization problem since searching for higher profits would lead to higher wastes only. Similarly, the curve D-E is also a non inferior solution curve.

Figure 5.4 can be better explained by means of an example. Let us assume that each of the clouds in figure 5.4 is a discrete alternative. Suppose the point A depicts the profit and waste for say, a heat exchanger with volume of 100 ft^3 and point B depicts the

profit and waste for another heat exchanger with volume of 200 ft^3 . Then, increasing the volume from 100 ft^3 to 200 ft^3 would lead to higher profits. Therefore, the physical significance of the search direction, u , would be the increase in volume.

Reiterating, in Figure 5.4 the curves G-F and D-E are non inferior solutions as changes on any point on these curves have a detrimental effect either on the profit or on the waste. Figure 5.5 shows how multiobjective optimization helps in saving time by using the process of elimination of continuous and discrete alternatives.

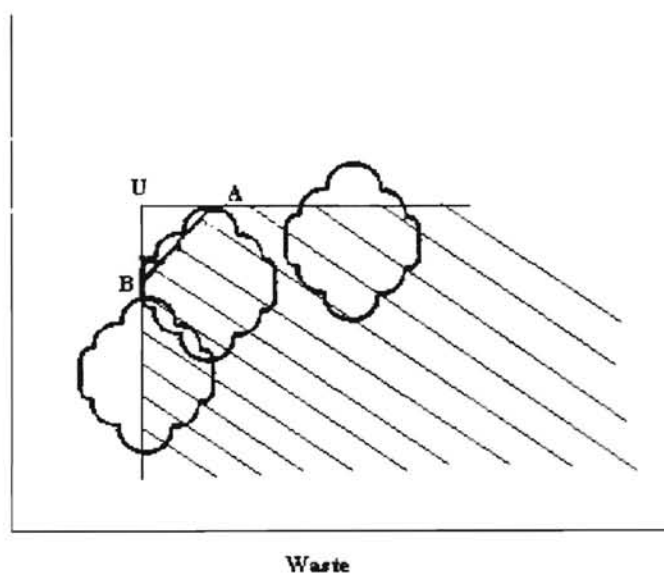


Figure 5.5: Identification of discrete non inferior regions by elimination.

Before multiobjective optimization is utilized, the discrete alternatives are identified. The extreme (upper and lower) approximators for the continuous portions of the non inferior curve is bounded. Figure 5.5 shows region 1 in which point A and point B are the maximum profit and the minimum wastes respectively for the integer combination studied. This helps in

- generating an underestimator (lower bound) line AB,

- eliminating the hatched region in the p-w space and
- binding the non inferior region for the particular discrete region.

This means that when each of the discrete alternatives are optimized for the maximum profits and the minimum waste generated and are connected by a straight line, we can quickly discard discrete alternatives based on the location of their respective lines. As a result of this, we eliminate the need to perform multiobjective optimization for all the discarded alternatives. Further, even for the undiscarded discrete alternative, the range of optimization study is reduced in terms of continuous variables. This helps in saving time.

Repeating this procedure for the other discrete alternatives or the integer combinations results in a identification of non inferior curves for each integer combination. The non inferior discrete solution set is the non inferior curve that is identified among all discrete alternatives.

This methodology is advantageous since it eliminates finding the maximum net profit for values of α for each of the discrete solutions other than the non inferior solution set. This methodology therefore prevents repetitive computation. An exhaustive search over the whole range of α would increase the computational effort unnecessarily.

5.2 Economic Model

It is essential to have an economic incentive in order to modify a process. This incentive can be derived by developing an economic model or by incorporating previously developed economic models such as the net present value method. Of the

methods discussed in Table 3.2, the net present worth method is rigorous and more complete, easy to compute and gives correct ranking in most project evaluations (Himmelblau, 1988). The net present worth is the difference between the present value of the annual cash flows and the initial capital investment.

The net present worth method takes into account the following factors:

- Fixed capital investment
- Working capital
- Annual income
- Annual manufacturing costs
- Annual depreciation
- Income after tax
- Discount factors

Since the base case represents the existing process in operation, it does not consider capital cost investment.

The total costs involved in the base case process, $M_{c,B}$ is shown by equation 5.5,

$$M_{c,B} = R_B + W_B + O_B \quad (5.5)$$

where:

- R = Raw materials cost (\$/yr.)
- W = Waste costs (\$/yr.)
- O = Operating costs (\$/yr.)

All waste treatment costs are considered to be part of the operating costs (see Equation 5.5),

$$O = \sum_{i=1}^Y (\text{utility consumption})_i (\text{utility cost})_i \quad (5.6)$$

where:

- Y = Total number of units

Based on the NPV method, considering the salvage value as zero, and rearranging terms, the economic model applied is presented in Equation 5.7 (Dantus, 1995)

$$NPV = \sum_{j=1}^{j=ny} [f_D (\Delta M_c (1 - T) + FCC * D_j * T)] - FCC \quad (5.7)$$

where:

NPV=net present value
 ny=number of years
 f_D =discount factor
 T=Tax rate
 FCC=Fixed capital cost
 D_j =Depreciation factor

The term ΔM_c in Equation 5.7 represents the savings in operating costs that are obtained with a specific retrofit alternative when compared to the base case (see Equation 5.8).

$$\Delta M_c = M_{c,B} - M_{c,alt} \quad (5.8)$$

where:

alt = process alternative

The discount factor f_D in Equation 5.7 is the factor that the company would have obtained if the initial capital was invested in a bank.

$$f_D = \frac{1}{(1+i)^j} \quad (5.9)$$

A suggested value for the interest rate is 15% (Peters, 1991). The economic model has been evaluated on an annual basis of 7920 hrs.

The depreciation factor D_f in Equation 5.7, is estimated using the sum-of-the-years digits method (Peters, 1991) (see Equation 5.10).

$$D_f = \frac{2 * (ny - j + 1)}{ny * (ny + 1)} \quad (5.10)$$

5.2.1 Capital Cost Estimation

There exist several types of estimates that can be used to determine the required capital investment. The use of cost indexes such as the Marshall and Swift Equipment Cost Index, and the Chemical Engineering Plant Cost Index (Peters and Timmerhaus 1991), can be helpful when capital cost information is available from some time in the past. An alternative method is to estimate the costs by scaling. If the new unit is similar to one of another capacity for which cost data is available (see Equation 5.11).

$$FCC_n = FCC_e \{Q_n / Q_e\}^\psi \quad (5.11)$$

where:

- Q = Plant or equipment capacity.
- FCC = Fixed capital cost
- e = Existing process
- n = New process
- ψ = Exponent 0.6 - 0.7

For reactors, pressure vessels and columns, the capital cost was calculated using Guthrie's correlation (Douglas, 1992) as seen in equation 5.12,

$$RCC = (M\&S) * (101.9 * D^{1.066} * H^{0.82} * F_c) / 280. \quad (5.12)$$

where

RCC	=	Reactor Capital Cost (S/yr)
M&S	=	M&S index.
D	=	Diameter(ft)
H	=	Height(ft)
F _c	=	F _m * F _p

A more detailed description of the NPV method can be obtained from (Dantus, 1995) and (Peters, 1991). A logic diagram for the procedure is given in Appendix A. The development and evaluation of process alternatives and incorporation of multiobjective optimization will be seen in the next chapter.

CHAPTER 6

PROCESS ALTERNATIVES

This chapter deals with identification and analysis of process alternatives for the acrylonitrile process. The concepts of multiobjective optimization discussed in the previous chapter will then be utilized to develop the sensitivity curve that depicts the optimal solution for the acrylonitrile production process. There are two types of variables that can be altered in a process. They are known as discrete and continuous variables.

6.1 Discrete Alternatives

Discrete variables are those alternatives that deal with change in process equipment. Process alternatives arising out of discrete variables are discrete alternatives. The discrete alternatives studied in the process were:

a) Separation and routing- The main product of the process is acrylonitrile. A byproduct, acetonitrile, is produced in very negligible quantity compared to the main product. The main byproduct formed is ammonium sulfate. An evaluation of the outlet streams shows that the separation is better achieved by rerouting the streams in the acrylonitrile purification system. Two new separation units are included in the modified process to increase the separation of the waste gases from the recycle stream. The modified process flow diagram is shown in Figure 6.1.

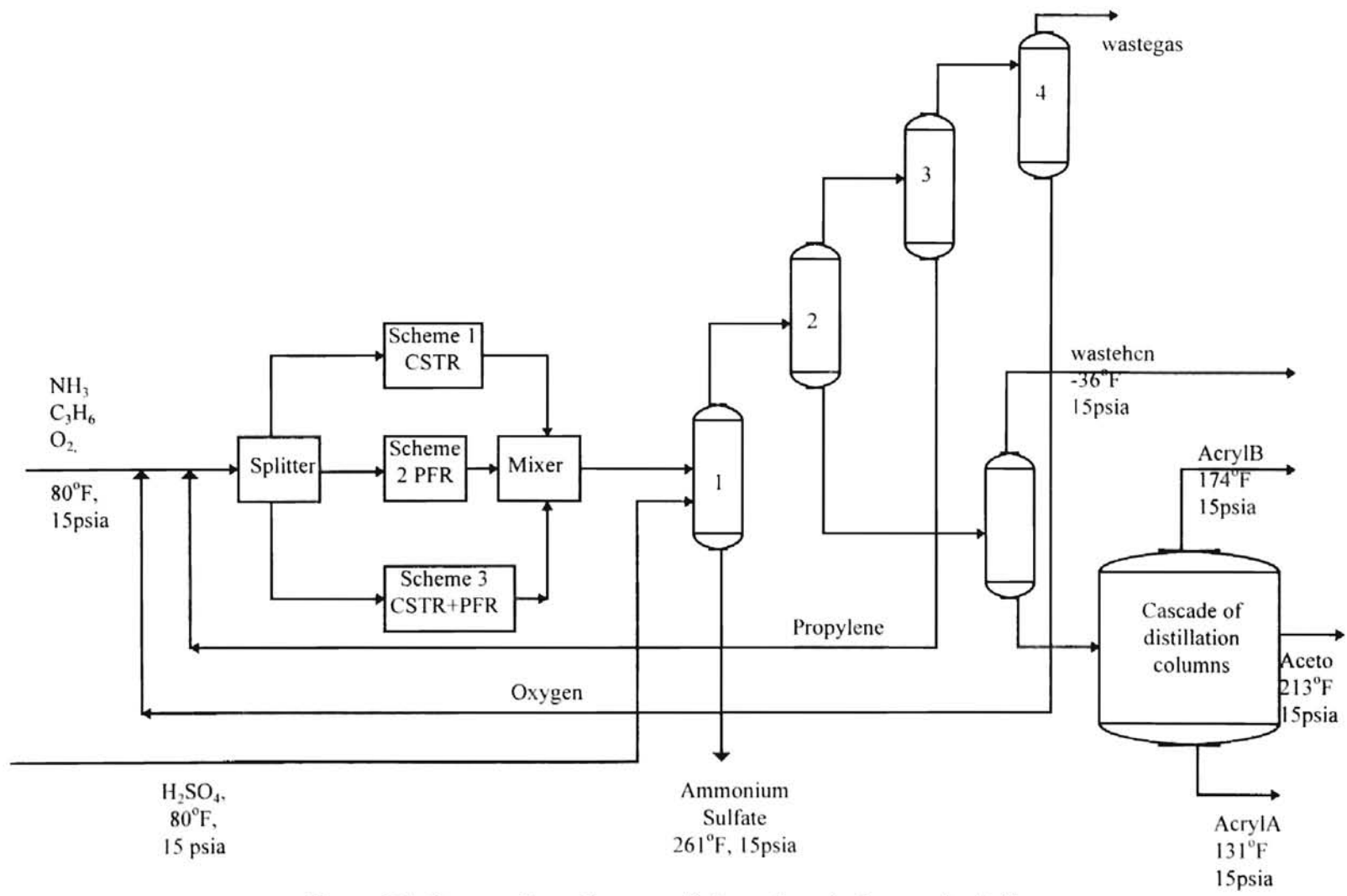


Figure 6.1: Process flow diagram of alternatives in the acrylonitrile process

b) Reactor Models-

- The Continuous Stirred Tank Reactor model(RCSTR model)-scheme I.
- The Plug Flow Reactor (RPFR model) scheme II.
- Combination of CSTR and PFR model in series scheme III.

$$\frac{V}{F_{A0}} = \left(\frac{1}{-r_A} \right) * X \quad (6.1)$$

where V is the reactor volume,

F_{A0} is the inlet mole flow rate,

$-r_A$ is the reaction rate and

X is the conversion.

The required conversion is set and as per equation 6.1 (Fogler, 1992), $1/r_A$ is obtained. The calculations and a plot of $-1/r_A$ vs X is generated (see Appendix A). This plot can be used for generating several other discrete alternatives to find the effect of different combination of reactors. In this research, a combination of a CSTR followed by a PFR has been used as an example. Since neither the intermediate conversion nor the volumes of the reactors were known, the intermediate conversion was calculated using a design specification was set on the outlet production of acrylonitrile. The outlet production was arbitrarily set to 145 lbmoles/hr. The CSTR and PFR model in series (scheme III) was modeled in a similar fashion as the CSTR and the PFR alternatives. The total volume of the two reactors is kept equal to the previous two cases as 800 ft³. The PFR parameters were then varied independently since neither the intermediate conversion nor the volumes of the reactors are known and, to reduce the complexity of varying every

parameter in all combinations in each of the reactors. Generally, discrete alternatives are selected based on experience and knowledge about the process as well as chemical engineering fundamentals. Modeling combinations of reactor and separation subsystems without prior knowledge of the process would be inefficient as there could be infinite such combinations.

6.2 Continuous Alternatives

Continuous variables are those variables that deal with individual process equipment's operating parameters. The continuous variables that were varied were:

- a) Residence time
- b) Reaction temperature
- c) Reaction pressure
- d) Inlet feed ratio - The inlet feed ratio was varied to get a constant mole flow of acrylonitrile.

6.2.1 Effect of Residence Time

The residence time of the inlet particles in the reactor is related to the volume of the reactor as per equation 6.2 (Fogler, 1992),

$$\tau = \frac{v}{V} \quad (6.2)$$

where

τ is the residence time.

v is Reactor volume in ft^3 .

V is the volumetric flow rate entering the reactor in ft^3/hr .

Therefore, varying the reactor volume effectively varied the residence time. A FORTRAN block was written for the RCSTR block to calculate the residence time according to equation 6.1.

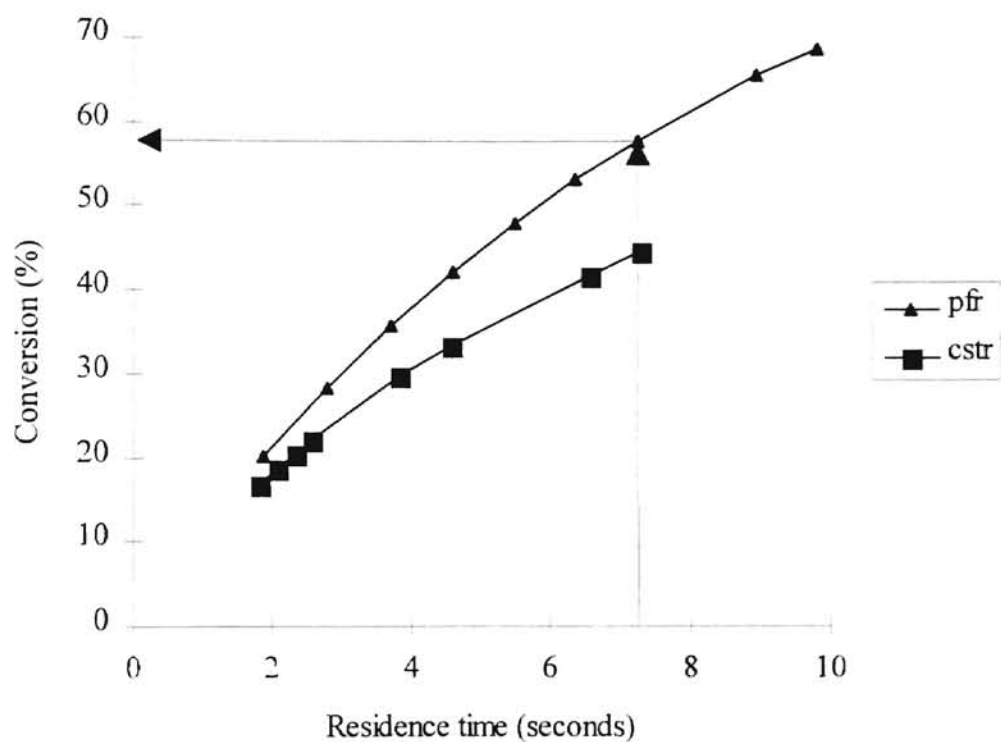


Figure 6.2: Effect of residence time on conversion.

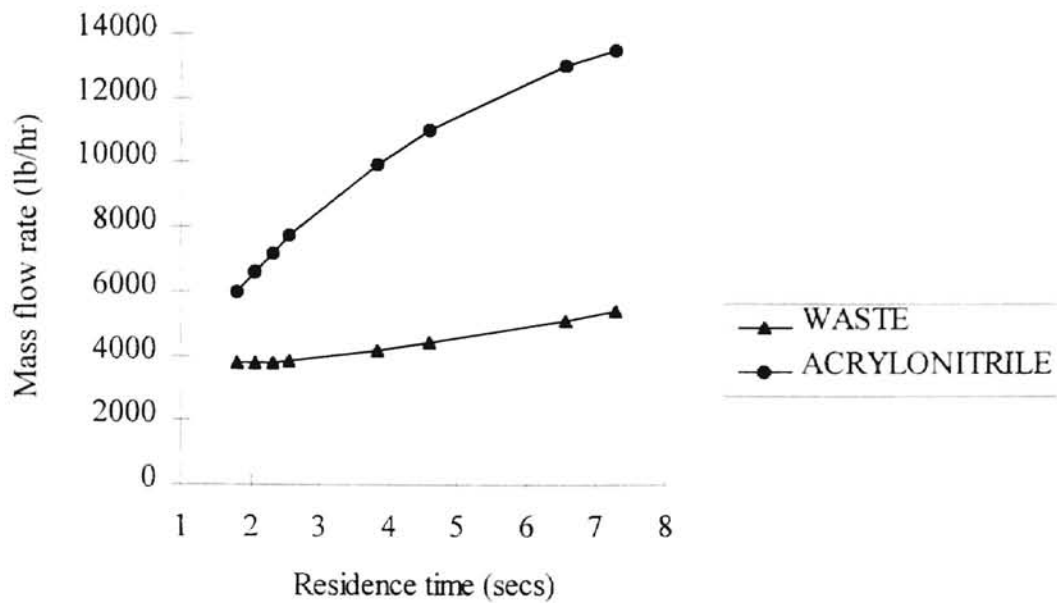


Figure 6.3 : Effect of residence time on product distribution using CSTR scheme.

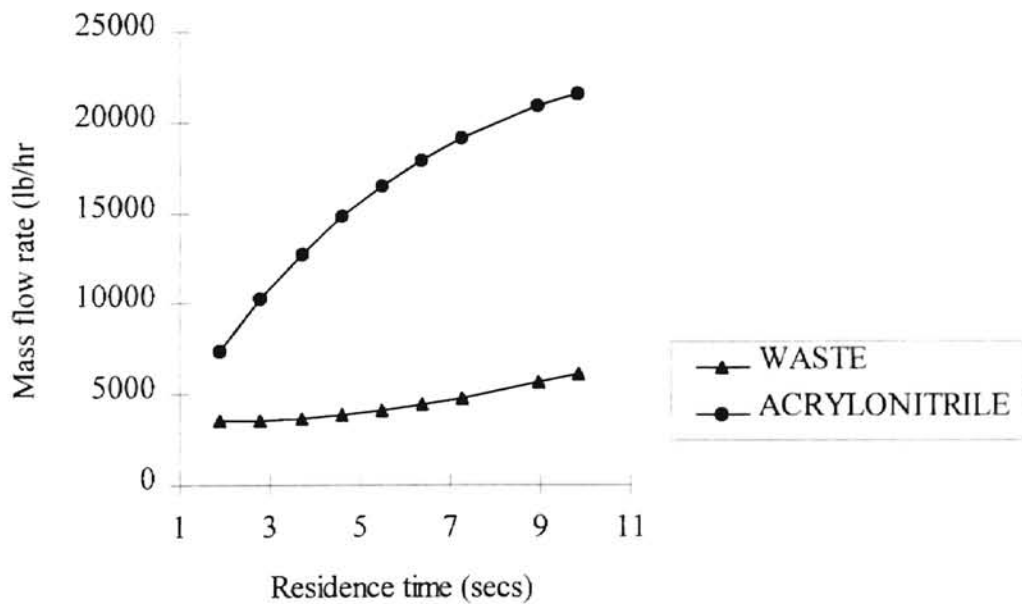


Figure 6.4 : Effect of residence time on product distribution using PFR scheme.

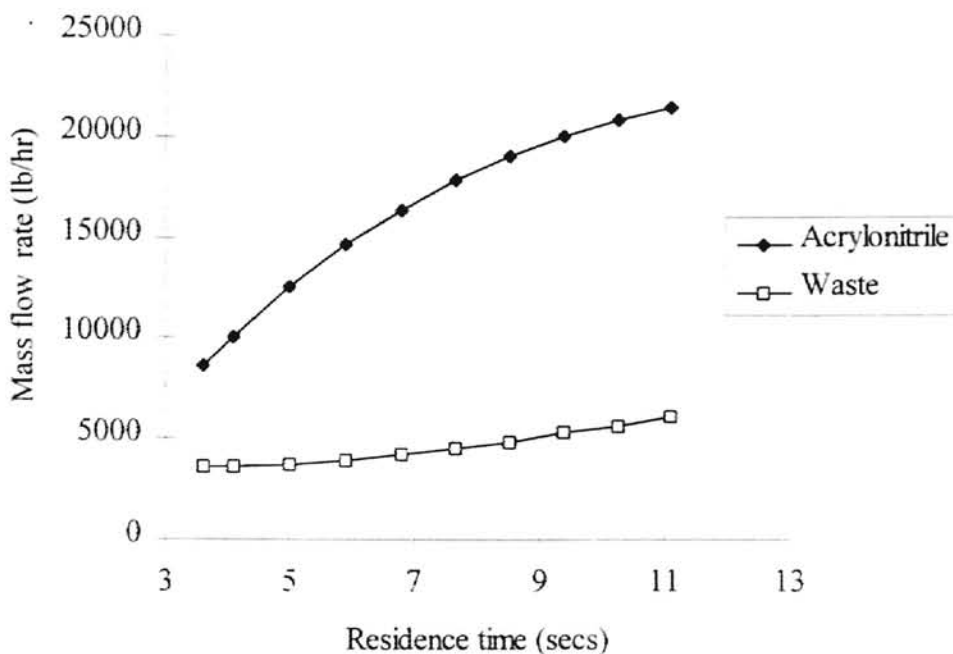


Figure 6.5: Effect of residence time on product distribution for scheme III.

The rate of conversion for the PFR and the CSTR schemes is shown in figure 6.2.

The key inlet component is propylene. It is seen that conversion of the key inlet component in both the PFR as well as the CSTR schemes increases as the residence times increases. The conversion increases from 16% to 44% for CSTR in 7.3 seconds while the conversion increases from 20% to 57% within 7.3 seconds in the PFR scheme. Figure 6.2 shows that the conversion for the PFR scheme has a higher conversion than that of the CSTR scheme.

Figures 6.3 through 6.5 show the effect of residence time on the product and the waste distribution for the discrete alternatives discussed. Larger amounts of product is formed in Schemes II and III compared to scheme I. It can be seen that when the residence time is increased from 1.88 to 9.82 seconds, there is a 193% increase in the product formed, while there is a 71% increase in the amount of waste formed using the

PFR model. This shows that the reaction kinetics supports increased formation of product compared to waste as the residence time is increased. Scheme III resembles a PFR model's results because the volume of the CSTR in scheme III, as discussed earlier, is kept constant and the volume of the PFR alone is varied to reduce the complexity.

6.2.2 Effect of Reaction Temperature

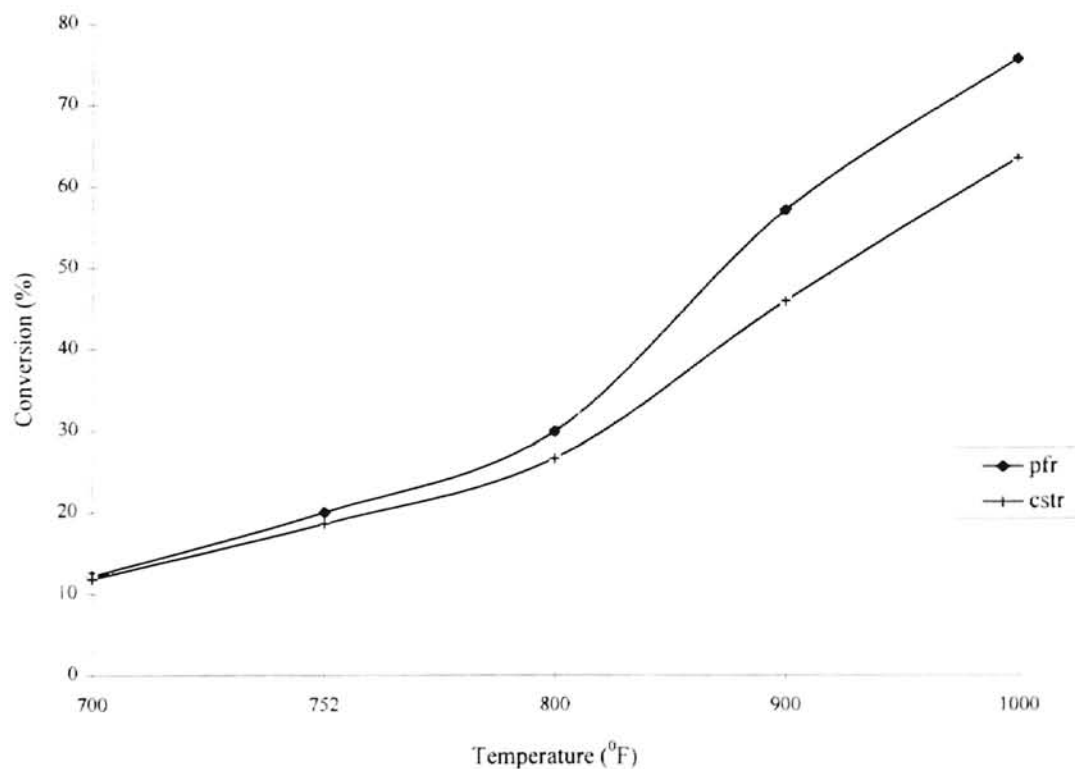


Figure 6.6: Effect of reaction temperature on conversion.

The conversion of the key inlet component in the PFR and the CSTR schemes increases as the temperature increases. The conversion increases from 11% to 63% for CSTR for a temperature range of 700°F to 1000°F. The conversion increases from 12%

to 71% when the reactor used is a PFR for the same temperature range. Figure 6.6 shows that the conversion for the PFR scheme has a higher conversion than that of the CSTR scheme.

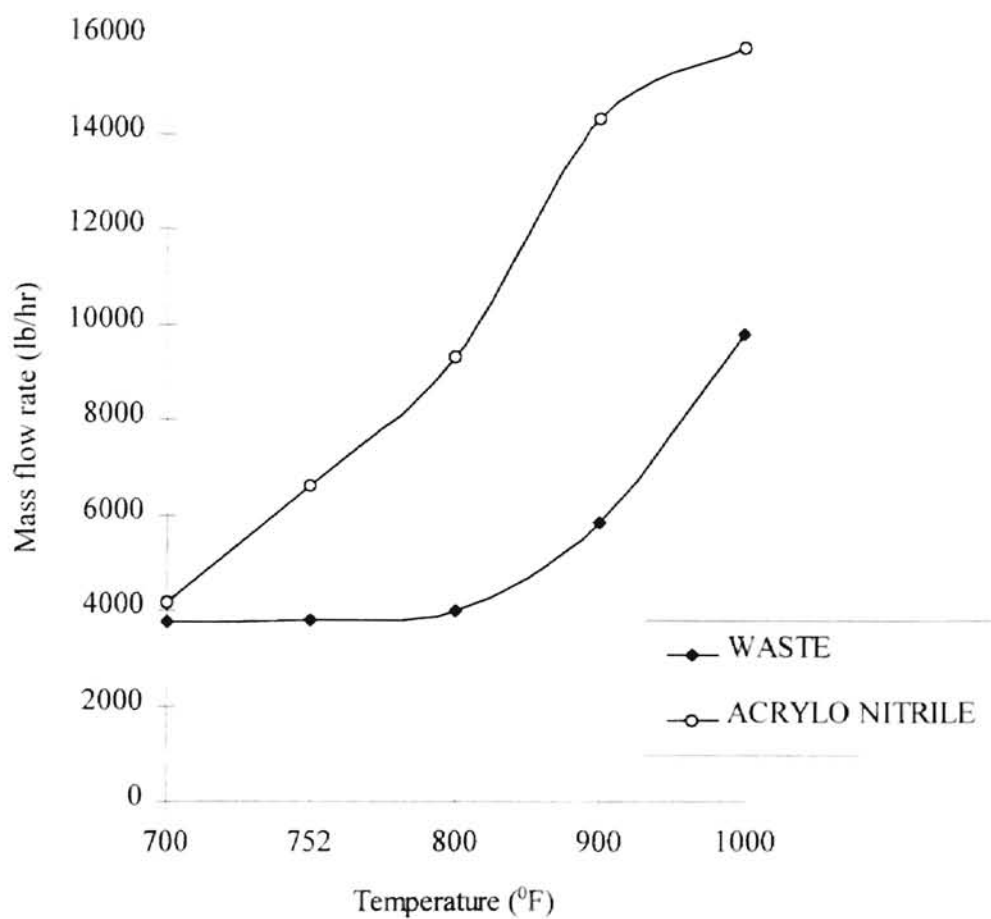


Figure 6.7: Effect of reaction temperature on the product distribution using CSTR scheme.

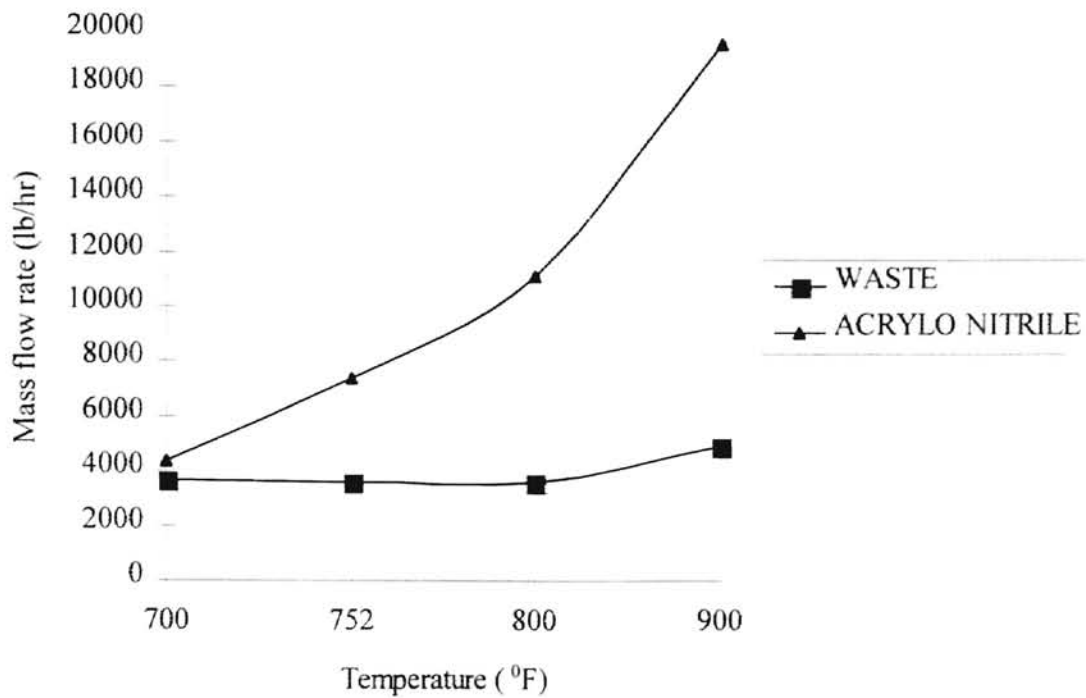


Figure 6.8: Effect of reaction temperature on the product distribution using PFR scheme

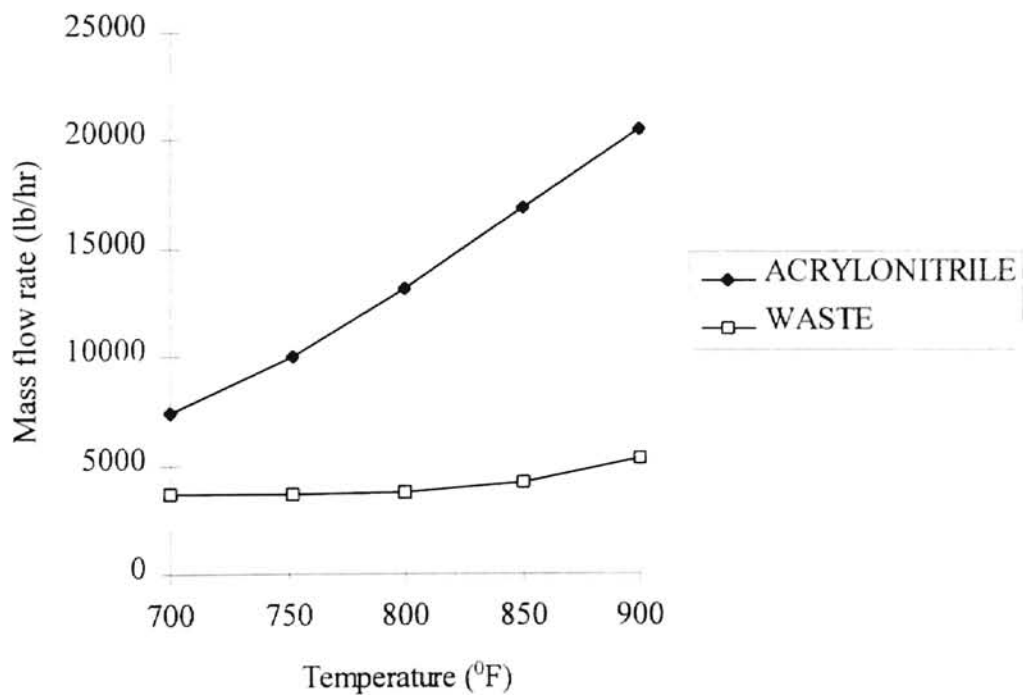


Figure 6.9: Effect of reaction temperature on product distribution using scheme III.

Figure 6.7 shows the product distribution using a CSTR scheme. When compared to the PFR model, the CSTR model produces considerably lesser quantities of product and waste. At 752°F (400°C), there is 11.3 % more product produced using PFR model compared to the CSTR model. There is almost 6% more waste generated at the same conditions for the CSTR compared to the PFR alternative.

Figure 6.8 shows the effect of temperature on the product and the waste distribution in the PFR model. It can be seen that when the temperature is increased from 700°F to 1000°F, there is a five fold increase in the product formed. The waste formed initially reduces and is minimum between 750 and 800°F after which it increases again. This can be attributed to the reaction kinetics.

6.2.3 Effect of Reaction Pressure

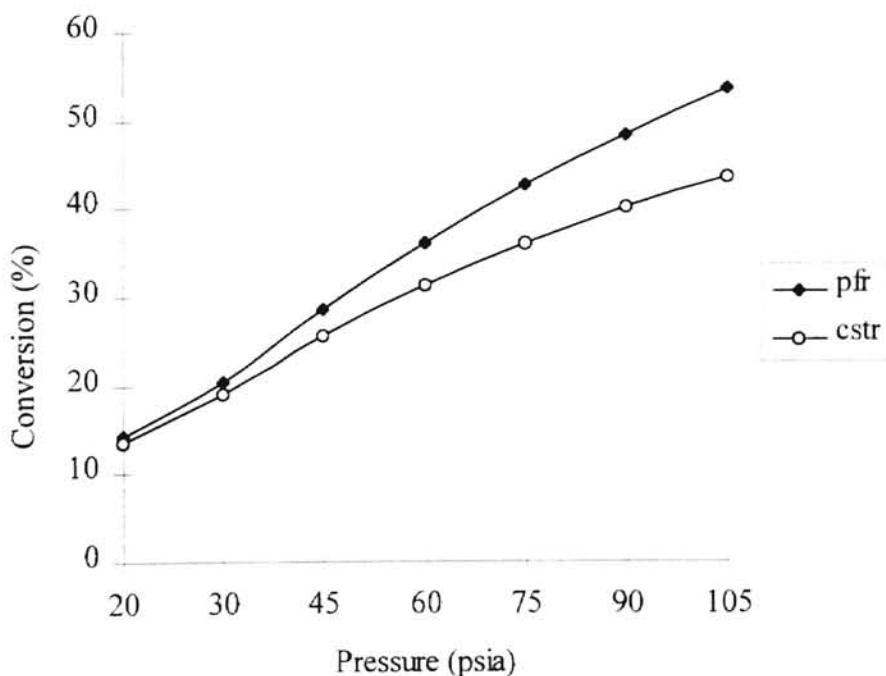


Figure 6.10: Effect of reaction pressure on conversion.

Figure 6.10 shows the effect of reaction pressure on the conversion. The conversion in a PFR scheme varies from 14% to 53%. The conversion increases for a CSTR too within the same pressure range from 13.5% to 43.8%. It can also be seen from the trend in Figure 6.6 that the conversion increases at a much higher rate for the PFR rather than a CSTR.

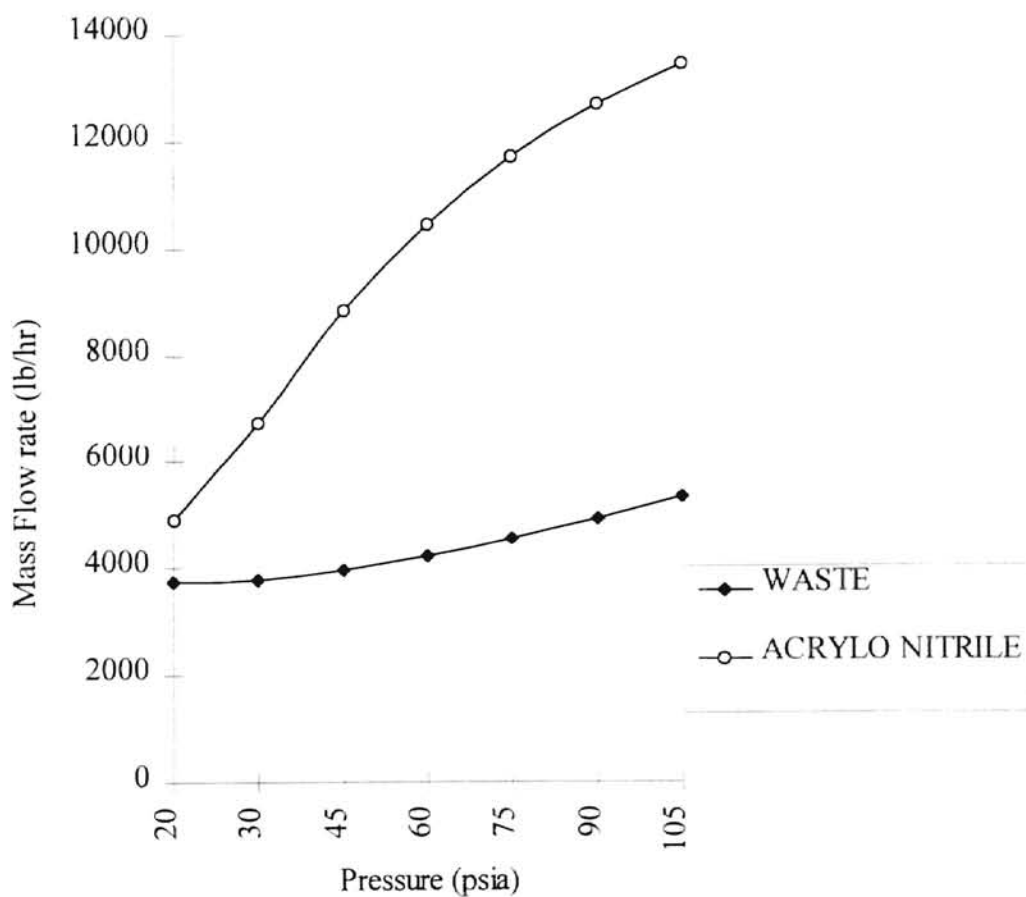


Figure 6.11: Effect of reaction pressure on the product distribution using CSTR scheme

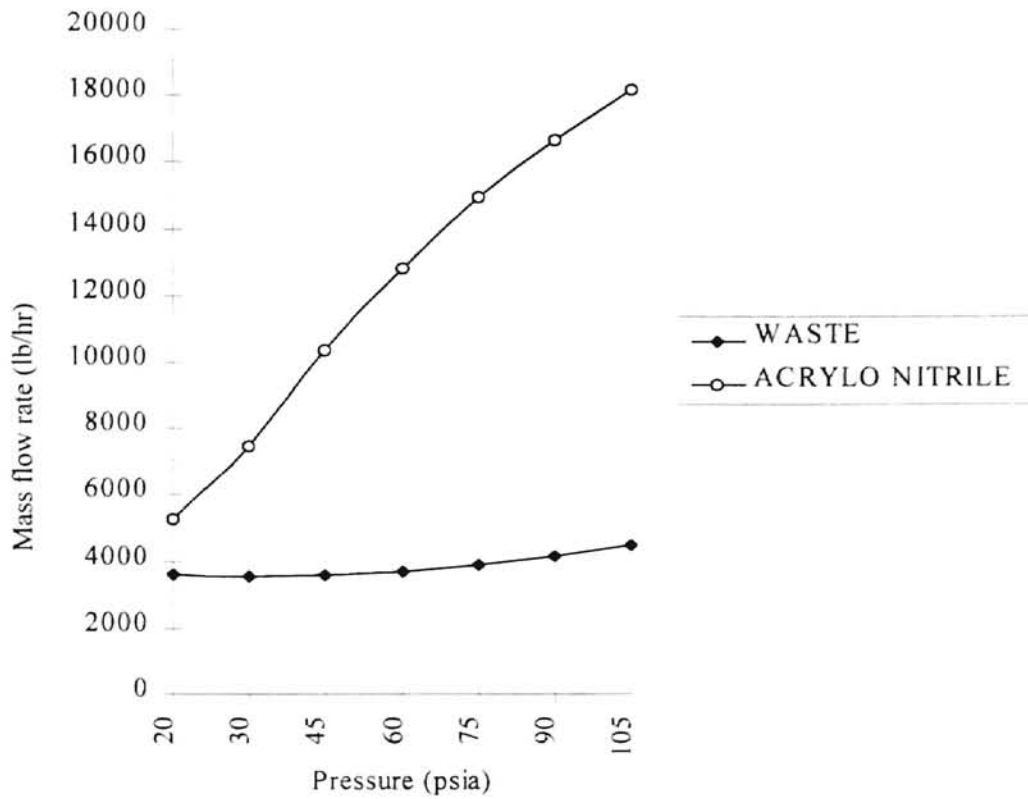


Figure 6.12 Effect of reactor pressure on product distribution using PFR scheme

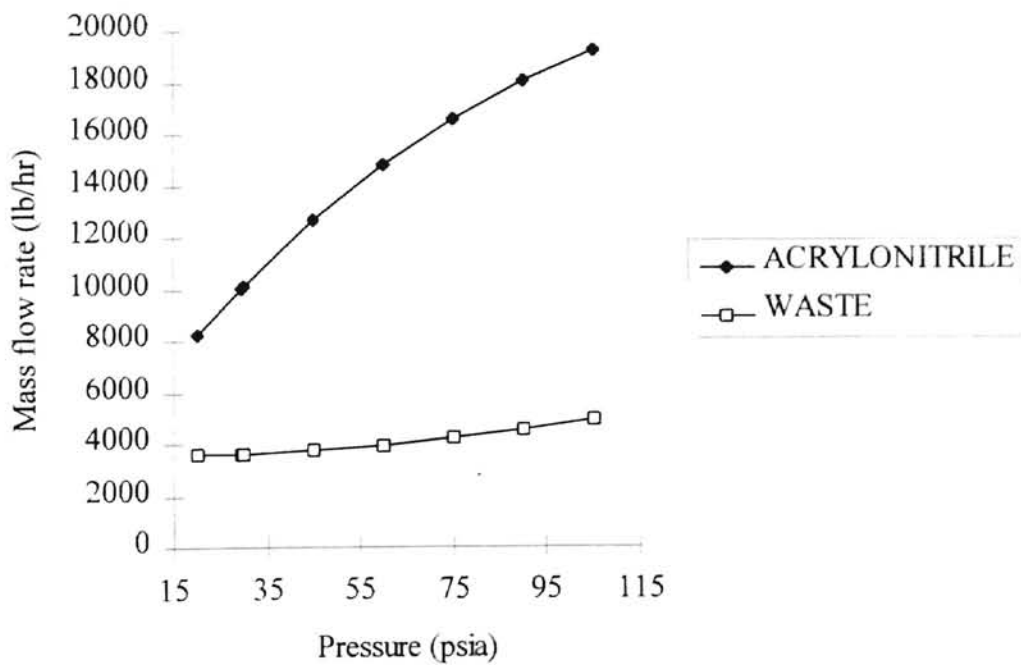


Figure 6.13 : Effect of reaction pressure on product distribution using scheme III.

Figure 6.11 and Figure 6.12 show the effect of the reactor pressure on the product and waste formation. The amount of product increases as the pressure increases. The amount of waste formed is constant until 60 psia after which there is a slow increase in the waste formation. The above mentioned trends are very much alike for both the models. However, the quantity of product formed is higher for a PFR compared to a CSTR. Scheme III, in comparison shows a 50% increase in product formation at 15 psia. However, as the pressure is increased within the same range, it behaves more like the PFR model.

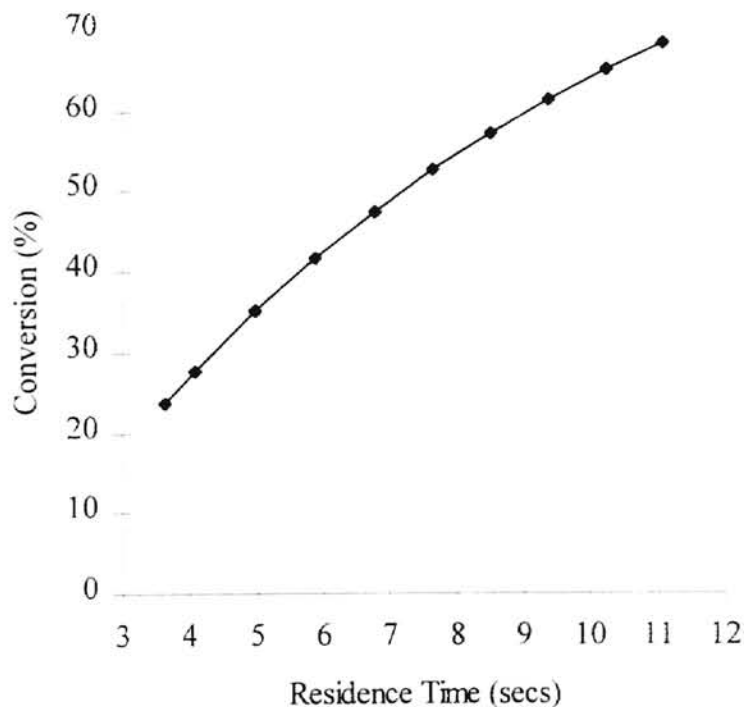


Figure 6.14 : Effect of Residence time on conversion using Scheme III.

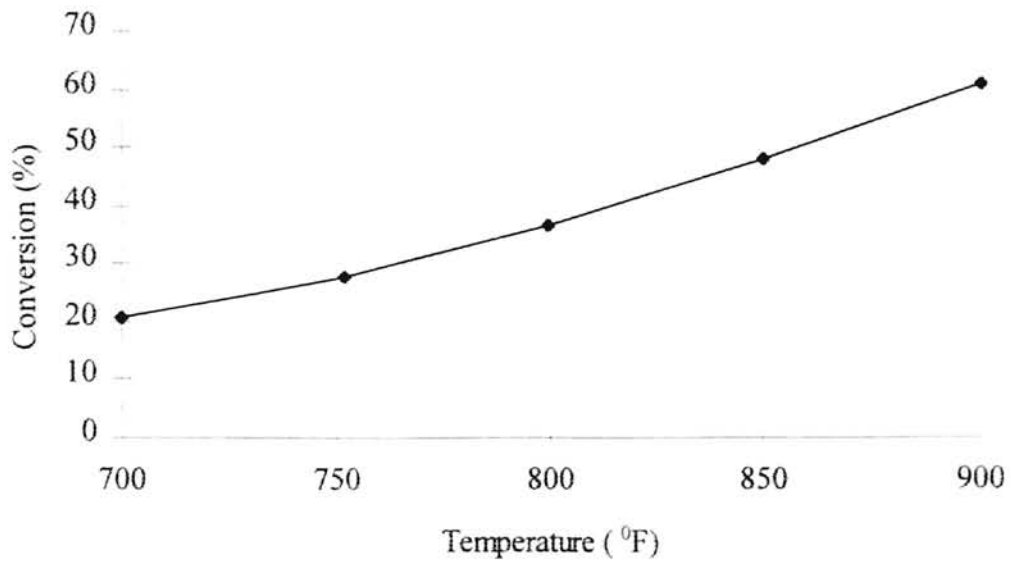


Figure 6.15 : Effect of temperature on conversion for scheme III.

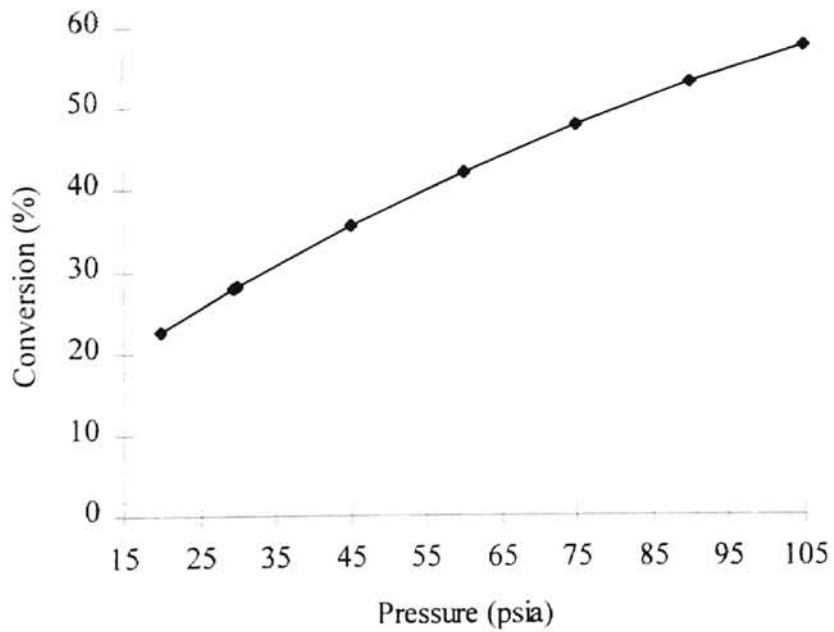


Figure 6.16: Effect of pressure on conversion using scheme III.

Although Figures 6.14 through 6.16 show that scheme III exhibits similar trends as in the CSTR and PFR schemes, the conversion for scheme III is lesser than Scheme I but greater than scheme II.

6.3 Summary of parameter variation results

Increase in continuous reaction parameters - reaction pressure, reaction temperature and residence time, generally increased the conversion with more product formation than waste formation in all the three schemes. However, the CSTR alternative seems to be the most advantageous in terms of conversion and amount of product formation and waste generation of all the studied alternatives. All the variations done on the discrete alternatives support usage of the PFR model as the reaction kinetics supports more formation of product rather than waste. Based on the parametric variation results, the PFR alternative was the better alternative.

6.4 Application of multiobjective optimization

The profit versus waste curve is plotted for each discrete alternative as shown in Figure 6.17. Based on the sensitivity analysis results, the PFR alternative seems to be the better alternative. Now each of the discrete alternatives are optimized for the maximum profit and the minimum waste and the comparison of the results as shown in Figure 6.17, proves that the a PFR reactor alone would be the better of the alternatives.

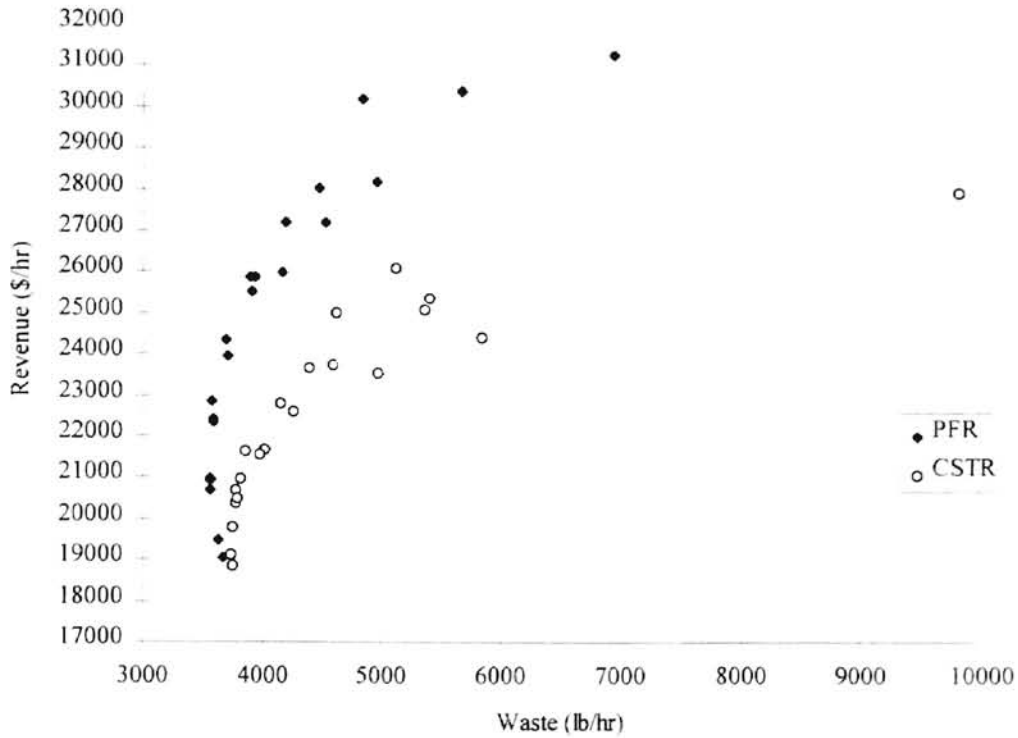


Figure 6.17: Profit vs. waste curves for discrete alternatives.

From figure 6.17, we can see that the PFR scheme is non inferior to the other discrete alternative. The PFR alternative was optimized for the maximum revenue.

The results of optimization of the PFR scheme for the maximum revenue earned having fixed the product formation to 145 mole/hr of product-acrylonitrile is shown in Table 6.1.

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TABLE 6.1

RESULTS OF OPTIMIZATION FOR MAXIMUM REVENUE

Variable	Value
Type of Reactor	PFR
Temperature of Reactor	710°F
Pressure of Reactor	30.17 psia
Volume of Reactor	953 ft ³
Capital cost	\$ 139400
Waste generated	5789 lb/hr
Net Present Value	\$ 2.64 x 10 ⁷

The net present value is calculated to be \$ 2.64 x 10⁷. The corresponding waste generated is 5789 lb./hr.

The PFR scheme is then optimized for the minimum waste that can be generated for the same amount of product outflow. The results of optimization of the PFR scheme for the minimum waste generated having fixed the product formation to 145 mole/hr of product acrylonitrile is shown in Table 6.2.

TABLE 6.2
RESULTS OF OPTIMIZATION FOR MINIMUM WASTE

Variable	Value
Type of Reactor	PFR
Temperature of Reactor	1000°F
Pressure of Reactor	20.34 psia
Volume of Reactor	663.8 ft ³
Capital Cost	\$ 124,404
Waste Generated	4153 lb./hr
Net Present Value	\$ 1.3 x 10 ⁷

The net present value thus found is \$1.3 x 10⁷ /hr and the corresponding waste generated is 4153 lb/hr.

Figure 6.18 shows a plot of the extremities got from the above two optimization runs. Point A depicts the optimization run for the minimum waste while point B depicts the optimization run for the maximum profit.

The data points for (revenue vs waste) for the maximum profit and the minimum waste runs that have been found are plotted and connected as shown in Figure 6.18. This line AB forms the under estimator. This is the line below which the optimum value cannot exist. The slope of this line is found and is used as a weighting factor for the waste in the objective function of the next optimization run.

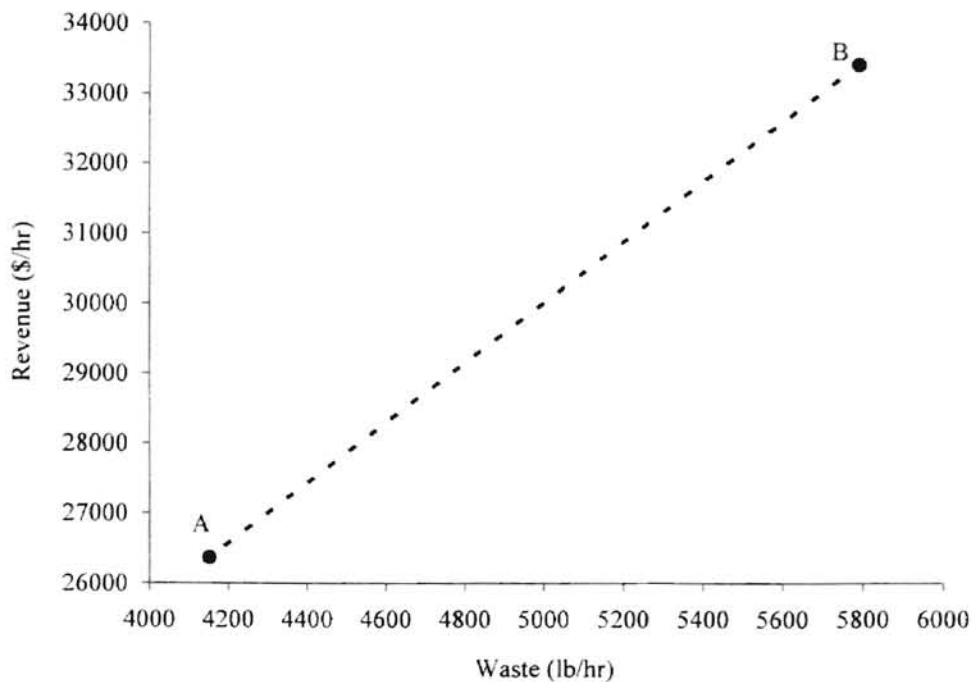


Figure 6.18: Plot of the extremities in the optimization runs.

The new sensitivity curve is obtained using the equation $NP = P - \alpha W$. The slope of line AB, α , is found to be 4.34. This value of α is now incorporated into the objective function. The number of years for the chemical plant's life has been assumed to be seven years. The results of the next iteration gives the data points of the (revenue, waste) to be (31507.4502). These data points are included in figure 6.18 to get the point C shown in figure 6.19.

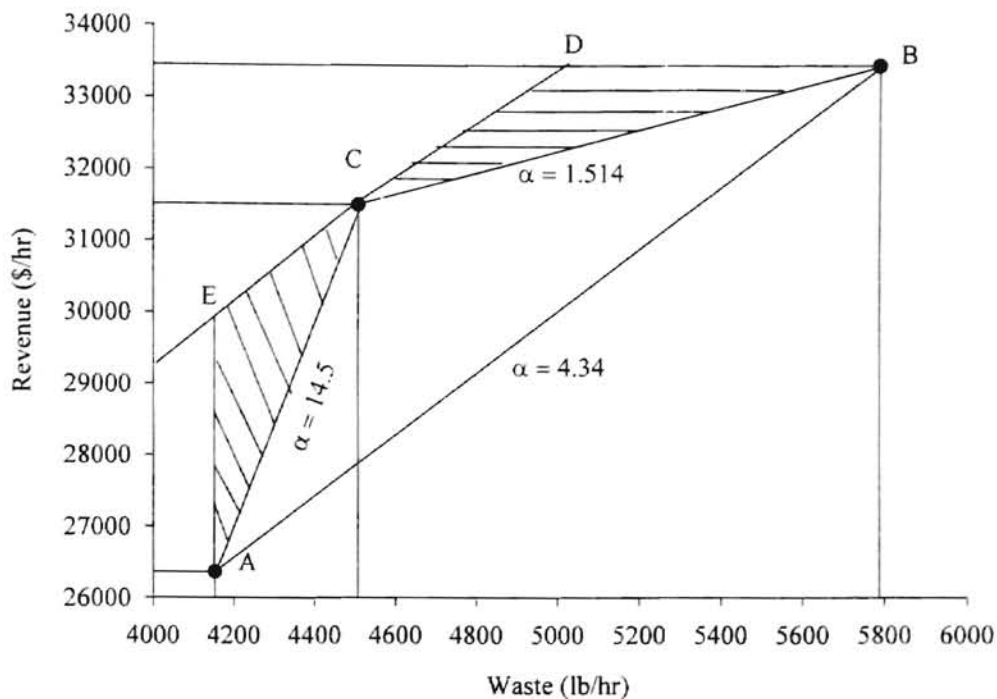


Figure 6.19: Development of sensitivity curve.

Lines AC and BC are connected to form the new under-estimators. The tangent to C forms the over-estimator. The slopes of AC and BC are again used as weighting parameters and the revenue earned is maximized. This in turn yield new points. By generating such points a curve is developed. The stopping criteria for this optimization is done by the following procedure. The tangent to intermediate point C is drawn and the areas under triangles AEC and BDC are calculated. If the areas of the triangles are so insignificant that further iteration would not make significant difference, the iterations could be stopped. This would lead to producing the final sensitivity curve as shown in figure 6.20.

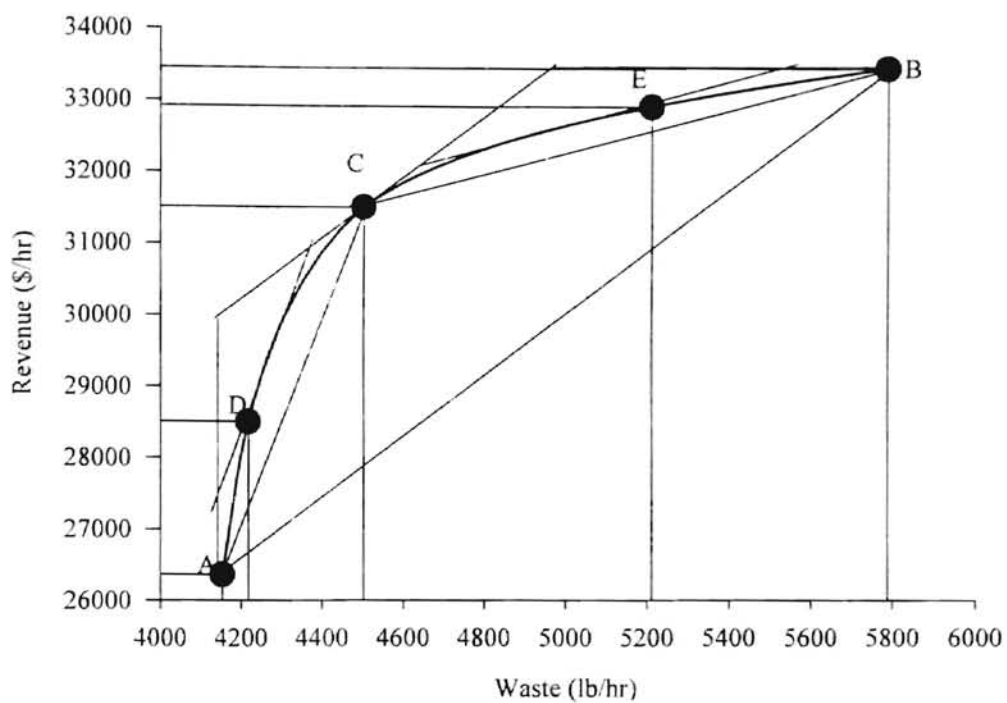


Figure 6.20: Sensitivity curve for Revenue vs. Waste.

The net present value is calculated using equation 5.7 for each of the points that have been found. The net present value versus the waste generated is shown in Figure 6.21.

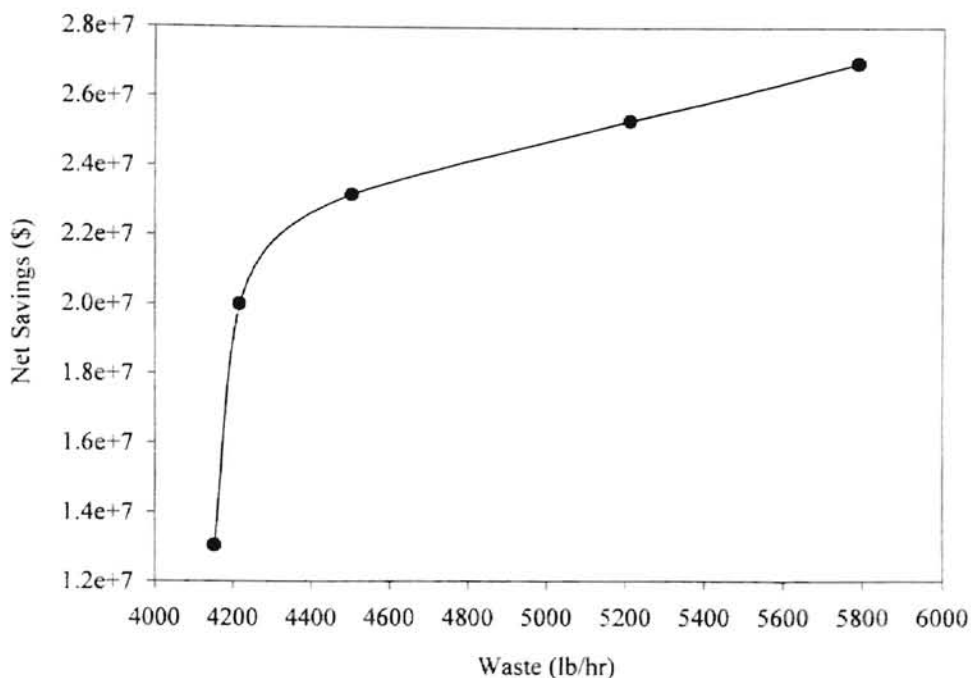


Figure 6.21: Plot of net savings vs. waste.

To summarize, the modified process can earn a maximum net savings of $\$ 2.64 \times 10^7$ in seven years, an increase of 69% over the base case. At the other end of the spectrum, the modified process could generate waste of 4153 lb./hr, a decrease of 38% compared to the base case. It is now left to the process designer to decide upon process alternatives based on the required net present value and the corresponding waste the process would generate.

Conclusions made based on the above mentioned results for the acrylonitrile process will be discussed in the next chapter.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The focus of this study was to develop a methodology using multiobjective optimization that would enhance a chemical process by increasing the overall revenue and also reducing the waste generated. This research has been done using the acrylonitrile process as a case study. A general methodology involving process modeling, generation of process alternatives and incorporation of multiobjective optimization was formulated.

ASPEN PLUS™ was the main tool that was used in this study. The modeling was done using constraints on the required outlet flow rate of the product. Since parameters such as the equipment sizes and operating conditions were not known, several sensitivity and optimization studies were done to study the methodology. The optimization algorithm of ASPEN PLUS™, SQP, is very time consuming. More robust algorithms or faster computing facilities such as the parallel processors may speed up optimization. In order to optimize the process using the SQP algorithm of ASPEN PLUS™, one needs to supply a good initial guess for the varied parameters. Evaluation of identified discrete process alternatives could be automated using a superstructure. The MINLP algorithm (Dantus, 1995) has been proven to be effective. However, every continuous variable is varied over the whole range for each of the discrete alternatives. This, in turn, causes high usage of CPU space as well as time when evaluating the whole flow sheet.

Discrete and continuous process alternatives were formulated to study the effectiveness of the proposed methodology. The discrete alternatives are listed below:

a) Variation in reactors used:

The various kinds of reactors studied were

- the plug flow reactor (PFR),
- the continuous stirred tank reactor (CSTR) and
- a combination of a CSTR and PFR in series.

b) Variation in separation sequence:

The waste and the product streams were identified on analysis of the stream summaries. Separation was enhanced on the waste streams to separate the raw materials which are then recycled to the feed. Further, the separation streams for acrylonitrile purification had been rerouted in order to be more effective.

The continuous alternatives that were studied are:

a) Reaction conditions

- Residence time in the reactor
- Reaction temperature
- Reaction pressure

b) Inlet Feed Rates.

It was found that increase in all of the above continuous alternatives resulted in production of more product as well as waste. Multiobjective optimization helps in screening the alternatives efficiently. This methodology is designed to enhance a process both economically as well as environmentally. Using this methodology, it is possible to

generate a non inferior curve which identifies the superior discrete alternative. This is then optimized using the slope of the non inferior curve as a weighting factor for the waste produced. This methodology helped in generating a tradeoff curve for the profit versus waste generated. It is then left to the decision maker to make the tradeoff as per requirements.

The following conclusions can be made on the basis of this study:

- 1) ASPEN PLUS™ was used successfully to incorporate the proposed methodology.
- 2) Development of the base case model and economic model can be used in comparing process alternatives.
- 3) The optimal process alternative can be obtained by usage of the proposed methodology.
- 4) In this case study, the variables that mainly affect the process have been identified and optimized. The variables that mainly affected the process were the reaction conditions of temperature, pressure and the residence time of the reactor and the inlet feed flow rates. Process kinetics was found to be the key factor in determining the better of the discrete alternatives.
- 5) It was found that usage of the plug flow reactor was the best discrete alternative for the modeled acrylonitrile process.
- 6) The multiobjective optimization methodology was followed. By using this methodology, a sensitivity curve, shown in Figure 6.21, of the net savings versus waste was developed after several optimization runs.

The recommendations for future study to improve the methodology are:

- 1) Association and incorporation of fuzzy factors such as safety, controllability etc. to economic or environmental value in the objective function.
- 2) Application of pinch technology to improve the heat and mass integration.
- 3) Evaluation of multiobjective optimization using more robust algorithms than the SQP optimizer of ASPEN PLUS.
- 4) Use of parallel processors to reduce the time required for optimization.

The recommendations for improving the process model studied are:

1. Investigating further approaches to reactor modeling:
 - i) Fluidized bed reactors are known to be better reactors for gas based reactions. Therefore, modelling using a fluidized bed reactor would be a better discrete alternative.
 - ii) Analyzing different combination of reactors using the $1/r_a$ vs. conversion curve developed in Appendix A for the least volume assuming a higher intermediate conversion.

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APPENDIX A

CALCULATIONS AND LOGIC DIAGRAM

Evaluation of Rate Equations

We know that $k_{t_1} = k_{t_2} \cdot e^{-(E/R)((1/t_1)-(1/t_2))}$

$R = 1.987 \text{ cal/mole K}$

$T = 470^\circ\text{C} = 743^\circ\text{K}$

Using data from Table 4.2 (pg. 28)

Therefore,

$$\begin{aligned}k_1 &= 0.40556 * e^{-(19000/1.987) * [1/T_1 - 1/743]} \\ &= 0.40556 * e^{-19000/(1.987 * 743)} * e^{-19000/RT_1} \\ &= 1.57498E+05 e^{-19000/RT_1}\end{aligned}$$

Similarly,

$$\begin{aligned}k_2 &= 0.00973 * e^{-(19000/1.987) * [1/T_1 - 1/743]} \\ &= 0.00973 * e^{-19000/(1.987 * 743)} * e^{-19000/RT_1} \\ &= 3.778E+03 e^{-19000/RT_1}\end{aligned}$$

$$\begin{aligned}k_3 &= 0.00973 * e^{-(7000/1.987) * [1/T_1 - 1/743]} \\ &= 0.00973 * e^{-7000/(1.987 * 743)} * e^{-7000/RT_1} \\ &= 1.99 e^{-7000/RT_1}\end{aligned}$$

$$\begin{aligned}k_4 &= 6.81341 * e^{-(7000/1.987) * [1/T_1 - 1/743]} \\ &= 6.81341 * e^{-7000/(1.987 * 743)} * e^{-7000/RT_1} \\ &= 780.82 e^{-7000/RT_1}\end{aligned}$$

$$\begin{aligned}k_5 &= 0.16222 * e^{-(19800/1.987) * [1/T_1 - 1/743]} \\ &= 0.16222 * e^{-19800/(1.987 * 743)} * e^{-19800/RT_1} \\ &= 1.08308E+05 e^{-19800/RT_1}\end{aligned}$$

$$\begin{aligned}
 k_6 &= 0.073 * e^{-(7000/1.987) * [1/T_1 - 1/743]} \\
 &= 0.073 * e^{-7000/(1.987 * 743)} * e^{-7000/RT_1} \\
 &= 8.3658 e^{-7000/RT_1}
 \end{aligned}$$

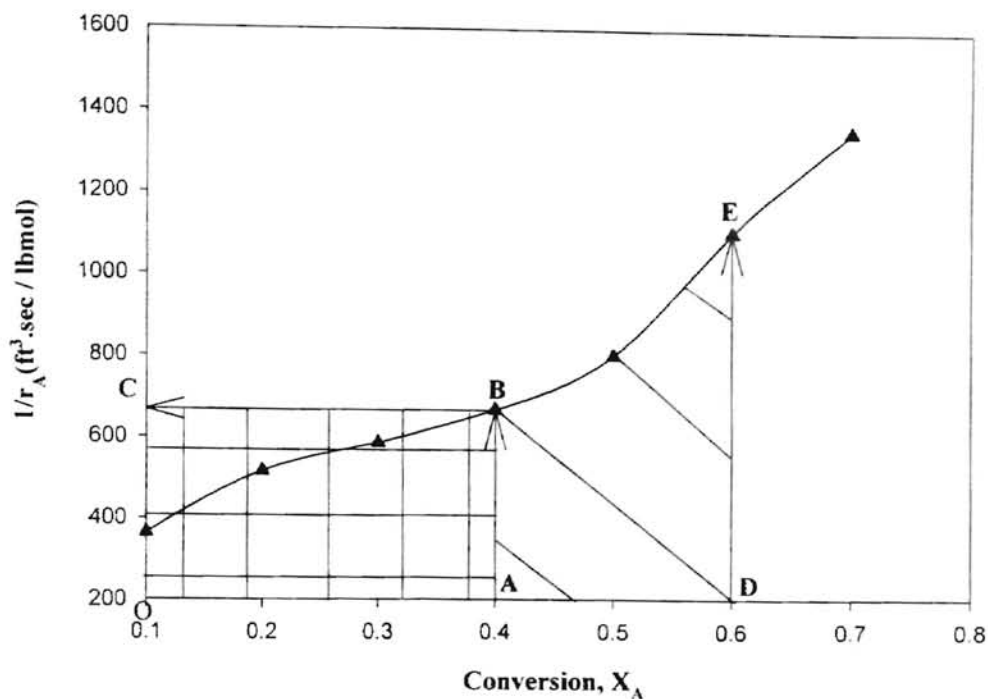
Evaluation of $1/r_A$ vs Conversion curve for further development of discrete alternatives using ASPEN.

Step 1: Create a design spec for the required conversion varying the volume of the reactor.

The results thus found are as follows:

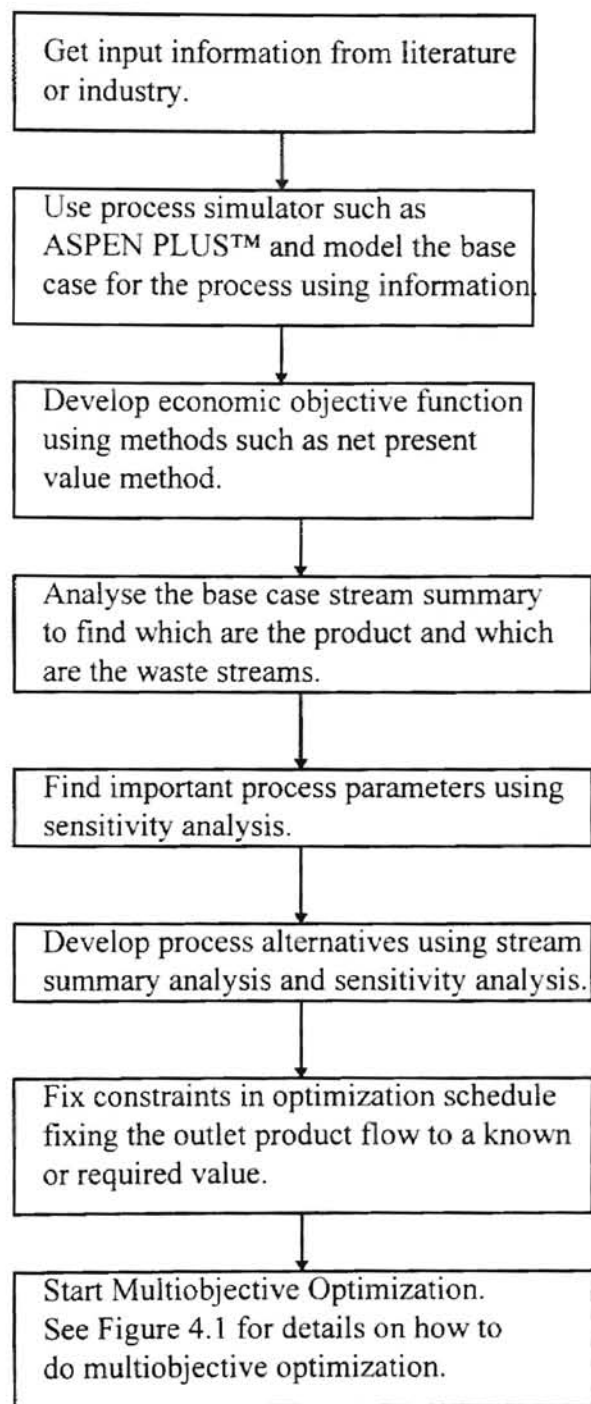
Conversion	Required volume(V) of reactor(ft ³)	$-1/r_A = V/X$
0.1	33.5	335
0.2	95	475
0.3	162	540
0.4	246	615
0.5	369	738
0.6	610	1016
0.7	873	1247

Step 2: Plot $1/r_A$ vs. X_A



Step 3: The volume under the curve for a known intermediate conversion will give the plug flow reactor volume. The product of the rectangle formed by the conversion and the corresponding $1/r_A$ gives the CSTR volume. For example for a cstr followed by a pfr with an intermediate conversion of 40% after the cstr and a desired overall conversion of 60% after the pfr, the required cstr volume would be the area formed by ABCO and the required pfr volume would be the area formed by ADEB.

LOGIC DIAGRAM



APPENDIX B

INPUT FILE FOR THE BASE CASE PROCESS

TITLE 'Acrylonitrile Process Basecase Simulation'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

SIM-OPTIONS RESTART=NO

RUN-CONTROL MAX-TIME=15000 MAX-ERRORS=1000 MAX-FORT-ERR=1000

DATABANKS PURECOMP / AQUEOUS / SOLIDS / INORGANIC / &
ASPENPCD

PROP-SOURCES PURECOMP / AQUEOUS / SOLIDS / INORGANIC / &
ASPENPCD

COMPONENTS

NH3 H3N NH3 /
H2O H2O H2O /
HCN CHN HCN /
CO CO CO /
O2 O2 O2 /
PROPYLEN C3H6-2 PROPYLEN /
CO2 CO2 CO2 /
ACETO C2H3N ACETO /
ACRYLO C3H3N ACRYLO /
ACROLEIN C3H4O ACROLEIN /
H2S04 H2SO4 H2S04 /
AMMSUL "(NH4)2SO4" AMMSUL

FLOWSHEET

BLOCK B1 IN=S-1 S-2 S-3 OUT=S-4
BLOCK B10 IN=S-13 OUT=S-16WAS S-15H2O
BLOCK B5 IN=S-7 S-8 OUT=S-7+8
BLOCK B3 IN=S-4 OUT=S-6
BLOCK B6 IN=S-7+8 OUT=57
BLOCK B26 IN=S-15H2O 48 OUT=38
BLOCK B12 IN=S-18 49 OUT=52
BLOCK B7 IN=S-6 OUT=S-7

BLOCK B2 IN=57 OUT=48 AMMSUL
BLOCK B8 IN=38 OUT=S-12GAS S-12
BLOCK B9 IN=S-12 OUT=S-14 S-13
BLOCK HCN-CO IN=S-14 OUT=S-17HCN S-18
BLOCK EXTRAC IN=52 OUT=S-19 S-24
BLOCK ACET-PUR IN=S-24 OUT=ACRYL3 ACETO
BLOCK ACR-I IN=S-19 OUT=49 S-21
BLOCK ACRY-II IN=S-21 OUT=ACRYLO ACRYL2

PROPERTIES ELECNRTL
PROPERTIES IDEAL

USER-PROPS DRUSR2 1 2 3

PROP-DATA NRTL-1
IN-UNITS ENG
PROP-LIST NRTL
BPVAL NH3 H2O -.16424220 -1849.5450 .20 .0 .0 .0 32.0 &
392.0
BPVAL H2O NH3 -.5440720 3021.2440 .20 .0 .0 .0 32.0 &
392.0
BPVAL H2O HCN .0 909.90 .30 .0 .0 .0 50.0 230.0
BPVAL HCN H2O .0 .0 .30 .0 .0 .0 50.0 230.0
BPVAL H2O CO2 10.0640 -5882.6430 .20 .0 .0 .0 32.0 &
392.0
BPVAL CO2 H2O 10.0640 -5882.6430 .20 .0 .0 .0 32.0 &
392.0

PROP-SET PS-1 VMX UNITS='CUFT/HR' SUBSTREAM=MIXED

STREAM ACRYL3

STREAM AMMSUL

STREAM S-1
SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW NH3 300

STREAM S-2
SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW PROPYLEN 400

STREAM S-3
SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW O2 600

STREAM S-8

SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW H2S04 1000.0

BLOCK B1 MIXER

BLOCK B5 MIXER

BLOCK B12 MIXER

BLOCK B26 MIXER

BLOCK B10 SEP

FRAC STREAM=S-15H20 SUBSTREAM=MIXED COMPS=NH3 H2O HCN CO &
O2 PROPYLEN CO2 ACETO ACRYLO ACROLEIN H2S04 FRACS=.0 &
1.0 .0 .0 .0 .0 .0 .0 .0 .0 .0
FLASH-SPECS S-15H20 TEMP=120.0 PRES=.0

BLOCK B2 FLASH2

PARAM TEMP=225 PRES=15

BLOCK ACET-PUR RADFRAC

PARAM NSTAGE=105
FEEDS S-24 53
PRODUCTS ACRYL3 1 L / ACETO 105 L
P-SPEC 1 15
COL-SPECS D:F=9.3E-3 MOLE-RDV=0 MOLE-RR=120

BLOCK ACR-I RADFRAC

PARAM NSTAGE=15
FEEDS S-19 9
PRODUCTS 49 1 L / S-21 15 L
P-SPEC 1 15
COL-SPECS D:F=0.032 MOLE-RDV=0 MOLE-RR=1.15

BLOCK ACRY-II RADFRAC

PARAM NSTAGE=100
FEEDS S-21 50
PRODUCTS ACRYLO 1 L / ACRYL2 100 L
P-SPEC 1 15
COL-SPECS D:F=0.95 MOLE-RDV=0 MOLE-RR=8.13

BLOCK B8 RADFRAC

PARAM NSTAGE=22

FEEDS 38 13
PRODUCTS S-12GAS 1 L / S-12 22 L
P-SPEC 1 15
COL-SPECS D:F=0.025 MOLE-RDV=0 MOLE-RR=.20

BLOCK B9 RADFRAC
PARAM NSTAGE=15
FEEDS S-12 7
PRODUCTS S-14 1 L / S-13 15 L
P-SPEC 1 15
COL-SPECS D:F=0.06 MOLE-RDV=0 MOLE-RR=41

BLOCK EXTRAC RADFRAC
PARAM NSTAGE=104
FEEDS 52 52
PRODUCTS S-24 104 L / S-19 1 L
P-SPEC 1 15
COL-SPECS D:F=0.153 MOLE-RDV=0 MOLE-RR=10

BLOCK HCN-CO RADFRAC
PARAM NSTAGE=15
FEEDS S-14 7
PRODUCTS S-17HCN 1 L / S-18 15 L
P-SPEC 1 15
COL-SPECS D:F=0.082 MOLE-RDV=0 MOLE-RR=0.66

BLOCK B6 RSTOIC
PARAM TEMP=100.0 PRES=15.0
STOIC 1 MIXED NH3 -2.0 / H2S04 -1.0 / AMMSUL 1.0
CONV 1 MIXED NH3 .960

BLOCK B3 RCSTR
PARAM VOL=2500 TEMP=752 PRES=30 ALGORITHM=INTEGRATOR
STOIC 1 MIXED PROPYLEN -1.0 / NH3 -1.0 / O2 -1.50 / &
ACRYLO 1.0 / H2O 3.0
STOIC 2 MIXED PROPYLEN -1.0 / O2 -1.0 / ACROLEIN 1.0 / &
H2O 1.0
STOIC 3 MIXED PROPYLEN -1.0 / NH3 -1.0 / O2 -2.250 / &
ACETO 1.0 / CO2 .50 / CO .50 / H2O 3.0
STOIC 4 MIXED ACROLEIN -1.0 / NH3 -1.0 / O2 -.50 / &
ACRYLO 1.0 / H2O 2.0
STOIC 5 MIXED ACRYLO -1.0 / O2 -2.0 / CO2 1.0 / CO &
1.0 / HCN 1.0 / H2O 1.0
STOIC 6 MIXED ACETO -1.0 / O2 -1.50 / CO2 1.0 / HCN &
1.0 / H2O 1.0

RATE-CON 1 157498 19000 <CAL/MOL>
RATE-CON 2 3778 19000 <CAL/MOL>
RATE-CON 3 1.990 7000 <CAL/MOL>
RATE-CON 4 780.82 7000 <CAL/MOL>
RATE-CON 5 108308 19800 <CAL/MOL>
RATE-CON 6 8.3658 7000 <CAL/MOL>
POWLAW-EXP 1 PROPYLEN 1.0
POWLAW-EXP 2 PROPYLEN 1.0
POWLAW-EXP 3 PROPYLEN 1.0
POWLAW-EXP 4 ACROLEIN 1.0
POWLAW-EXP 5 ACRYLO 1.0
POWLAW-EXP 6 ACETO 1.0

BLOCK B7 MULT
PARAM FACTOR=1.0

DESIGN-SPEC DS-1
DEFINE INAMM MOLE-FLOW STREAM=57 SUBSTREAM=MIXED &
COMPONENT=AMMSUL
DEFINE OUTAMM MOLE-FLOW STREAM=AMMSUL SUBSTREAM=MIXED
&
COMPONENT=AMMSUL
F RATIO = OUTAMM/INAMM
SPEC "OUTAMM/INAMM" TO "0.99"
TOL-SPEC "0.05"
VARY BLOCK-VAR BLOCK=B2 VARIABLE=PRES SENTENCE=PARAM
LIMITS "0 " "70"

DESIGN-SPEC DS-2
DEFINE INH20 MOLE-FLOW STREAM=57 SUBSTREAM=MIXED &
COMPONENT=H20
DEFINE OUTH20 MOLE-FLOW STREAM=48 SUBSTREAM=MIXED &
COMPONENT=H20
SPEC "OUTH20/INH20" TO "0.95"
TOL-SPEC "0.05"
VARY BLOCK-VAR BLOCK=B2 VARIABLE=TEMP SENTENCE=PARAM
LIMITS "200" "600"

DESIGN-SPEC DS-3
DEFINE MOLH2S MOLE-FLOW STREAM=S-8 SUBSTREAM=MIXED &
COMPONENT=H2S04
DEFINE MOLNH3 MOLE-FLOW STREAM=S-7 SUBSTREAM=MIXED &
COMPONENT=NH3
SPEC "MOLH2S" TO "MOLNH3/2"
TOL-SPEC "5"

VARY MOLE-FLOW STREAM=S-8 SUBSTREAM=MIXED
COMPONENT=H2S04
LIMITS "25" "1000"

DESIGN-SPEC DS-4

DEFINE ACRYL MOLE-FLOW STREAM=S-6 SUBSTREAM=MIXED &
COMPONENT=ACRYLO
SPEC "ACRYL" TO "145"
TOL-SPEC "0.05"
VARY BLOCK-VAR BLOCK=B3 VARIABLE=VOL SENTENCE=PARAM
LIMITS "700" "4000"

CONV-OPTIONS

PARAM TOL=.010
WEGSTEIN MAXIT=200 QMIN=-20.0
SECANT MAXIT=60 XTOL=1E-03

ECONOMIC-REP CASH-FLOW=ANNUAL

;
;
;
;
;
;

APPENDIX C

INPUT FILE FOR OPTIMIZED PROCESS

TITLE ' Optimization of Modified Acrylonitrile Process '

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

RUN-CONTROL MAX-TIME=1000 MAX-ERRORS=9999 MAX-FORT-ERR=9999

DATABANKS PURECOMP / AQUEOUS / SOLIDS / INORGANIC / &
ASPENPCD

PROP-SOURCES PURECOMP / AQUEOUS / SOLIDS / INORGANIC / &
ASPENPCD

COMPONENTS

NH3 H3N NH3 /
H2O H2O H2O /
HCN CHN HCN /
CO CO CO /
O2 O2 O2 /
PROPYLEN C3H6-2 PROPYLEN /
CO2 CO2 CO2 /
ACETO C2H3N ACETO /
ACRYLO C3H3N ACRYLO /
ACROLEIN C3H4O ACROLEIN /
H2S04 H2SO4 H2S04 /
AMMSUL "(NH4)2SO4" AMMSUL

FLOWSHEET

BLOCK B1 IN=S-1 S-2 S-3 OUT=S-4
BLOCK B5 IN=S-7 S-8 OUT=S-7+8
BLOCK EXTRAC IN=52 OUT=S-19 S-24
BLOCK HCN-CO IN=S-14 OUT=WASTEHCN S-18
BLOCK B6 IN=S-7+8 OUT=57
BLOCK B8 IN=38 OUT=36 S-12
BLOCK B26 IN=48 S-13 OUT=38
BLOCK B9 IN=S-12 OUT=S-14 S-13
BLOCK B12 IN=49 58 S-18 OUT=52
BLOCK B19 IN=51 OUT=58 ACETO
BLOCK B20 IN=S-24 OUT=ACRYLB 51

BLOCK B7 IN=S-6 OUT=S-7
BLOCK B2 IN=57 OUT=48 AMMSULP
BLOCK B11 IN=S-19 OUT=49 ACRYLA
BLOCK REACTOR IN=S-4 OUT=S-6
BLOCK B4 IN=36 OUT=37
BLOCK B10 IN=35 OUT=WASTEGAS REOXYG
BLOCK B13 IN=37 OUT=35 REPROP

PROPERTIES ELECNRTL
PROPERTIES IDEAL

USER-PROPS DRUSR2 1 2 3

PROP-DATA NRTL-1
IN-UNITS ENG
PROP-LIST NRTL
BPVAL NH3 H2O -.16424220 -1849.5450 .20 .0 .0 .0 32.0 &
392.0
BPVAL H2O NH3 -.5440720 3021.2440 .20 .0 .0 .0 32.0 &
392.0
BPVAL H2O HCN .0 909.90 .30 .0 .0 .0 50.0 230.0
BPVAL HCN H2O .0 .0 .30 .0 .0 .0 50.0 230.0
BPVAL H2O CO2 10.0640 -5882.6430 .20 .0 .0 .0 32.0 &
392.0
BPVAL CO2 H2O 10.0640 -5882.6430 .20 .0 .0 .0 32.0 &
392.0

STREAM S-1
SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW NH3 1100

STREAM S-2
SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW PROPYLEN 850

STREAM S-3
SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW O2 1350

STREAM S-8
SUBSTREAM MIXED TEMP=80.0 PRES=14.70
MOLE-FLOW H2S04 500

BLOCK B1 MIXER

BLOCK B5 MIXER

BLOCK B12 MIXER
PARAM TOL=0.01

BLOCK B26 MIXER

BLOCK B19 SEP
FRAC STREAM=ACETO SUBSTREAM=MIXED COMPS=NH3 H2O HCN CO &
O2 PROPYLEN CO2 ACETO ACRYLO ACROLEIN H2S04 AMMSUL &
FRACS=.0 .0 .0 .0 .0 .0 .0 1.0 .0 .0 .0 .0

BLOCK B4 HEATER
PARAM TEMP=100 PRES=0

BLOCK B2 FLASH2
PARAM TEMP=225 PRES=15

BLOCK B8 DSTWU
PARAM LIGHTKEY=PROPYLEN RECOVL=.97 HEAVYKEY=HCN
RECOVH=.01 &
PTOP=15.0 PBOT=20.0 NSTAGE=10 FLASH-TOL=0.01 K-TOL=0.01

BLOCK B9 DSTWU
PARAM LIGHTKEY=ACRYLO RECOVL=.990 HEAVYKEY=H2O RECOVH=.250
&
PTOP=15.0 PBOT=15.0 RR=-1.2 FLASH-TOL=0.1 K-TOL=0.1

BLOCK B10 DSTWU
PARAM LIGHTKEY=CO RECOVL=0.95 HEAVYKEY=O2 RECOVH=0.05 &
PTOP=15 PBOT=15 RR=-1.2 FLASH-TOL=0.1

BLOCK B11 DSTWU
PARAM LIGHTKEY=PROPYLEN RECOVL=0.95 HEAVYKEY=ACROLEIN &
RECOVH=0.05 PTOP=15 PBOT=15 NSTAGE=15

BLOCK B13 DSTWU
PARAM LIGHTKEY=CO2 RECOVL=0.95 HEAVYKEY=PROPYLEN &
RECOVH=0.05 PTOP=15 PBOT=15 RR=-1.2

BLOCK B20 DSTWU
PARAM LIGHTKEY=ACRYLO RECOVL=.950 HEAVYKEY=ACETO &
RECOVH=.050 PTOP=15.0 PBOT=15.0 RR=-1.2

BLOCK EXTRAC DSTWU

PARAM LIGHTKEY=ACRYLO RECOVL=.950 HEAVYKEY=ACETO &
RECOVH=.050 PTOP=15.0 PBOT=15.0 RR=-1.2 FLASH-MAXIT=60

BLOCK HCN-CO DSTWU

PARAM LIGHTKEY=HCN RECOVL=.950 HEAVYKEY=ACROLEIN &
RECOVH=.10 PTOP=15.0 PBOT=15.0 NSTAGE=15

BLOCK B6 RSTOIC

PARAM TEMP=100.0 PRES=15.0
STOIC 1 MIXED NH3 -2.0 / H2S04 -1.0 / AMMSUL 1.0
CONV 1 MIXED NH3 .960

BLOCK REACTOR RPLUG

PARAM TYPE=T-SPEC LENGTH=20 DIAM=7 PRES=29.5
T-SPEC 0.25 752
STOIC 1 MIXED PROPYLEN -1 / NH3 -1 / O2 -1.5 / ACRYLO &
1 / H2O 3
STOIC 2 MIXED PROPYLEN -1 / O2 -1 / ACROLEIN 1 / H2O &
1
STOIC 3 MIXED PROPYLEN -1 / NH3 -1 / O2 -2.25 / ACETO &
1 / CO2 .5 / CO .5 / H2O 3
STOIC 4 MIXED ACROLEIN -1 / NH3 -1 / O2 -0.5 / ACRYLO &
1 / H2O 2
STOIC 5 MIXED ACRYLO -1 / O2 -2 / CO 1 / CO2 1 / &
H2O 1 / HCN 1
STOIC 6 MIXED ACETO -1 / O2 -1.5 / CO2 1 / HCN 1 / &
H2O 1
RATE-CON 1 157498 34200
RATE-CON 2 3778 34200
RATE-CON 3 1.99 12600
RATE-CON 4 780.82 12600
RATE-CON 5 108308 35640
RATE-CON 6 8.3658 12600
POWLAW-EXP 1 PROPYLEN 1
POWLAW-EXP 2 PROPYLEN 1
POWLAW-EXP 3 PROPYLEN 1
POWLAW-EXP 4 ACROLEIN 1
POWLAW-EXP 5 ACRYLO 1
POWLAW-EXP 6 ACETO 1

BLOCK B7 MULT

PARAM FACTOR=1.0

DESIGN-SPEC DS-1

DEFINE INAMM MOLE-FLOW STREAM=57 SUBSTREAM=MIXED &

```

      COMPONENT=AMMSUL
      DEFINE OUTAMM MOLE-FLOW STREAM=AMMSULP SUBSTREAM=MIXED
&
      COMPONENT=AMMSUL
F      RATIO = OUTAMM/INAMM
      SPEC "OUTAMM/INAMM" TO "0.99"
      TOL-SPEC "0.05"
      VARY BLOCK-VAR BLOCK=B2 VARIABLE=PRES SENTENCE=PARAM
      LIMITS "0 " "70"

DESIGN-SPEC DS-2
      DEFINE INH20 MOLE-FLOW STREAM=57 SUBSTREAM=MIXED &
      COMPONENT=H2O
      DEFINE OUTH20 MOLE-FLOW STREAM=48 SUBSTREAM=MIXED &
      COMPONENT=H2O
      SPEC "OUTH20/INH20" TO "0.95"
      TOL-SPEC "0.05"
      VARY BLOCK-VAR BLOCK=B2 VARIABLE=TEMP SENTENCE=PARAM
      LIMITS "200" "600"

DESIGN-SPEC DS-3
      DEFINE MOLH2 MOLE-FLOW STREAM=S-8 SUBSTREAM=MIXED &
      COMPONENT=H2S04
      DEFINE MOLNH3 MOLE-FLOW STREAM=S-7 SUBSTREAM=MIXED &
      COMPONENT=NH3
      SPEC "MOLH2" TO "MOLNH3/2"
      TOL-SPEC "5"
      VARY MOLE-FLOW STREAM=S-8 SUBSTREAM=MIXED
      COMPONENT=H2S04
      LIMITS "200" "1200"

DESIGN-SPEC DS-4
      DEFINE ACRYL MOLE-FLOW STREAM=S-6 SUBSTREAM=MIXED &
      COMPONENT=ACRYLO
      SPEC "ACRYL" TO "145"
      TOL-SPEC "5"
      VARY BLOCK-VAR BLOCK=REACTOR VARIABLE=DIAM
      SENTENCE=PARAM
      LIMITS "2" "20"

CONSTRAINT C-1
      DEFINE PACRYA MOLE-FLOW STREAM=ACRYLA SUBSTREAM=MIXED &
      COMPONENT=ACRYLO
      DEFINE PACRYB MOLE-FLOW STREAM=ACRYLB SUBSTREAM=MIXED &
      COMPONENT=ACRYLO

```

F PRODUT=PACRYA+PACRYB
 SPEC "PRODUT" EQ "140"
 TOL-SPEC "5"

OPTIMIZATION O-1

 DEFINE NH3IN MOLE-FLOW STREAM=S-1 SUBSTREAM=MIXED &
 COMPONENT=NH3
 DEFINE PROPIN MOLE-FLOW STREAM=S-2 SUBSTREAM=MIXED &
 COMPONENT=PROPYLEN
 DEFINE O2IN MOLE-FLOW STREAM=S-3 SUBSTREAM=MIXED &
 COMPONENT=O2
 DEFINE PRO1 MOLE-FLOW STREAM=S-4 SUBSTREAM=MIXED &
 COMPONENT=PROPYLEN
 DEFINE PRO2 MOLE-FLOW STREAM=S-6 SUBSTREAM=MIXED &
 COMPONENT=PROPYLEN
 DEFINE RDIA BLOCK-VAR BLOCK=REACTOR VARIABLE=DIAM &
 SENTENCE=PARAM
 DEFINE RLEN BLOCK-VAR BLOCK=REACTOR VARIABLE=LENGTH &
 SENTENCE=PARAM
 DEFINE RES BLOCK-VAR BLOCK=REACTOR VARIABLE=RES-TIME &
 SENTENCE=PARAM
 DEFINE RPRES BLOCK-VAR BLOCK=REACTOR VARIABLE=PRES &
 SENTENCE=PARAM
 DEFINE RTEMP BLOCK-VAR BLOCK=REACTOR VARIABLE=TEMP &
 SENTENCE=T-SPEC ID1=1
 DEFINE WSWAS STREAM-VAR STREAM=WASTEGAS SUBSTREAM=MIXED
 &
 VARIABLE=MASS-FLOW
 DEFINE WSHCN STREAM-VAR STREAM=WASTEHCN SUBSTREAM=MIXED
 &
 VARIABLE=MASS-FLOW
 DEFINE PACRA MASS-FLOW STREAM=ACRYLA SUBSTREAM=MIXED &
 COMPONENT=ACRYLO
 DEFINE PACRB MASS-FLOW STREAM=ACRYLB SUBSTREAM=MIXED &
 COMPONENT=ACRYLO
 DEFINE PACETO MASS-FLOW STREAM=ACETO SUBSTREAM=MIXED &
 COMPONENT=ACETO
 DEFINE PSAMMS MASS-FLOW STREAM=AMMSULP SUBSTREAM=MIXED
 &
 COMPONENT=AMMSUL
 DEFINE QB2 BLOCK-VAR BLOCK=B2 VARIABLE=QCALC
 SENTENCE=PARAM
 DEFINE QHHCN BLOCK-VAR BLOCK=HCN-CO VARIABLE=REB-DUTY &
 SENTENCE=RESULTS
 DEFINE QCHCN BLOCK-VAR BLOCK=HCN-CO VARIABLE=COND-DUTY &

```

SENTENCE=RESULTS
DEFINE QHEXTR BLOCK-VAR BLOCK=EXTRAC VARIABLE=REB-DUTY &
  SENTENCE=RESULTS
DEFINE QCEXTR BLOCK-VAR BLOCK=EXTRAC VARIABLE=COND-DUTY &
  SENTENCE=RESULTS
DEFINE QHB20 BLOCK-VAR BLOCK=B20 VARIABLE=REB-DUTY &
  SENTENCE=RESULTS
DEFINE QCB20 BLOCK-VAR BLOCK=B20 VARIABLE=COND-DUTY &
  SENTENCE=RESULTS
DEFINE QHB11 BLOCK-VAR BLOCK=B11 VARIABLE=REB-DUTY &
  SENTENCE=RESULTS
DEFINE QCB11 BLOCK-VAR BLOCK=B11 VARIABLE=COND-DUTY &
  SENTENCE=RESULTS
DEFINE QHB9 BLOCK-VAR BLOCK=B9 VARIABLE=REB-DUTY &
  SENTENCE=RESULTS
DEFINE QCB9 BLOCK-VAR BLOCK=B9 VARIABLE=COND-DUTY &
  SENTENCE=RESULTS
DEFINE QHB8 BLOCK-VAR BLOCK=B8 VARIABLE=REB-DUTY &
  SENTENCE=RESULTS
DEFINE QCB8 BLOCK-VAR BLOCK=B8 VARIABLE=COND-DUTY &
  SENTENCE=RESULTS
DEFINE QB3 BLOCK-VAR BLOCK=REACTOR VARIABLE=QCALC &
  SENTENCE=PARAM
DEFINE QB6 BLOCK-VAR BLOCK=B6 VARIABLE=QCALC
SENTENCE=PARAM
DEFINE RPRO MASS-FLOW STREAM=REPROP SUBSTREAM=MIXED &
  COMPONENT=PROPYLEN
DEFINE RO2 MASS-FLOW STREAM=REOXYG SUBSTREAM=MIXED &
  COMPONENT=O2
DEFINE QB4 BLOCK-VAR BLOCK=B4 VARIABLE=QCALC
SENTENCE=PARAM
DEFINE QHB10 BLOCK-VAR BLOCK=B10 VARIABLE=REB-DUTY &
  SENTENCE=RESULTS
DEFINE QCB10 BLOCK-VAR BLOCK=B10 VARIABLE=COND-DUTY &
  SENTENCE=RESULTS
DEFINE QHB13 BLOCK-VAR BLOCK=B13 VARIABLE=REB-DUTY &
  SENTENCE=RESULTS
DEFINE QCB13 BLOCK-VAR BLOCK=B13 VARIABLE=COND-DUTY &
  SENTENCE=RESULTS
C   VOLUME CALCULATIONS
F   RAD=RDIA/2
F   LEN=RLEN
F   RVOL=22/7*RAD*RAD*LEN
C   RESIDENCE TIME CALCULATIONS
F   REST=RES*3600

```



```

F   TWAS=WSHCN+WSWAS
F   TACRY=PACRA+PACRB
F   TACETO=PACETO
F   TAMM=PSAMMS
C   ECONOMY
F   CO2=0.1
F   CNH3=0.209
F   CPROP=0.2325
F   CACETO=1.0
F   CAMMSL=0.085
F   CACRYL=0.53
F   CWASTE=0.108
F   CH2SO4=0.075
F   CQH=3.24E-6
F   CQC=-6.59E-6
F   CWAS=TWAS*CWASTE
F   REVEN=CACRYL*TACRY+CACETO*TACETO
F   BYPROD=TAMM*CAMMSL
F   CRAW=MNH3*CNH3+MPROP*CPROP+MO2*CO2+MH2SO4*CH2SO4
F   HET=QHHCN+QHEXTR+QHB20+QHB11+QHB9+QHB8+QB2+QB3+
    QHB10+QHB13+QB4
F   CHEAT=CQH*HET
F   CCOOL=(QCHCN+QCEXTR+QCB20+QCB9+QCB11+QCB8+QB6+QCB10+
    QCB13)*CQC
F   CUTIL=CCOOL+CHEAT
F   TREVEN=(REVEN+BYPROD-CRAW-CUTIL)/100
F   CONV=(PRO1-PRO2)/PRO1*100
F   YREVEN=TREVEN*330*24*100
F   IF (YREVEN.GE.1E10)YREVEN=0
F   IF (CUTIL.GE.1E10)CUTIL=0
F   WRITE(*,*)TWAS,TACRY,YREVEN,REST,CONV,RVOL,CUTIL
F   WRITE(*,*)'*****'
F   WRITE(*,*)RTEMP,RPRES,RVOL,PROPIN,NH3IN,O2IN
MAXIMIZE "TREVEN"
VARY BLOCK-VAR BLOCK=REACTOR VARIABLE=TEMP SENTENCE=T-
SPEC &
    ID1=1
    LIMITS "700" "1000"
    VARY BLOCK-VAR BLOCK=REACTOR VARIABLE=PRES
SENTENCE=PARAM
    LIMITS "20" "100"
    VARY BLOCK-VAR BLOCK=REACTOR VARIABLE=LENGTH
SENTENCE=PARAM
    LIMITS "10" "80"
    VARY MOLE-FLOW STREAM=S-1 SUBSTREAM=MIXED COMPONENT=NH3

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LIMITS "700" "1700"
VARY MOLE-FLOW STREAM=S-2 SUBSTREAM=MIXED
COMPONENT=PROPYLEN
LIMITS "800" "1500"
VARY MOLE-FLOW STREAM=S-3 SUBSTREAM=MIXED COMPONENT=O2
LIMITS "1200" "2100"

CONV-OPTIONS
PARAM TOL=0.01
WEGSTEIN MAXIT=200 QMIN=-20.0
DIRECT MAXIT=100
SECANT MAXIT=100 XTOL=1E-03
SQP WAIT=4 QMIN=-50

REPORT UTILITIES ECONOMIC

STREAM-REPOR MOLEFLOW MASSFLOW

ECONOMIC-REP CASH-FLOW=ANNUAL

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VITA

SATISH VENKATARAMAN

Candidate for the Degree of

Master of Science

Thesis: PROCESS ENHANCEMENT BY PROCESS SIMULATION AND
MULTIOBJECTIVE OPTIMIZATION

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Kumbakonam, TamilNadu, India, on July 9, 1972, to Venkataraman and Raji Venkataraman.

Education: Graduated from Gill Adarsh Matriculation Higher Secondary School, Madras, India in May 1989; received Bachelor of Engineering (Hons.) degree in Chemical Engineering from Birla Institute of Technology and Science, Pilani, India in June 1993. Completed the requirements for the Master of Science degree with a major in Chemical Engineering at Oklahoma State University in December 1996.

Experience: Summer Internship at Tamil Nadu Science & Technology Center, Madras, India, 1991; Six month internship at Neyveli Lignite Corporation, Neyveli, India, 1993., Employed as a marketing executive for Indian Commercial Company from October 1993 to June 1994; employed as Research Assistant by the School of Chemical Engineering, Oklahoma State University, August 1994 to July 1996.