PROCESS ANALYSIS OF SULFOLANE PROCESS: DEVELOPMENT AND APPLICATION OF PROCESS RETROFIT METHODOLOGY

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NOMENCLATURE

a_b	Bubble surface area (interfacial area)
a_c	Specific catalyst surface area
$C_{a,s}$	Concentration of gas at the external surface of catalyst
C_b	Concentration of gas in the bulk liquid
C_i	Concentration of gas at bubble interface
$C_{p,mix}$	Specific heat of the mixture
C_p°	Ideal gas heat capacity
d_B	Average bubble diameter
d_I	Diameter of impeller
d_p	Diameter of catalyst particle
d_T	Diameter of reactor
$D_{H2,mix}$	Diffusivity of hydrogen
$\Delta H^\circ_{f,298}$	Heat of formation at 298 K
k	Specific reaction rate constant
k_b	Mass-transfer coefficient for bubbles
k_c	Mass-transfer coefficient for catalyst particles
L	Total height of reaction mixture above entrance of gas bubbles
m	Mass concentration of catalyst
N	Molar flux rate
N	Speed of agitation
n	Reaction order
N_{Pe}	Peclet number

N_{Sh}	Sherwood number
P	Power consumption for agitation
P_c	Critical pressure
P^{sat}	Vapor pressure
Q	Volumetric flow rate of gas
R_A	Overall rate of reaction
$r_{A,s}$	Specific reaction rate if entire catalyst is exposed to surface concentration absorbed gas
S_T	Surface tension of mixture
T	Temperature
T_c	Critical temperature
u_g	Superficial velocity of gas in reactor
u_t	Terminal velocity of catalyst particle
V_L	Volume of reaction mixture
η	Catalyst effectiveness factor
ρ_p	Density of catalyst particle
ρ_g	Density of gas
ρ_f	Density of reaction mixture
ε_g	Gas hold-up
μ_f	Viscosity of reaction mixture

CHAPTER I

INTRODUCTION

Process enhancement strategies have become critical to present day operation of chemical industries. Since the regulatory nature of operation has become very stringent, a industry must anticipate changes and be prepared to upgrade its process to remain profitable. Regulatory compliance pressures and environmental awareness have increased the economic and social incentives for making processes cleaner. Redesigning existing processes for waste reduction is thus becoming a top priority. Therefore, it has become essential to develop methodologies that include environmental criteria in economic comparisons of improvement alternatives. The objective of this work is to develop such a methodology and to apply it to the sulfolane process of Phillips Petroleum Company.

The retrofit of existing processes is a challenging task. Retrofit actions typically include, in order of increasing investment, (1) optimization of operating conditions, (2) repiping, (3) equipment modification, and (4) new equipment purchases (Gundersen, 1989). Usually, these efforts focus on a single aspect of a process, such as, saving energy, reducing wastes, increasing production or enhancing the flexibility of production. Under economic scenarios different from those during the inception of the process, retrofit measures reestablish the optimum tradeoffs between energy, raw materials, and environmental liabilities. Three approaches have emerged towards systematic retrofit design. They are the 'evolutionary' (pinch technology), 'mathematical' (non-linear integer programming), and the 'hierarchical' approaches. These are traditionally process synthesis approaches applied to continuous processes, which have been modified to accommodate the retrofit scenario.

The methodology proposed in this work is based on a concept termed 'process model based engineering.' The tools of the methodology are process modeling, economi analysis, and optimization. Process modeling using commercial simulators is an importa area of computer applications in chemical engineering. Simulation models are now routinely being used for the synthesis, analysis, and control of processes. Useful economic analysis can be carried out if the costs of operation are incorporated into the process model. The utility of the resulting economic model is greatly enhanced if the environmental costs of operation are also incorporated. Specifically, tradeoffs between waste treatment and waste reduction approaches can be clearly studied. Optimization and evaluation of alternatives can then be carried out using the economic model of the process. Economic justification for evaluating environmental considerations in processes has been found to be lacking in conventional retrofit approaches.

The sulfolane process of Phillips Petroleum Company was chosen because of its potential for change. Sulfolane is a highly stable, non-toxic industrial solvent. Its environmentally friendly characteristics make it a popular solvent for several processing applications. The raw materials and the wastes from the process are being regulated by the Environmental Protection Agency (EPA). Sulfur dioxide, a reactant, is currently being regulated under the Clean Air Act (CAA) and 1,3-butadiene, another reactant, is expected t be regulated under the hazardous organic National Emission Standards for Hazardous Air Pollutants (NESHAP). Also, this process has features typical of many industrial processes, such as stoichiometric and catalytic chemical reactions, and solid, liquid, and gaseous wastes. Thus, there is much impetus to study the process and devise alternatives for increasing production while reducing the waste generation.

The process can be broken down into three basic sections: synthesis, purification, and waste treatment. The synthesis consists of three steps. In the first step, excess sulfur dioxide and 1,3-butadiene react to form sulfolene. Side reactions leading to the formation of polybutadiene and polysulfone are known to occur in this step. The products of the sulfolene formation reaction are then sent to a flash chamber where a solvent (e.g., methanol, water, sulfolane, etc.) is added. This step is designed to remove as much of th sulfur dioxide (gaseous waste) as possible to prevent poisoning in the subsequent step. After the sulfur dioxide has been removed, the mixture is transferred to a reactor for catalytic hydrogenation to form sulfolane. Several side reactions involving the catalyst occur in this reactor and lead to the formation of unwanted products. After the sulfolane synthesis section, a series of filters and dehydrators are used to purify the product and remove used solvent and spent catalyst (solid waste). The sulfur dioxide and 1,3-butadiene removed in the flash chamber are treated in scrubbing towers with caustic soda (liquid waste) before being vented through the flares. To investigate waste reduction options, the synthesis section of the process was considered, as it is the source of waste generation .

A batch process for the three steps of sulfolane synthesis was assumed and modeled. The commercial steady-state simulator ASPEN PLUS was used for this purpose. This package contains a batch reactor module which can be integrated into an otherwise steady state flowsheet structure. Additional features of ASPEN PLUS used include physical property estimations, sensitivity analyses, optimization routines and user-programmed FORTRAN subroutines. In order to develop a valid process model several issues such as physical property approximations, incorporation of non-ideality of equipment, steady-state approximation of batch operations, and assumptions to overcome lack of data were carefully considered. The limitations of the model were analyzed. More than one model was developed for each step. Comparisons between them were carried out on the basis of complexity, accuracy, and ease of computational solution. Finally, the appropriate model was validated by comparing predicted values of key process parameters such as reactor conversions, stream compositions, and an overall material balance, with operating plant data.

Based on the overall process model, the base case economics of the process were calculated. The economic base case could not explicitly account for the environmental cos because such data were not available from Phillips Petroleum Company. These costs wer included into an overhead account, a breakdown for which was not available. However, approximate environmental costs were assumed.

The base case provided adequate direction to pursue waste reduction studies. As expected, the process was found to be quite insensitive to minor changes in operating conditions. As with a majority of retrofit studies on batch processes, the two key issues were found to be de bottlenecking and rescheduling. The hydrogenation step was studied in detail, and a preliminary understanding of its operation and its limitations could be reached. By addressing the bottleneck in the sulfolane process, alternatives for improving the process efficiency were evaluated within the framework of the proposed methodology.

In summary, the main objective of this work was to improve the efficiency of the existing sulfolane process of Phillips Petroleum Company through waste reduction. This was accomplished through the development and application of a general methodology for process retrofit. In this report the discussion of the efforts is structured into sections dealing with,

1) Background on existing methodologies
2) Description of the sulfolane process
3) Proposed methodology
4) Application of the methodology to the sulfolane process
    a) Process modeling
    b) Economic analysis
    c) Process retrofit alternatives
5) Conclusions and recommendations of the study

CHAPTER II

BACKGROUND

In this chapter a background of the sulfolane process, the motivation to study it, the existing methodologies available for process improvement, and concepts important to the development of a proposed methodology are discussed.

Process Description

The process can be broken down into three basic sections: synthesis, purification, and waste treatment. The synthesis consists of three steps :

1. Reaction
2. Treatment
3. Hydrogenation

The sulfolene formation reaction is limited by equilibrium and complete conversion is never achieved. The equilibrium mixture of sulfolene, sulfur dioxide, and butadiene is then sent to a treatment tank where the mixture is added to a solvent. This solvent, apart from being the hydrogenation solvent, stabilizes sulfolene and keeps the mixture above its freezing point. The unreacted sulfur dioxide and butadiene are separated from the reaction mixture by flashing the mixture under vacuum conditions. The gases are scrubbed with caustic soda before being burned in the flare. The treated mixture is then sent to the hydrogenation reactor where sulfolene is hydrogenated in the presence of a catalyst to form sulfolane. Several side reactions involving the catalyst occur in the hydrogenation step leading to the formation of unwanted by-products. The hydrogenation step is the time and the waste bottleneck of the process.

Motivational Background

For the sulfolane process, existing regulations under the CAA constrain the emission of sulfur dioxide, a raw material, and new regulations under the NESHAP target 1,3-butadiene, another raw material (Bryant, 1992). In addition to these air pollutants, the process generates solid wastes in the form of spent catalyst, and liquid wastes through the treatment of the air pollutants. Phillips Petroleum Company is committed to improving the environmental, health, and safety aspects of its operation. This commitment has been formalized as a company policy defined 'Principles of Performance' (Environmental Report, PPCo, 1993). All these factors contribute as justifications for looking into the sulfolane process critically and devising methods of reducing its environmental impact, while increasing its productivity and efficiency.

Existing Methodologies For Process Retrofit

The redesign of processes is generally referred to as retrofit. Retrofit typically involves change of operating conditions, repiping, minor equipment modifications or purchase of new equipment. Several retrofit approaches have been reported in the literature in the past 8-10 years (Gundersen, 1989). However, most of these approaches are process design or synthesis approaches which have been modified for the retrofit scenario. Each of these methods suffers from some limitation. A brief discussion of the existing methods and their limitations follows.

The hierarchical approach suggested by James Douglas (1987) utilizes a short cut approach to narrow the range of retrofit alternatives. It combines heuristics with the use of cost diagrams to evaluate modifications in both the structure of the flow sheet and in equipment sizes for a fixed flow sheet. It is generally applicable to continuous processes. The main draw back in this method is the use of simple equipment models leading to alternatives which do not consider full use of the existing equipment.

The mathematical approach is probably the most rigorous process synthesis metho that is presently used. Several investigators such as Grossmann (1987) and Biegler (1989 have studied the use of mathematical techniques for retrofit situations. More recently, Reklaitis (1993) has used MINLP techniques to study retrofitting of multiproduct batch processes. These techniques rely on optimization of an objective function subject to flow sheet configuration and equipment size constraints. The former consists of discrete variables and the latter of continuous variables. This is mathematically converted into a mixed integer non-linear programming (MINLP) formulation. The non-linearity of the process model equations and the magnitude of possible flow sheet configurations require enormous computational resources which limits the utility of this method.

Pinch technology is based on a heat flow analysis of the process (Linhoff, 1988). It was developed during the energy crisis of the late 1970s and 1980s. By not utilizing conventional process design tools such as flow sheets, it allows the process engineer to obtain a clear understanding of the interactions within the process and its utilities. This technology has been successfully applied to retrofit of processes (Rossiter, 1991). The range of alternatives is, however, limited to energy integration of the process. Though this is the most practical and widely used method in the process industries, it suffers from its inability to couple the energy issues with the process flow issues, which for some processes might hold more incentive for improving process efficiency.

The application of these three methodologies to waste minimization has not been reported extensively in the literature. Fonyo (1994) and others have reported the use of Douglas's hierarchical method for waste minimization under the retrofit scenario. This represents the most systematic effort developed by chemical engineers so far to address pollution prevention in the chemical process industries.

The logic behind this work is to address some of the limitations inherent in the existing methods. The three basic elements in the proposed methodology are process modeling, economic modeling, and optimization. Additional elements such as forecasting are considered to enhance the utility of the methodology. The applicability and usefulness of the proposed methodology was evaluated by applying it to the sulfolane process. In order to understand the tools of the proposed method, it is essential to review some basic concepts.

Process Analysis Through Modeling

Process analysis is fundamentally different from process design. Analysis deals with existing processes and breaks it apart for study, whereas design deals with the creation of new processes. Process analysis is of significance during redesign.

Process modeling is fast becoming the focal point of computer applications in chemical engineering. Applications such as process synthesis, analysis, control, and optimization derive their basis from a well formulated process model. The use of commercial process flow sheet simulators for process modeling has increased dramatically in the past two decades. Packages such as ASPEN PLUS, PRO II, HYSIM, ChemCAD, SPEEDUP, etc., are now routinely used for plant design, improvement of safety and control features, debottlenecking, and operator training (Fouhy, 1991). The extensive use of simulation packages has been aided by the growth of computer hardware in the past five years (Grinthal, 1993). Most of these packages offer unit operation models, physical property databases, data regression systems, and graphical user interfaces.

The analysis of process efficiency using models is a quick and economical alternative when compared to experimentation. However, both these approaches are essential to understanding and analyzing a process. The trade-offs between the two are accuracy, effort, and investment. In current operating environments extensive experimentation for process improvement is not a feasible solution. This is because product life cycles are short, market conditions change constantly, and capital investment is harder to justify. Thus, the emphasis has shifted to improving design, analysis, control, and optimization of a process with the aid of a simulated process model.

The use of process modeling for environmental applications is a relatively new application. Several applications of ASPEN PLUS for modeling pollution prevention have been reported in the literature (Wu, 1992). Diverse pollution issues such as waste water minimization, desulfurization, etc., have been studied using ASPEN PLUS (ASPEN Tech.brochure, 1993). In this study, a simulated process model of the sulfolane process, developed using ASPEN PLUS, has been used to study the environmental and production parameters of process efficiency.

Economic Analysis

Any retrofit measure requires economic justification. Therefore, one needs to first evaluate the base-case profitability of the process. Incentives of modifying the process will be weighed against this base-case. One needs a cost model of the process to be able to evaluate profitability under existing or changing conditions.

The profit levels of a process are a combination of the efficiency of the process and the market conditions affecting both the inputs and outputs of the process. Thus, both of these aspects of profitability need to be incorporated when developing a cost model for optimization. Such a cost model can be developed by linking the process model with economic data. It is essential to include the environmental costs of operation into this cost model in order to evaluate the environmental impact of the process.

When looking at the benefits of pollution prevention, environmental costs will play an important role in determining the course of action. Purely financial analysis of the benefits of pollution prevention can be obtained through Total Cost Assessment (TCA) of processes. This concept considers the usual costs (fixed and production), the 'hidden' costs (e.g., compliance and permits), liability costs (e.g., penalties/fines), and the less tangible costs (e.g., consumer response and employee relations) in evaluating the long term costs and savings from a pollution prevention opportunity (Freeman,1992). However, an integrated process and economic modeling approach targeted towards reducing environmental impact has been lacking in the open literature.

This work provides a framework in which the integrated cost model will be used as a tool to provide direction and quantitative justification for waste minimization alternatives.

Optimization

Chemical process optimization is that mathematical activity that finds the values of process variables that maximizes or minimizes a given performance criteria. The three key components of optimization of a chemical process are the objective function, the equality, and the inequality constraints (Himmelblau,1988). The objective function, sometimes known as the 'economic model', is usually a measure of profitability; yet other criterion may be used. The constraints are usually defined by the process model.

Optimization can be carried out on different types of models. Models can be generally classified into the following types (Himmelblau,1988):

Linear vs. non-linear
Steady state vs. unsteady state
Lumped parameter vs. distributed parameter
Continuous vs. discrete

In a process, equipment sizes, process flow rates, and operating conditions can be considered as continuous variables. The existence of a particular piece of equipment can be represented by discrete variables. The most common form of process models is non-linear, steady-state, lumped, and continuous.

The relevance of optimization to the present study can be easily identified. If the objective function were defined to be waste generation, then the set of process variables that reduce this quantity can be determined. If profit defined as the difference between revenue from sales and the production cost, is considered as the objective function, then once again, the optimum set of process variables can be found. However, while doing so one must make sure that the environmental costs are incorporated into the objective function. Thus, in the case of this work, optimization is a natural extension of the use of a integrated process model. Waste minimization alternatives may typically include change in operating conditions, or modification of equipment, etc. By using optimization techniques, one can determine the optimum way of carrying out each alternative. Then, by comparing the relative incremental savings of each alternative, the best alternative can be selected for implementation.

In summary, the sulfolane process offers us a typical industrial process with stoichiometric and catalytic reactions, as well as solid, liquid, and gas phase waste streams. The motivation for studying this process comes from waste minimization incentives. Several methods exist for analyzing and retrofitting an existing process through evaluation of improvement alternatives. These methods were originally design procedures which have been modified for the retrofit case. Moreover, the application of these methods for waste minimization has not been reported extensively. In this work, a general methodology has been proposed which will address some of the limitations from which existing methods suffer. The important elements of such a methodology are process modeling, economic analysis, and optimization.

The remaining chapters are devoted to a detailed description of the sulfolane process, the development of a general methodology for process improvements and details of the application of such a methodology to the sulfolane process of Phillips Petroleum Company.

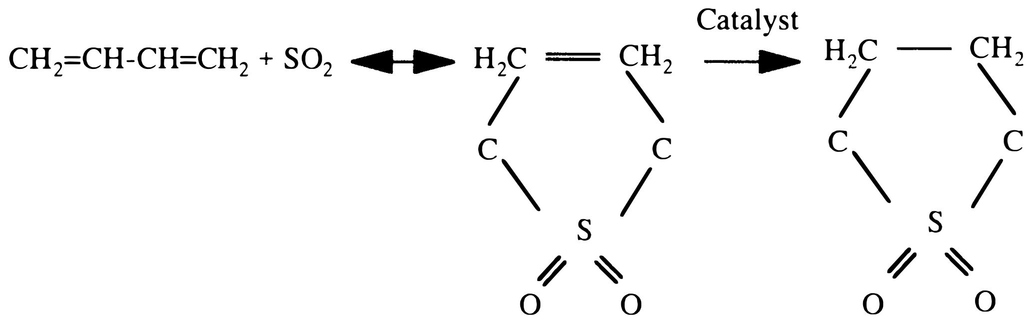
CHAPTER III

PROCESS DESCRIPTION

Sulfolane is a colorless, water-soluble, non-toxic, bio-degradable, and highly polar compound. Its thermal stability, chemical inertness, and solvent properties make it a very popular industrial solvent. Roughly about eighteen to twenty million pounds of sulfolane are consumed annually for a variety of applications such as extraction of aromatics, removal of acidic compounds from natural gas streams, and as solutions for polymerization. Currently, sulfolane is produced by Phillips Petroleum Company and Shell Chemical Company, using processes based on chemistry first described in the early 1900s. A brief description of the process chemistry and the patented production process is provided in this chapter.

Process Chemistry

The basic reaction scheme involves the reaction of 1,3-butadiene with sulfur dioxide to produce 3-sulfolene (2,5-dihydrothiophene-1,1-dioxide), which then undergoes catalytic hydrogenation to yield sulfolane (2,3,4,5-tetrahydrothiophene-1,1-dioxide).



sulfolene sulfolane

The intermediate product, 3-sulfolene, belongs to the generic group of compounds called 'sulfolenes' which consist of substituted or unsubstituted unsaturated compounds containing a sulfolene nucleus. A sulfolene nucleus is a five-membered ring with a single olefinic linkage between adjacent carbon atoms of the ring, and two oxygen atoms each of which is directly attached to the sulfur atom. Sulfolanes refer to saturated sulfolene compounds that may be substituted or unsubstituted.

The yield of 3-sulfolene from the first reaction is limited by a chemical equilibrium between 3-sulfolene, sulfur dioxide, and 1,3-butadiene, as well as poorly characterized polymer-producing side reactions. Three types of polymers are usually formed. Polymerization of butadiene and sulfur dioxide (usually in the gas phase) in the presence o free radicals and low temperatures leads to the formation of copolymers. These may also link to form 'block' polymers. Polybutadiene is also formed under the conditions described previously. Additionally, polybutadiene may cross link to form what is commonly referred to as 'popcorn' polymer. The free radical initiated break up of 3-sulfolene molecules may lead to the formation of polysulfone. Generally, these polymerization reactions tend to occur above a temperature of 210°F. On the other hand, 3 sulfolene is known to crystallize at a temperature of about 150°F. This effectively sets the operational temperature range of 150-210°F for the reaction between sulfur dioxide and 1,3-butadiene. Kinetic studies on this reaction have been reported by Drake and others (Drake, et al., 1946).

In the catalytic hydrogenation reaction of 3-sulfolene to sulfolane, side reactions consume the metal catalyst and yield mixtures of oligomers and polymers containing metal ions and organic components. Decomposition of 3-sulfolene, solvent, temperature, and th activity of the catalyst may affect the extent of the side reactions. Mashkina et al. (1962) have reported a kinetic study of the 3-sulfolene hydrogenation reaction on a nickel-chromium catalyst. The poisoning of the catalyst during hydrogenation was also studied (Mashkina et. al, 1966).

These side reactions are the major causes of waste generation in the sulfolane process. In order to achieve acceptable conversion of reactants to products in this proces one has to contend with the equilibrium consideration in the first reaction and the side reactions in the hydrogenation reaction. Industrially, process conditions are set accordin to these considerations.

Production Process

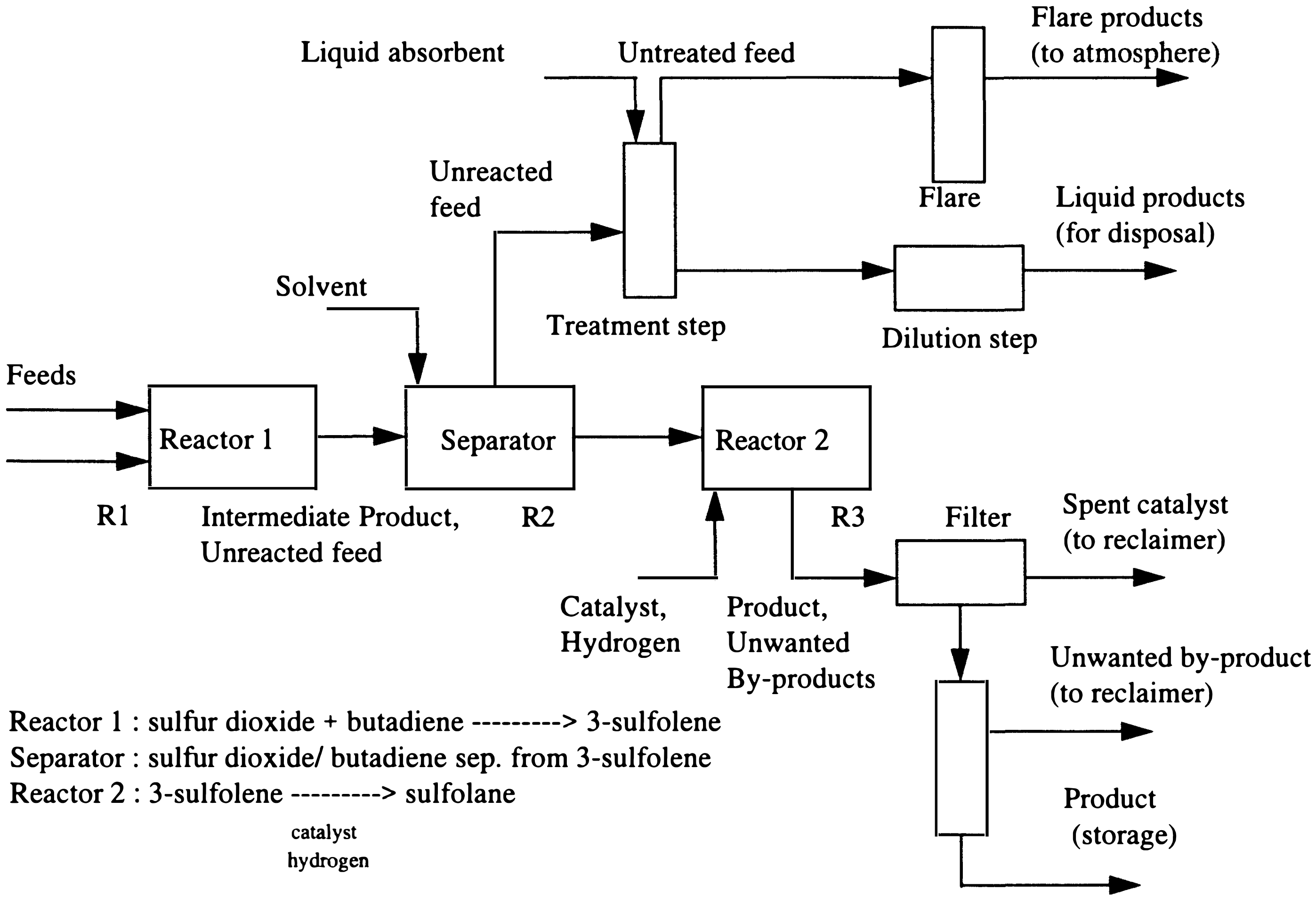
A brief description of Phillips Petroleum Company's sulfolane process is provide in this section. The details can be found in a U.S Patent which was approved in 1971 (Willis, 1971).

The process can be broken up into three basic sections - synthesis, purification, a waste treatment (Fig. 1). Sulfolane is manufactured in the synthesis section, and is then purified to required specifications in the purification section. The air pollutants produced during synthesis and purification are treated in the waste treatment section before being released into the atmosphere. A batch mode of process operation has been assumed for t study. The focus of our research was to study the synthesis section of the sulfolane process. Thus, the process description will concentrate on the synthesis section.

Synthesis

The synthesis section can be further broken down into three steps. These three steps include :

1) Manufacture of 3-sulfolene - the reaction step,
2) Neutralization of the reaction mixture - the treatment step, and,
3) Hydrogenation of the 3-sulfolene - the hydrogenation step.



Reactor 1 : sulfur dioxide + butadiene ---------> 3-sulfolene
Separator : sulfur dioxide/ butadiene sep. from 3-sulfolene
Reactor 2 : 3-sulfolene ---------> sulfolane
catalyst
hydrogen

Figure 1. Schematic diagram of sulfolane process

These steps are carried out in batch stirred tank reactors. In the reaction step, the reactants, sulfur dioxide and 1,3-butadiene, are introduced as liquids into the reactor. The reaction is limited by equilibrium and complete conversion is never achieved. The mixture is then neutralized to remove excess sulfur dioxide and butadiene through the addition of a suitable solvent and application of vacuum. This is done to prevent poisoning and destruction of the catalyst in the subsequent step. The sulfolene-solvent mixture is then hydrogenated with excess hydrogen in the presence of a suitable hydrogenation catalyst to produce sulfolane. Each of these steps is explained in detail below.

Reaction step The sulfur dioxide is first charged to reactor R1. The 1,3-butadiene is then slowly added to the reactor. Both of the reactants are liquids during the charge. The molar ratio of sulfur dioxide to 1,3-butadiene is in the range of about 1:1 to 1.5:1. Polymerization inhibitors such as pyrogallol, pyrocatechol, and phenyl-b-napthylamine, ar added separately or with the 1,3-butadiene. The temperature of the reactor is allowed to rise slowly during the addition of 1,3-butadiene. Once the addition is complete the reactor is operated isothermally. The temperature in the reactor is maintained in the range of 150°F to about 300°F, and the pressure is generally in the range of about 100 to 600 psig. The reaction mixture is allowed to remain in the reactor for a suitable time to permit substantial completion of the reaction. Once the reaction is complete, the contents of the reactor, i.e., the unreacted sulfur dioxide, 1,3-butadiene, and 3-sulfolene are transferred to the next step i.e., the neutralization step.

Treatment step The molten reaction mixture from R1 is transferred into treatment tank R2 which contains a suitable hydrogenation solvent, examples of which include water aqueous alkalies, and alcohols (such as methanol, ethanol, isopropanol, etc.). The unreacted sulfur dioxide and 1,3-butadiene are removed by pulling a vacuum on the mixture and transporting the gases to the waste treatment steps. The removal of sulfur dioxide from this mixture is important because it poisons the hydrogenation catalyst in the next step. The temperature and pressure in R2 during the degassing is generally in the range of about 75°F to about 150°F and from about 2 psia to 5 psia in order to 'flash' the mixture. In addition to this, the removal of sulfur dioxide can be enhanced by sparging th mixture with nitrogen. The concentration of sulfur dioxide in the resulting mixture is reduced to about 0.1 weight percent. The remaining sulfur dioxide is oxidized to sulfuric acid by addition of hydrogen peroxide. The sulfuric acid is neutralized by addition of an aqueous caustic solution. The mixture is then filtered and transferred into the hydrogenation reactor.

Hydrogenation step. The neutralized mixture from treatment vessel R2 is transferred to the hydrogenation reactor. The reactor is charged with a hydrogenation catalyst, one to five percent by weight based on the sulfolene charge. Commonly used hydrogenation catalysts include nickel, cobalt, copper, palladium, or platinum. These ca be unsupported or supported on kieselguhr, aluminum oxide, or diatomaceous earth. Raney nickel, which is a catalyst in finely divided form, is often used for hydrogenation. The reactor is then pressurized with hydrogen to provide sufficient hydrogenation pressu The temperature and pressure are maintained at 50 to 120°F and 50 to 500 psig, respectively. After the reaction is completed the reactor is vented to remove the excess gases and cooled. Next, the reaction mixture is filtered to remove the catalyst and sent to the downstream purification steps.

CHAPTER IV

GENERAL METHODOLOGY

In this chapter the development of a general methodology for process retrofit will b reviewed. The implementation of the general methodology requires resource investments. Typically, these comprise resource persons from the process plant and R&D, and a commercial process simulator. The general methodology can be broken down into a sequence of three logical steps (Figure 2).

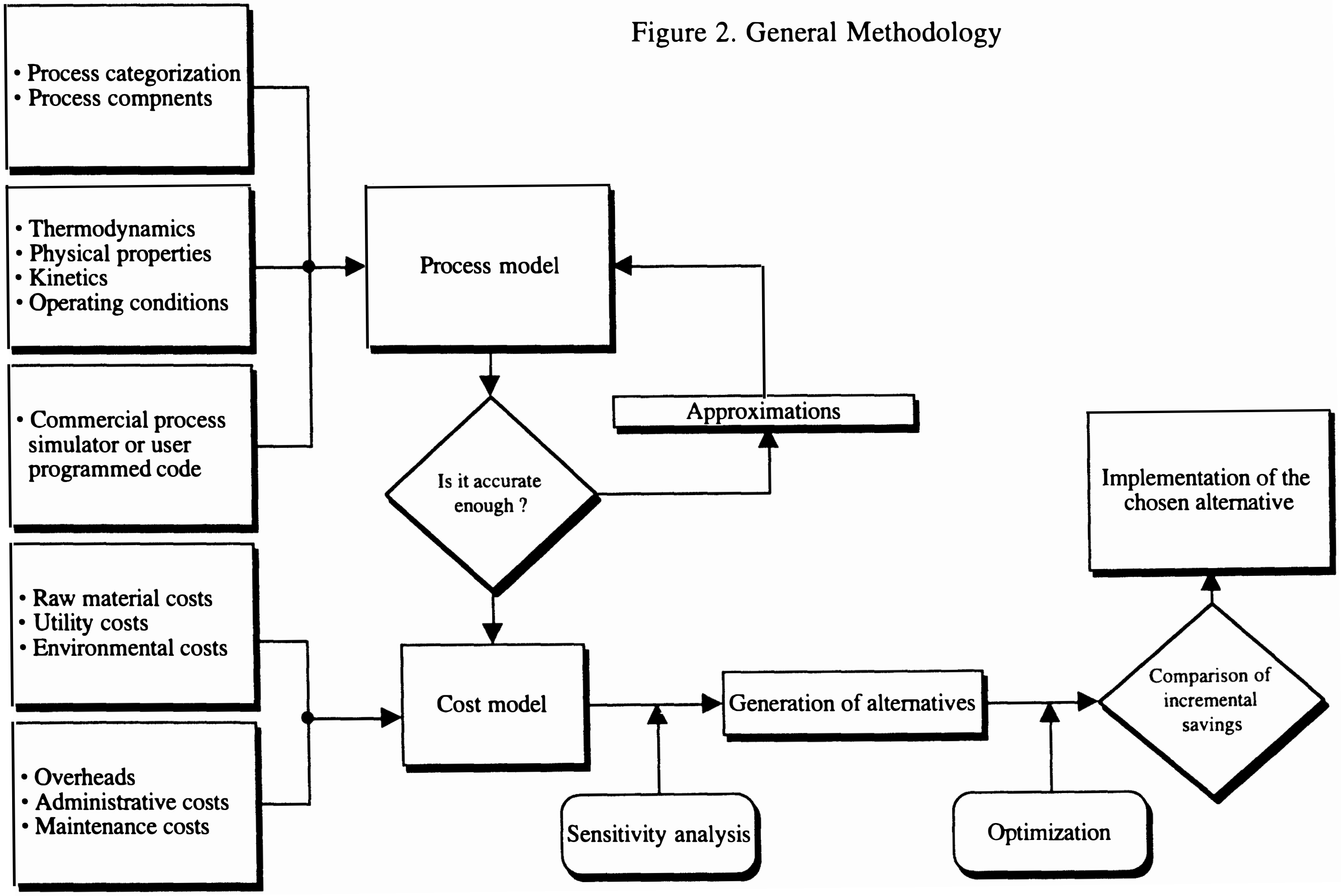
1. Process modeling
2. Economic analysis
3. Generation, optimization, and selection of retrofit alternatives

Additional concepts such as forecasting have been considered for improving the effectiveness of the methodology (Shyamkumar, 1993). A detailed description of the sequence of sub-tasks for each of the three steps is provided below.

Process Modeling

A process model serves to emulate the actual process. Mathematical modeling of a process allows one to essentially perform "experiments" using simulation techniques. Physical experiments, on the other hand, allow one to directly observe the effects of proces changes. Both of these approaches are essential to analyzing and understanding a process. The trade-offs between the two are accuracy, effort, and investment. For process retrofit, preliminary analysis using simulations is advised, because it can reduce the range of feasibl solutions. Physical experimentation can then confirm the most promising solutions. The approach proposed in this research is composed of six steps.

Figure 2. General Methodology



1) Categorize process as batch, semi-batch, or continuous.
2) List components involved in the process. This list must include wastes generated i the process. Sometimes these wastes cannot be characterized accurately, in which case approximations should be applied.
3) List data requirements for model development. Typically, these include,
    a) physical property data,
    b) kinetic data,
    c) thermodynamic data, and
    d) plant measurements
        i) operating conditions,
        ii) flow rates,
        iii) equipment geometry, and
        iv) operational constraints.
4) Ascertain physical and kinetic property data availability. In case data are not available, check on the feasibility of either theoretical estimation or experimental determination of the data. Another option is to approximate the properties of a give material with that of a chemically and structurally similar compound.
5) Select appropriate tools for formulating the model. Two options are available for developing a model. One could either use a commercial process simulator or develop a code. Common features of simulators include databases on physical property of compounds and unit operation modules. Some examples of process simulators are ASPEN PLUS, SPEEDUP, PRO II, ASCEND II, FLOWTRAN, etc.
6) Once the tool has been chosen and a rough model incorporating all the unit operations has been developed, the results from the model should be analyzed. On must decide on key process variables which would serve as criterion for validation

of the model and then determine the availability of data for these variables. Analyzing the results of the rough model will show areas in which the accuracy of the model needs to be improved. The reasons for discrepancy between the predicted and actual values should be analyzed. Methods of incorporating modifications into the model must be studied. An iterative procedure should be carried out until the criterion for validation can be satisfactorily matched.

Economic Analysis

Economic justification for process retrofit can be provided using a cost model for the process. Such a model can be developed by linking the process model with economic data. The costs of operating a process are typically divided into capital and total product costs. Generally, product costs are broken down into four categories (Peters & Timmerhaus, 1980).

1) Direct production costs
    a) raw material costs
    b) utility costs
    c) maintenance costs
    d) labor costs
2) Fixed charges
    a) depreciation
    b) taxes
    c) insurance
3) Plant overhead costs
    a) safety
    b) laboratories
    c) storage
4) Administrative and product distribution costs.

For many processes, the costs of waste reduction and disposal significantly impact the overall profitability of the process. This research proposes that environmental costs should be included into the total product costs as direct production costs. This is done to reflect the relative incentives for waste minimization or treatment. An important step in this general methodology is to incorporate the environmental costs into the process and cost models for optimization purposes. The development of a total product cost model for the process can be broken down into the following steps:

1) For purposes of developing a cost model, the process model can be used to generate a material balance of the components in the process.
2) Cost data for the raw materials and waste treatment should be gathered. This data can then be incorporated into the process model. This essentially means multiplication of the material stream quantities by the stream costs. A good estimate of the direct production costs can then be obtained using the process model.
3) The remaining costs including fixed charges, plant overheads and administrative costs can be obtained from company records. It is sufficient to use rough estimates of these costs for preliminary optimization. All these costs can then be combined into an aggregate fixed charge.
4) The sum of the direct production costs and the aggregate fixed charges will then give the total product cost, i.e.,

Total product costs = *direct production costs + aggregate fixed charges*

where,

direct production costs = *f (raw material costs, utility costs, environmental costs)*

aggregate fixed charges = *f (overheads and administrative costs).*

The profit can then be calculated, given the selling price of the product. The profit on an annualized basis can be written as,

Annual profit = *production rate (lb./yr.) x selling price ($/lb.) - total product cost($/yr.).*

This represents the base-case profitability. Thus, using a valid process model, we can develop a reasonably accurate cost model for the process.

Generation, Optimization, and Selection of Retrofit Alternatives

The first step in optimization is to target key variables which can be manipulated to maximize the profitability of the process. The economic base case gives a good idea of the significant costs of operation. A sensitivity analysis provides, by elimination, specific process variables for manipulation. In the next step, one uses engineering creativity and judgment to develop alternatives based on changes in the significant variables. Using this methodology, the incentives of varying either one or a combination of the significant variables can be compared with the base-case profitability. For each alternative, the additional constraints imposed on the system due to the changes should be incorporated into the process model. The main steps in generating, optimizing, and selecting retrofit alternatives can be summarized as follows:

1) Analyze function for its sensitivity to process variables.
2) Target the significant process variables.
3) Develop alternatives for process improvements based on these significant variables
4) Incorporate additional constraints corresponding to the alternatives into the process model.
5) Use mathematical techniques to optimize the process model.
6) Compare optimized profitability of alternatives with the base-case profitability.

So far the discussion has pertained to optimizing the current process conditions. This was essential, because the operating conditions of the original plant design are different than the present conditions. Extending the argument, future conditions may change the profitability of the process drastically. Such a scenario is very plausible considering the impact of regulatory compliance. Thus, there is impetus for anticipating changes and being prepared to take appropriate action. This methodology proposes that

CHAPTER V

PROCESS MODEL

A process model is usually developed to predict the response and sensitivity of existing equipment to changes in operating configuration or conditions. Through these applications the profitability of a chemical process is to be controlled and optimized. In this work, a model of the synthesis section of the sulfolane process has been developed for retrofit applications. The synthesis section has been considered because it is the source of waste generation in the process.

Process Characterization

A batch mode of operation for the sulfolane process has been assumed and modeled. The main components in the process are sulfur dioxide, 1,3-butadiene, 3-sulfolene, sulfolane, hydrogenation solvent, and a hydrogenation catalyst.

The physical properties for most of these compounds are available and accessible in the open literature. Data does not exist for either the pure component or mixture properties of the intermediate compound, 3-sulfolene. Data for sulfolane are available in the Design Institute of Physical Property Research (DIPPR) database; however, most of these properties are estimated. In this work, properties of 3-sulfolene have been estimated for use in simulations.

Some kinetic data are available for both of the reactions in the synthesis step. Drake et al. (1946) have published data for the reaction of sulfur dioxide with 1,3-butadiene to form 3-sulfolene. These data have been found to be inapplicable to the reaction occurring in reactor R1 (Jayagopal, 1994). Proprietary kinetic data provided by Phillips Petroleum

Company was used to simulate this reactor. Mashkina et al. (1966) have studied the hydrogenation of 3-sulfolene over nickel-chromium catalyst and the effect of poisoning on the activity of the catalyst. These data were not used for the simulation of reactor R3, because they are inaccurate and not reproducible.

Proprietary operating conditions and equipment geometry data were provided by Phillips Petroleum Company. These data included typical ranges of reactor temperatures, pressures, batch sizes, and waste material balances. In addition, Phillips experimental dat were made available. These helped substantially in confirming, discarding, or revising some of the conclusions derived from the process model.

In summary, apart from the physical properties of 3-sulfolene and kinetic data for the hydrogenation reaction, all other data requirements for modeling the process were satisfactorily met.

Process Modeling Tool

In this work, the steady state simulator ASPEN PLUS released by Aspen Technology has been used. ASPEN PLUS has several features that make it user friendly and powerful. The graphical user interface ModelManager is an expert system guidance tool that allows complete specification of the flowsheet at every stage of model development. The package has an extensive database for pure component properties. Almost forty equation-of-state models provide for thermodynamic properties required in th simulations. Additional features include property estimation system, sensitivity blocks, optimization routines and flowsheet sectioning. It contains an ideal batch reactor module which can be integrated into a continuous process flowsheet, through the use of accumulation tanks. It also contains models of typical pollution control equipment such as cyclones, scrubbers, etc.

Although ASPEN PLUS is probably the most popular flowsheet simulator at the current time its applications to solving practical industrial problems have not been widely reported in the literature. Some investigators report the use of ASPEN PLUS for environmental applications (Wu, 1992). Others have reported the use of ASPEN PLUS for innovative applications such as determining the effect of process parameter uncertainty on the outcome of a simulation (Diwekar, 1992). In this work, ASPEN PLUS has been used to simulate the sulfolane process.

Physical Property Estimation For 3-sulfolene

There is little experimental data on 3-sulfolene. ASPEN PLUS does not contain th pure component physical properties of 3-sulfolene. In this study these properties have been estimated using group contribution methods. The selection of these methods was based on their use for sulfolane. Since the structure of these two compounds is very similar it is a reasonable approximation to use the same group contribution methods for the estimation of pure component physical properties. The properties of 3-sulfolene were either estimated manually or using ASPEN PLUS. The details of these estimations are provided below.

1) The molecular weight of 3-sulfolene is equal to the sum of the molecular weights o sulfur dioxide and 1,3-butadiene. For this study, the molecular weight of 3-sulfolene has been assumed to be 118.156.

54.092	+	64.063	=	118.156
sulfur dioxide		1,3-butadiene		sulfolene

2) 3-sulfolene is known to decompose at temperatures close to its normal boiling point. Therefore, there are no experimental data on the normal boiling point. Through extrapolation of a plot of boiling point as a function of the normal boiling point has been estimated to be 304 F.

3) The critical temperature and pressure of 3-sulfolene can be determined using the Lyderson group contribution method. This method was selected because it has been used to estimate the critical properties of sulfolane (DIPPR). Due to similarity

in chemical structure this approximation may be justifiable. The values used for th critical properties are (Jayagopal, 1994):

a) Critical temperature, T_c: 707.68 F

b) Critical pressure, P_c: 774.92 psia.

4) The heat of formation of 3-sulfolene and the ideal gas heat capacity can be determined using the Benson group contribution method. This method generally provides quite accurate results for sulfur containing compounds. This is because group contribution factors for ring compounds containing sulfur are available in thi method (Reid et al., 1987). The heat of formation and the ideal gas heat capacity polynomial as estimated using the Property Constant Estimation System (PCES) in ASPEN PLUS, are (Appendix A):

   a) Heat of formation $\Delta H^\circ_{f,298} = -2.586 \times 10^8$ J/kmol.

   b) Ideal gas heat capacity polynomial

   $C_p{}^\circ = -81388.0 + 775.27 \cdot T - 0.72205 \cdot T^2 + 0.26086 \times 10^{-3} \cdot T^3$

   for $280 < T < 1100$ (temperatures in Kelvin).

Experimental verification for the heat of formation can be found in literature. However, these values fall in a range, the average of which is quite close to the estimated value. Therefore, we shall go with the estimated value.

5) The vapor pressure data were estimated using the Reidel method (Jayagopal, 1994) Using these data the Antoine parameters for the vapor pressure of 3-sulfolene were estimated with the PCES module in ASPEN PLUS. The estimated Antoine's polynomial is shown below (Appendix A):

$$\ln p^{sat} = 67.87 - \frac{7671.3}{T} + 0.483 \times 10^{-3} \bullet T - 6.358 \bullet \ln T$$

The value of the vapor pressure calculated using this polynomial provides for interesting results. It is found that the vapor pressure of 3-sulfolene is three orders of magnitude greater than the vapor pressure of sulfolane at the same temperature.

This could be due to errors introduced into the estimation through the use of approximate normal boiling point and estimated critical properties.

Comparison with sulfolane properties

The use of good physical properties is essential to any simulation. Approximations have to be often applied to overcome lack of data. For instance, the properties for 3-sulfolene were approximated with those of sulfolane. The simulated process model was run with both estimated and approximated 3-sulfolene properties. It was found that the use of sulfolane properties for 3-sulfolene gives more accurate results than using the estimated 3-sulfolene properties. Therefore, in this work, the properties of 3-sulfolene have been approximated with those of sulfolane. A brief summary and comparison of physical properties of both compounds is shown in Table 1.

TABLE 1

COMPARISON OF ESTIMATED PHYSICAL
PROPERTIES OF 3-SULFOLENE AND SULFOLANE

Property	3-Sulfolene	Sulfolane
Molecular weight	118.156	120.172
Normal boiling point (NBP)	303.8 F	548.3 F
Critical temperature, T_c	707.7 F	1075.8 F
Critical pressure, P_c	774.92 psia.	728.33 psia.
Heat of formation, $\Delta H^\circ_{f,298}$	-2.59×10^8 J/kmol	-3.9×10^8 J/kmol
Ideal gas heat capacity @170 F, C_p°	1.13×10^5 J/kmol K	1.33×10^5 J/kmol K
Vapor pressure @ 170 F, P^{sat}	1.04 psia.	0.005 psia.

Process Model Of The Sulfolane Process

The discussion of the individual equipment models has been structured in the following format. The discussion will consist of :

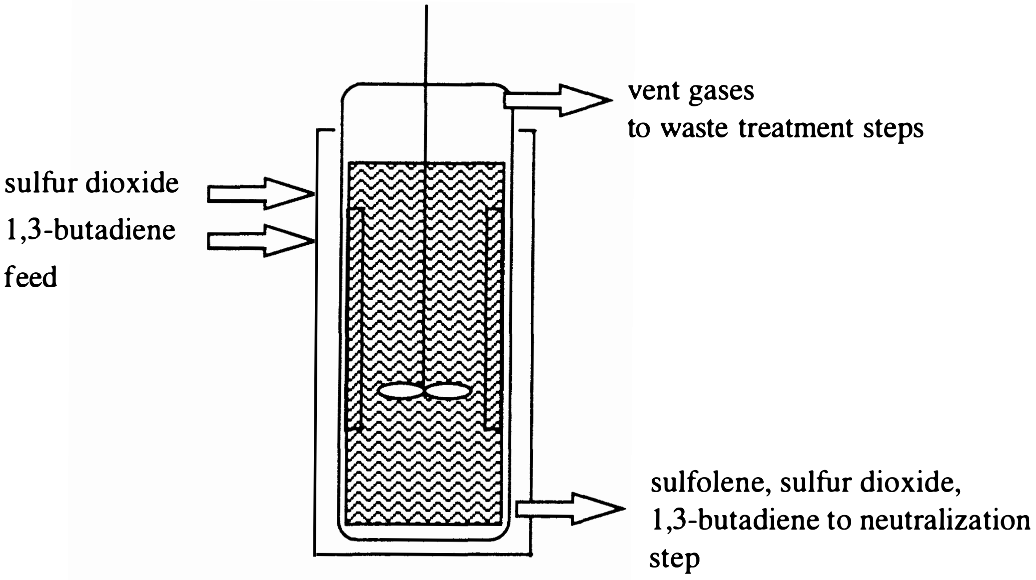
1) Operating procedure and conditions
2) Physical and kinetic property data
3) Assumptions
4) Model development
5) Results

Since most of this information is proprietary, details of the assumptions and model development will be provided in this chapter. A discussion of the actual operating conditions and the results of the models are provided elsewhere (Technical Report, 1994).

Reaction step - Reactor R1

R1 Operational procedure and conditions

Reactor R1 is a semi-batch reactor in which the reactants sulfur dioxide and 1,3-butadiene react to form 3-sulfolene. Fresh feed is introduced into the reactor over a period of approximately two hours. At the end of the batch cycle only a part of the reaction mixture is removed from the reactor. The portion of the reaction mixture remaining in the reactor shall be referred to as the 'heel'. The heel acts as a heat source to maintain the temperature of the reaction mixture at the desired value. The operation of the reactor is isothermal and the temperature is controlled by means of an external cooling jacket and internal cooling coils. A schematic diagram of the reactor and the operating conditions can be found in Fig.3.



Operating conditions

Feed	sulfur dioxide, 1,3-butadiene
Feed ratio (SO2/Bd)	Between 1.0 and 1.5
Temperature	150-200 F
Pressure	100-200 psig.
Batch time	6-8 hours

Figure 3. Schematic diagram of sulfolene production reactor R1

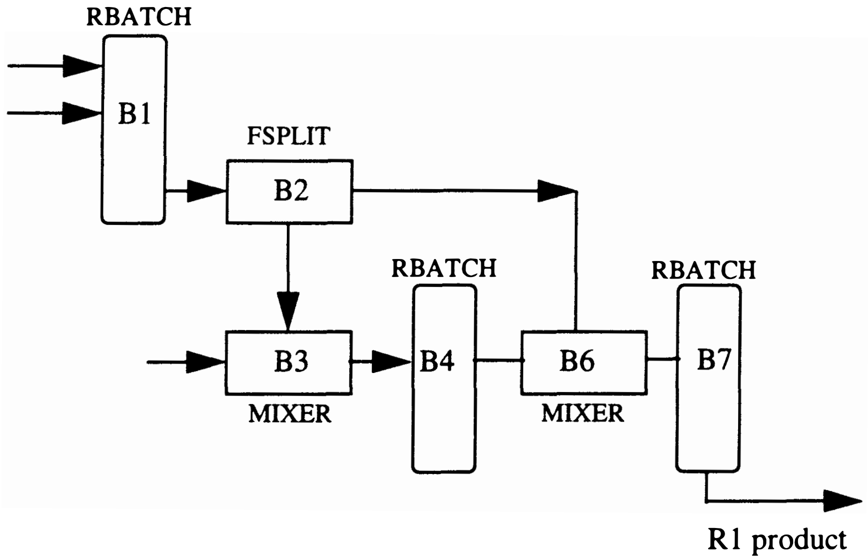


Figure 4. Block diagram of ASPEN PLUS model for R1

Physical property and kinetic data for R1

1) Simulations were performed with both estimated 3-sulfolene and sulfolane properties.
2) Kinetic data provided by Phillips Petroleum Company were used. These data can be found in the Technical Report (1994).
3) The Peng-Robinson equation of state (EOS) was found to be the most accurate for the simulation of R1. Even though the components of the mixture are highly polar this EOS seems to give better results than others models. The other EOS that is appropriate for this system is the Redlich-UNIFAC EOS developed by Aspen Technology. This EOS model uses binary interaction parameters of mixtures for which data is available in the databases. This model is usually used when the liquid mixture is polar and non-ideal.

R1 Modeling Assumptions

1) Both the reactants are charged into the reactor at the same temperature and pressure.
2) The reactor is operated isothermally.
3) The pressure relief valve of the reactor is set at a constant value.
4) The only reaction occurring in the reactor is the reversible and exothermic formation of 3-sulfolene.
5) The extent of the reaction is measured in terms of the percent conversion of 1,3-butadiene charged.
6) The heel is at equilibrium composition of sulfur dioxide, 1,3-butadiene, and 3-sulfolene.
9) The liquid phase is homogenous, i.e., there are no immiscible liquid phases of a particular component.
10) The reactor can be represented by a series of two ideal batch reactors.

R1 Model development

Based on the assumptions outlined above, R1 was modeled using the RBATCH, MIXER, and FSPLIT modules in ASPEN PLUS (ASPEN PLUS, Users guide). The model of this reactor has been iteratively improved as more information on its configuration could be obtained.

The refinement of the model from the initial to the final form results from a better understanding of the mixing occurring inside the reactor. The evolution of the model is du to the work done on this reactor by Jayagopal (1994). The difference in the final results, i.e., the prediction of the exit composition is not significant from one model to another. However, the final form of the model can be considered predictive as opposed to the correlative nature of the initial model.

In the final model (Fig. 4) the reactor operation is represented by a series of three batch reactors. The first reactor, block B1, is used to produce the heel that is present in the beginning of the batch cycle. This heel is then split into two equal portions in block B2. Block B3 and B4 represent the top zone of the reactor to which fresh feed is added. A portion of the product from B4 is removed and added to the second zone of the reactor represented by block B7. A part of the product is removed from block B7. This represent the product removal from reactor R1 (Technical Report, 1994).

R1 Results

A comparison of the results showed that the conversions and molar volume of reaction mixture predicted using 3-sulfolene properties were higher than those predicted using sulfolane properties. The criterion for validating the model were the exit compositions of the reactor stream. The variable with the most impact on the exit composition was found to be the batch cycle time.

Treatment step - Vessel R2

R2 Operational procedure and conditions

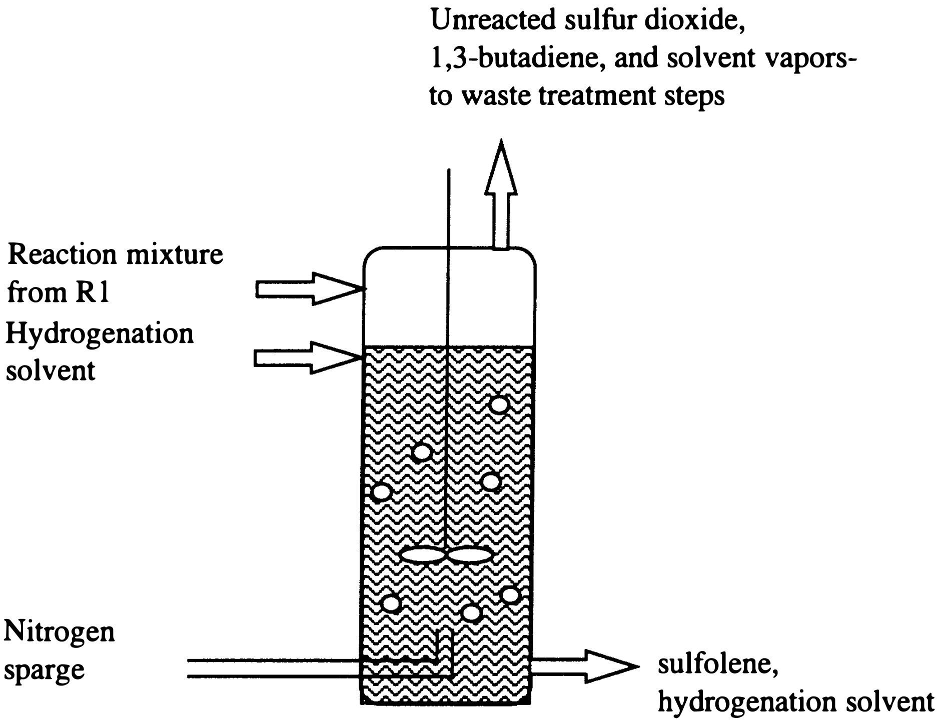
R2 is a agitated flash vessel in which the reaction mixture from R1 is added to a solvent and then treated to remove the unreacted sulfur dioxide and the butadiene. This is done through a combination of flashing the mixture and sparging it with an inert gas such as nitrogen (Fig. 5). The process is kept isothermal. The unreacted sulfur dioxide and butadiene gases are swept along with the solvent vapors to the waste treatment section of the process where they are treated with caustic before being sent to the flare. See Technical Report (1994) for actual operating conditions.

Physical property and kinetic data for R2

1) For the simulation of this step the properties of sulfolene were approximated with those of sulfolane.
2) The kinetic data for this step pertains to the decomposition of sulfolene is the solvent-sulfolene mixture. These data have been obtained through experimental measurements made by Phillips.
3) The Redlich-UNIFAC EOS was found to be suitable for the simulation of this step.

R2 Modeling Assumptions

1) Decomposition of sulfolene has been neglected for the steady state model.
2) A pressure profile exists during the evacuation of R2. This profile starts with atmospheric pressure and ends with a pressure of about 2 psia.
3) The liquid mixture inside R2 is well-mixed, homogeneous, and no immiscible liquid phases exist.
4) Nitrogen is used to sparge the mixture and is fed continuously into the vessel.



<u>Operating conditions</u>	
Feed	Reaction mixture and hydrogenation solvent
Temperature	75-150 F
Pressure	2-5 psia.
Batch cycle time	2-4 hours

Figure 5. Schematic diagram of treatment vessel R2

R2 Model development

Three models were constructed for the simulation of this step. They were:

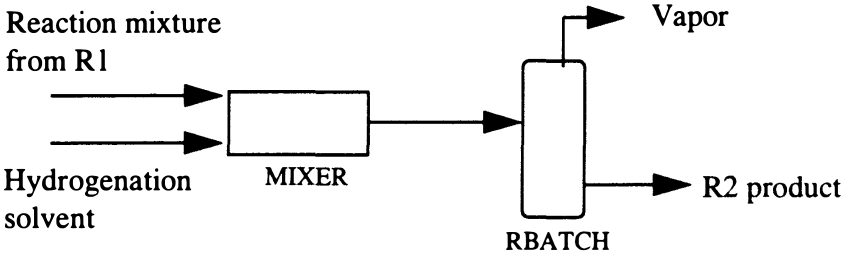
1) Batch reactor model (Model 1)
2) Steady state flash vessels in series (Model 2)
3) Batch reactor and flash vessel in series (Model 3)

The decomposition of sulfolene was neglected in the steady state model (model 2) because simultaneous phase and chemical equilibrium could not be incorporated. The ASPEN PLUS module which allows this - REQUIL is known to have convergence problems, and this was experienced during the simulation of R2. The assumption regarding pressure profile was made because it represents the transient response of the system to the evacuation of the treatment vessel. Though this transience cannot be incorporated per se into the steady state model, it can serve as an approximation of the batch process through the series representation.

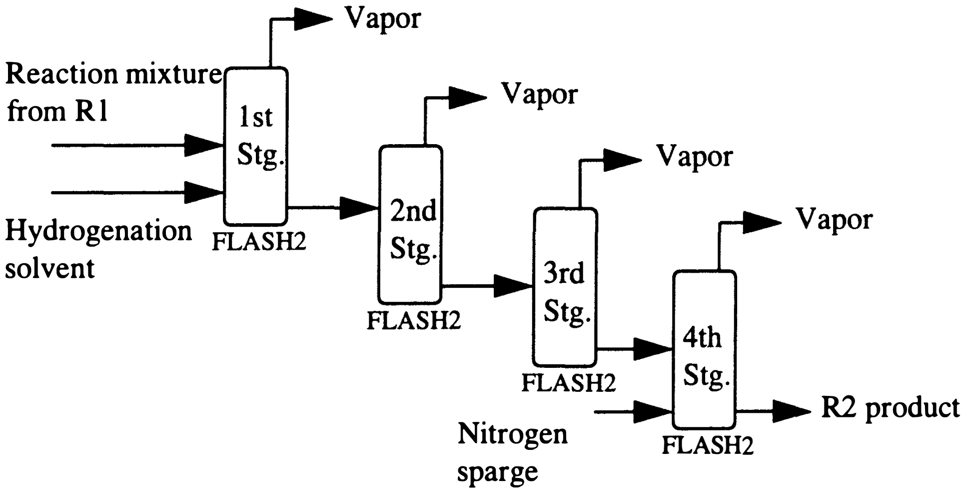
If we assume that the pressure inside the vessel varies with time, then the progression of the pressure can be represented by a set of discrete points. Steady state vessels can then be used to simulate each discrete pressure condition (keeping the temperature constant). The assumption regarding perfect mixing is justifiable considering the small volume of the mixture. This assumption simplifies the thermodynamic aspects of the flash calculations for R2.

The nitrogen sparging is an important step in the treatment in R2 because it reduces the mass-transfer limitations of sulfur dioxide removal from the liquid mixture. Nitrogen gas can strip solvent vapors. This should to be avoided, because the solvent concentration in the liquid must be maintained at a certain level to prevent freezing of the sulfolene. The incorporation of nitrogen sparging into the model is thus very important. The details of the three models are provided below.

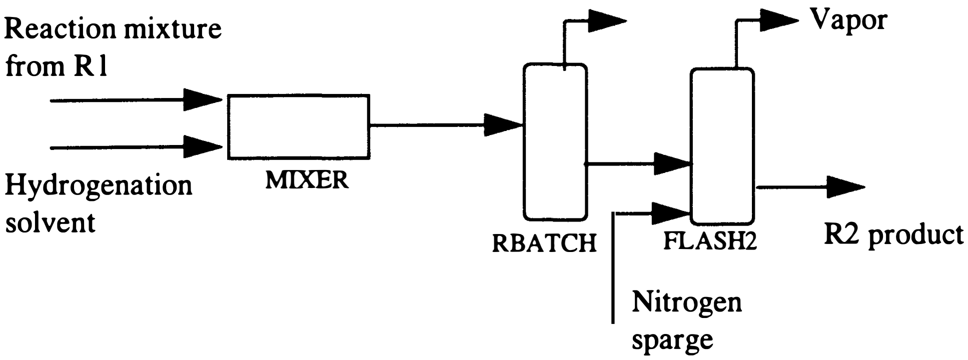
Model 1 The batch reactor model consists of the RBATCH and MIXER modules (Fig. 6). The reaction mixture from R1 and the solvent are first mixed in the MIXER



(a) Model 1



(b) Model 2



(c) Model 3

Figure 6. Block diagram of ASPEN PLUS models of R2

model. The product from this module is then sent to the RBATCH model. Decomposition kinetics of sulfolene are provided for this module. The product from the RBATCH module is considered equivalent to the R2 output.

Model 2 The steady state model of R2 consists of a series of FLASH2 modules (Fig. 6). The reaction mixture from R1 is mixed with the solvent in the first stage. The liquid from each stage is fed into the next stage. The vapor streams from each stage are taken out as product streams. In the last stage, in addition to the liquid feed from the previous stage, an additional stream simulating the nitrogen sparge is incorporated. The liquid stream from the last stage is considered equivalent to the R2 output.

Model 3 The third model consists of a batch reactor and a flash vessel in series (Fig. 6). The model consists of RBATCH, FLASH2 and MIXER modules. The reaction mixture from R1 is added to the solvent in the MIXER module. The product is then transferred to the batch reactor and the product of this reactor is then sent to the flash vessel where the mixture is sparged with nitrogen. The product of this FLASH2 module is considered equivalent to the R2 output.

R2 Results

Several trade-offs were applied in selecting the appropriate model. The batch model (Model 1) allows us to study the transient response of the system including the changes in the composition of the vapor and the liquid. It also allows us to incorporate the decomposition kinetics of the sulfolene. However, the nitrogen sparge cannot be added to this model. An attempt was made to include the nitrogen sparge in a FLASH2 module connected to the outlet of the batch reactor (Model 3). However, this model predicts a lower sulfur dioxide concentration in the liquid than measured experimentally. The results from the steady state model (Model 2) were found to match with the pilot plant data quite closely. Since this model allows incorporation of nitrogen sparging and provides reasonable results, it was chosen as the representative model (Technical Report, 1994).

The simulation results for this step were found to be very sensitive to the properties of sulfolene and the EOS used. The improper selection of these quantities led to gross errors in the prediction of vapor-liquid equilibrium in this step.

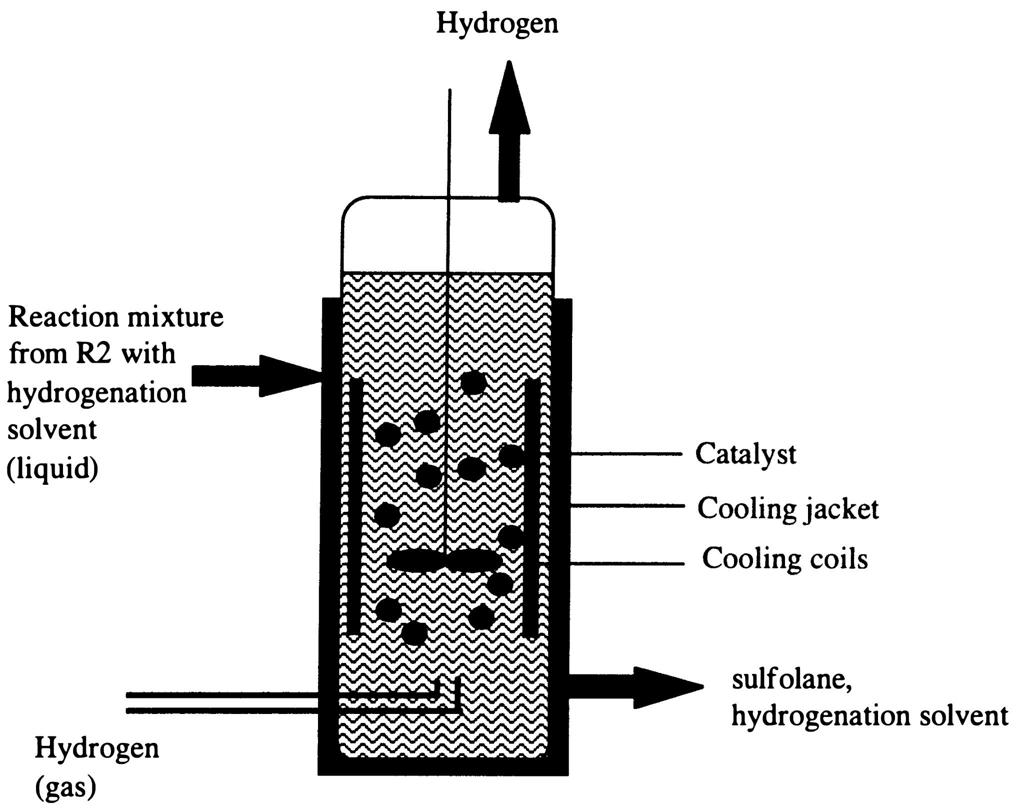
Hydrogenation step (R3)

R3 - Operational procedure and conditions

R3 is a stirred reactor in which the sulfolene-solvent mixture is catalytically hydrogenated to produce sulfolane (Fig. 7). The catalyst is charged at the beginning of the batch and pressurized hydrogen is fed continuously into the reactor throughout the batch cycle. The reactor is operated isothermally. The heat of the reaction is removed through a cooling jacket and internal cooling coils. The completion of the reaction is determined by monitoring the heat removal from the reactor. At the end of the reaction cycle the reactor is vented to remove excess gases and the sulfolane is transferred to a set of downstream processes for purification.

Physical property and kinetic data for R3

1) For the simulation of this step, the sulfolene properties were approximated with those of sulfolane. This was necessary because transport properties of the hydrogenation mixture were needed.
2) No data are available on the intrinsic kinetics of the hydrogenation reaction of sulfolene. An effort was made to regress kinetic data based on the heat removal data obtained from the plant. However, the assumptions regarding the mechanism of the reaction were not justifiable. A discussion of the conventional mechanism of heterogeneous reactions is provided in the next section.
3) The Redlich-UNIFAC equation of state was used to simulate the properties for this step.



<u>Operating conditions</u>	
Feed	sulfolene, hydrogenation solvent, hydrogen, catalyst
Temperature	50-120 F.
Pressure	50-500 psig.
Batch cycle time	3-6 hours.

Figure 7. Schematic diagram of the hydrogenation reactor

R3 Modeling assumptions

Reactors Liquid phase hydrogenation reactions are usually carried out in either slurry reactors or fluidized bed reactors. In a slurry reactor, the solid catalyst is suspendec in a liquid which contains the material to be hydrogenated. Gas is bubbled through this slurry and the hydrogenation occurs on the catalyst particle surface. The slurry reactor which is common in specialty chemical manufacture can be usually operated in batch, semi batch or continuous mode. The advantages of this type of reactor are good temperature control and easy heat recovery.

Mechanism There are classically two approaches to determining the kinetics of a heterogeneous reaction.

1) Power law kinetics
2) Langmuir-Hinshelwood kinetics

The latter is a mechanistic representation of the reaction. The power law kinetics on the other hand are a representation of the kinetics in terms of component concentrations which affect the rate of a reaction significantly. A comprehensive discussion of the advantages and pitfalls of each approach is available by Welier (1956).

The most conventional interpretation of the mechanism of a heterogeneous reaction is represented by the following general sequence of steps:

1) absorption from gas phase into liquid phase at the bubble surface,
2) diffusion in the liquid phase from bubble surface to bulk liquid,
3) diffusion from bulk liquid to external surface of the catalyst,
4) internal diffusion of reactant in the porous catalyst,
5) reaction within the porous catalyst.

The products then follow similar steps in the reverse order. Each step is a resistanc to the overall rate of the reaction. Following these set of steps, the overall rate of reaction can be expressed as,

$$\frac{C_i}{R_A} = \frac{1}{k_b \cdot a_b} + \frac{1}{m}\left(\frac{1}{k_c \cdot a_c} + \frac{1}{k \cdot \eta}\right)$$

where, the first term on the right hand side represents the resistance to gas absorption, the second term the resistance to transport to the surface of the catalyst particle, and the third term the diffusion to (internal) and reaction within the catalyst particle. These resistances act in series as can be recognized by the equation.

There is, however, another proposed mechanism in which the resistances of gas absorption and external diffusion act in parallel. This mechanism is described as the "shuttle" mechanism (Alper,1981). This occurs when the catalyst particles are very fine and leads to enhanced gas absorption rates. Usually the enhancement reaches a limit when the diameter of the catalyst particle is roughly equal to the thickness of the liquid film surrounding the catalyst particle. Under these conditions the well established design equation mentioned above does not apply. However, quantitative representation of this concept is still lacking in the literature.

In this study, we will assume that the standard Langmuir-Hinshelwood kinetic mechanism applies. Apart from this, the following assumptions are made:

1) The conversion of sulfolene to sulfolane is assumed to be 98%.
2) The hydrogen is assumed to be at ambient temperature.
3) The side reactions occurring in this step have been neglected.

R3 Model development

This step has been simulated with a RSTOIC module (Technical Report, 1994). The sulfolene-solvent mixture from R2 is provided as feed for this block. The conversion for sulfolene is specified. The products of the RSTOIC block (vapor and liquid streams) are assumed to represent the R3 output. The property set facility of ASPEN PLUS was used to estimate the mixture properties of the hydrogenation mixture.

R3 - Results

The results of this block were mainly the property estimations that were required to determine the rate limiting step in the process (Table 4, Chapter 7). The amount of sulfolane produced per batch cycle was chosen as the variable for validating the model. The results indicated that the overall material balance for the process could be satisfied through the use of the RSTOIC module.

Overall Process Model

The most appropriate model for each step was selected. These were then combined into one flow sheet to form the overall process model. Thus, a complete material and energy balance for the first three steps of the process could be generated using ASPEN PLUS. This shall be referred to as the 'base-case'. The particulars for the overall model are:

1) Reaction step - Refined two-zone batch reactor model
2) Treatment step - Steady state flash vessels in series model
3) Hydrogenation step - Stoichiometric reactor model

These selections were based on accuracy of results, computational ease, and ease of interface with each other. Some important process variables were selected to validate the overall process model. These variables were:

1) Reaction step - Outlet composition of reaction mixture
2) Treatment step - Sulfur dioxide concentration in the exit liquid stream
3) Hydrogenation step - Sulfolane production per batch.

The input file for the ASPEN PLUS simulation of the overall process model and the detailed material and energy balances are available in the Technical Report (1994). A synopsis of the results is shown in Table 2.

In this chapter we have reviewed, a) process characterization, b) physical property estimation for 3-sulfolene, c) operational details of equipment, d) development of ASPEN

PLUS models to simulate each piece of equipment, e) analysis and selection of appropriate models for each piece of equipment, and, f) the results from the base case simulation of the overall process. In summary, the work presented in this chapter represents the application of the first step of the general methodology to the sulfolane process, namely, process modeling.

Using this overall process model as the base case material and energy balance the economics of the current operation will be evaluated. This discussion is presented in the next chapter.

TABLE 2

BASE CASE RESULTS

Outlet composition of the reaction mixture from R1 (in terms of mole fractions)	
sulfolene	0.763
sulfur dioxide	0.140
butadiene	0.097
Concentration of liquid product from R2 (in terms of mass fraction)	
sulfur dioxide	710 ppm
butadiene	515 ppm
sulfolene	0.684
solvent	0.314
Sulfolane production per batch (in terms of lb. sulfolane/ lb. sulfur dioxide feed)	

$$\frac{\text{lb. sulfolane}}{\text{lb. butadiene}} = 0.746$$

CHAPTER VI

ECONOMIC ANALYSIS

Process retrofit requires economic justification. Today, most of the economic incentive for modifying a process comes from reducing its environmental impact. In order to look at the incentives for improving the sulfolane process, an economic analysis of the existing process needs to be performed. In this chapter, a base case economic analysis will be reviewed.

Review Of Approach For Economic Analysis

A cost model for the process can be developed by linking the process model with economic data. The costs of operating a process are typically divided into capital and total product costs. Generally, product costs are broken down into four categories.

1) Direct production costs
2) Fixed charges
3) Plant overhead costs
4) Administrative and product distribution costs

For many processes, the costs of waste reduction and disposal significantly impact the overall profitability of the process. This research proposes that environmental costs should be included into the total product costs as direct production costs. However, industrially these costs are assigned to an overhead account (Freeman, 1992). This is one of the main obstacles in determining the incentives for waste minimization. The development of a total product cost model for the sulfolane process is discussed in the next section.

Base Case Economics of Sulfolane Process

A total product cost model has been developed for the sulfolane process. The majo components of the total products costs are :

1) raw material costs
2) utility costs
3) maintenance costs
4) plant overhead costs
5) waste treatment /disposal costs

Based on these costs annualized profit can be expressed as,

Profit = *production rate x selling price - total product costs*

The total product costs term can be expanded to the following form,

Product costs = *raw material usage x raw material costs + utility usage x utility costs + waste generation x waste treatment/ disposal costs + plant overhead costs + maintenance costs*

Data availability

In this analysis, approximate values for treatment and disposal of wastes will be assumed since accurate figures for the environmental costs are not available. Then, using these costs, the annualized waste treatment and disposal costs will be calculated. This amount will be subtracted from the plant overhead account to which it is presently being charged. The utility and maintenance costs for individual sections of the process are not available. Thus, these costs will be assumed to vary linearly with production levels. In summary, the main assumptions are,

1) Waste treatment and disposal costs assumed
2) Maintenance and overhead costs vary linearly with production levels
3) Process equipment is fully depreciated

Cost data

The cost data used for this economic analysis have been summarized below. These values are estimates and have been obtained from Chemical Marketing Reporter.

1) Raw materials

Butadiene	\$0.20 / lb.
Sulfur dioxide	\$0.115 / lb.
Catalyst	\$7.15 / lb.
Nitrogen	\$0.70 / MSCF
Hydrogen	\$0.131 / lb.
NaOH	\$0.165 / lb.

2) Utilities

Steam	\$3.08 / Mlb.
Electricity	\$0.0345 / kWhr

3) Waste treatment / disposal costs

Spent liquid absorbent disposal costs	\$0.01/ gallon.
Solid waste reclamation (disposal) costs	\$750 / ton.
Gaseous waste treatment costs	\$ 0.165 /lb.

Since the overhead and maintenance cost figures are proprietary, these values can be found in the Technical Report (1994) along with the results of the base case economics.

Economic analysis

The material balance generated using the overall process model was used to calculate the annual costs of sulfolane production. The break down of the calculated costs is available in the Technical Report (1994). The catalyst and sodium hydroxide usage figures are based on plant data and are not based on the predictions of the overall process model.

Based on the material balance generated by the process model, the economics of the base case process were calculated. The results of such an analysis indicates that the process costs are dominated by raw material costs. The catalyst cost is the most significant among the raw material costs. This was found to be nearly 20% of the overall costs of the process. The catalyst use figure is, however, uncertain and due to this, the costs could vary from 20 to 35% of the overall costs of the process.

The environmental costs were found to be nearly 2% of the overall costs of the process. This cost is very uncertain due to lack of data on sodium hydroxide usage. For this economic analysis it has been assumed that for every pound of sulfur dioxide to be scrubbed, one pound of sodium hydroxide is needed. If the use of sodium hydroxide is closer to 10 pounds per pound of sulfur dioxide then this amounts to nearly 20% of the overall costs. This is mainly due to the high raw material costs associated with sodium hydroxide. The costs of treating and disposing the liquid discharges were found to be insignificant compared to the overall process costs. The reclamation costs associated with the solid sludge were recovered through the value of the reclaimed catalyst.

The environmental costs discussed in this section pertain solely to the treatment and or disposal of wastes. While measuring the incentives of waste reduction, one needs to consider the hidden incentives such as retroactive liability imposed by EPA, customer response to environmentally friendly technology, a more efficient raw material utilization etc.

In summary, based on the economic analysis it can be concluded that there exists much incentive (10-15% savings on the product costs) for implementing waste reduction measures through more efficient utilization of the raw materials in the process. In the next chapter the generation, selection and optimization of improvement alternatives will be considered.

Chapter VII

PROCESS RETROFIT ALTERNATIVES

In the previous two chapters the development of an overall process model and its use to perform an economic analysis has been reviewed. In this chapter the use of these two steps for generating and selecting alternatives will be discussed.

Sensitivity Analysis

The sensitivity of the annual profit to a particular process variable is a useful way of targeting the key optimization variables. The economics dictate the magnitude of impact each process variable has on the overall profitability. Therefore, even though the process model might be extremely sensitive to some parameter such as temperature or pressure of a reactor, changes in that parameter may not affect the profit levels of the process. Thus, a sensitivity analysis is important not only for the development of the process model but also for the optimization of the process. In this chapter, the sensitivity of the economic model will be discussed.

Sensitivity of process economics

From the base case economics the following conclusions can be drawn about the relative magnitudes of costs. The process is dominated by raw material costs. The variable costs with the next highest impact are the waste treatment/ disposal costs, followed by plant overhead, maintenance and utility costs. Plant overhead costs tend to be a significant portion of the total product costs when a variety of miscellaneous costs are combined under it. In order to avoid this in this work, the waste treatment and disposal costs have been separated from the overhead, leaving the remaining portion to account for costs associated with administrative and product distribution activities. Specifically, the following inferences can be drawn from the economic analysis.

1) The catalyst cost is the most important variable. The catalyst is very expensive. It gets poisoned in the hydrogenation step and cannot be recovered for reuse. The poisoning of the catalyst also leads to the formation of unwanted by-products (solids sludge) the disposal of which is an additional economic burden. The poisoning of the catalyst reduces its activity thus affecting the rate of the reaction and consequently the batch cycle times. Also, the quality of catalyst is not consistent from one batch to another. All these factors lead to the hydrogenation step being the time and waste bottleneck of the process. The improvement and optimization of this step holds the maximum environmental and economic incentive.
2) Next to the catalyst costs, the important variables are the raw material costs of the reactants sulfur dioxide and butadiene. A more efficient utilization of the raw materials either through better conversion or recycle holds incentive not only from a regulatory point of view but also from a raw material conversion efficiency point of view.
3) The utility costs are not significant for this particular process. However, in case retrofit involves addition of new equipment or change of an existing equipment for which the energy consumption is increased (e.g., increase in steam consumption to effect better separation) then these costs may become more significant.

In the following section possible scenarios which highlight the importance of the above mentioned variables will be discussed.

Forecasting Future Scenarios

Consider the following scenarios which further highlight the incentive for efficient raw material utilization.

1) Butadiene emission levels are regulated
2) Allowable sulfur dioxide emission levels are lowered
3) Demand for sulfolane increases
4) Catalyst reclaimer is subjected to new environmental regulations
5) Raw material prices increase
6) Reduction of emissions from one facility qualifies as a trade-off for another facility

Scenario 1:

The process plant usually operates under permitted levels of gaseous emissions and waste water discharges. Currently, the amount of butadiene is not regulated, and prevention of butadiene from entering either the gaseous emissions or the waste water is not an important consideration. By 1995 the levels of butadiene will be regulated, and process modifications will have to be made to reduce the butadiene in the gaseous emissions and the waste water to allowed (permitted) levels.

Scenario 2:

The allowable levels of sulfur dioxide emissions from a plant are subject to revision. These emission requirements may become more stringent. With existing equipment it might be infeasible to reduce sulfur dioxide levels to the permissible levels. In this case the only alternative would be to reduce at the source, i.e., through better raw material utilization.

Scenario 3:

The demand for sulfolane may increase in the future. This would require an increase in the production levels of the process. This will affect the amount of wastes generated and consequently the economics of the process. It would be worthwhile to investigate the case of increased production and determine ways in which this can be achieved without adversely affecting the profit levels of the process.

Scenario 4:

The catalyst reclaimer may increase the price of reclaiming the catalyst. This could be due to increased environmental regulations that the reclaimer may face in the future. This would affect the amount of solid waste that the process can dispose. If the costs of reclamation are not offset by the value of the disposed solid waste, then it would be beneficial to reduce the generation of these wastes.

Scenario 5:

The price of raw material may increase in the future. Raw materials such as sulfur dioxide and butadiene may become more expensive. This would increase the incentives for better raw material utilization.

Scenario 6:

Reduction in emissions from one part of the plant may qualify as a trade-off for emission levels from another part of the plant or from another facility. In fact this provision is already in place. This is additional incentive for reducing emissions from any plant.

Under all these scenarios, waste minimization through better raw material utilization will carry high incentives. Thus, it can be seen that incentives for waste minimization exist not only for the current operating scenario but more so for the future, considering the trend of environmental regulations. The following sections will be devoted to the application of the proposed methodology for generating, optimizing and selecting alternatives for improving the sulfolane process.

Generation, Selection, and, Optimization of Alternatives

Based on the sensitivity of the economics of the process, catalyst cost and raw material costs have been identified to be the significant costs of operation. Following these are the environmental costs, which have been calculated by assuming approximate values of waste treatment of solid, liquid, and, gaseous emissions from the process. Based on these indicators, the following alternatives are worth investigating.

1) Conservation and optimization of raw material usage in the reactor R1.
2) Improvement of sulfur dioxide removal in treatment tank R2.
3) Change of hydrogenation solvent in treatment tank R2.
4) Mitigation of rate limitation in the hydrogenation reactor R3.

Each of these alternatives is discussed in detail below.

Conservation and optimization of raw material usage in reactor R1

This alternative is important to ensure that there is no raw material loss through the vent of the reactor. When fresh feed is added at the beginning of the batch, the composition of the top zone of the reactor changes. The concentration of the more volatile components, i.e., sulfur dioxide and butadiene is high. The heat of the reaction causes some of the reactants to vaporize. This leads to the accumulation of the gaseous reactants in the head space of the reactor. As the vapor in the head space of the reactor builds up the operating pressure of the reactor increases till it reaches vent pressure. Once this pressure is achieved the reactor vents. In actual operation the reactor is found to vent at the beginning of the batch and then stabilize to equilibrium pressure as the batch cycle proceeds. This is because as the reaction proceeds the composition of the reaction mixture changes and more of the non-volatile component, i.e., sulfolene is present at the end of the batch than at the beginning. This aspect of R1 operation has consequences on not only raw material utilization, but also on waste formation. High build up of butadiene in the gaseous phase can lead to the formation of polybutadiene polymers. Also, the reactor vent stream would contain sulfur dioxide and butadiene which are transported to the waste treatment steps of the process. Therefore, any alternative that reduces the emissions from the reactor vent and conserves raw material within the reactor without leading to polymer formation would be beneficial.

To understand the vaporization taking place at the beginning of the batch cycle the bubble point of the mixture needs to be considered. The change of bubble point with composition also needs to be considered. Simulations of the P-T envelope can be carried out in ASPEN PLUS. The bubble points of the mixture are estimated as a function of the reaction rate. The main assumption in this analysis is that the temperature of the reactor is kept constant at the operating temperature. This can be verified by a study of the heat transfer occurring in the reactor through cooling coils and the external jacket. It has been theoretically determined that sufficient heat transfer capacity exists in the R1 cooling system to maintain the temperature of the top half of the reactor at the operating temperature (Jayagopal, 1994). The variation of the bubble point with batch time are shown in Table 3.

At the beginning of the batch assuming that the reactor contents are considered saturated liquids (i.e., at saturated pressure of 65 psia) at or close to equilibrium composition, the addition of fresh feed would be followed by immediate vaporization of reactants because the system pressure is lower than the bubble point of the mixture (~125 psia). Therefore as an operating policy it would be helpful to maintain the reactor vent pressure above this pressure so that even with rapid vaporization, the build up in the head space is never sufficient to cause the reactor to vent.

TABLE 3

REACTION MIXTURE COMPOSITION AND BUBBLE POINTS

Time	Composition (mole fraction) SO_2 / C_4H_6 / $C_4H_6SO_2$	Bubble point pressure
Beginning of cycle	0.27/ 0.23/ 0.50	125 psia
2 hrs	0.20/ 0.16/ 0.64	100 psia
4 hrs	0.17/ 0.13/ 0.70	80 psia
6 hrs	0.16/ 0.12/ 0.72	75 psia
Equilibrium composition	0.14/ 0.09/ 0.77	65 psia

There are two issues to consider in optimizing the R1 reactor with respect to utilization of the raw materials. One is to ensure that the products removed from the reactor are at equilibrium conversion and secondly to produce sufficient moles of sulfolene per batch. Since the reactants are charged over a period of time it would be worthwhile to investigate the effect of the feed charge times on the extent of the reaction (in terms of percent conversion of butadiene charged). This can be studied by utilizing the optional continuous stream available as input to RBATCH module in ASPEN PLUS.

The effect of butadiene charge times on the extent of reaction was studied. For this study the top zone of the reactor was considered. It is assumed that the fresh feed is well mixed with the heel present in the top half of the reactor. The feed charge time was varied between 1 and 6 hours.

It was observed that the conversion of fresh feed to sulfolene in the heel decreases with increasing feed times (Fig.8). Correspondingly, the number of moles of sulfolene in the product decreases. Therefore, it is advisable to charge the fresh feed in as small a time as possible. However, the optimum feed time is constrained by the heat transfer capacity of the reactor cooling system. Charging the reactor too quickly would lead to a temperature runaway and vaporization of the reaction mixture, both of which are detrimental to achieving equilibrium conversion. Since a feed time of 2 hrs. is found to cause venting of R1 in process plant operation, it is suggested that the feed time be increased. To make up for the reduced conversion, as quantified in Fig.8, the feed should be introduced continuously while allowing the reaction mixture to stay in the reactor for a longer time (i.e., increasing the residence time). This can be done by reducing the mixing within the reactor and operating it in a plug flow type of configuration (Jayagopal, 1994).

Improvement of sulfur dioxide removal from reaction mixture

The unreacted sulfur dioxide and butadiene are separated from the reaction products of reactor R1 in this step. The sulfur dioxide poisons the catalyst in the hydrogenation step. Thus, apart from changing the hydrogenation solvent, reducing the sulfur dioxide levels in the R3 feed is potentially an alternative to reduce the waste generation in the hydrogenation step. The main consideration in R2 is maintain the sulfolene mixture above its freezing point. The other consideration is to avoid high temperatures at which the decomposition rates of sulfolene would be significant. Subject to these two constraints the removal of sulfur dioxide from the reaction mixture can be improved it would reduce the poisoning in the hydrogenation step.

The main constraint in the removal of sulfur dioxide is the mass-transfer limitation that dominates after a major part of the removal has been accomplished. To overcome this, the mixture is sparged with nitrogen. The nitrogen sparging can enhance the removal of sulfur dioxide, but nitrogen strips solvent. The change in the liquid composition increases the likelihood of the sulfolene mixture freezing. An increase of nitrogen sparging rate may therefore not be a feasible alternative. Through a sensitivity analysis carried out on the R2 model, it is found that the removal of sulfur dioxide is

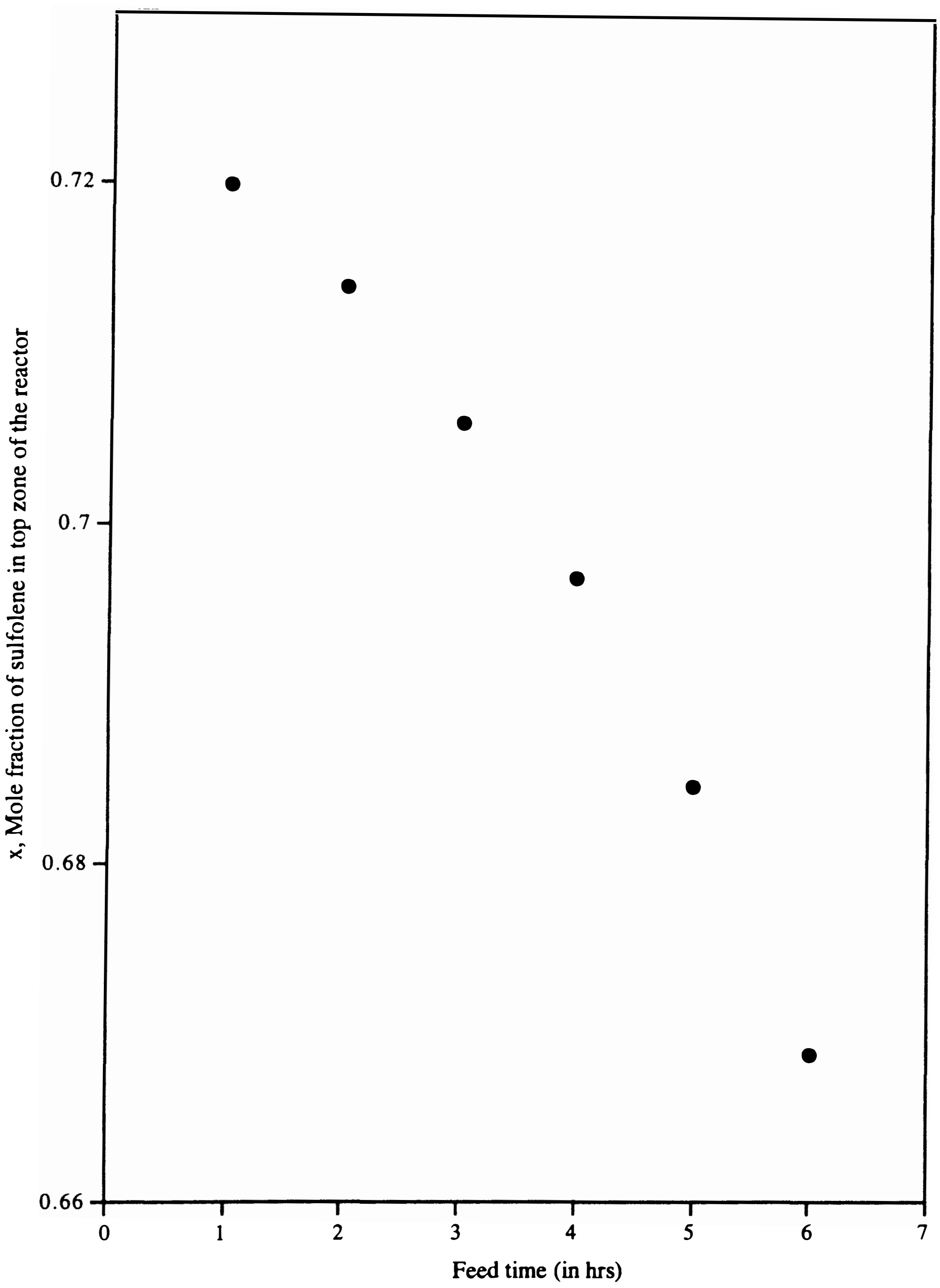


Figure 8. Butadiene feed time versus sulfolene mole fraction in the top zone of R1

sensitive to the temperature of operation. In this work, an increase in the operating temperature of R2 has been considered as an alternative for improving the removal of sulfur dioxide from the reaction mixture. An optimization block was incorporated along with the simulated ASPEN PLUS process model. The range of temperature was restricted to the limits set by the decomposition characteristics of sulfolene. Based on the results of the optimization block it was found that an increase in the temperature of R2 operation by roughly about 10°F can reduce the sulfur dioxide levels to almost 100 ppm. There is increased solvent vaporization at the optimized conditions; however, not sufficient to adversely affect the freezing point of the mixture. Therefore, an increase in temperature can reduce the sulfur dioxide concentrations from the present 800 ppm to roughly 100 ppm. From an operability point of view, the increased solvent vaporization may affect the vacuum and the condensing system attached to R2. Through an analysis of the condenser and the vacuum system capacities, the feasibility of this alternative can be confirmed. A comparison of the unoptimized and optimized runs for the R2 is shown in Fig 9.

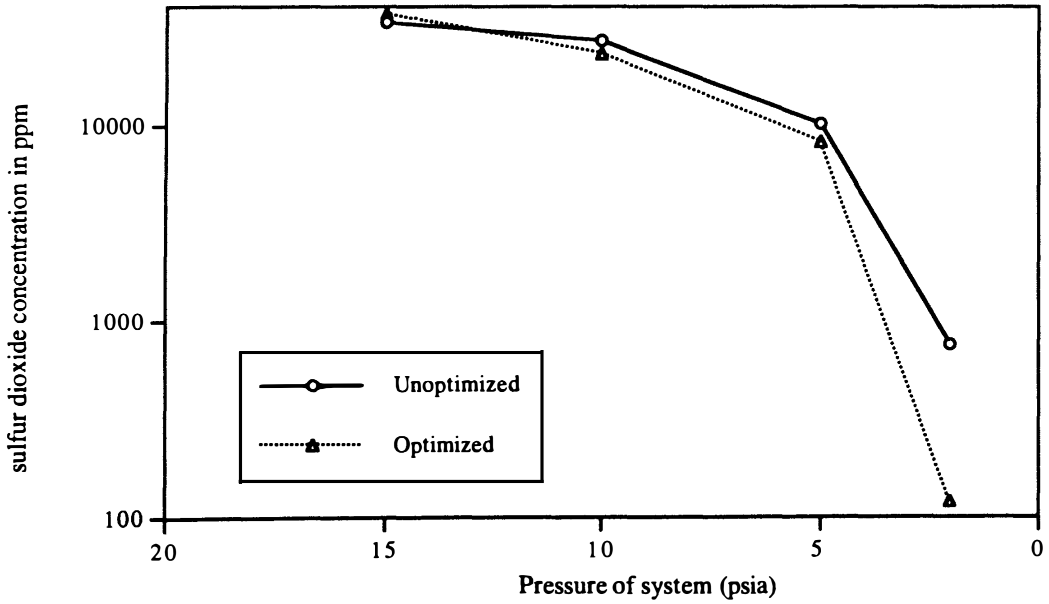


Figure 9. Effect of temperature on sulfur dioxide removal

In the base case simulation the freezing point of the sulfolene mixture was 20°F below the operating temperature. In the optimized case, the temperature difference between the operating temperature and the freezing point is about 30°F. Thus, the optimized temperature is safe from an operating standpoint. In summary, the major benefits of increasing temperature of R2 operation are:

1) Reducing sulfur dioxide levels in the outlet to ~ 120 ppm.
2) Reducing solvent content in the outlet (roughly 22% compared to 30%)
3) Increasing the temperature difference between the sulfolene mixture freezing point and the operating temperature of R2.

Change of hydrogenation solvent in treatment tank R2

One of the alternatives for improving process efficiency is change of the hydrogenation solvent. By using a solvent that reduces the poisoning of the hydrogenation catalyst, a significant reduction in the generation of the wastes can be affected. Preliminary calculations can be performed to evaluate alternative solvents. In order to make a comparison between solvents the important or critical qualities of a solvent must be listed. For sulfolane hydrogenation, the following characteristics are desirable.

1) Highly polar
2) Non-volatile
3) High solubility of hydrogen
4) High heat capacity
5) Chemically inert under hydrogenation conditions

The solvent should be polar because it should be able to dissolve sulfolene and sulfur dioxide, both of which are polar. The non-volatility ensures that under vacuum conditions appreciable vaporization doe not take place. This is important to maintain the sulfolene solution above its freezing point. The solvent should be able to dissolve hydrogen so that the hydrogenation reaction is not limited by the rate of hydrogen absorption and diffusion. Finally, the solvent should not be involved in competing reactions with the catalyst which could lead to unwanted by-product formation. On the basis of these criteria, three solvents have been chosen for evaluation:

1) isopropyl alcohol
2) sulfolane
3) water

The solvent properties have mostly been estimated through ASPEN PLUS simulations.

Polarity Accentric factor (omega) is usually defined as a measure of the nonsphericity of a molecule (Reid et al., 1987). Usually, the accentric factor is a parameter which reflects the geometry and polarity of molecules. High omega implies high polarity of the molecule. Isopropyl alcohol may be considered to be the most polar among the three choices (Table 4).

Volatility Vapor pressure of a pure substance is a suitable measure of its volatility. The uncertainty in the values for sulfolane is the highest because there are no experimental data . However, the vapor pressure parameters for isopropyl alcohol and water are well documented. The vapor pressures for the pure solvents at a temperature of 140°F have been compared in Table 4. Based on these calculations it can be observed that sulfolane is the most non-volatile solvent followed by water and lastly by isopropyl alcohol.

Solubility of hydrogen in the solvent This criterion is important to ensure that the hydrogenation reaction is not rate limited by the solubility and thus absorption of hydrogen A rough comparison of the solubilities based on thermodynamic predictions or experimental data can be carried out. Experimental data is available for the solubility of hydrogen in pure water. The remaining solubilities can be estimated through thermodynamic predictions using ASPEN PLUS. These calculations have been done for a temperature of 140 F and a pressure of 500 psig, both of which are typical conditions for hydrogenation. For these conditions the solubilities have been tabulated in Table 4.

TABLE 4

PHYSICAL PROPERTIES OF ALTERNATIVE SOLVENTS

Property	Isopropyl alcohol	Sulfolane	Water
Molecular wt.	60.1	120.17	18.01
Freezing point (F)	-127.2	80.3	32.0
Boiling point (F)	180.0	548.3	212
Critical temperature (F)	455.3	1075.8	705.5
Critical pressure (psia)	690.4	728.3	3205.3
Accentric factor	0.665	0.378	0.344
Vapor pressure @ 140°F (psia)	5.63	2.89	0.002
Solubilities of hydrogen (reported in mole fraction)	$1.37\text{x}10^{-2}$	$6.5\text{x}10^{-3}$	$4.57\text{x}10^{-4}$
Heat capacity (Btu/lbmol R)	43.75	42.95	19.43
Latent heat of vaporization (Btu/lbmol)	$1.54\text{x}10^{4}$	$2.58\text{x}10^{4}$	$1.68\text{x}10^{4}$

From the results it can be inferred that hydrogen is most soluble in isopropyl alcohol when compared to other solvents. Hydrogen is found to be least soluble in water.

Heat capacity of the solvent The heat capacity of the solvent is an important variable for consideration because if the hydrogenation is carried out in a slurry reactor typ of operation the advantage of good temperature control of reactor can be derived from the high heat capacity of the slurry which includes the solvent. A comparison of the heat capacities and the latent heats of vaporization for the three solvents are shown in Table 4. The heat capacities of both sulfolane and isopropyl alcohol are very high.

Chemical inertness under hydrogenation conditions This is probably the most important consideration. The primary reason for changing solvents was to avoid the generation of unwanted by-products during the hydrogenation reaction. The kinetics or mechanism of sulfolene hydrogenation and the side reactions occurring with use of the current solvent are not fully understood. It is quite difficult to predict the effect of a new solvent on the selectivity of the reaction. It is expected that isopropyl alcohol and sulfolane will not promote unwanted side reactions because of their chemical reactivity.

Comparison and selection of alternative solvent Based on the comparison of the three different solvents, isopropyl alcohol can be selected as a suitable alternative solvent. I is highly polar, has a high heat capacity, and is expected to be chemically inert under hydrogenation conditions.

Overcoming Rate Limitation in the Hydrogenation Step

The hydrogenation reactor represents the time and waste bottleneck of the process. The mechanism and the kinetics of the sulfolene hydrogenation are presently not known. Results of previous studies (Mashkina et al., 1967) are not applicable for use in modeling the R3 reactor. Additionally, the unwanted by-products produced in this step have not been characterized, nor has the reaction mechanism been understood. The only alternative for improving this reactor is to estimate the relative resistances of gas absorption and external diffusion and to devise ways of overcoming the rate limitation.

In Chapter 5, the mechanism of catalytic three-phase hydrogenation was briefly discussed. Assuming that the sulfolene hydrogenation reaction follows a conventional Langmuir-Hinshelwood type of mechanism, the sequence of steps involved in the heterogeneous reaction may be summarized by the following equations (Fogler,1986):

Rate of gas absorption,

$$R_A = k_b \cdot a_b \cdot (C_i - C_b) \qquad \text{gmol/ cm}^3\text{•sec} \tag{7.1}$$

Rate of transport to catalyst,

$$R_A = k_c \cdot a_c \cdot (C_b - C_{A,s}) \qquad \text{gmol/ cm}^3\text{•sec} \tag{7.2}$$

Rate of diffusion and reaction in catalyst pellet,

$$R_A = m \cdot \eta \cdot (-r_{A,s}) \qquad \text{gmol/ cm}^3\text{•sec} \tag{7.3}$$

Rate law for the reaction on the surface of catalyst,

$$-r_{A,s} = k \cdot C_{A,s}{}^{n} \tag{7.4}$$

Based on these rates the overall rate of reaction can be expressed as,

$$\frac{C_i}{R_A} = \frac{1}{k_b \cdot a_b} + \frac{1}{m}\left(\frac{1}{k_c \cdot a_c} + \frac{1}{k \cdot \eta}\right) \tag{7.5}$$

where,

k_b = mass-transfer coefficient for bubbles, cm/ sec

k_c = mass-transfer coefficient for catalyst particles, cm/ sec

k = specific reaction rate constant

a_b = bubble surface area (interfacial area), $\text{cm}^2/\text{ cm}^3$

a_c = specific surface area, $\text{cm}^2/\text{ gm}$

m = mass concentration of catalyst, gm/ cm^3 slurry

η = effectiveness factor

$-r_{A,s}$ = specific reaction rate if entire catalyst is exposed to surface concentration of the adsorbed gas, gmol/ gm. catalyst • sec

C_i = concentration of gas at the bubble interface, gmol/ cm^3

C_b = concentration of gas in the bulk liquid, gmol/ cm^3

$C_{A,s}$ = concentration of gas at the external surface of catalyst, gmol/ cm^3

n = reaction order

The basic assumptions involved in carrying out this analysis are:

1) liquid phase is well mixed,
2) catalyst particles are uniformly distributed,
3) gas phase is in plug flow,
4) during the initial reaction, the concentration of the liquid remains practically constant, and,
5) reaction conditions are isothermal.

From this form of the design equation it can be seen that the resistances of gas absorption, external diffusion, and, surface reaction act in series. R_A represents the overall or 'observed' rate of reaction whereas the term k_η represents the intrinsic or 'actual' rate of reaction. Usually, experiments are performed to measure the intrinsic kinetic parameters of a reaction by minimizing the absorption and diffusional resistances so that the 'observed' rate of reaction represents the 'actual' or the intrinsic rate of reaction.

For the sulfolene hydrogenation reaction, the following data is available.

1) The reactor heat removal profile
2) Feed material balance

The physical properties required for carrying out the rate limitation analysis were obtained through a combination of manual estimations and using the PROP-SET option in ASPEN PLUS. A summary of the properties estimated is presented in Table 5. These values have been reported in SI units because the correlations used to calculate the mass transfer coefficients have been written for SI units.

Since the intrinsic kinetics of the sulfolene hydrogenation reaction are not available we cannot predict the magnitude of the intrinsic reaction rate given by equation 7.4. We can however attempt to calculate the remaining three terms in the equation.

TABLE 5.

HYDROGENATION MIXTURE
ESTIMATED PROPERTIES

Solubility of hydrogen in hydrogenation mixture	$1.18\text{x}10^{-5}$ cm^3 slurry
Diffusivity of hydrogen in the reaction mixture, $D_{H2,mix}$	$4.6\text{x}10^{-5}$ cm^2/ sec.
Density of hydrogen, ρ_g	$2.19\text{x}10^{-2}$ gm/ cm^3
Viscosity of mixture, μ_f	1.1 cP
Surface tension of mixture, S_T	51 dyne/ cm
Density of mixture, ρ_f	1.392 gm/ cm^3
Specific heat of mixture, $C_{p,mix}$	2.79 Kj/ kg.K
Diameter of catalyst particle, d_p	60 micron
Density of catalyst particle, ρ_p	4.0 gm/ cm^3

Rate of external diffusion In a book on mass transfer in heterogeneous catalysis Satterfield (1970) discusses an example in which quantitative justification has been provided to prove the absence of diffusion effects in a slurry reactor. This method has been applied to investigate diffusion effects in R3. The data used for the calculation is shown in Table 6.

First, the terminal velocity of the settling catalyst particles is calculated. Satterfield (1970) suggests in his example the use of Stokes law for calculating the terminal velocity. However, Stokes law can be used only when the particles are 10-20 micron in size. Since the assumed particle size is 60 micron applying Stokes law would lead to considerable error. The Theodore and Buonicore correlation (Alley,1986) can be used for particles

TABLE 6

DATA FOR EXTERNAL DIFFUSION RATE CALCULATION

Concentration of hydrogen at bubble interface, $C_{H_2,i}$	$1.18\text{x}10^{-5}$ gmol/ cm^3 slurry
Diffusivity of hydrogen in the reaction mixture, $D_{H_2,mix}$	$4.6\text{x}10^{-5}$ cm^2/ sec.
Viscosity of mixture, μ_f	1.1 cP
Density of mixture, ρ_f	1.392 gm/ cm^3
Diameter of catalyst particle, d_p	60 micron
Density of catalyst particle, ρ_p	4.0 gm/ cm^3
Catalyst loading, m	0.014 gm/ cm^3 slurry

larger than 20 micron. The correlation has the following form:

$$u_t = \frac{0.153 d_p^{1.14} \rho_p^{0.71} g^{0.71}}{\mu_f^{0.43} \rho_f^{0.29}} \tag{7.6}$$

where g is the acceleration due to gravity (cm/sec). Substituting the values, the terminal velocity u_t is calculated to be 1.01 cm/sec. Based on this terminal velocity, the Peclet number can be calculated as,

$$N_{Pe}^{*} = \frac{d_p u_t}{D_{H2,mix}} = \frac{60\text{x}10^{-4} \text{ x } 1.01}{4.6\text{x}10^{-5}} \sim 132 \tag{7.7}$$

The Peclet number can then be related to the Sherwood number through a correlation proposed by Brian and Hales and represented graphically in Fig 2.4 of Satterfield (1970). The Sherwood number is given by,

$$N_{Sh} = \frac{k_c d_p}{D_{H2,mix}} = (4.0 + 1.21 N_{Pe}^{2/3})^{1/2} \tag{7.8}$$

or, $\quad k_c = 0.0456 \text{ cm / sec}$

The turbulence that results from the agitation of the reaction slurry enhances this mass transfer coefficient. In reality, the mass transfer coefficients are roughly two to four times the calculated values. Taking twice the calculated value we obtain,

$$k_c = 0.0912 \text{ cm / sec}$$

The rate of mass transfer from the bulk liquid to the external catalyst surface is given by (Satterfield, 1970):

$$N = k_c \frac{6m}{d_p \rho_p}\left(C_{H2,i} - C_{H2,s}\right) \text{ gmol / sec} \bullet \text{cm}^3 \qquad (7.9)$$

where, $C_{H2,s}$ is the concentration of hydrogen on the catalyst surface. If we assume that the reaction rate is controlled by the mass-transfer rate, i.e., the rate at which the hydrogen is transported from the bulk liquid to the catalyst surface, then we can assume that the surface concentration of hydrogen on the catalyst surface is zero. Applying equation 7.9, we can then calculate the maximum rate of external diffusion rate.

$$N = \frac{0.0912 \text{ x } 6 \text{ x } 0.014 \text{ x } 1.18\text{x}10^{-5}}{60\text{x}10^{-4} \text{ x } 4.0} = 3.76\text{x}10^{-7} \text{ gmol / sec}\cdot\text{cm}^3$$

<u>Rate of gas absorption</u> In a comprehensive review of three phase catalytic reactors Chaudhari and Ramachandran (1980) have presented correlations for predicting the gas-liquid mass transfer coefficient. Calderbank and Moo-Young (1961) suggested the following correlation for liquid side mass transfer coefficient.

$$k_L = 0.42\left[\frac{(\rho_f - \rho_g)\mu_f g}{\rho_f^2}\right]^{1/3}\left[\frac{D\rho_f}{\mu_f}\right]^{1/2} \qquad (7.10)$$

where, ρ_g is the density of the gas, and other terms are defined above.

The value for k_L can be calculated as follows,

$$k_L = 0.42\left[\frac{(1.392-0.022) \text{ x } 0.011 \text{ x } 981}{(1.392)^2}\right]^{1/3}\left[\frac{4.6\text{x}10^{-5} \text{ x } 1.392}{0.011}\right]^{1/2}$$

$$= 0.063 \text{ cm / sec}$$

The gas-liquid interfacial area was related by Calderbank (1958) as follows:

$$a_b = 1.44 \frac{\left(\frac{P}{V_L}\right)^{0.4} \rho_L^{0.2}}{S_T^{0.6}} \left(\frac{u_g}{u_t}\right)^{0.5} \qquad (7.11)$$

a_b = effective gas-liquid interfacial area per unit volume of slurry, cm^2/cm^3

P = power consumption for agitation, gm/ cm^2/ sec^3

V_L = total volume of slurry, cm^3

S_T = surface tension of the liquid, gm/ sec^2

u_t = terminal gas bubble velocity, cm/ sec

u_g = superficial velocity of gas in reactor, cm/ sec

The power consumption per unit volume is given by Prasher and Williams (1973) as:

$$\frac{P}{V_L} = \frac{8 N^3 d_I^5 \psi \rho_f}{d_T^2 L} \qquad (7.12)$$

where,

N = speed of agitation of slurry, sec^{-1}

d_I = diameter of impeller, cm

d_T = diameter of slurry reactor, cm

L = total height of slurry above the entrance of the gas bubbles, cm,

and the correction factor ψ is given as,

$$\psi = 1.0 - 1.26\left[\frac{Q}{N d_I^3}\right], \text{ for } \frac{Q}{N d_I^3} < 3.5 \times 10^{-2} \qquad (7.13)$$

$$\psi = 0.62 - 1.85\left[\frac{Q}{N d_I^3}\right], \text{ for } \frac{Q}{N d_I^3} > 3.5 \times 10^{-2} \qquad (7.14)$$

Where, Q is the volumetric flow rate of the gas (cm^3/ sec).

For our case,

$$\frac{Q}{N d_I^3} = \frac{1.8 \times 10^4}{2.1 \text{ x } (38.0)^3} = 0.155$$

The correction factor is then calculated to be:

$$\psi = 0.62 - 1.85(0.155) = 0.33$$

The power consumption per unit volume is further calculated to be:

$$\frac{P}{V_L} = \frac{8 \text{ x } (2.1)^3 \text{ x } (38.0)^5 \text{ x } 0.33 \text{ x } 1.392}{(137.2)^2(140.0)} = 1037$$

To account for the multiple impeller in the process reactor, an enhancement factor of three is considered. Therefore, the actual power consumption is calculated to be 3110. Based on this power consumption, the superficial gas velocity, and the surface tension of the liquid, the gas hold-up, ε_g, can be calculated by the following equation.

$$\varepsilon_g = \left[\frac{u_g \varepsilon_g}{u_t}\right]^{1/2} + 0.0216 \frac{\left[\frac{P}{V_L}\right]^{0.4} \rho_L^{0.2}}{S_T^{0.6}} \left[\frac{u_g}{u_t}\right]^{1/2} \qquad (7.15)$$

For our case, this equation reduces to,

$$\varepsilon_g = \left[\frac{1.22 \varepsilon_g}{26.0}\right]^{1/2} + 0.0216 \frac{(3110)^{0.4}(1.392)^{0.2}}{(51.0)^{0.6}} \left[\frac{1.22}{26.0}\right]^{1/2} \Rightarrow \varepsilon_g = 0.07$$

where, the superficial gas velocity has been calculated as,

$$\frac{\text{Gas flow rate}}{\text{Cross - sectional area of the reactor}} = \frac{18000 \text{ cm}^3/\text{sec}}{14775.6 \text{ cm}^2} = 1.22 \text{ cm}/\text{sec}$$

The terminal bubble velocity has been approximated to be 26 cm/sec (Chaudhari, 1980). The value of the gas hold-up was calculated to be 0.07, implying that the amount of gas available to diffuse to the catalyst surface is roughly 7% of the total volume of the liquid.

This value is considerably low. The average bubble diameter d_B can be calculated using the gas hold-up by the following equation:

$$d_B = 4.15 \frac{S_T^{0.6}}{\left[\frac{P}{V_L}\right]^{0.4} \rho_L^{0.2}} \varepsilon_g^{1/2} + 0.09 \tag{7.16}$$

Substituting values we get d_B to be 0.52 cm. The usual values are in the range of 0.2-0.5 cm. These values are directly related to the gas hold-up. The higher the gas hold-up (due to higher power input per unit volume), the smaller the bubble diameter. Using the calculated bubble diameter, the following criterion needs to be evaluated before the interfacial area can be calculated.

$$\left[\frac{d_I^2 N \rho_L}{\mu_L}\right]^{0.7} \left[\frac{N d_B}{u_g}\right]^{0.3} < 20{,}000 \tag{7.17}$$

For our case, the value of this parameter is less than 20,000. The value of the interfacial area is calculated as follows:

$$a_b = 1.44 \frac{(3110)^{0.4}(1.392)^{0.2}}{(51.0)^{0.6}} \left(\frac{1.22}{26.0}\right)^{0.5} = 0.8 \text{ cm}^2/\text{cm}^3$$

Using the calculated value of the gas liquid mass transfer coefficient, k_L, and the interfacial area, a_b, the rate of gas absorption can be calculated. If gas absorption is the controlling mechanism then the bulk concentration of hydrogen in the liquid can be considered to be zero. The driving force for the absorption process is provided by the concentration gradient across the bubble interface and the bulk liquid. The concentration of hydrogen at the bubble-liquid interface is essentially the equilibrium concentration of hydrogen. Therefore, the hydrogen absorption rate is given by equation 7.1 as,

$$N = k_L a_b (C_{H2,i} - C_{H2,b}) \text{ gmol / sec} \bullet \text{cm}^3$$

where, $C_{H2,b}$ is the bulk liquid concentration of hydrogen. Substituting the calculated values we obtain,

$$N = 0.063 \times 0.8 \times (1.18\times10^{-5} - 0) = 5.9\times10^{-7} \text{ gmol / sec}\bullet\text{cm}^3$$

Overall rate of reaction The overall rate of reaction is the 'observed' rate of reaction. The overall rate of reaction is dependent on the magnitudes of the resistances of each of the heterogeneous processes, i.e., gas absorption, external diffusion, and, internal diffusion and reaction (intrinsic kinetics).

In the case of the sulfolene hydrogenation reaction, data are not available for the intrinsic kinetics of the reaction. At the present time an experimental apparatus for measuring the reaction rates is being set up by the Department of Chemistry, OSU. Similarly, data on the observed rate of reaction (at conditions under which the reaction is carried out in the process plant) are not available either in literature or from Phillips experimental measurements.

The objective of this analysis is obtain an approximate value for the maximum observed 'process' rate from plant data . This has been done using the heat removal data for the process hydrogenation reactor. The assumptions involved in carrying out this analysis are,

1) The heat removal profile is representative of the heat evolution due to the heat of reaction, i.e., the nature of the curve for both the heat removal and the evolution of the heat of reaction are the same.
2) The only reaction with a significant heat of reaction is the sulfolene hydrogenation reaction. Side reactions leading to unwanted by-products are known to occur in this reactor. Neither the mechanism nor the thermo-kinetics of these reactions are known. Therefore, this assumption is necessary.

The use of reaction calorimetry to measure the overall rate of reaction is an extreme approximation. Hernández et al. (1993) have developed a mathematical model for the analysis and optimization of batch reactors for heterogeneous liquid-liquid reactions. They have predicted kinetic parameters for the toluene mononitration reaction through an experimental apparatus which measures heat removal by recording reactor temperatures. Their approach is rigorous and presumes certain data availability. Since data availability is scarce in the case of sulfolene hydrogenation reaction, it is justifiable to retain the basic premise of Hernández and others (1993) work. Measuring the rate of reaction through reaction calorimetry must be considered only a prediction of 'process rate' trends rather than a quantitative description of the reaction rates.

Heat of reaction: The heat of reaction for sulfolene hydrogenation can be calculate from the heats of formation of the reactants and the products. The reaction stoichiometry is

$$C_4H_6SO_2 \underset{\substack{H_2 \\ \text{Catalyst}}}{\rightarrow} C_4H_8SO_2$$

The heat of formation of the components involved are,

$$\Delta H^{\circ}_{f@298K,sle} = -2.59\text{x}10^{8}\ \text{J / Kmol}$$

$$\Delta H^{\circ}_{f@298K,sla} = -3.90\text{x}10^{8}\ \text{J / Kmol}$$

$$\Delta H^{\circ}_{f@298K,hyd} = 0\ \text{(since it is an elemental compound)}$$

Based on a simulation carried out using the RSTOIC module in ASPEN PLUS, the heat of the sulfolene hydrogenation reaction at 100°F can be calculated to be 63,275 Btu/ lbmol.

Reactor heat removal data: The heat removal in the reactor by the cooling water is monitored by computer control based on inlet and outlet temperature of cooling water, flowrate of cooling water, and the reactor temperature. The temperature and flow sensors record measurements at regular intervals, and the data are used to control the reactor. The reaction is assumed to be complete when no more heat is being removed by the cooling water.

Analysis If we assume that, 1) the heat removed during a batch is proportional to the heat evolved during the batch due to the reaction, and 2) the average moles of sulfolane produced in a batch are known, then the heat of reaction per mole of sulfolane formed can be found by dividing the total heat evolved over a batch by the average number of sulfolane moles produced per batch. The average heat of reaction calculated in this way is ~ 540 Btu/ lbmol. This is roughly 1% of the actual heat of reaction. The cooling water system cannot remove just 1% of the total heat. This would mean that the temperature of the reactor would rise to very high levels. Since in process plant operation the temperatures are not found to increase beyond a few degrees of the desired reaction temperature this explanation is not justifiable. A further analysis reveals the following points:

1) Some of the heat is carried away by the hydrogen which is kept in high circulation during the batch. Since the heat required to bring the temperature of hydrogen from ambient conditions to the reaction conditions is roughly about 4% of the total heat evolved this cannot account for a large part of the total heat evolution.
2) Some of the heat is accumulated in the reactor walls and some of it is dissipated as radiation losses. However, once again the magnitudes of these losses cannot be more than 5% of the total heat of the reaction.

Therefore, the only other explanation is that calibration of the flow meters measuring the cooling water rate is faulty. Even though this might be the case the present control system for the reactor is adequate because it is more important to know the profile of heat removal than the actual values of heat removed.

By normalizing the heat removal in each time period by the total heat removed during that batch, the number of moles sulfolane moles formed in that time period can be calculated. Since the volume of the slurry is known and the time period is known, the heat data can be converted into a 'process rate' data. This 'process rate' data is plotted against time for six batches for which plant data is available. The data is shown in Fig. 10.

Results, Sensitivity, and, Comparisons The following is a comparison of the observed reaction rate, the gas absorption rate and the external diffusion rates.

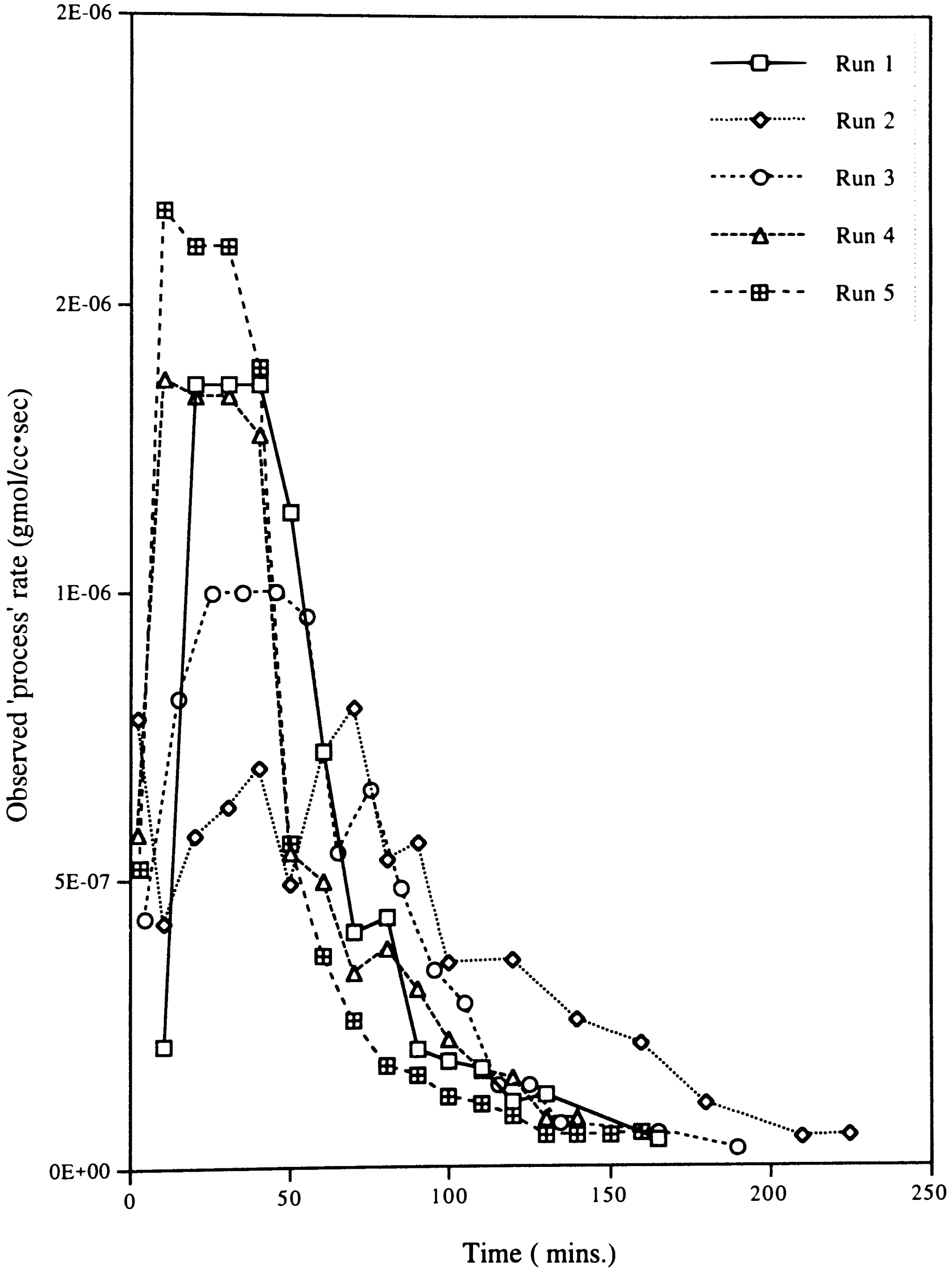


Figure 10. Reaction profiles for five R3 batches

Observed reaction rate	1.68×10^{-6} gmol/sec•cm^3
External diffusion rate	3.76×10^{-6} gmol/sec•cm^3
Gas absorption rate	5.9×10^{-7} gmol/sec•cm^3

Considering that the 'shuttle' mechanism of gas absorption (see chapter 5) is very likely (since the assumed catalyst particle size is very small) there could be considerable enhancement of the gas absorption rates. Therefore, the actual value may be significantly higher than the calculated value. As mentioned earlier the enhancement factor cannot be accurately quantified. However a factor of 10-100 might be appropriate. In which case it is most likely that the gas absorption does not present the major resistance to the rate of the reaction.

The maximum calculated value of the 'observed' rate of reaction or 'process' rate is equal to the rate of external diffusion. From this analysis it can be concluded that the external diffusion rate is the limiting step under the process conditions. It is important to study the sensitivity of the calculated external diffusion rate to the input parameters. A quantitative sensitivity analysis of the absorption rate cannot be carried out because there are several variables involved. However, qualitatively it is found that the calculations are sensitive the estimation of the gas hold-up. An additional issue is the use of the single impeller correlations for estimating the power consumption per unit volume in multiple impeller configurations.

Since many parameters in both the absorption and diffusion calculations are highly uncertain, a sensitivity analysis would indicate which parameter affects the calculated value the most. This would be a valuable guide for setting up experimental studies during the measurement of intrinsic kinetics.

Sensitivity of external diffusion rate calculations : The physical property inputs for these calculations are:

1) Diameter of catalyst particle
2) Density of catalyst particle
3) Viscosity of reaction slurry
4) Density of reaction slurry
5) Diffusivity of hydrogen in reaction slurry

The results of the sensitivity analysis indicates that the diffusivity of hydrogen in the reaction slurry affects this calculation the most. The rest of the parameters do not affect the order of magnitude of the calculated external diffusion rate. The range of values considered for the different variables are shown in Table 7.

TABLE 7

RANGE OF INPUT VARIABLES FOR EXTERNAL DIFFUSION RATE CALCULATION

Density of catalyst particle	2-7 gm/cm^3
Diameter of catalyst particle	60-100 μ
Viscosity of slurry	300-1000 cm/ gm•sec
Density of slurry	0.8175-1.5 gm/cm^3
Diffusivity of hydrogen	2×10^{-5} - 2×10^{-3} cm^2/sec

Alternatives The alternatives that are available to overcome or reduce the effect of external diffusion limitation of the hydrogenation reaction have been discussed by Chaudhari and Ramachandran (1980). These alternatives can be divided into categories depending upon their impact. They are shown in Table 8.

TABLE 8

EFFECT OF PARAMETERS ON OVERCOMING EXTERNAL DIFFUSION LIMITATION.

Major influence	Minor influence	Insignificant influence
Amount of catalyst	Temperature	Concentration of liquid phase reactant (i.e., sulfolene)
Catalyst particle size	Stirring rate	
Concentration of reactant in gaseous phase (i.e., hydrogen)	Reactor design	Concentration of active component(s) on catalyst
	Viscosity	
	Relative densities	

Let us consider the variables with the major influence.

1) Amount of catalyst: Since many reactions involving the catalyst are known to occur in this step, addition of more catalyst will increase the rate of the reaction and increase the amount of unwanted by-products formed during the batch. Therefore the trade-offs are increased production versus the costs of waste disposal (sludge disposal). This alternative will have to be looked at in more detail, if the scenario of increased production becomes important or possible. For the current operation of the process, this alternative is not very attractive because the incentive for increasing production does not exist.

2) Catalyst particle size: The catalyst particle size used presently is quite small. Further decrease in particle size may not be feasible. The cost of a smaller catalyst may be significantly higher, and the effect on the rate of sulfolene hydrogenation and by-product formation is not known. Therefore, once again this alternative is not feasible in most of the scenarios.

3) Concentration of hydrogen: This alternative seems to be the most attractive. By increasing the concentration of hydrogen in the liquid it can be ensured that the diffusivity of the hydrogen in the liquid is increased and that more hydrogen is available on the surface of the catalyst for reaction. There are a variety of ways in which this can be achieved.

   a) *Increase the pressure of the reactor* : This will affect the solubility of hydrogen in the liquid, and increase the concentration in the liquid (as long as gas absorption is not limiting).

   b) *Change the solvent for the hydrogenation step* : As discussed earlier, a comparison of alternative solvents reveals that the solubility of hydrogen in some solvents is better than others. For example, the solubility of hydrogen in isopropyl alcohol is twice that in sulfolane. Therefore, this is potentially a way of overcoming diffusion limitations in the liquid mixture. The change in solvent will also affect the by-product formation. Through experimental verification it can be determined whether an alternative solvent reduces by-product formation. Through change of solvent both the rate limitation and waste generation bottleneck of the hydrogenation reactor can be overcome.

In summary, four different alternatives for process improvement were investigated.

1) Conservation and optimization of raw material usage in the reactor R1.
2) Improvement of sulfur dioxide removal in treatment tank R2.
3) Change of hydrogenation solvent in treatment tank R2.
4) Mitigation of rate limitation in the hydrogenation reactor R3.

With further experimentation and data availability, economic justification for the alternatives can be put forward. This concludes the chapter on the process retrofit alternatives.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

The sulfolane process of Phillips Petroleum Company was analyzed for process improvements. The focus of the study was on investigating alternatives for reducing the wastes in the process and increasing production. An approach involving process modeling, economic analysis, and selection and evaluation of retrofit alternatives was utilized to accomplish the objective. A general methodology involving these elements was formulated.

Using the general methodology, the following tasks were accomplished. An overall process model for the sulfolane process was developed. The development of the model involved estimation of physical properties for an intermediate compound in the process, 3-sulfolene, incorporation of non-ideality of process equipment, approximation of batch processing with steady-state analyses, and use of stoichiometric model to overcome lack of data. Based on the process model, a material balance for the synthesis step of the sulfolane process was generated.

The process model gave more consistent results with substituted sulfolene properties (sulfolane properties) than with the estimated sulfolene properties. The estimation of the sulfolene properties were based on group contribution methods used for sulfolane in the DIPPR database. In this study, sulfolene properties were approximated with sulfolane properties since no uncertainty limits could be established for the estimated sulfolene properties. The property approximations were validated by comparing the results of the simulated model with process plant data.

In the simulation of both R1 and R2 the most important sulfolene property was the vapor pressure. The vapor pressure input did not affect R1 simulation very drastically because the operating pressures are quite high and the reaction mixture remains as liquid for most of the batch cycle. However, in the case of R2, the operation is under vacuum conditions and vapor pressure parameters affect the simulation results drastically. This is the reason for substituting sulfolene properties with sulfolane properties. This has a direct effect on process economics because R2 simulation calculates the vaporization losses of sulfolene if any, which in turn affects the batch charge for hydrogenation.

Apart from vapor pressure the other significant variable is the density of pure sulfolene and sulfolene mixtures. The density parameter affects the estimation of batch charge and product volumes which becomes important while considering alternatives for increasing production or determining equipment bottlenecks.

For the simulation of R3, the most important properties pertained to the transport characteristics (e.g., viscosity, diffusivity, etc.) of the sulfolene-solvent mixture. Equally important was the solubility of hydrogen in sulfolene mixtures. As discussed earlier solubility and diffusivity of hydrogen in the sulfolene-solvent mixture were found to affect the external diffusion rate calculation the most. In terms of economics, a better knowledge of these variables along with the mechanism and rate data for the hydrogenation reaction would help overcome the rate limitation of the present operation.

In summary, from a point of improving model accuracy and selecting economically significant physical property variables for sulfolene, the following properties are important: vapor pressure and density of pure sulfolene and sulfolene mixtures, transport properties of sulfolene mixtures, and solubility of hydrogen in sulfolene mixtures. The above information may be used for future estimation and experimentation work on sulfolene properties.

An economic analysis was performed on the basis of the material balance. It was found that the raw material costs dominated the overall costs of the process. The catalyst costs were found to account for nearly 20% of the overall costs of the process, followed b raw material and the overhead costs for the process. The waste treatment and disposal costs were found to account for 2-20% of the overall costs. Such a wide range exists for these costs because they are highly uncertain. These costs are based on an assumed use of sodium hydroxide. Since this use is not taken into account explicitly in the process model and had to be assumed, the uncertainty was unresolved. Based on the economic analysis, it was found that the profit levels of the process were highly sensitive to the catalyst and other raw material costs. There is a high incentive (10-15% of the total product costs) for better utilization of raw materials and reduction of wastes in the process.

Incentive for waste reduction is further highlighted by the expected regulation of butadiene under NESHAP. By 1995, the levels of butadiene discharges either in the gaseous form or through waste water are going to be regulated. Also, since the catalyst is heavy metal, spent catalyst sludge will continue to be regulated. From a regulatory point o view, this process will be further regulated. The incentives for pro-active modifications should consider not only compliance benefits but also intangible benefits such as environmental stewardship, avoidance of retroactive liability, and positive consumer response.

On the basis of the economic analysis and its sensitivity, four alternatives for improving the process were investigated. These were,

1) Conservation and optimization of raw material usage in the reactor R1.
2) Improvement of sulfur dioxide removal in treatment tank R2.
3) Change of hydrogenation solvent in treatment tank R2.
4) Mitigation of rate limitation in the hydrogenation reactor R3.

From the process model and economic analysis it was determined that the hydrogenation step is the time and waste bottleneck of the process. The processes upstream of the hydrogenation step are held up due to the batch cycle times of the hydrogenation step. Also, this step produces unwanted by-products through side reactions involving poisoning of the catalyst. Since the catalyst costs account for nearly 20% of the total costs, the improvement and optimization of the hydrogenation reactor, R3, provides maximum environmental and economic benefits.

A conclusive economic comparison of the alternatives could not be carried out because of lack of data regarding the mechanism and kinetics of the hydrogenation reaction. The causes and extent of side reactions due to the use of the present hydrogenation solvent are not fully understood. Thus, it is very difficult to analyze alternatives for improving this step. Two alternatives were considered. The first one was evaluating the feasibility of using alternative solvents such as sulfolane and isopropyl alcohol. The second was a study of ways to overcome the rate limitation of the hydrogenation step. The major assumption with the latter analysis was that the reaction calorimetry is an approximate measure of the reaction rate. Approximate values for the rates of the other heterogeneous process, i.e., gas absorption and external diffusion were calculated. The sensitivity of these calculations were studied because the input variables were found to be quite uncertain.

Based on a comparison of the alternatives in the long term, the best alternative is to change the hydrogenation solvent. This will affect catalyst usage and by-product formation in the hydrogenation step. In the short term, alternatives such as conserving raw materials in the reaction step, improving the removal of sulfur dioxide in the treatment step, and overcoming the rate limitation in the hydrogenation step should be considered. Conclusive economic justification for these alternatives can be provided once kinetic data for the hydrogenation can be obtained.

The optimization of the sulfolane process was not carried out because the hydrogenation reactor R3 could not be adequately modeled due to lack of information on kinetic mechanism and rates. The development of a hydrogenation model is especially important because the R3 reactor is the time and waste bottleneck of the process. Another limitation was the use of ASPEN PLUS to model a time-dependent process. Though ASPEN PLUS has strong optimization capabilities, it cannot be fully utilized for batch processing. On the other hand, dynamic simulation packages such as BATCHCAD and SPEEDUP are suitable for developing predictive process models but do not contain optimization modules. A brief discussion of ASPEN PLUS limitations follows.

The limitations of ASPEN PLUS were mainly with the RBATCH module, REQUIL module convergence, and accessibility of the physical properties. On the other hand the optimization and property estimation features available in ASPEN PLUS were found to be useful.

The RBATCH module in ASPEN PLUS can be used to simulate isothermal, adiabatic, temperature or duty specified batch reactors. A batch charge stream and a reactor product stream is required, whereas a continuous feed stream and vent product streams are optional. The continuous feed stream allows the simulation of semi-batch reactors in which one of the reactants is continuously introduced into the reactor throughout the batch cycle. As the RBATCH module is to be interfaced with a flowsheet which is steady-state, ASPEN PLUS accepts batch charge inputs and computes reactor products based on continuous streams. It uses the concepts of feed times and cycle times to compute actual batch charge. The main limitation with the use of RBATCH is that one cannot sequence periodic feed additions or limit addition from a continuous stream to a fraction of the total cycle time. This makes it difficult to simulate industrial operation of batch reactors which often involve feed addition over a fraction of the total batch time and also alternate and periodic addition of the reactants.

The other limitation of the RBATCH module is that one cannot generate the heat profile of the reactor over the batch time. This has to be accomplished by creating a property set which records the enthalpy profile of the reaction mixture over the batch time. Then, one needs to consider the enthalpy difference over a time interval to determine the heat release in that interval. This amounts to a tedious procedure. Conventional batch simulation software such as BATCHCAD contain in-built functions for generating heat profiles and tuning controller parameters to achieve stable temperature control.

REQUIL is an equilibrium reactor module which can be used to calculate simultaneous phase and chemical equilibrium. An attempt was made to use this module for simulating R2 operation where the relevant reaction was the decomposition of sulfolene. Further, this model was used to optimize the steady-state operating parameters for R2 operation. However, there were severe convergence problems with the mass balance for the system. This is most probably due to faulty development of the REQUIL module. It is not advisable to use this module for optimization purposes.

In the production of specialty chemicals, it is quite difficult to obtain accurate physical property data because it is not feasible or economical to perform extensive experimentation. In such cases, one has to use estimated properties. While using estimated properties in a process model, it is worthwhile to investigate the sensitivity of the results to physical property parameters. Additionally, when the process model is combined to an economic model, the effect of physical property estimations on economic predictions can provide directions for physical property research. ASPEN PLUS contains sensitivity modules which allows users to access stream or block variables and study the effect of these on the simulation results. However, ASPEN PLUS lacks the facility whereby the physical property inputs can be accessed. This has to be accomplished by a user-programmed FORTRAN subroutine.

In summary, ASPEN PLUS was found to be a powerful simulation tool with useful features such as property estimation, sensitivity, case study, and optimization modules. It contains extensive databases on pure component and mixture properties. The RBATCH module in ASPEN PLUS can be used to simulate a batch reactor and interface it with an otherwise steady-state flowsheet. However, there exist some limitations with the use of RBATCH, primary among which are lack of feed sequencing and heat profile generation capabilities. Some of these limitations can be overcome with batch reactor software such as BATCHCAD. The following discussion pertains to an optimization strategy which can be used once data and appropriate modeling tools are available.

The optimization of batch processes involves the prediction of optimal profiles for the operating variables. The feasibility of optimizing a process can be determined by the availability of robust and predictive process models, experimental data and verification, and powerful and flexible computational tools.

Specifically for the sulfolane process, the three main steps of the synthesis section should be modeled individually. Once a sufficient degree of accuracy can be achieved these individual models should be linked. The use of dynamic simulation in improving the predictive capabilities of the process model should be investigated. Operational constraints and environmental cost data should be gathered. The feasibility of optimizing the overall process model should then be determined. If it is found that optimizing the entire process model is not possible, the equipment models should be optimized individually while carefully considering the effect on downstream variables.

The optimization of each of three synthesis steps is discussed below. R1 operation can be optimized by considering variables such as feed charge time, cycle time, feed ratio, and alternative configurations. This requires a reactor model which can predict heat transfer characteristics. The physical property and kinetic data presently available are sufficient for optimization purposes. The vapor pressure of sulfolene is critical to the simulation and the optimization of this reactor because it affects the prediction of the vaporization of the reaction mixture.

Optimizing R3 requires information regarding the mechanism of the main and waste forming reactions. This should be supplemented with quantitative data on the rates of the heterogeneous process occurring during the reaction. This can be obtained through experimentation on a laboratory and process scale. A thorough knowledge of the reactor configuration and its cooling system is also essential. Since changing the hydrogenation solvent is an attractive option in terms of waste minimization, experimental study of solvent characteristics would help in choosing an 'optimal' alternative solvent. Based on these data the catalyst loading, alternative solvent operation, and cycle times for R3 can be optimized.

The operation of R2 can be optimized for alternative solvents. The optimal temperature, pressure, and solvent amount and its effect on the decomposition and freezing characteristics of the reaction mixture can be investigated through experimentation and thermodynamic modeling.

If the optimization is carried out using ASPEN PLUS, one would need to define an objective function and the applicable constraints. This is accomplished quite easily with the input language for ASPEN PLUS. Thus, in summary full optimization of the sulfolane process requires a combination of dynamic simulation, experimental data, and flexible optimization tools. The optimization of dynamic models is an extremely difficult task. However, this obstacle can be overcome by the use of a case study approach where the significant variables are varied manually within specific limits.

The following recommendations can be put forward on the basis of this study.

1) Vent relief pressure of the first reactor (R1) should be increased.
2) R1 should be operated with a butadiene charge time greater than 2 hours.
3) Continuous operation of the first reactor (R1) should be considered along with a reduction of the mixing in the reactor.
4) Improved sulfur dioxide removal in the treatment step should be accomplished by increasing the temperature of operation by about 10°F.
5) The operating pressure of the hydrogenation reactor should be increased to increase the solubility of hydrogen.
6) Change of the hydrogenation solvent should be considered. Suitable alternative solvents are sulfolane and isopropyl alcohol.

The primary recommendations for future study are:

1) To develop a quantitative understanding of the hydrogenation kinetics of sulfolene.
2) To perform experimental analysis of the effect of solvent, catalyst activity, and side reactions on the poisoning of the catalyst.

3) To study the possibility of recycling of sulfur dioxide and butadiene from the separation step (R2) to the first reactor (R1), and to identify the potential future scenarios in which this would be economically feasible.

4) To develop a dynamic model of the process using either SPEEDUP or BATCHCAD. Use the dynamic model to study the transient behavior of the first reactor (R1). Also, use the dynamic model to improve the predictive capabilities of the existing equipment models.

5) To perform a sensitivity analysis on the process model to determine the effect of uncertainty of property estimations and input variables on the model results.

6) To investigate how the uncertainty in process model inputs affects the predictions of the economics of the process, especially the environmental costs.

7) To formulate a general approach to forecast possible future scenarios and quantify the uncertainties involved in these scenarios.

8) Design alternative processes either with the existing process chemistry or with better and improved chemistries.

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APPENDICES

APPENDIX A

ASPEN PLUS INPUT FILES

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TITLE "ESTIMATION OF ANTOINE'S CONSTANTS FOR
SULFOLENE"

 PCES

 COMPONENTS SULFOLEN

 ESTIMATE ONLY
      PL SULFOLEN DATA

 PCES-PROP-DATA
       IN-UNITS SI
       PL SULFOLEN 310 900.9 / 320 1604.3 / 330 2743.2 /
                340 4521.5 / 350 7207.8 / 360 11145.5/
                370 16761.6 / 380 24574.3 / 390 35197.5/
                400 49344.1 / 410 67825.9 / 420 91552.4/
                430 121526.6
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TITLE "ESTIMATION OF HEAT OF FORMATION & SPECIFIC HEAT
OF  SULFOLENE"

 PCES


 IN-UNITS ENG

 DATABANKS ASPENPCD

 PROP-SOURCES ASPENPCD

 COMPONENTS
    C4 * C4

 PROP-DATA C4
    IN-UNITS ENG TEMPERATURE=C
    PROP-LIST TB
    PVAL C4 151

 ESTIMATE ALL

 STRUCTURES
    STRUCTURES C4 C1 C2 S / C2 C3 D / C3 C4 S / C4 S5  &
       S / S5 C1 S / S5 O6 D / S5 O7 D

 PROPERTY-REP PCES PROP-DATA
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VITA

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