A METHODOLOGY FOR INTEGRATING PROCESS DESIGN ELEMENTS WITH LABORATORY EXPERIMENTS

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A METHODOLOGY FOR INTEGRATING PROCESS DESIGN ELEMENTS WITH LABORATORY EXPERIMENTS

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A METHODOLOGY FOR INTEGRATING PROCESS DESIGN ELEMENTS WITH LABORATORY EXPERIMENTS

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Jeffrey Richard Seay was born in Montgomery, Alabama, on September 3, 1973. He graduated from Auburn University in Auburn, Alabama in 1996 with a Bachelor of Chemical Engineering, and from the University of South Alabama in Mobile, Alabama in 2004 with a Master of Science in Chemical Engineering. Jeffrey is a member of the Tau Beta Pi Engineering Honor Society, the Honor Society of Phi Kappa Phi, the Alpha Theta Chi Collegiate Honor Society, the Golden Key International Honour Society and is a member of the American Institute of Chemical Engineers. Jeffrey is currently employed by Evonik Degussa Corporation as a Senior Process Engineer and is a registered Professional Engineer in the state of Alabama. He currently resides in Mobile, Alabama, with his wife Lisa and his son William.

DISSERTATION ABSTRACT

A METHODOLOGY FOR INTEGRATING PROCESS DESIGN ELEMENTS WITH LABORATORY EXPERIMENTS

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This dissertation is the result of a joint project between industry and academia. The research was originally conceived as an industrial process development project based on the manufacture of industrial products from the catalytic dehydration of glycerol. However, as it has developed from an industrial research project into an academic dissertation, it has become a study in the development of a methodology for integrating the elements of conceptual process design and performance optimization with laboratory experimentation, minimization of potential environmental impacts and inherently safe process design. Therefore, the original research goal of developing an industrial glycerol dehydration process is presented as a detailed case study to illustrate this proposed

integration methodology. By taking a wider angle view, the benefits of this type of approach become clear.

A key element of the development of a truly integrated conceptual process design methodology is the laboratory data describing the system chemistry and operating conditions. This element is critical because the work of the process design engineer rests on a foundation of good data; however this data is often conceived and collected independently from the process design activities. This disconnect can often constrain the creativity of the design engineer. Indeed, the resulting process may in fact be driven not by the design engineer but rather by the conditions originally studied in the laboratory.

Therefore the primary purpose of this dissertation is to describe a methodology that integrates the simulation, modeling and process integration tools available to the design engineer with laboratory experimentation. Using the conceptual process design of the glycerol dehydration process as a detailed case study example, this proposed methodology will be illustrated. Although previous work on the glycerol dehydration process has so far failed to result in a commercially viable process, by the application of this methodology, this research shows that an industrially feasible process is possible.

Due to the proprietary nature of the data gathered as part of this research, this dissertation consists of two volumes. Volume one will be public and contain non-proprietary data and results. Volume two contains all proprietary data, and will be available only to the dissertation committee and industrial sponsor.

ACKNOWLEDGEMENTS

The project undertaken for this research has involved collaboration between two universities, an industrial partner and researchers on two continents. Due to this complexity the guidance and assistance of many people was needed to make it a success, all of whom I would like to thank and acknowledge. First I would like to thank my research committee, Mario Eden, Chris Roberts, Tom Thomas, Jin Wang and Robert D'Alessandro for guidance and support during this research project. I would also like to thank Herbert Riemenschneider, Evonik Degussa Director of Technology and Process, for his support of this project and the Evonik Degussa GmbH Feed Additives business unit for providing funding and facilities for this research. Additionally, I would like to thank the following people, without whom this project would not have been possible: All the Mobile Site FA personnel, especially Kerry Raynor, Kerry Hill, Alan Brewer, Kevin Jordan and Butch Maddox; my colleagues on the Mobile Site who worked so hard to help me keep my laboratory equipment working, Shawn Eley, Ed Harris, Ken Mead, Jim Cook, Ted McCafferty, Joe Duke and Tracey Mole; Evonik Degussa intern students Astrid Roesner, Maria Schley, Mareike Schaum, Stephan Adelmann and Holger Werhan, who I hope enjoyed learning as much as I enjoyed teaching them; and finally, my research colleagues from Evonik Degussa in Hanau, Germany, Christoph Weckbecker, Hubert Redlingshoefer and Klaus Huthmacher. To each of you – Thank you.

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NOMENCLATURE

Symbol		Units
C_{A0}	Concentration of Component A	kmol/m^3
F_{A0}	Flow rate of Component A	kmol/hr
ΔH_f	Heat of Formation	kJ/kmol
ΔH_r	Heat of Reaction	kJ/kmol
I_t	Amount of PEI of the chemical process plus energy generation process	PEI/kg
$\dot{I}_{in}^{(cp)}$	Input rate of PEI impact to the chemical process	PEI/kg
$\dot{I}_{out}^{(cp)}$	Output rate of PEI impact to the chemical process	PEI/kg
$\dot{I}_{in}^{(ep)}$	Input rates of PEI impact to the energy generation process	PEI/kg
$\dot{I}_{out}^{(ep)}$	Output rate of PEI impact to the energy generation process	PEI/kg
$\dot{I}_{we}^{(cp)}$	Output of PEI for waste energy lost from the chemical process	PEI/kg
$\dot{I}_{we}^{(ep)}$	Outputs of PEI for waste energy lost from the energy generation process	PEI/kg
$\dot{I}_{gen}^{(t)}$	Rate of generation of PEI inside the system	PEI/kg
k_j	Rate Constant of Reaction *j*	s^{-1}
k^0_j	Frequency Factor for Reaction *j*	mol/kg·s·bar
M_T	Thiele Modulus	[-]
R	Recycle Rate	[-]
r_{ij}	Reaction Rate of Reaction *j* Component *i*	kmol/m^3·s

t	Time	s
U	Control Signal	[-]
V	Volume	m^3
W	Mass Flow Rate	kg/s
X	Reaction Conversion	[-]
Y	Control Variable	[-]
Y_s	Control Variable Set Point	[-]

CHAPTER 1

INTRODUCTION

The research project undertaken for this dissertation is a collaborative effort between Evonik Degussa Corporation in the United States, Evonik Degussa GmbH in Germany, Auburn University and the University of South Alabama. Organizing a dissertation project among industrial and academic partners can be challenging enough, but what has made this project unique is that the laboratory research has been carried out on the Evonik Degussa Corporation site in Mobile, Alabama. Additionally, the required coursework has been completed through the Auburn University Graduate Outreach Program.

This research project was originally conceived as a conceptual process development project for the production of an industrial chemical from renewable, bio-based feed stocks. The original objectives included the development of a conceptual process and an assessment of its overall performance. In general, there are multiple ways of evaluating process performance. In the case of this research, the metrics used to determine the performance of the process will not be revealed due to the business sensitive nature of this information. Therefore, performance will be reported as a normalized index value. For this analysis, a minimum value of the normalized performance index will indicate a better performing process.

In addition to the conceptual process development activities, laboratory experiments were to be carried out to gather the data needed for the process design activities. However, this industrial project in and of itself would not necessarily have contained sufficient academic rigor for a Ph.D. dissertation. To address this concern, the original project scope was expanded and incorporated into other research work being done at Auburn University in systems engineering. In this way, the project was given a broader scope, yet the original goals were preserved by including the industrial application as a case study. The unique organization of this project and the challenges of working with such diverse groups of researchers are described in Chapter 3. This chapter was originally written as a journal article co-authored with Mario Eden titled “Challenges of Implementing a Joint Industrial - Academic Partnership” and has been accepted for publication in the *Journal of Chemical Engineering Education* (Seay and Eden, 2008-1).

The aspect of this dissertation that links the industrial case study with the research in systems engineering is the development of a conceptual process. Although the field of chemical engineering has expanded greatly in scope over the last few decades, the primary function of a chemical engineer in modern industry remains the design, construction, safe operation, management, and maintenance of chemical production facilities. The scope of this dissertation will center on the activities of conceptual process design. Process design requires that the design engineer has achieved an ability to apply the tools of heat and material balances, thermodynamics, reactor design, unit operations, process control and transport phenomena to a wide range of potential processes. Furthermore, a thorough conceptual process design must also include an assessment of the safety, environmental and performance impacts of the proposed process. Indeed, the culmination of an education in chemical engineering is proving the ability to turn these elements into commercially viable and technically feasible processes. That said, the foundation of an integrated process based on novel chemistry is good laboratory data, gathered under conditions that lead to viable and technically feasible processes. Therefore, the purpose of this dissertation is:

To provide a means for ensuring that the experimental data for process design are gathered under conditions that will lead to technically feasible and viable processes in terms of overall performance.

Based on this stated purpose, the central theme of this dissertation is the integration of laboratory experimentation with process simulation and modeling in the design and development of a conceptual process. The primary contribution of this research can therefore be described as:

The development of a concise and widely-applicable methodology for integrating conceptual process design activities with laboratory experimentation, environmental impact assessment and inherently safe process design.

The methodology developed to achieve this stated research objective consists of five steps:

- Data gathering and preliminary laboratory investigations to determine the feasibility of the proposed process chemistry.
- Application of simulation and optimization methodology to determine the options for process development. The result of this step is the determination of the initial design conditions.

- Laboratory experimentation to validate the assumptions made during the initial simulations and optimization steps.
- Additional application of the simulation and optimization methodology to incorporate the laboratory results.
- Additional laboratory experiments to validate process changes suggested by simulation results and to optimize the reactor operating conditions.

To illustrate this proposed methodology, a flow chart will be presented that outlines the five individual steps included in the procedure. This flowchart will serve as the model for the integration activities included in this research. This flowchart and a description of each of the five steps are included in Chapter 4. This chapter is a revised and expanded version of a journal article titled "Integration of Process Modeling with Laboratory Experiments in Conceptual Design: Bio-based Glycerol Dehydration Case Study". The article, co-authored with Mario Eden, Robert D'Alessandro, Thomas Thomas, Hubert Redlingshoefer, Christoph Weckbecker and Klaus Huthmacher, was published in 2007 in the Elsevier book series *Computer Aided Process Engineering* Volume 22A, edited by V. Plesu and P.S. Agachi (Seay *et al.*, 2007). Subsequent chapters describe how each step of the methodology was applied to the industrial case study used as the basis for the research.

Step 1 of the methodology involves gathering the initial data for the proposed process and is described in more detail in Chapter 5. This preliminary data can be gathered from literature sources or collected from preliminary laboratory experimentation. The primary purpose of Step 1 is to determine the general technical feasibility of the process chemistry and to determine the general process operating conditions of the proposed reactions. Sections of Chapter 5 have been previously published in a journal article titled “Sustainable Production of Industrial Chemical Products from Bioresources”. The article, co-authored with Mario Eden, Robert D’Alessandro and Christoph Weckbecker was published in 2006 in the Elsevier book series *Computer Aided Process Engineering* Volume 21A, Edited by W. Marquardt and C. Pantelides (Seay *et al*., 2006).

Step 2, which is described in Chapters 5, 6 and 7, consists of applying a generalized process design methodology. In this stage of the development, process configuration and recycle options are proposed and evaluated using standard design heuristics. Once the models are created, an evaluation based on overall process performance and potential environmental impacts can be completed, as described in Step 2 of the methodology. The results from Step 1 and Step 2 are then used to guide the laboratory experiments, which make up Step 3 of the proposed methodology. An example of the application of risk assessment and inherently safe design practices is included in Chapter 6. This chapter is adapted from a journal article co-authored with Mario Eden titled “Incorporating Risk Assessment into Chemical Engineering Education“ which has been accepted for publication in the *Journal of Chemical Engineering Education* (Seay and Eden, 2008 – 2).

Step 3 of the methodology is the validation of the simulation models by laboratory experimentation. The design and function of the laboratory scale mini-plant used to test and validate the proposed process is described in Chapter 8. Using the experimental results, the process simulation models are updated to reflect the measured process data. This is accomplished by once again applying the generalized process design methodology. This procedure is Step 4 of the methodology, described in detail in Chapter 9. In this way, the experimental work and the simulation are integrated to ensure that not only are the proposed simulations based on technically feasible operating conditions, but also that the experiments are carried out with operating ranges that lead to viable processes in terms of performance. Because of this integration of laboratory work and simulation work, this step holds the greatest potential for innovation.

Step 5 of the methodology is to optimize the operating conditions for the conceptual process resulting from Step 4. Statistical design of experiments (DOE) techniques are used to determine the optimum process operating conditions. This optimization work is described in Chapter 10. By following the proposed methodology illustrated by the industrial case study, it is shown that by integrating laboratory experimentation and environmental impact assessment with the standard heuristics of process design and heat integration, a truly optimized process can be achieved. The research presented in Chapter 10 is adapted from a journal article co-authored with Mario Eden, Robert D'Alessandro, Thomas Thomas, Hubert Redlingshoefer, Christoph Weckbecker and Klaus Huthmacher titled "Integrating Laboratory Experiments with Process Simulation for Reactor Optimization" which has been accepted for publication in the Elsevier book series *Computer Aided Process Engineering* (Seay *et al,* 2008).

In order to design and build an industrial scale reactor, information about the detailed reaction kinetics is needed. The development of a simplified kinetic model is described in Chapter 11. The use of sophisticated computer tools to automate the search for an appropriate kinetic model based on the proposed mechanism for the reaction system is also described. Finally, the research achievements and conclusions from this dissertation are described in Chapter 12.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Introduction

This dissertation is the result of a joint research project between Evonik Degussa Corporation, the University of South Alabama and Auburn University. The purpose of the research project is to develop a methodology for integrating laboratory experiments with process design. This methodology incorporates laboratory experimentation with process simulation and optimization techniques based on standard process design heuristics. Furthermore, potential environmental impacts and inherently safe design practices are incorporated into the process development methodology. The proposed methodology is illustrated using a case study example based on the development of an industrial process for the catalytic dehydration of glycerol. The justification for this process is to utilize the crude glycerol generated as a side product from the production of biodiesel from fatty acids. The successful implementation of a process based on the results of this research will also benefit the performance and overall sustainability of the biodiesel process by providing commercially viable uses for the glycerol side product.

2.2 Process Design and Synthesis

2.2.1 Hierarchical Approach

A chemical process can be divided into a few general and widely applicable systems. These sections may include:

- Raw material storage and delivery systems
- Reaction systems
- Separation systems
- Recycle and integration systems
- Product storage and transport systems.

By considering how each of these individual systems works together, a holistic approach can be applied to the conceptual design problem. Early work on the development of a structured approach to process design based on hierarchical techniques and standard design heuristics has been described by Douglas (1988) in his book, *Conceptual Design of Chemical Processes*. In this work, the development of a conceptual process design is divided into 5 levels (Douglas, 1985)(Douglas, 1988):

- Level 1: Batch vs. continuous
- Level 2: Input-output structure of the flow sheet
- Level 3: Reactor and recycle structure of the flow sheet
- Level 4: Separation system synthesis
- Level 5: Heat recovery network.

Since then, the work of Douglas has been further advanced in widely used process design textbooks by Seider (1999) and Biegler *et al.*, (1997). Biegler states that the principle steps of process synthesis are as follows:

- Gathering information
- Representation of alternatives
- Assessment of preliminary designs
- Generation and searching among alternatives.

In general, these techniques rely on a knowledge-based approach. Although these techniques can be applied quite successfully to systems based on well established chemistry, they do not address the gathering of the experimental data needed to design a process based on newly developed chemistry.

2.2.2 Integration of Laboratory Experimentation

This omission has begun to be addressed in other ongoing work in this area by Kiss *et al.* (2006), regarding the linking of experiments to modeling in biodiesel production. The purpose of the research study presented by Kiss *et al.* is the development of a new catalyst for biodiesel manufacturing. In this research, process simulation is used to set the design targets for the laboratory experimentation. The experimental program for the new chemistry proposed is streamlined by ensuring that the experiments are based on parameters that lead to feasible processes. The methodology proposed by Kiss *et al.* is illustrated in Figure 2.1, below.

Kiss *et al.* points out that the disconnect between the chemists who typically carry out the kinetic experiments and the design engineers who must use the data to develop conceptual process models can lead to design failures since the conditions considered in the lab may not lead to feasible conceptual processes. Using the methodology developed by Kiss *et al.*, economic considerations based on simulation models are used to set the minimum kinetic requirements for the catalysts being evaluated for biodiesel production. Therefore, the process development can be streamlined.

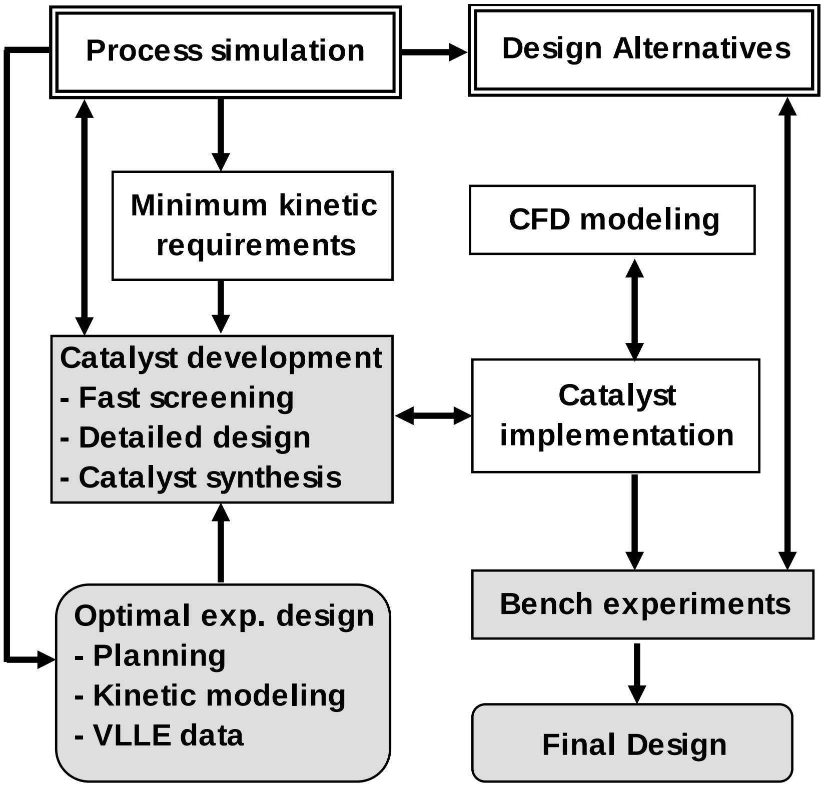

Figure 2.1. Methodology for linking simulation to experimentation (Kiss *et al.*, 2006).

In the contribution from Kiss *et al.*, the scope of the process design activities has been expanded to include the additional elements of laboratory experimentation. The research presented in this dissertation further advances this work to broaden the scope of conceptual process design by including laboratory experimentation, environmental considerations and inherently safe process design.

2.3 Process Design for Sustainability

2.3.1 System-based Environmental Management

In recent years, much attention has been focused on the impact human activities have on the global environment. The effects of using crude oil derived fuels and feed stocks on the global climate, and the importance of pursuing the use of sustainable raw material feed stocks has been well documented (Clift, 2005)(Hoel and Kverndokk, 1996)(Vicente, 2004). One of the principle challenges in the quest for sustainable process design is determining exactly what sustainable design means. One definition that has been proposed is as follows (Sikdar, 2003): *Sustainability occurs when we maintain or improve the material and social conditions for human health and the environment over time without exceeding the ecological capabilities that support them.*

Another definition proposed by Bakshi *et al.* (2003), is as follows: *A sustainable product or process is one that constrains resource consumption and waste generation to an acceptable level, makes a positive contribution to the satisfaction of human needs and provides enduring economic value to the business enterprise.*

Although these proposed definitions are easy to understand on a conceptual level, they remain vague in defining how sustainability can be quantified. A more systematic approach is needed to define what is meant by sustainable design. Recently, the idea of system-based environmental management has been proposed (Clift, 2005). This idea is based on the fusion of chemical engineering principles with the tools of other disciplines, such as environmental sciences, toxicology and economics. Clift summarizes three tools for applying a system-based approach to sustainable design:

- Material Flow Accounting (MFA)
- Life Cycle Assessment (LCA)
- Industrial ecology.

These tools can be used in different ways to determine the impact of a process on the environment. MFA is a material balance approach that can be used to estimate raw material consumption and waste generation. Whereas MFA is applied more to an individual process, LCA focuses on the impacts of the entire supply chain. The LCA approach is referred to as a “cradle to grave” approach because it encompasses the entire lifecycle of a product or process (Clift, 2005). Finally, industrial ecology is based on minimizing the impact of processes through interconnection between processes or groups of processes. One example of industrial ecology is finding economically viable uses for the waste products generated from a process, so that those wastes do not end up being discharged to the environment. This aspect of sustainable development is the focus of this dissertation, by identifying industrial uses for the glycerol generated as a byproduct of biodiesel manufacturing.

2.3.2 Impacts of Bio-based Resources

Since 1750 AD, the carbon dioxide content in the world atmosphere has increased from 280 ppm (+/- 10) to 360 ppm (DeNevers, 2000). This corresponds to an annual increase in carbon dioxide concentration of 1.5 ppm/year (DeNevers, 2000). Because of the potential adverse effects of increased atmospheric carbon dioxide concentration, it is imperative to develop technologies that minimize the generation of carbon dioxide.

In terms of energy production, biodiesel is the only alternative with an overall positive lifecycle energy balance (Buczek and Czepiriski, 2004). Therefore use of biodiesel and its byproducts may have a positive impact on global climate change. In addition, according to the U.S. Department of Energy's 2003 *World Energy Report*, at current rates of consumption, crude oil reserves may be depleted in 80 to 120 years (DOE, 2003). This provides an additional incentive for replacing crude oil derived fuel sources with sustainable sources, such as biodiesel.

Recent estimates predict that the demand for biodiesel will grow from 6 to 9 million metric tons per year in the United States and from 5 to 14 million metric tons per year in the European Union in the next few years (Blume and Hearn, 2007). The vegetable oils used as biofuel sources have viscosities 20 or more times higher than standard petroleum based diesel fuel (Barnwal and Sharma, 2005). Therefore, the triglycerides that compose vegetable oil must be split into the component fatty acids and glycerol. It is the fatty acids that are then used as the source of the biodiesel fuel. The glycerol from the triglyceride molecule is then left as a waste product. In fact, for every 9 kilograms of biodiesel produced, 1 kilogram of crude glycerol is formed as a byproduct (Chiu *et al.*, 2005). Therefore, the identification of novel industrial uses for this glycerol is important to the economic viability of biodiesel (USDA, 2003).

2.4 Process Integration

2.4.1 Scope of Process Integration

An important aspect of systems engineering is the evaluation of multiple process options to determine the most technically feasible and economically viable process configuration. Process integration is a holistic approach to process design that emphasizes the unity of the process (El-Halwagi, 1997). El-Halwagi defines three key components of process integration:

- Process synthesis
- Process analysis
- Process optimization.

Process synthesis is the step in which individual unit operations are linked to create an interconnected process. The ultimate goal of this step is a flow sheet that meets the design objectives of the process. The second step, process analysis, involves decomposing the process into its individual elements so that the performance of each element can be studied separately (Biegler *et al.*, 1997)(El-Halwagi, 1997). The process analysis step may involve using such tools as mathematical models, empirical correlations or computer aided simulation tools (El-Halwagi, 1997). Additionally, lab experimentation may be included in the process analysis. Finally, the process optimization step involves the selection of the “best” solution from among a set of potential process options (El-Halwagi, 1997).

Energy integration, an important subset of process integration, has been introduced in recent years. Energy integration has been defined by El-Halwagi (1997) as: *A systematic methodology that provides a fundamental understanding of energy* *utilization within the process and employs this understanding in identifying targets and optimizing heat-recovery and energy-utility systems.*

This systematic methodology is used to determine the optimum utilization of heating and cooling energy within a process. Thermal pinch analysis is the principle tool for determining this optimum.

2.4.2 Heat Exchanger Networks

Due to the rising costs of energy in the United States, developing heat integrated processes is important to achieve a process that is optimized in terms of performance. An important tool for achieving this goal is thermal pinch analysis. The goal of heat integration is the development of a heat exchanger network (HEN) that distributes the energy requirements throughout a process in order to optimize the external utility requirements. Increased energy integration enables higher utilization of raw materials and minimizes the use of external utilities (El-Halwagi and Spriggs, 1998)(Linnhoff *et al*., 1979). In general the identification of the minimum external utility requirement of a process is done by identifying the hot and cold streams within a process. By definition, a cold stream is a stream requiring heating and a hot stream is a stream requiring cooling. The minimum external utility requirement is then determined by matching the cooling potential of cold streams with the heating potential of hot streams. After making all thermodynamically possible matches between hot and cold streams, the left over heating and cooling duty is the minimum external requirement. The HEN is then designed by optimizing the cost of the external utilities with the cost of the heat exchangers required to transfer the process heat loads. The solution to the optimal HEN design can be achieved by providing answers to the following questions (El-Halwagi, 1997):

- Which heating and/or cooling utilities should be used?
- What is the optimal energy load to be removed or added by each utility?
- How should the process hot and cold streams be matched, i.e. stream pairings?
- What is the optimal system configuration, i.e. how should the heat exchangers be arranged? Do any streams require mixing or splitting?

Preliminary work on developing methods for identifying the minimum utility requirements for a HEN was done by Hohmann (1971). Other early research to develop this technique was done by Linnhoff *et al*. (1979), Linnhoff and Hindmarsh (1983), Linnhoff and Ahmad, (1990-1) and Linnhoff and Ahmad (1990-2). The tool used for determining the potential for the internal transfer of heat between process streams is thermal pinch analysis. The thermal pinch is a thermodynamic boundary that allows the heat integration problem to be solved by dividing it into two smaller subproblems with their own solutions, one above the thermal pinch and one below (Ebrahim, 2000).

In determining the thermal pinch for a given process, a graphical technique is often employed to easily identify the pinch location. This graphical technique involves the construction of composite curves for the hot (heat supplying) and cold (heat gaining) process streams. The heat exchange capacity for each hot and cold stream is calculated. This heat exchange capacity is then plotted for the temperature range over which the hot streams must be cooled and the cold streams must be heated. From the plot of these two composite curves, the thermal pinch point is identified. In addition, the minimum hot utility and cold utility requirements can be easily identified. The minimum utility requirement is simply the left over heating and cooling requirements after all feasible transfer of process heat has occurred. An example of this graphical technique is illustrated in Figure 2.2, below (Ebrahim, 2000). In this example, the process consists of three hot streams and three cold streams. From this example, the location of the thermal pinch and the minimum external hot and cold utility requirements are easy to determine. The minimum ΔT is simply the minimum temperature driving force required to reasonably transfer heat between hot and cold streams. The ΔT of the system is the principle optimization variable. Lower ΔT leads to a decrease in the use of required external heating and cooling utilities; however, it also leads to an increased capital cost due to the increase in heat transfer area required for the HEN.

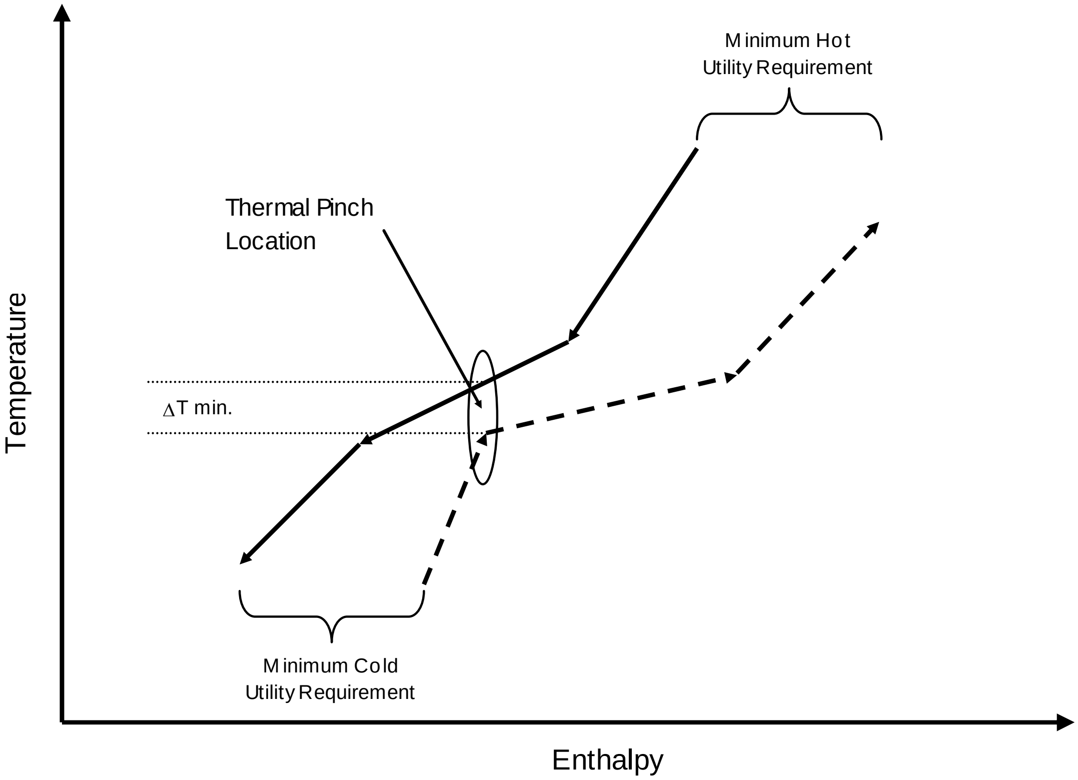

Figure 2.2. Hot and cold composite diagram example (Ebrahim, 2000).

After identifying the pinch, the HEN can be designed based on three rules (Linnhoff, 1983):

- Do not transfer heat across the pinch.
- Do not use external cooling utilities above the pinch.
- Do not use external heating utilities below the pinch.

A HEN designed based on these rules will achieve the minimum external utility requirement. A violation of any of the above stated rules will result in the additional usage of external heating or cooling utilities. Recently this technique has been incorporated into a software package called HX-Net currently marketed by Aspen Technology in Cambridge, MA (2006). Integrating the use of this tool into the early stages of design will ensure that the proposed conceptual processes are designed with optimal energy utilization.

2.5 Environmental Impact Assessment

2.5.1 Design Integration of Environmental Assessment

Often the criteria used in developing conceptual options for a proposed process is based solely on performance criteria. Although the importance of process performance should not be minimized, the environmental impacts of a new process should not be ignored. There are a multitude of potential benefits for minimizing the environmental impacts of a proposed conceptual process:

- Potential new environmental regulations
- Emissions trading opportunities
- Potential increased costs of “after the fact” means of emissions abatement.

2.5.2 Waste Reduction Algorithm

By taking an integrated approach, an optimized design that considers both business viability and minimum environmental impacts can be proposed. An available tool for calculating the potential environmental impact (PEI) of a process is the Waste Reduction (WAR) algorithm developed by Cabezas *et al.* (1999), for the U.S. Environmental Protection Agency. Further work by Young and Cabezas (1999) and Young *et al*. (2000) presents case studies detailing the use of the WAR algorithm as an integrated part of process design. These works demonstrate a significant step in the use of environmental impact assessment tools in the development of conceptual processes.

The PEI is a quantitative means of indicating the environmentally friendliness of a process (Young and Cabezas, 1999)(Young *et al*., 2000). The PEI of a given quantity of material and energy can be defined as the effect this material or energy would have if it were emitted directly to the environment (Young and Cabezas, 1999)(Young *et al*., 2000). The PEI for a process is made up of 8 categories of environmental impacts (Cabezas, *et al.*, 1999). The individual weighting for each of these categories can be changed, depending on the emphasis of the study.

- Human Toxicity: Ingestion
- Human Toxicity: Dermal/Inhalation
- Aquatic Toxicity
- Terrestrial Toxicity
- Global Warming
- Ozone Depletion
- Photochemical Oxidation

- Acidification.

Based on the categories above, the PEI balance for a process and energy generation system can be shown by equation 2.1.

$$\frac{\partial I_t}{\partial t} = \dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} - \dot{I}_{we}^{(cp)} - \dot{I}_{we}^{(ep)} + \dot{I}_{gen}^{(t)} \qquad \text{(Eqn. 2.1)}$$

In this equation, I_t is the amount of PEI of the chemical process plus energy generation process, $\dot{I}_{in}^{(cp)}$ and $\dot{I}_{out}^{(cp)}$ are the input and output rates of PEI impact to the chemical process, $\dot{I}_{in}^{(ep)}$ and $\dot{I}_{out}^{(ep)}$ are the input and output rates of PEI impact to the energy generation process, $\dot{I}_{we}^{(ep)}$ and $\dot{I}_{we}^{(ep)}$ are the outputs of PEI associated with waste energy lost from the chemical process and energy generation process and $\dot{I}_{gen}^{(t)}$ is the rate of generation of PEI inside the system (Young and Cabezas, 1999).

For steady state processes, equation 2.1 can be simplified, as shown in equation 2.2.

$$0 = \dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} - \dot{I}_{we}^{(cp)} - \dot{I}_{we}^{(ep)} + \dot{I}_{gen}^{(t)} \qquad \text{(Eqn. 2.2)}$$

This equation can be further simplified by assuming that the waste energy emissions for the chemical process and energy process are negligible (Young and Cabezas, 1999). The result of this simplification is shown in equation 2.3.

$$0 = \dot{I}_{in}^{(cp)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} + \dot{I}_{gen}^{(t)} \qquad \text{(Eqn. 2.3)}$$

Equation 2.3 can be further rewritten as shown in equation 2.4,

$$0 = \dot{I}_{in}^{(t)} - \dot{I}_{out}^{(t)} + \dot{I}_{gen}^{(t)} \tag{Eqn. 2.4}$$

where, $\dot{I}_{in}^{(t)}$ is defined as the total PEI that resides in the mass inputs to the manufacturing / energy generation process (Young and Cabezas, 1999). The result of this balance is the PEI for a process. This balance is illustrated in Figure 2.3, below.

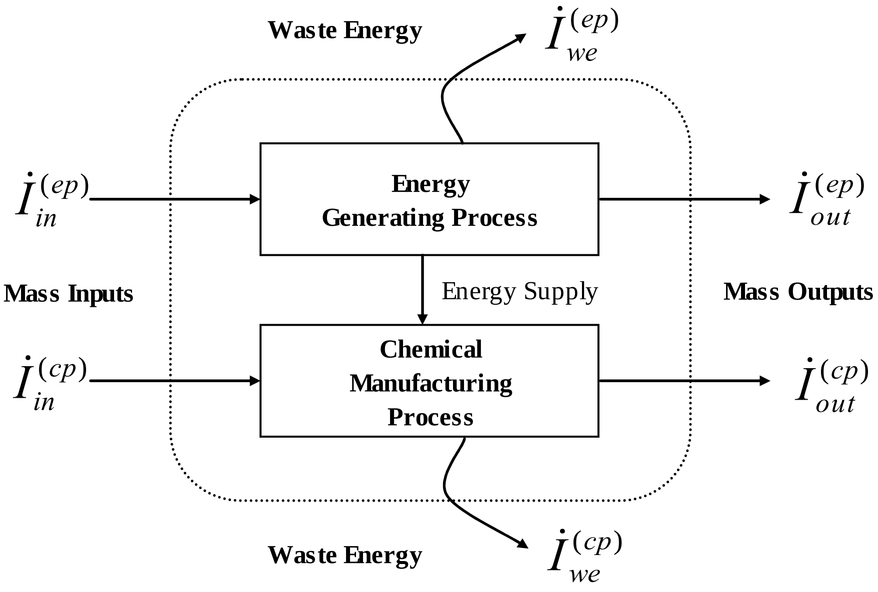

Figure 2.3. Inputs and outputs incorporated into the WAR algorithm (Young and Cabezas, 1999).

It should be noted that there are some important limitations to using the WAR algorithm for an analysis of this type. Although the WAR algorithm provides an effective means of comparing process options with a similar basis, it cannot evaluate the impacts of switching from a crude oil to a renewable, biomass derived feed stock. Therefore one should use caution when directly comparing the PEI calculated for sustainable processes with that calculated for processes based on crude oil derived feedstocks.

2.6 Inherently Safe Process Design

Process safety is a fundamental component of sound process design. Although the chemical industry has demonstrated an excellent safety record over the years (Sanders, 2005), the quantities and hazardous nature of many of the substances typically handled by chemical manufacturers make the potential for large scale disasters a constant concern. In industry, the concept of process safety is firmly rooted in the concept of risk. From government regulatory requirements, such as those outlined by OSHA and the EPA (Nelson, 2003)(EPA, 2005)(OSHA, 2005), to industry initiatives such as Responsible Care®, the requirement of quantifying and managing risk is paramount. In addition to working within performance and environmental constraints, the process design engineer is also tasked with reducing the risk of operating a chemical manufacturing process to a level acceptable to employees, regulatory authorities, insurance underwriters and the community at large.

2.6.1 Quantifying Risk

In order to begin understanding the benefits of inherently safer process design, it is important to first understand the concept of risk. The concept of risk is often misunderstood by both chemical engineers and the general public. It is important to separate the concept of risk, from the concept of hazard. While the concept of hazard relates to the *potential* for adverse consequences, risk is rather a combination of both the *severity* of an upset scenario and the *likelihood* of that event occurring. This is an important distinction. The potential hazard associated with a substance or process is an inherent property that cannot be changed. The risk associated with handling a substance or operating a process can be high or low, depending upon the safeguards that are included in the design. Thus, for chemical engineers, the most important distinction between hazard and risk is that risk can be reduced through process design.

In order to begin to discuss risk, the process design engineer must first consider potential upset scenarios. In other words, answer the question, “What is the worst thing that can happen?” Answers to this question typically involve loss of containment of a process chemical with causes ranging from failure of control loops and operator errors to external events such as fire, among many others. It is critical to note that the answers to the aforementioned question must be considered independently of the likelihood of the worst case scenario occurring. Again, it is the combination of both the severity and the likelihood that determines the risk. In order to ensure a complete and consistent assessment of potential upset scenarios, a structured approach must be applied. The need for such an approach is the basis for a Process Hazard Analysis.

2.6.2 Process Hazard Analysis

A Process Hazard Analysis (PHA) is a methodology for reviewing and assessing the potential hazards of a chemical process by utilizing a structured, facilitated team brainstorming approach. A PHA is typically facilitated by a trained team leader and attended by a wide variety of plant personnel, including engineers, managers, operators, maintenance technicians and safety, health and environmental (SHE) personnel.

Although several techniques are available for performing PHAs (EPA, 2005), the goal of the PHA is always the same – to identify the potential hazards of a process and determine whether sufficient safeguards are in place to mitigate those hazards.

Typically, however, a PHA is conducted at a later stage of engineering development. Although the PHA is a vitally important tool, it is very beneficial to begin evaluating inherently safer design strategies at the earliest stages of process development, when the process design engineer has the greatest opportunity to affect the safety aspects of the process.

2.6.3 Design for Safety

Inherently safe process design practices can generally be grouped into five categories (Kletz, 1998)(CCPS, 1993):

- Intensification
- Substitution
- Attenuation
- Limitation of effects
- Simplification.

Some examples of how each of these categories can be applied are listed in Table 2.1 below.

Table 2.1. Potential opportunities for making inherently safer design choices (Kletz, 1998).

Process Design Choice	Inherently Safe Design Category	Potential Process Safety Impact
Reactor type	Intensification	Continuous reactors are typically smaller than batch reactors for a given production volume.
Feed stocks	Substitution	Less hazardous raw materials may be available to make the same products.
Process solvents	Substitution	Less hazardous and/or less volatile solvents may be available.
Reaction mechanism	Attenuation	Endothermic reactions present less potential for runaway.
Operating conditions	Attenuation	Temperatures and pressures close to ambient are typically less hazardous.
Process utilities	Attenuation	Low pressure utilities such as hot oil may be a safer choice than high pressure steam.
Alternative technology	Attenuation	Use of alternative technology, for example pervaporation instead of azeotropic distillation using a solvent entrainer.
Production rate	Limitation of effects	A continuous process making just what is required can be safer that a batch process with a large hold-up volume.
Storage volume	Limitation of effects	Minimization of volume limits the potential effects of a release.
Equipment layout	Simplification	Utilizing gravity flow minimizes the need for rotating equipment.
Cooling by natural convection	Simplification	Utilizing natural convection simplifies the process and eliminates the potential for process upsets due to loss of utilities.

Initially, inherently safer designs may seem to be more expensive than applying traditional safeguards to processes. However when the total cost of the process is considered, the inherently safer design is often more cost effective. Installing and maintaining multiple independent layers of protection can be quite expensive, however these costs are often ignored during initial cost estimates. Conceptual phase cost estimates are usually based on stand-alone major equipment costs that are simply multiplied by factors to obtain the total installed cost. These factors are intended to account for instrumentation and controls, among other items needed for the complete process installation. However, to apply the same factors to traditional and inherently safer processes can lead to an erroneous comparison and conclusion. Inherently safer processes will typically require fewer safety controls which leads to lower installation and operating costs. These factors should be considered when evaluating processes during a hierarchical approach to process design. Additional cost savings for inherently safer processes that are often overlooked include insurance costs and the costs associated with regulatory compliance.

The research presented on the development of a conceptual process for glycerol dehydration based on integrating design and simulation with laboratory experimentation incorporates the fundamentals of inherently safe process design. This integration ensures that safety, along with economics and environmental protection, is a vital element of the conceptual design process (Ulrich and Palligarnai, 2006).

2.7 Reaction Pathway Discovery

Previous research has suggested that the catalytic dehydration of glycerol can be successfully carried out in either the liquid or vapor phase (Neher *et al*., 1995). It has also been shown that the dehydration reaction can be carried out in the supercritical water phase (Ramayya *et al*., 1987). A wide variety of industrially important chemical products are possible from this dehydration reaction. Hydroxyacetone (acetol), 3-hydroxypropionaldehyde, acrolein, acetaldehyde and formaldehyde are all potential chemical products (Neher *et al*., 1995)(Chiu *et al.*, 2006)(Antal *et al.*, 1985)(Ramayya *et al*., 1987). Further reactions with these products can lead to other industrially important chemical species. Hydrogenation of hydroxyacetone or 3-hydroxypropionaldehyde can produce 1,2-propanediol (also called propylene glycol) and 1,3-propanediol respectively (Zhu and Hofmann, 2004)(Miyazawa, 2006)(Casale and Gomez, 1993)(Casale and

Gomez, 1994)(Chiu *et al.*, 2006). Hydrogenation of acrolein can produce propanol, propionaldehyde or allyl alcohol (Smith, 1963). Oxidation of acrolein can produce acrylic acid (Neher *et al*., 1995)(Weigert and Haschke, 1976)(Etzkorn *et al.*, 2001)(Ramayya *et al*., 1987)(Bub *et al.*, 2006). The identity and yield of the dehydration products are a function of the catalyst used and of the operating conditions of the reactor. This research will focus on the acid catalyzed dehydration of glycerol, as described by Neher *et al*. (1995). However, the integration methodology developed from this research is general in form and could successfully be applied to the development of a process for the manufacture of any of these chemical species. Only the operating conditions and catalyst would need to be customized for the desired product.

2.7.1 Initial Glycerol Dehydration Step

The initial step in the proposed pathway is the elimination of one mole of water from the glycerol. This reaction can result in two possible products, hydroxyacetone or 3-hydroxypropionaldehyde (Miyazawa, 2006)(Chiu *et al.*, 2006). This reaction is illustrated in Figure 2.4, below. Under the reaction conditions considered for this research project, the formation of 3-hydroxypropionaldehyde is favored.

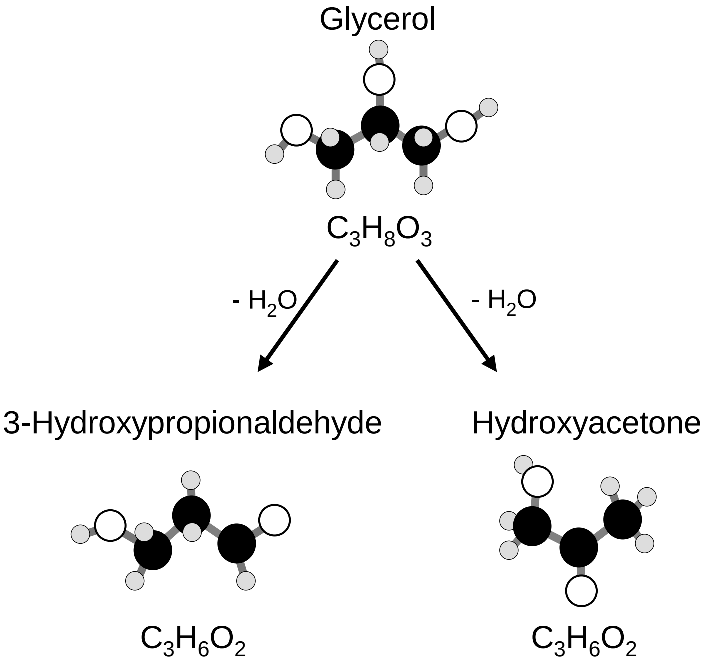

Figure 2.4. Initial acid catalyzed glycerol dehydration step.

2.7.2 Reaction with Hydroxyacetone

In an inert gas or water vapor atmosphere, the hydroxyacetone generated in the initial dehydration step is stable and can be collected as a product. However, under certain conditions it can undergo further reactions. The principle reaction of industrial importance among these occurs in the presence of hydrogen where hydroxyacetone can be hydrogenated to produce 1,2-propanediol (Casale and Gomez, 1993)(Casale and Gomez, 1994)(Chiu *et al.*, 2006) or as it is also called, propylene glycol (Chiu *et al.*, 2006). This reaction is illustrated in Figure 2.5, below.

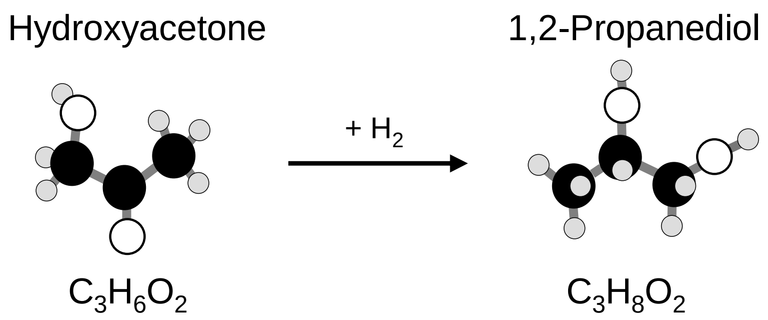

Figure 2.5. Catalyzed hydrogenation of hydroxyacetone.

2.7.3 Reactions with 3-Hydroxypropionaldehyde

The 3-hydroxypropionaldehyde generated in the initial dehydration step is highly reactive and will further react in the presence of the acid catalyst to generate a number of additional products, depending on the conditions in the reactor. In one possible reaction, the 3-hydroxypropionaldehyde directly decomposes to form acetaldehyde and formaldehyde.

It should be noted that formaldehyde is generally unstable under high temperature conditions and will further decompose into hydrogen and carbon monoxide (Ramayya *et al.*, 1987). In addition, the 3-hydroxypropionaldehyde can be further dehydrated to form acrolein (Neher *et al.*, 1995). In the presence of hydrogen, it can be hydrogenated to produce 1,3-propanediol (Miyazawa, 2006)(Chiu *et al.*, 2006). These reactions are illustrated in Figure 2.6, below.

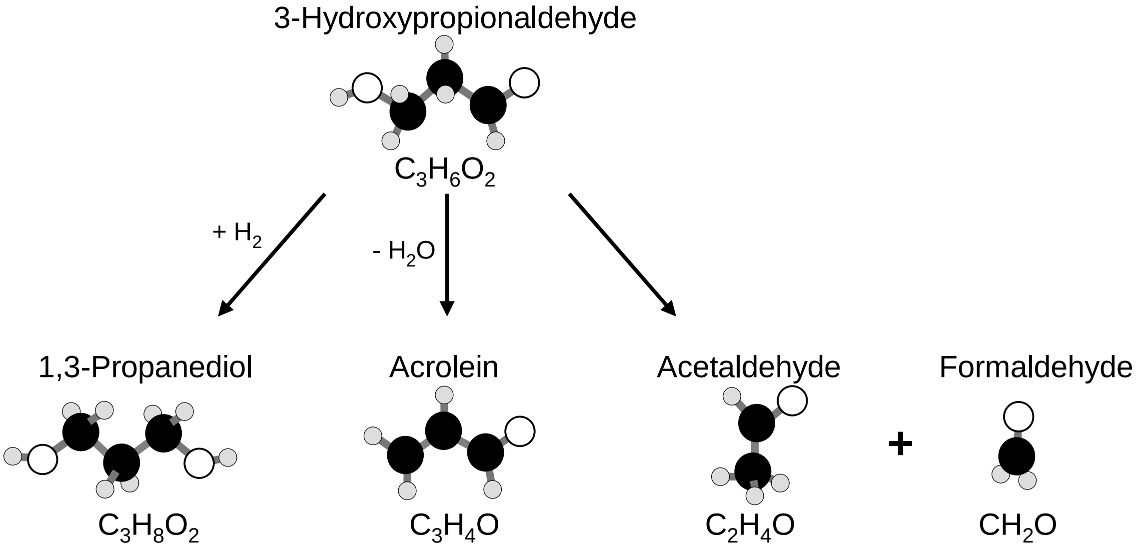

Figure 2.6. Acid catalyzed reactions with 3-hydroxypropionaldehyde.

2.7.4 Reactions with Acrolein

The final reactions to be considered as part of this proposed pathway are the additional reactions possible with the acrolein formed from the 3-hydroxypropionaldehyde. In the presence of hydrogen, the acrolein can be hydrogenated to produce either propionaldehyde or allyl alcohol, depending on the conditions in the reactor. In the presence of oxygen, it can be oxidized to produce acrylic acid (Neher *et al.*, 1995). These reactions are illustrated in Figure 2.7, below.

2.7.5 Complete Reaction Pathway

Putting all the above described reactions together, an overall simplified pathway of the glycerol dehydration chemistry can be proposed. This system of reactions is illustrated in Figure 2.8, below.

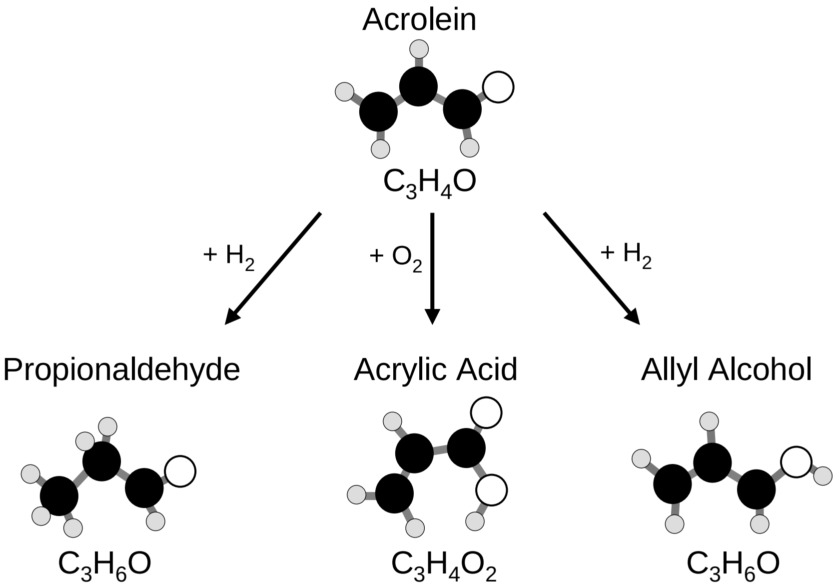

Figure 2.7. Acid catalyzed reactions with acrolein.

In this illustration, all of the reactions described previously are combined to show the entire proposed pathway. It has been reported that various polymers as well as solid carbon deposits are also formed during the glycerol dehydration process (Neher *et al.*, 1995)(Dubois *et al.*, 2006). These unwanted byproducts are difficult to quantify and are not included in the proposed pathway. However, the potential formation of these products is important due to the potential to shorten the catalyst life due to fouling and should be noted.

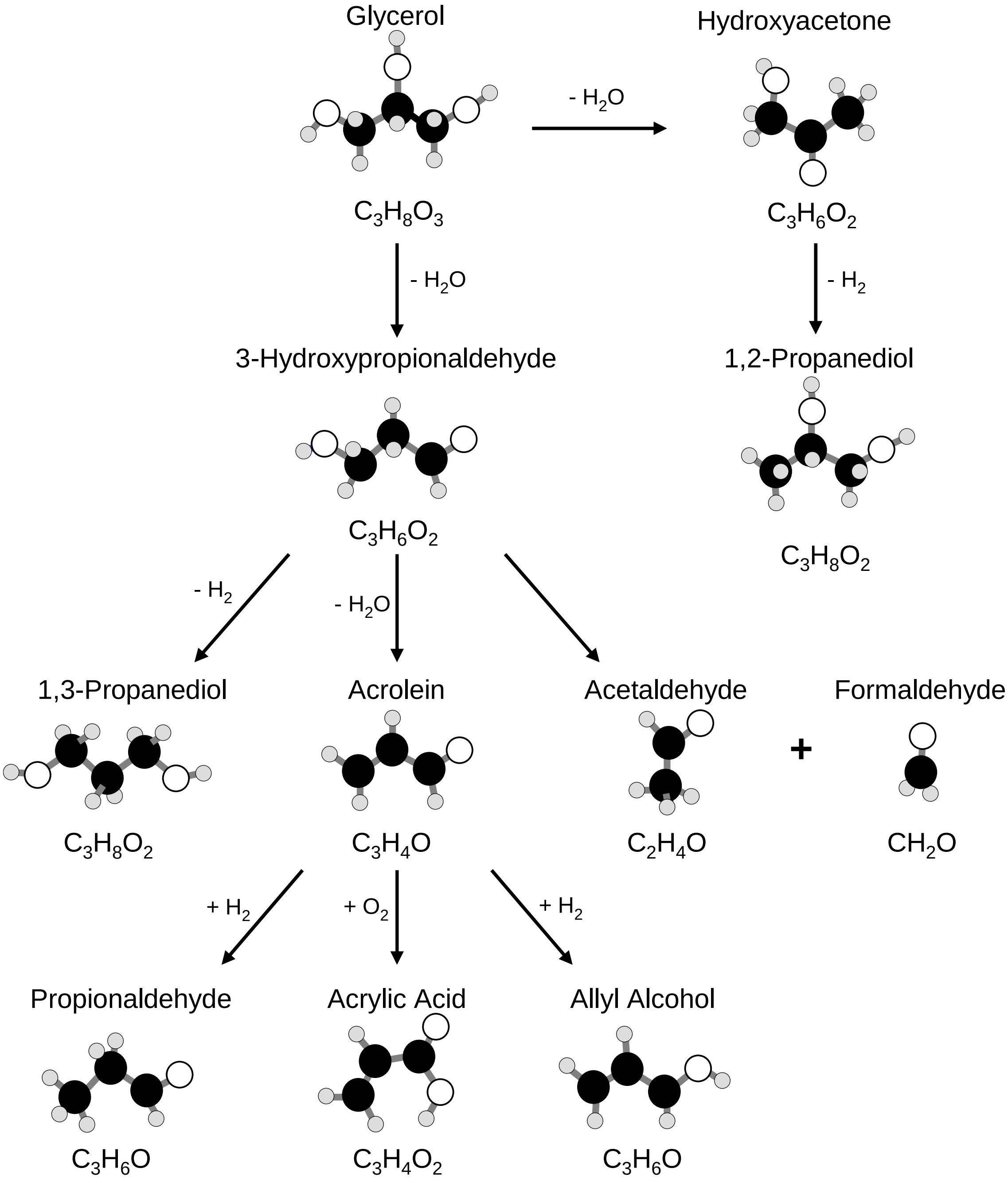

Figure 2.8. Proposed chemical pathways of glycerol dehydration.

2.8 Reaction Kinetic Models

An analysis of the kinetics of the glycerol dehydration reaction system based on the proposed pathway is necessary to predict the size of an industrial scale reactor. Properly sizing the reactor is an important consideration in determining the economic or performance feasibility of a process. The first step in this process is determining the reaction rate. Many factors can affect the rate of a heterogeneously catalyzed reaction, such as (Levenspiel, 1998):

- Surface reaction
- Pore diffusion
- Temperature gradient within the catalyst particle
- Temperature gradient at the particle – fluid interface
- Film mass transfer.

The degree to which each of these factors effect the overall reaction rate varies depending on the characteristics of the reacting system. These effects must be determined experimentally in the laboratory.

2.8.1 Experimental Methods for Determining Rates

Levenspiel describes four categories of experimental reactors for determining reaction rates (Levenspiel, 1998):

- Differential (flow) reactor
- Integral (plug flow) reactor
- Mixed flow reactor
- Batch reactor.

The particular reactor model chosen is based on the assumed conditions in the reactor. The first type of experimental reactor mentioned is the differential flow reactor. This reactor is based on the assumption that the rate of reaction is constant at all points within the reactor. This assumption is typically only valid for low conversion reactions. As described by Levenspiel, for each run in a differential reactor the plug flow performance equation can be written as:

$$\frac{W}{F_{A0}} = \int_{X_{Ain}}^{X_{Aout}} \frac{dX_A}{-r'_A} = \frac{1}{(-r_A)_{Ave}} \int_{X_{Ain}}^{X_{Aout}} dX_A = \frac{X_{Aout} - X_{Ain}}{(-r'_A)_{Ave}} \qquad \text{(Eqn. 2.5)}$$

In this equation, W is the mass flowrate, F_{A0} is the inlet flowrate of species A, X_A is the conversion of species A and r_A is the reaction rate. From equation 2.5, the average rate for each experimental run can be determined. A series of experimental runs to gather a set of rate versus concentration data can be analyzed to give a rate equation (Levenspiel, 1998).

The second type of experimental reactor is the integral reactor. An integral reactor is chosen when the assumption of constant reaction rate throughout the reactor is not valid. Two procedures are available for searching for the rate equation for an integral reactor; integral analysis and differential analysis. Using integral analysis, the plug flow performance equation is integrated to give (Levenspiel, 1998):

$$\frac{W}{F_{A0}} = \int_{0}^{X_A} \frac{dX_A}{-r'_A} \qquad \text{(Eqn. 2.6)}$$

Although the integral analysis procedure is straightforward for simple rate equations, it often becomes cumbersome for more complicated rate expressions

(Levenspiel, 1998). In these cases, differential analysis is preferred. Using this procedure, Eqn. 2.6 may be differentiated to give:

$$-r'_A = \frac{dX_A}{dW/F_{A0}} = \frac{dX_A}{d(W/F_{A0})} \qquad \text{(Eqn. 2.7)}$$

The third type of reactor is the mixed flow reactor. In this case, the design equation is based on the assumption of uniform concentration throughout the reactor. Experiments based on this model require a special type of reactor. Devices proposed by Carberry (1964) and Berty (1974) come close to approximating the ideal mixed flow reactor. For the mixed flow reactor, the design equation is written as:

$$\frac{W}{F_{A0}} = \frac{X_{Aout}}{-r'_{Aout}} \qquad \text{(Eqn. 2.8)}$$

Using this equation, each experimental run directly gives a value for the rate at the composition of the exit fluid (Levenspiel, 1998). A recycle reactor can also approach mixed flow conditions if the recycle rate is large enough. In the case of a recycle, the procedure requires inserting the kinetic expression into the performance equation for a recycle reactor with recycle rate, *R*, as follows (Levenspiel, 1998):

$$\frac{W}{F_{A0}} = (R+1)\int_{(R/R+1)X_{Af}}^{X_{Af}} \frac{dX_A}{-r'_A} \qquad \text{(Eqn. 2.9)}$$

The final type of experimental reactor is the batch reactor. In this system, the change in concentration is tracked versus time. The rate is determined using the batch reactor performance equation, as follows (Levenspiel, 1998).

$$\frac{t}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{V}{W}\int \frac{dX_A}{-r'_A} \qquad \text{(Eqn. 2.10)}$$

Based on the types of experimental reactors described above, Levenspiel offers some comparisons for determining which type is appropriate for the system of reactions being considered (Levenspiel, 1998). These comparisons are summarized as follows:

- The integral reactor can have significant temperature variations, especially with gas-solid systems. If this is the case, a mixed flow reactor may be a better choice.
- Integral reactors are useful for modeling operations of larger packed bed units with all their heat and mass transfer effects, particularly for system with a variety of feed and product materials.
- Differential and mixed flow reactors give the reaction rate directly, so they are more useful for complex systems.
- The small conversions needed for differential reactors require more accurate measurements than other reactors.
- Recycle reactors with large recycle flowrates can approximate a mixed flow reactor.
- When considering heat and mass transfer effects, the integral reactor most closely models a larger fixed bed, while mixed flow and batch reactors are more suited to avoiding regimes where the rate is hindered by these effects.
- Batch gas-solid reactors, like integral reactors, give cumulative effects, thus are useful for tracking multiple reactions.
- Because of the ease of interpreting the results, mixed flow reactors are often best for studying the kinetics of solid catalyzed reactions.

2.8.2 *Controlling Resistances in Rate Determination*

Interpreting experimental results can be difficult when more than one resistance affects the reaction rate (Levenspiel, 1998). Because of this, it is useful to carry out preliminary experiments to determine the ranges of operation where the various resistances are unimportant. This technique will allow the selection of operating conditions where the individual resistances can be studied separately.

The first step should be to determine if film resistances of any kind should be considered (Levenspiel, 1998). This is done experimentally by carrying out runs to determine if the conversion changes at different gas velocities but at identical weight-time. If the runs give different results, film effects are important.

Next, the effects of pore resistance must be determined. The pore resistance is accounted for by the effectiveness factor, defined as the inverse of the Thiele Modulus, M_T. The presence of pore resistance can be determined experimentally by noting the change in rate for different catalyst pellet sizes.

Finally, nonisothermal effects must be considered. Temperature gradients may be present in either the gas film or within the catalyst particle. If experiments show that gas film resistance is absent, the catalyst particle can be assumed to be at the same temperature as the surrounding fluid (Levenspiel, 1998).

2.8.3 Software Tools for Evaluating Kinetic Models

Because of the complexity of testing models for determining the reaction rate and the effect of resistances, sophisticated software tools are available for automating the process. One such available tool is the REX Suite from Optience Corporation. This software automates the process of selecting a kinetic model based on a proposed mechanism and experimental data. This software allows the user to evaluate many potential kinetic models to determine which ones best fit the experimental data. Using this software, a complete kinetic model for the glycerol dehydration reaction system can be proposed.

2.9 Laboratory Experimentation

2.9.1 Laboratory Scale Design and Control

Based on the glycerol dehydration chemistry, a laboratory scale mini-plant has been designed and built. The mini-plant consists of a packed bed reactor and the associated feed, preheating and sampling equipment. Based on the particular operating conditions required for carrying out the glycerol dehydration chemistry, the design of the lab scale mini-plant presented some specific challenges. The primary design challenges include the following:

- High boiling point of glycerol (288°C).
- Preventing condensation in interconnecting tubing.
- Potential for polymerization of glycerol and dehydration products, i.e. acrolein and acrylic acid.
- Sampling of gas phase reaction product.

However, the most important aspect of the mini-plant is the control system. In order to conduct experiments for determining the optimum operating conditions and kinetic parameters, accurate control is required. The primary control variables are composition, flow rate and temperature. Since the feed concentration is prepared manually, flow rate and temperature are the principle control variables. The flow rate of the liquid feed is controlled by use of a syringe pump. The syringe pump works by allowing adjustment of the speed of a stepper motor that depresses the plunger of a syringe filled with the feed liquid. The gas flow is controlled manually by using a rotameter type flow controller. Finally, the temperature is controlled automatically with multiple programmable PID controllers. Each temperature loop is controlled independently by its own automatic controller.

The universal PID controller is used to compensate for deviations (control differences) between the set point Y_s and the control variable Y by the signal U. The PID controllers used to maintain temperature for the lab scale mini-plant work in a closed-loop system/feedback control loop as an on/off controller. This system is illustrated in Figure 2.9, below.

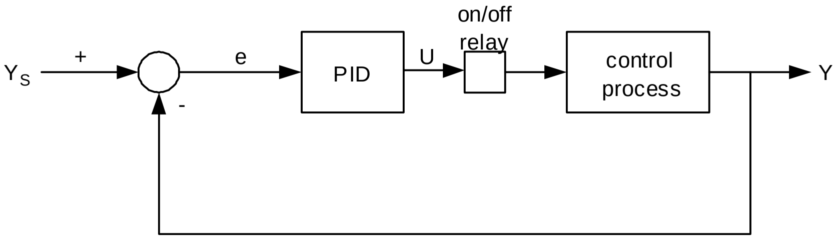

Figure 2.9. Block diagram of a feedback control system.

As illustrated in Figure 2.9, the signal U is sent to the process where a new output Y is obtained. This new output is compared with the desired set value Y_s which leads to a new error signal e. The controller takes the new error and sends a new signal U. This process continues as longs as the control loop is active. The closed-loop is defined as a strategy, where the control variable Y is permanently recorded and compared with the desired variable Y_s. The output U of the PID controller is a linear combination of the actual input, the integral of the previous input and the derivative of the future input. In other words, with proportional action the controller output is proportional to the error, with integral action the controller output is proportional to the amount of time the error is present and with derivative action the controller output is proportional to the rate of change of the error.

In tuning the controllers, two methods are possible, manual and automatic. Manual tuning for a closed loop system can be done using the continuous cycling method, which is a trial and error method proposed by Ziegler and Nichols (Seborg *et al.*, 1989). Because it involves trial and error, this method can be time consuming. For tuning the temperature control loop for the lab scale mini-plant, the automatic, or auto tuning, method is used. This method was selected because it is generally faster and easier than manual tuning. The procedure outlined by the controller manufacturer was followed to auto tune the Omega Type CN 4730 PID Controllers (Omega, 1998).

2.9.2 Analytical Techniques

For analyzing the reactor product gas chromatography is used. The function and operation of a gas chromatograph is well described in the text, *Basic Chromatography*, by McNair and Miller (1998). The set up and configuration of a gas chromatograph basically consists of the following steps:

- Selection of injector type – split versus splitless injector.

- Selection of column type – packed versus capillary - for separating the components that make up the sample.
- Selection of the detector type – Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD) are the most common types.

Determining the appropriate type of each of these components is of critical importance in ensuring accurate analytical results. In addition, calibration of the system and development of an analytical method must be completed in order to use the gas chromatograph.

2.9.3 Statistical Design of Experiments (DOE)

The primary purpose of the laboratory experiments is to determine the optimum operating conditions for the glycerol dehydration reactor. A typical technique for determining the optimum operating conditions for a system is called the "one factor at a time" (OFAT) approach. Using this technique, the variables influencing the behavior of the system are varied independently, holding the other variables constant. However, this approach doesn't provide data on the interaction of the factors (Anderson and Whitcomb, 1996). This potential problem with the OFAT technique is illustrated with an example from Box, Hunter and Hunter (1978).

In this example, experiments are to be carried out to determine the optimum yield of a chemical reaction. The variables of reaction time and reaction temperature are varied to determine the optimum conditions. Using the "one factor at a time" technique, experiments are carried out by first varying reaction time from 60 to 180 minutes at a constant reactor temperature of 225°C. These results indicated than the maximum yield occurred at 130 minutes. Next, holding reaction time constant at 130 minutes, the reaction temperature was varied from 210 to 250°C. From these experiments, it was determined that the maximum yield occurred at a temperature near the original value of 225°C. According to this example, by applying the "one factor at a time" approach it would be reasonable to conclude that the maximum yield occurs at a time of 130 minutes and a temperature of 225°C. However, when the reaction time and temperature are varied together, the true optimum value is revealed. This example is illustrated in Figure 2.10, below.

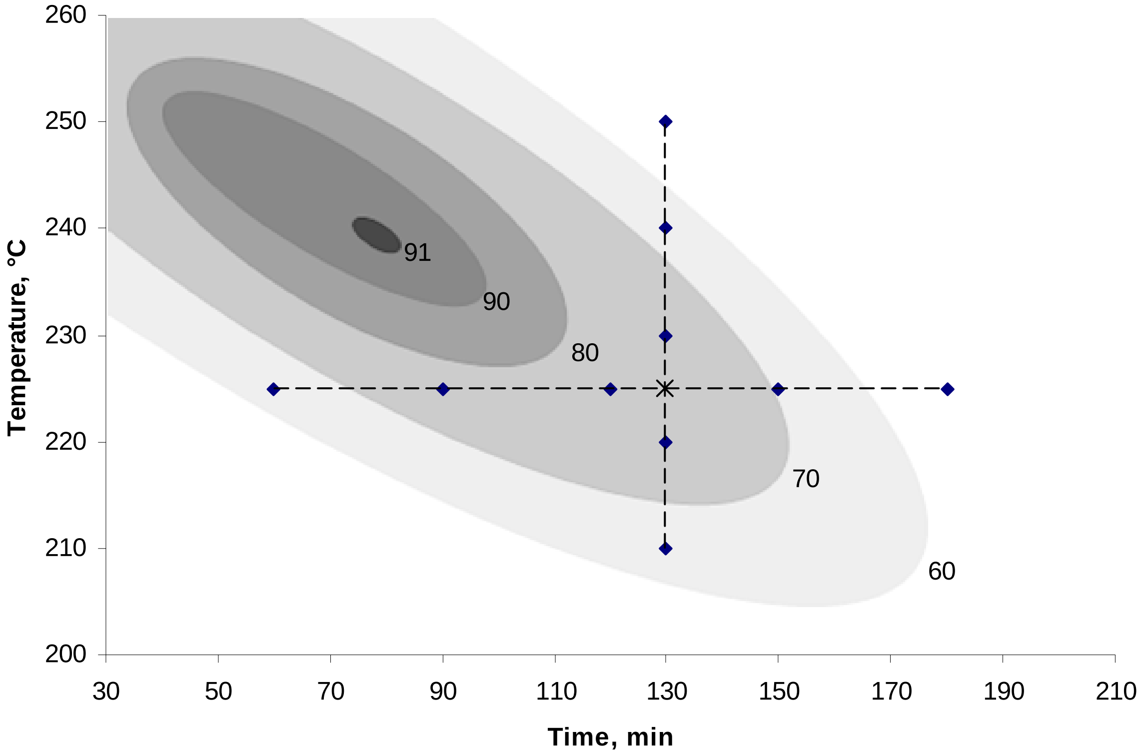

Figure 2.10. Response surface analysis vs. one factor at a time (Box *et al.*, 1978).

The dashed lines from the "one variable at a time" experiments are superimposed over the response surface generated from the experiments when time and temperature are varied together. From this figure it can be seen that a yield of 91 grams can be achieved at a time of about 80 minutes and a temperature of about 240°C.

As illustrated in this example, statistical design of experiments is preferred over the “one factor at a time” approach. By using a design of experiments approach, the experimenter can determine the effects of variables in concert, rather than only seeing the effects of each variable independently. One of the principle works describing the use of statistical techniques for the optimization of experimental results is *Statistics for Experimenters* by George E. P. Box, William G. Hunter and J. Stuart Hunter (1978). The objectives of statistical design of experiments have been further outlined by Montgomery *et al*. and are as follows (Montgomery *et al*., 2000):

1. Determine which variables are most influential on the response(s),
2. Determine where to set the influential variables so that the response(s) are almost always near their desired target values,
3. Determine where to set the influential variables so that the variability in the response(s) are small, or
4. Determine where to set the influential variables so that the effects of the uncontrollable variables on the response(s) are small.

For the glycerol dehydration reaction system, response surface modeling (RSM) is appropriate. Experiments designed based on RSM are based on a standard general linear model where the responses are assumed to be linear with uncorrelated errors and homogeneous variances (Khuri, 2001). Most design methods for RSM models were developed around industrial and laboratory experiments (Khuri, 2001). There are generally two types or response surface designs, central composite and Box-Behnken.

Box-Behnken designs (BBD) have fewer design points than central composite designs, so they require fewer experiments, and are therefore faster and less expensive to run (Minitab, 2006). Because of this, a BBD was chosen, since the primary purpose of the experimental optimization is to screen operating conditions to find the best parameters for running the reactions. A BBD is a spherical design with no edge points, in contrast to the central composite design which is a face centered cube (Myers and Montgomery, 1995). These two designs are illustrated in Figure 2.11, below. From this illustration, it can be seen that the BBD indeed requires fewer experiments than the central composite design.

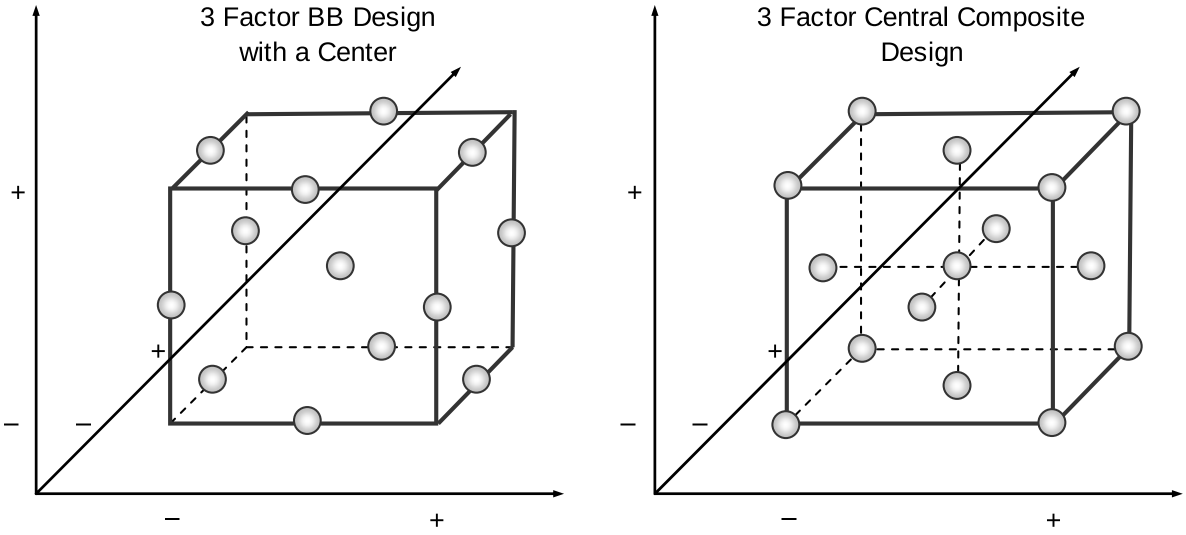

Figure 2.11. Box-Behnken and Central Composite design of experiments.

Because the experimental work for this research project is integrated with the process simulation work, the ranges for the system variables are determined based on the optimized operating conditions in terms of overall performance as determined by the process simulation. RSM is used to develop the required list of laboratory experiments to be carried out using the mini-plant to determine the operating conditions in the reactor that maximize the overall conversion and yield. The software package Minitab 14 is used to develop the list of experiments using RSM and to randomize the run order.

2.10 Summary

Based on the theoretical background presented in this chapter, it should be clear that there is indeed an opportunity to advance the science of process systems engineering by the application of this proposed methodology. Integration of laboratory experiments, minimization of environmental impacts and inherently safe process design with the standard heuristics of process design is an important step toward insuring that proposed conceptual processes are based on the most attractive in terms of performance, technically feasible, environmentally benign and inherently safe process conditions. Furthermore, developing a commercially viable process based on glycerol dehydration as illustrated by the case study example is an additional advance, since previous efforts in this area have not yielded a competitive processes that met the required performance targets, when compared with processes for manufacturing the same products based on crude oil derived feed stocks. Finally, since glycerol is produced as a side product of biodiesel manufacture, the results of this research, if implemented into a commercial process, can improve the overall sustainability of the biodiesel process.

CHAPTER 3

ORGANIZING AN INDUSTRIAL DISSERTATION

3.1 Introduction

To many people, the notion of a distance education Ph.D. may seem ridiculous enough by itself, but to add to it the fact that the prospective student intends to maintain full time employment with a chemical manufacturing company, and the ridiculous notion almost becomes an impossibility. Despite the potentially daunting obstacles, through a unique partnership between Evonik Degussa Corporation in the United States, Evonik Degussa GmbH in Germany, Auburn University and the University of South Alabama, this impossible proposition has become a reality. This relationship is illustrated in Figure 3.1. This chapter describes the conception and organization of this unique and non-traditional research project. At each step along the way, compromises from all parties involved have been required, but in the end, an environment was established whereby everyone stood to gain from the process. As each step of the process is described, it is accompanied by some first hand lessons learned from the experience.

3.2 A Win-Win-Win Scenario

The real key to making this unlikely dissertation project a reality was to negotiate a scenario where all parties involved – the student, the universities, and the company –

have something to gain from a successful collaboration. For the student the benefit is clear, the chance for achieving the Doctor of Philosophy degree while maintaining a career. For the universities, the benefits include exposure to industrially relevant research and processes and the opportunity to apply theory to real applications. Additionally, the universities can benefit greatly from the improved intellectual diversity due to addition of industrial experience to academic research groups. For the company, the benefits come from the creative thinking required of the Ph.D. student, which can lead to an increased potential for innovation.

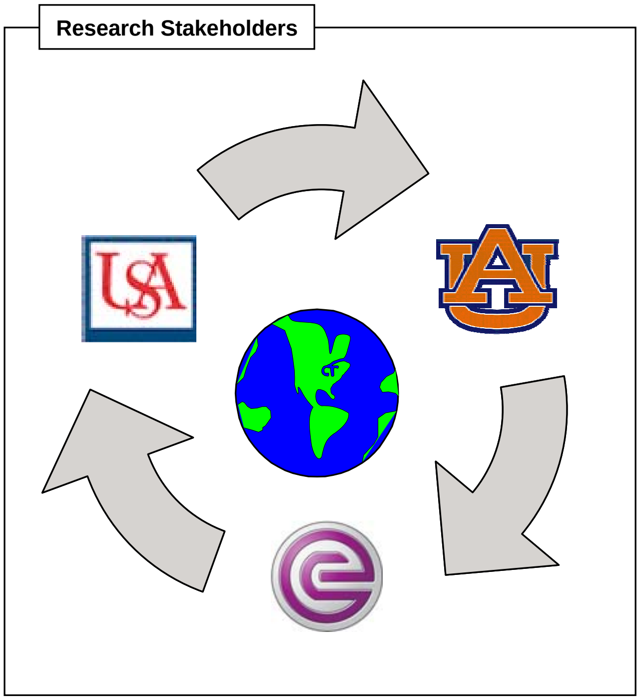

Figure 3.1. Stakeholders in the research project.

3.3 Research Objectives

The research project was originally conceived as a conceptual process development project for the production an industrial chemical from renewable, bio-based feed stocks (Seay *et al*., 2006). The original objectives included the development of a conceptual process, including an assessment of its viability in terms of process performance. In addition, laboratory experiments were to be carried out to gather the data needed for the process design activities. However, this industrial project in and of itself would not necessarily have contained sufficient academic rigor for a Ph.D. dissertation. To address this potential shortcoming, the original project has been incorporated into other research work being done at Auburn University in systems engineering. In this way, the project was given a broader scope, yet the original goals were preserved by including the industrial application as a case study (Seay *et al*., 2007).

With any collaborative research project, the different parties involved do not necessarily share the same objectives. This project is no different; therefore it is important to ensure that the objectives of both the university and the industrial partner are defined and addressed. The academic objectives are usually based on a "process of discovery" where scientific merit is favored over specific results. From the perspective of the university, the ultimate goal is the advancement of scientific knowledge on a research subject. The objectives of the corporation, however, usually have a different focus. In industry, the objectives are usually based on predefined deliverables with economic viability being considered at each step. From the perspective of the corporation, the ultimate goal is a positive return on the research investment. Framing the research project to incorporate the objectives of both the university and the industrial partner is important for a successful collaboration. Developing a clear scope of work with the principle objectives defined improves the likelihood of satisfying the expectations of all the research parties.

3.4 Organizational Challenges

When defining the scope of the research project, several organizational challenges had to be addressed in order to ensure a successful collaboration. First and foremost is establishing the need for flexibility from the student, the university and the industrial partner. Research is a fluid process and it is nearly impossible to force the process to fit into a rigid schedule. From the student, flexibility with regard to work and study schedules is needed; from the university, flexibility with regard to residency requirements and in what order the individual requirements of the Ph.D. degree are met is needed; and from the industrial partner, flexibility with regard to work hours and vacation schedules are tremendously beneficial.

Nearly as important as establishing the need for flexibility is establishing channels of communication so that no one is left out of the loop. With research partners in two universities and on two continents, good communication is critical. Determining a schedule for update meetings and status reports early in the process can help to ensure that everyone involved is informed regarding the progress of the research.

Another key item to consider during the organization of this project is determining where and how this research fits in with the current research being done at Auburn University. Since this research was conceived outside the university, organizing the funding for the project could have been a challenge. In this case, the research is wholly funded by Evonik Degussa; however, for others considering a similar partnership, grant money may also be a potential source for research funding. Regardless of the source, it is important to accurately forecast the total cost of the project. By spending the time to estimate the total cost over the life of the project, the issue of running out of money before all the academic requirements are met can be avoided. Some lessons learned from the budgeting process of this project are listed in Figure 3.2.

Lessons Learned

- Accurately determine the expected duration of the research project. The dissertation will include additional elements beyond the industrial portion of the research, so it is important to include these when estimating the project duration.
- Decide how university tuition and fees will be paid. Since the research was not conceived at the university, funds for tuition waivers or stipends may not be available.
- Determine who will be responsible for travel costs for both the student and academic advisor. Additional costs for attending technical conferences and seminars may also need to be included.

Figure 3.2. Some lessons learned regarding the budgeting process.

Finally, since this research must fit in with the normal job function of the student, it is important to organize how hours during the work day will be allocated between the research project and other job functions. This research project has been organized as an Evonik Degussa engineering project with a fixed budget to account for research hours spent during the work week. One potential problem is drawing the line between what part of the research is focused on meeting the goals of the company, and what part is solely focused on meeting academic requirements. Clearly, activities such as completing coursework requirements are solely academic. However, since the development of a Ph.D. candidate requires time to be spent exploring various avenues of research, it can be difficult to determine what is “company work” and what is “school work”. Therefore it is important to establish research goals and milestones upfront so progress can be easily measured.

In summary, it is important to realize that balancing work, school and sanity is not always easy. Any student considering this path must have advanced time management skills. In other words, personal organization is as important as the organization of the project. Without good organization, it is easy to feel overwhelmed by the demands of school and career. Understanding of these demands from supervisors at work and from the academic advisor can help make this burden manageable.

3.5 Potential Sources of Conflict

Even with the most well organized projects, conflict between the partners will arise. To help minimize this potential conflict, it is important to consider where conflict might arise and take preemptive action to avoid it. One primary source of potential conflict is over the ownership of intellectual property generated as a result of the research. In the case of this project, a thorough research contract has been entered into between Evonik Degussa and the two universities. In the process of negotiating these contracts, it became clear that there were two competing interests regarding intellectual property: the university does not want to “give away” its innovations, and the company does not want to pay royalties to use its own technology. Clearly, addressing intellectual property issues before they become conflicts is wise. In the case of this research project, the scope was divided between academic objectives and industrial objectives to help settle any intellectual property conflicts that may arise.

Another potential source of conflict is the duration of the research project. Because the Ph.D. student must be allowed time to develop creative solutions to problems and explore alternate avenues of research, the pace of the project may be slower than the pace industry is accustomed to. To avoid a possible conflict, it is important to outline a schedule up front, including milestones and a general timeline. In the case of this research project, a three-year timeline was proposed to meet the industrial and academic requirements. This timeline was acceptable to Evonik Degussa and reasonable for a Ph.D. student already holding a master's degree. Some lessons learned regarding identifying potential sources of conflict are listed in Figure 3.3.

Lessons Learned

- Definition of pre-existing intellectual property. It is important to establish what each side already knows with regard to the proposed research.

- Ownership of any patents that arise from the research. Patent ownership can be a huge source of conflict. Negotiating an ownership and royalty agreement up front may help to avoid this potential conflict.

- Publication of research findings. Since the research may contain business sensitive information it is important to determine what can and cannot be published and who will make this decision.

Figure 3.3. Some lessons learned regarding identifying potential sources of conflict.

Conflict is a normal part of business, and this collaborative research project is no exception. Even though conflict cannot be avoided entirely, brainstorming to look for possible sources of conflict and addressing them from the onset can help to streamline the process. Although there is no universal right way to address potential conflicts, it is well worth the time to look for and discuss them before any money or time is invested on collaborative research.

3.6 Meeting Coursework Requirements

Since the requirements for the Doctor of Philosophy degree include coursework as well as research, being located so far from campus presents challenges for a prospective student. Obviously, driving over 200 miles just to attend class is not practical. Fortunately, in this case, all graduate courses in engineering at Auburn University are available through distance education. The distance education option is really a necessity for a non-traditional student. Another avenue to explore is transfer credit. Since many universities allow at least some transfer credit, it may be possible to take some courses at a nearby university to avoid have to take all classes via distance education. Auburn University allows up to twelve hours of transfer credit to count towards the thirty hours of graded coursework required. Therefore, twelve hours of elective credit were transferred from the University of South Alabama, with the remaining eighteen hours being completed through distance education. In addition to the thirty hours of traditional graded coursework, Auburn University requires an additional 30 hours of ungraded coursework as well. This requirement was met by using research and dissertation and directed study credit.

Not only does the geographic distance create challenges for completing coursework, it can also be an obstacle for the normal interaction between a student and advisor that is so critical to the student's development. To help bridge this gap, it is critical that both the student and the advisor be comfortable using long distance collaboration tools like e-mail, video conferencing, instant messaging and web based meeting tools. If used effectively, these tools can create an open forum for communication and discussion. Despite the advances in technology, the use of long distance collaboration tools can never completely take the place of face to face conversations. Because of this, regular visits to Auburn by the student and to Evonik Degussa by the advisor were important.

3.7 Participation in a Research Group

In order to truly develop as a Ph.D. candidate, participation in a research group is also important. From the academic side, this research is folded into the research group of the academic advisor. This was a tremendous advantage of the partnership with Auburn University. Since the research project fit well with other research already being done at Auburn, there has been ample opportunity to learn from, and contribute to, other research in this area. Because of this it is important to spend time interacting with the other students in the research group, not just the advisor, during scheduled visits to campus. Interacting with other students can enhance creativity due to an exchange of ideas from others working on similar projects. In addition to campus visits, participation in technical conferences and seminars with other members of the research group is a good way to achieve this interaction.

3.8 Conclusions and Final Thoughts

Integrating industrially relevant research topics into an academic setting is an important goal for providing balance to a chemical engineering department. Through collaboration with an industrial partner on an academically interesting and industrially important research topic, this goal can be achieved. Although this project is unique for all parties involved, the results of the collaboration have so far been very successful. This experience can serve as a model for other manufacturing companies, looking to bring an academic perspective to a research project, and for universities looking to bring an industry focus to chemical engineering education.

In conclusion, this unique and non-traditional research project has been a tremendous learning opportunity for both the student and the advisor. Although sometimes challenging, the success of this project has been the result of hard work, careful planning and good communication along the way. Based on this experience, some final lessons learned are listed in Figure 3.4.

Lessons Learned

- Negotiate as much as possible up front.
- Brainstorm early and often to anticipate potential roadblocks.
- Secure management commitment up front.
- Be prepared for surprises along the way!

Figure 3.4. Some final lessons learned regarding the non-traditional Ph.D. process.

CHAPTER 4

PROJECT OVERVIEW AND BACKGROUND

4.1 Introduction

In this work the development of a methodology for integrating process simulations with laboratory reaction experiments is presented using a case study for the conceptual design of a process for manufacturing an industrially important chemical product from sustainable, bio-based glycerol. The objective of this research is to identify optimized processes with minimized environmental impacts that can utilize the glycerol produced as a side product of biodiesel manufacturing. The environmental impacts are potentially significant, since current industrial production processes are based on using crude oil-derived feedstocks (Weigert and Haschke, 1976)(Etzkorn *et al.*, 2001).

Using simulation models, the most viable in terms of performance and technically feasible process for further study in the laboratory is identified. This chapter illustrates how process simulation tools are used in conjunction with experimental laboratory studies to develop an optimized process for switching production of an industrially important chemical from crude oil-derived to sustainable, biomass-derived feed stocks.

4.2 Background

The process investigated in this research is the catalytic dehydration of glycerol using an acid catalyst. Previously published literature on this reaction identified only the overall conversion and yield of the primary product (Neher *et al*., 1995). These results have been published for both high pressure liquid and low pressure vapor phase reaction systems, however, the identity and yield of the side products were not reported. Therefore, significant additional work remains to be done to develop the parameters for this system of reactions. This chapter will illustrate how process simulations are used to guide the design and operation of a lab scale mini-plant to carry out the required reaction experiments. Furthermore, it will be demonstrated how the laboratory results are used to update the process simulation models to complete the process optimization. This approach not only ensures that the processes developed for the separation and purification of the product are based on performance optimized targets, but also minimizes the required laboratory work, since the experimental parameters are always based on viable and feasible operational boundaries. This serves to minimize the expenditure of both time and money for process development.

4.3 Methodology Development

It is proposed that by integrating process simulation tools with laboratory experiments, the development of an optimized industrial process can be streamlined. The methodology proposed for process development can be summarized by a flowchart, illustrated by Figure 4.1, below.

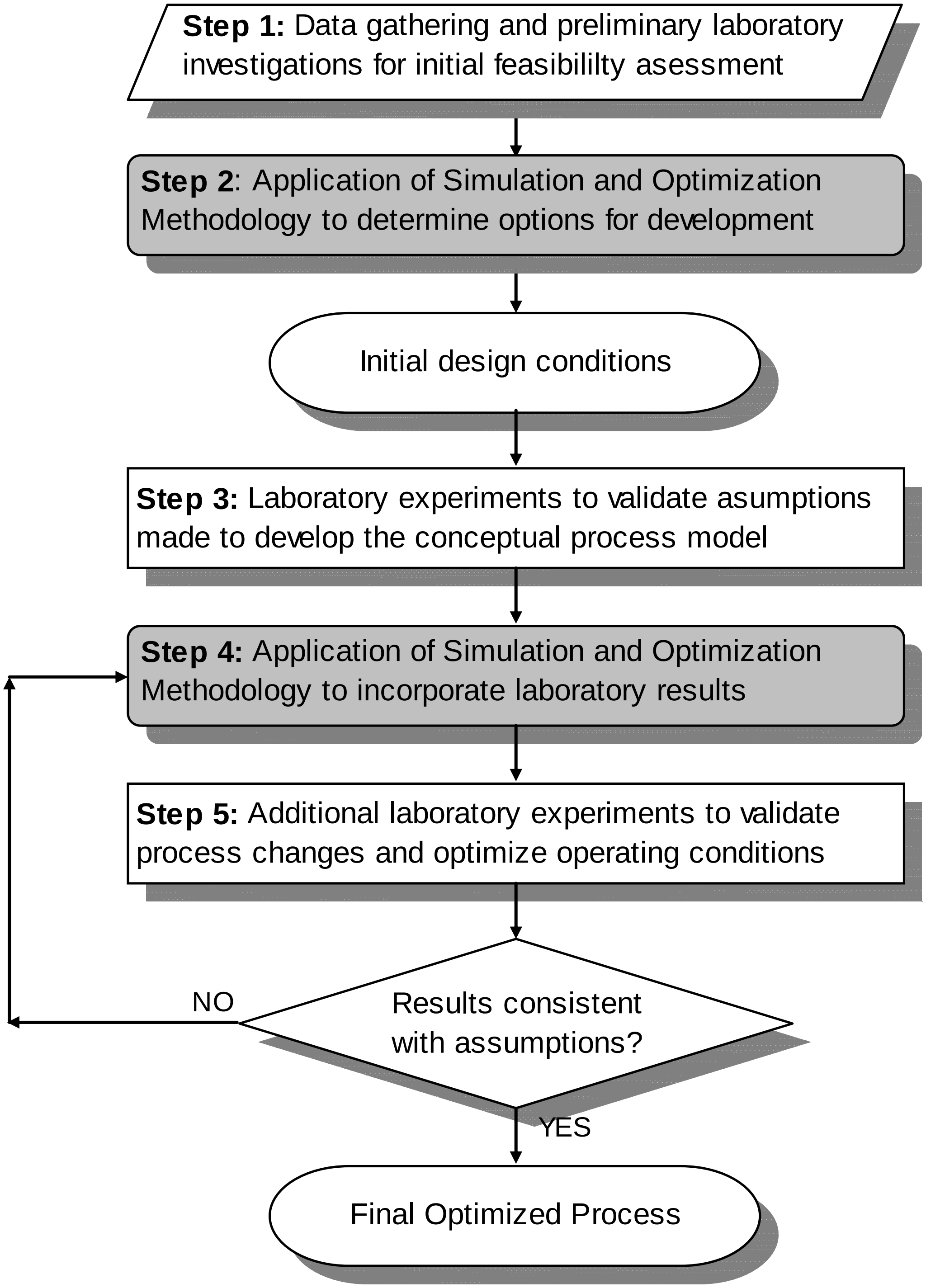

Figure 4.1. Flowchart for integrating process simulation work with experiments.

From this flowchart, it can be seen that process simulation and optimization is integrated with laboratory experiments to ensure that the results are always based on technically feasible and performance optimized conditions. In this way, the process simulations are used to direct the laboratory work, thus eliminating time spent on parameters that do not lead to optimized solutions. This can also potentially reduce the total expenditure of time and money in the laboratory as a result of streamlining the process.

As stated previously, the purpose of this methodology is to integrate process simulation and optimization with laboratory experimentation. In this methodology, reference is made to a simulation and optimization methodology. This methodology is illustrated in Figure 4.2, below.

The process simulation and optimization methodology illustrated in Figure 4.2 is an extension of the traditional process design activities due to the inclusion of process optimization, risk assessment and environmental impact assessment. These elements have typically been included “after the fact”, i.e., once the conceptually design is finalized. This traditional approach constrains the creativity of the design engineer by narrowing the options for achieving safety and environmental benchmarks. By including these elements in the earliest stages of conceptual process development, it can be ensured that not only will the final design meet all safety and environmental requirements, but it will be based on conditions that lead to optimal process performance.

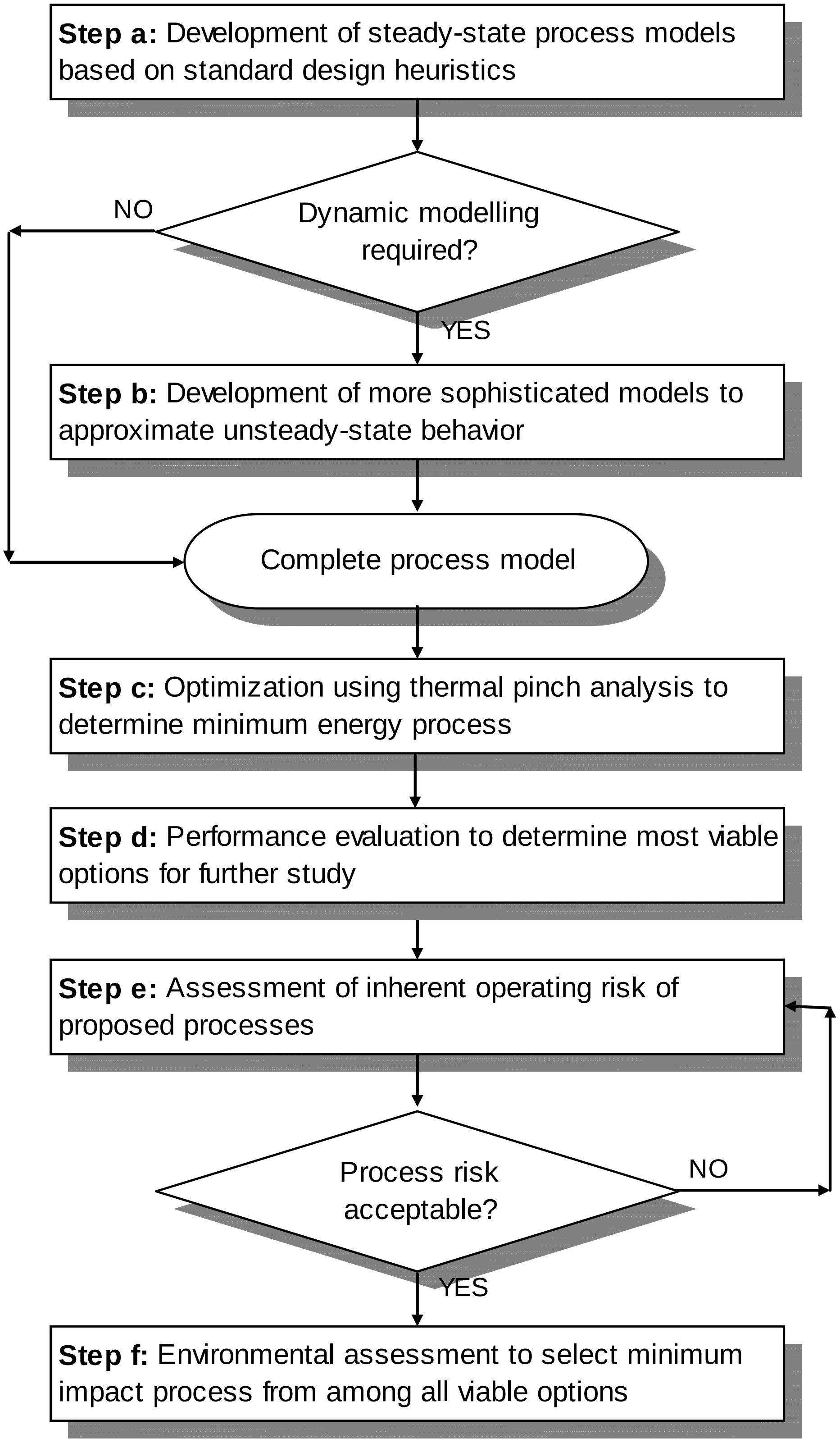

Figure 4.2. Process simulation and optimization methodology flowchart.

4.4 Case Study Example

The case study presented below is based on the application of the methodology to an actual process development project. Through the case study, each step in the methodology is illustrated. In this chapter, the framework of the methodology will be introduced. Subsequent chapters will detail the application of the individual steps to the case study example.

4.4.1 Integration Methodology Step 1

The first step in the application of the methodology is the determination of the chemical feasibility of the proposed process. For chemistry not previously described in literature, this step could involve preliminary laboratory experimentation to determine the general parameters of the process. These parameters may include the phase in which the reaction occurs, whether high, low or sub-atmospheric pressure is required, whether the reaction is endothermic or exothermic and whether or not a catalyst is required.

For the case study considered as part of this research, these preliminary laboratory investigations had been completed previously and the results were available in literature (Neher *et al*., 1995). Therefore, it was possible to simply gather this existing data. Two potential reaction processes had previously been described – one based on high pressure liquid phase conditions and one based on low pressure vapor phase conditions – this formed the basis for the initial process simulation and optimization studies (Neher *et al*., 1995).

4.4.2 Integration Methodology Step 2

The second step of the methodology is the application of the previously described simulation and optimization methodology. This step includeds the preparation and analysis of a computer simulation of the entire process. The result of this analysis is described in detail in Chapters 5, 6 and 7. Since these results indicated that the vapor phase glycerol process held the best chance for overall process viability in terms of performance, the laboratory experiments were based on this process.

4.4.3 Integration Methodology Step 3

The third step is the validation of the simulation assumptions in the laboratory. The equipment used for the laboratory experiments is designed to model the feed vaporizer and packed bed reactor required for the vapor phase glycerol dehydration process. A schematic of this equipment is illustrated in Figure 4.2, below. The product gas leaving the reactor is extracted via the sample port, QE, and analyzed using a gas chromatograph. Utilizing this equipment, the primary side products were identified and the overall system conversion and yield were measured.

This laboratory mini-plant, including a description of the specific equipment and control systems used is described in detail in Chapter 8. In addition, the gas chromatgraph used to measure the reactor conversion and yield are also described in Chapter 8.

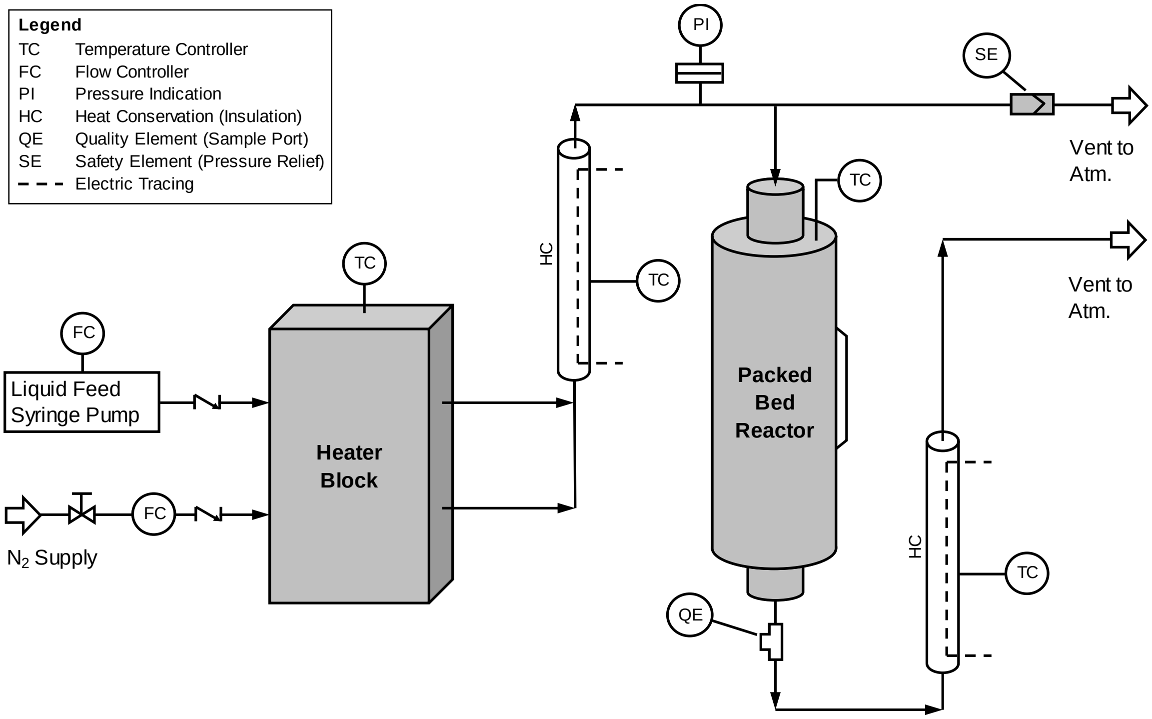

Figure 4.2. Schematic of laboratory equipment used in case study example.

4.4.4 Integration Methodology Step 4

Step 4 of the methodology is to update the process simulation model with the experimental data and again apply the simulation and optimization methodology to enable a more detailed analysis. Use of a process simulation model allows more in-depth analysis of each component of the proposed industrial process. The results of this study indicated that the vapor phase process, although more attractive in terms of overall performance than the liquid phase process, was, for the conditions considered in this research study, still not competitive with the industry standard process based on using crude oil derived raw materials (Weigert and Haschke, 1976)(Etzkorn *et al.*, 2001).

The analysis of each component of the process indicated that the primary cause of the higher performance index of the vapor phase glycerol process relative to this standard process is the contribution of the cost of energy per kilogram of product. Further analysis identified that the energy associated with vaporizing the feed was the largest contributor to the utility cost. This is due to the fact that the glycerol feed must be highly diluted in order to prevent the glycerol from reacting with itself. An engineering solution to avoid the problem of spending large amounts of energy vaporizing the diluent water must be found to make this glycerol dehydration process competitive.

As a result of the insights learned from the revised simulation model based on laboratory data, a new process has been developed to address the problem of vaporizing the large quantities of water required for the vapor phase process. This new process has been modeled using the Aspen Engineering Suite to determine its overall viability. This analysis is described in detail in Chapter 9. Since this new process is based on assumptions, the next step is to return to the laboratory to ensure that the assumptions made regarding glycerol conversion and product yield are valid.

4.4.5 Integration Methodology Step 5

Step 5 of the methodology is then to determine if the laboratory results of the experiments using the new process conditions are consistent with the simulation results. If not, the process simulations are modified again, followed by a return to the laboratory for further validation. Step 5 of this methodology is also described in detail in Chapter 9.

4.5 Results and Conclusions

In conclusion, it can be seen that by the use of this methodology for integrating the laboratory experiments with the process simulation, innovative process designs can be discovered. In the following chapters it is shown that by including process simulations with the laboratory experiments, more attractive process conditions in terms of overall performance are discovered. From the glycerol dehydration case study, the benefits of applying this methodology are shown.

CHAPTER 5

DESIGN AND OPTIMIZATION OF STEADY STATE MODELS

5.1 Introduction

At the current rate of consumption, conservative estimates predict the depletion of fossil fuel resources in 80-120 years (DOE, 2003). As prices for crude oil increase, a similar increase is seen in the price of crude oil-derived chemical feed stocks. Thus there is a growing need for the development of novel production processes, which are based on cost effective, renewable raw materials. In addition to the potential process performance benefits, the use of renewable bio-based feed stocks decreases greenhouse gas emissions as carbon sources are switched from crude oil to agricultural products (DOE, 2003). Additionally, the development of industrial processes utilizing bio-based feed stocks will enhance the markets for these products, thus encouraging the development of more consistent supplies.

The objective of this work is to utilize systematic process systems engineering methods to screen candidate conceptual processes for the production of important chemicals and chemical intermediates from bio-based glycerol. This screening procedure allows the process with the greatest potential for overall viability to be selected before beginning detailed process design and engineering.

Historically, glycerol has been produced as a byproduct of the manufacture of soap by hydrolysis of animal fats. However more recently, glycerol has been generated as a byproduct of biodiesel manufacture. Due to its high viscosity, glycerol must be removed from the biodiesel product, thus reducing the carbon utilization. Therefore, the identification of novel industrial uses for glycerol can improve the overall carbon utilization and possibly the profitability of the biodiesel process (USDA, 2003).

5.2 Development of Steady-State Process Models

The purpose of this investigation is to evaluate the potential for switching the production pathways of industrially important chemicals from utilizing crude oil-derived raw material feed stocks to bio-based glycerol. As described in Chapter 4, in the application of the proposed methodology, the first step is the screening of potential conceptual processes.

This research case study is based on developing new reaction pathways for chemical products currently manufactured using crude oil derived feedstocks. Many chemical products currently produced from the catalytic oxidation of crude oil derived feedstocks, can also be manufactured via the dehydration of glycerol. Several examples of these chemical products are as follows:

- Acrylic acid, which is used in the manufacture of acrylate ester polymers. These polymers have application in the coatings industry, as non-woven fabric binders, as textile and leather finishers as well as in the oil additives industry (Weigert and Haschke, 1976).

- Acrolein, which is a widely-used intermediate in the production of building materials, herbicides, amino acids, and water chemicals (Weigert and Haschke, 1976).
- 1,3-Propanediol (PDO), which is used in the manufacture of 1,3-propanediol terephthalate. This fiber molecule is used for textiles in the garment industry (DuPont, 2005).

Other products include 1,2-propanediol and hydroxyacetone. The identity and yield of the product is determined by the catalyst used and the reactor operating conditions. The case study presented in this chapter provides a generic framework for analyzing the performance potential for switching from crude oil derived raw materials to glycerol as a feed stock.

5.3 Sustainable Production Case Study

Current production schemes for the chemicals targeted in this study are based on the catalytic partial oxidation of crude oil derived feedstocks. The identity and yield of the products of this process is primarily dependent on the catalyst used; however, the side products of these reactions will generally include carbon oxides, light aldehydes and organic acids (Weigert and Haschke, 1976)(Etzkorn *et al.*, 2001). The oxidation reaction is exothermic and is carried out at low pressure. As an alternative reaction pathway, the catalytic dehydration of glycerol has been proposed. The dehydration reaction is endothermic and potential side products include light aldehydes, mid-boiling ketones and polyglycerols (Neher *et al.*, 1995). Recent studies have indicated that dehydration of glycerol can be carried out in either the liquid or vapor phase (Neher *et al.*, 1995), however the complete kinetics of these reactions have not yet been identified.

5.4 Conceptual Process Development

To illustrate the previously introduced 5-step methodology, an initial screening using process simulation tools were used for determining the performance potential of switching from production pathways based on crude oil derived feed stocks to bio-based glycerol. This screening encompasses Step 1 of the methodology. A case study is developed to compare processes based on oxidation of crude oil derived raw materials with processes based on glycerol dehydration. As the actual reaction pathway of the glycerol dehydration reaction is unknown, a number of pseudo components were included to represent the potential byproducts. To ensure a realistic process, the components were chosen so low and high boiling side products are present in the reactor effluent.

5.4.1 Process Simulation Models

For the initial step, both liquid and vapor phase production processes are considered. Multiple reaction temperatures and conversions were considered to cover a wide range of possible operations. Various recycle options and side product purification options were also studied. Initially, five liquid phase (Case L1–L5) and five vapor phase (Case V1–V5) glycerol based production schemes were investigated and compared with the traditional manufacturing process (Case S1). A description of these initial process simulation cases are listed in Table 5.1, below.

For the glycerol processes, the options were based on the temperature, pressure and compositions reported in previous studies (Neher *et al.*, 1995), along with various recycle options for unreacted glycerol and excess water. Process simulation models were developed for all cases and subsequently optimized by process integration methods to provide a systematic framework for evaluating the technical, process performance and environmental feasibility of switching to a bio-based feedstock.

Table 5.1. List of initial simulation cases for glycerol dehydration process.

Industry Standard Process Based on Crude Oil Derived Feedstocks	
S1	Base Case Process Using Crude Oil Derived Feed Stock
Vapor phase processes for initial screening	
V1	Vapor Phase Base Case
V2	Base Case with No Water Recycle
V3	Vapor Phase Base Case with Waste Water Stripping
V4	Base Case with Alternate Recycle Configuration
V5	Base Case with Higher GLY/WTR Feed Ratio
Liquid phase processes for initial screening	
L1	Liquid Phase Base Case
L2	Base Case with Alternate Recycle Configuration
L3	Base Case with Alternate Recycle Configuration and Wastewater Stripping
L4	Base Case with Alternate Recycle Configuration and Elevated Temperature
L5	Base Case with Alternate Recycle Configuration and Elevated Temperature

Figure 5.1 illustrates the base conceptual process for the vapor phase reaction. Since essentially complete conversion (+99.9%) of glycerol can be achieved in the vapor phase reaction process, only two columns are required to purify the product (Neher *et al.*, 1995).

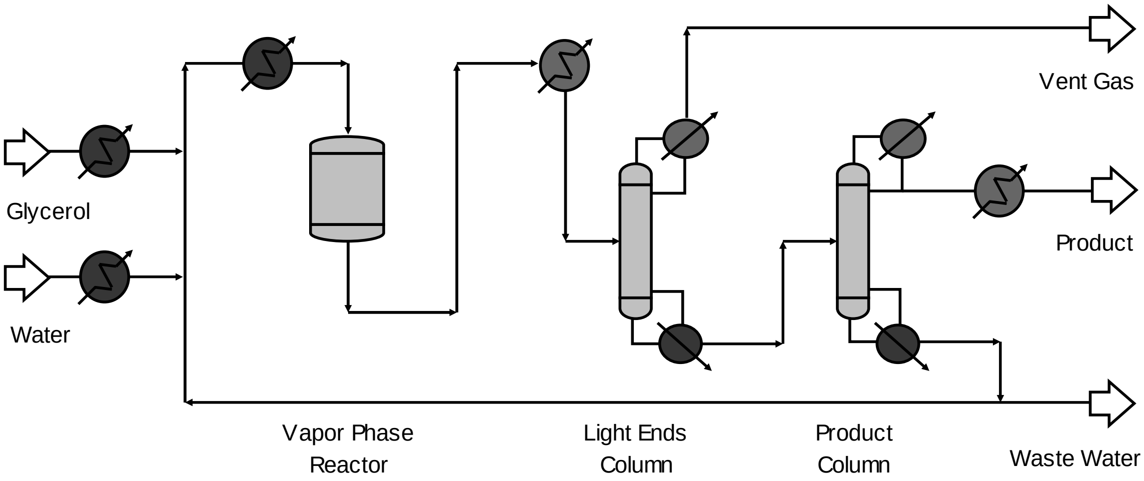

Figure 5.1. Schematic representation of a conceptual vapor phase glycerol process.

Analogously, Figure 5.2 illustrates the base conceptual process for the liquid phase reaction. Because less than 25% glycerol conversion can be achieved in the case considered for study, three columns are required to purify the product (Neher *et al.*, 1995). A primary difference between the liquid phase and vapor phase processes is that in the liquid phase, the product is collected as a bottoms product, while it is an overhead product in the vapor phase process. The effect on quality of a bottoms product must be carefully considered in future stages of conceptual process development due to the potential of collecting heavy contaminants in the product stream.

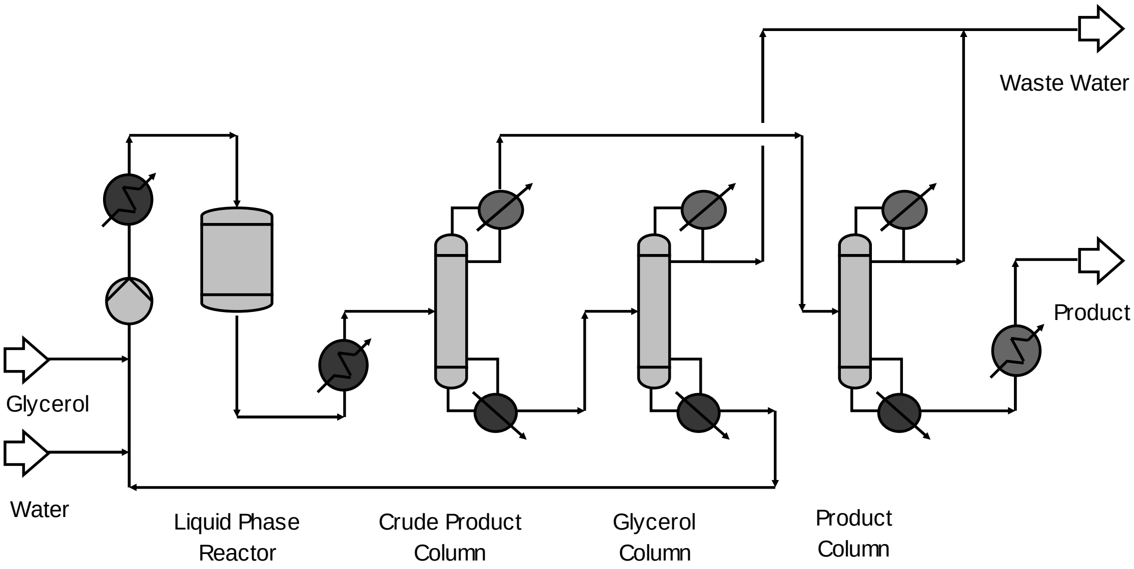

Figure 5.2. Schematic representation of a conceptual liquid phase glycerol process.

For the purposes of assessing the true performance potential of these processes both the liquid phase and vapor phase processes will be compared to the current industry standard process (Weigert and Haschke, 1976)(Etzkorn *et al.*, 2001). This process is illustrated in Figure 5.3, below.

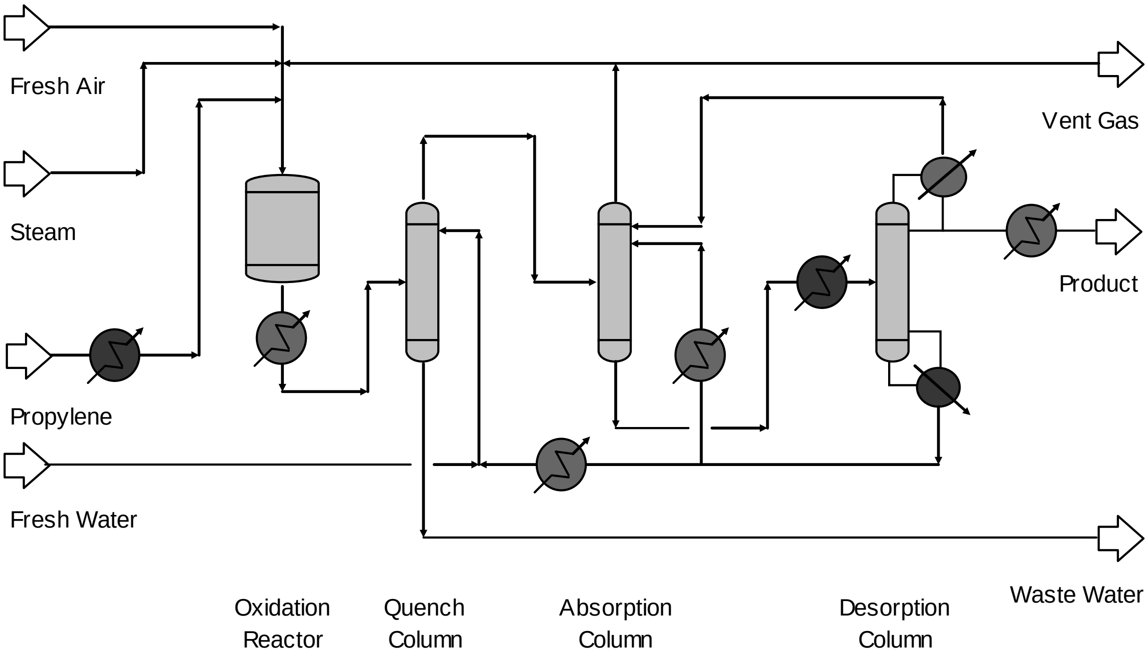

Figure 5.3. Schematic representation of industry standard production process.

5.4.2 Process Integration Analysis

Once the candidate conceptual processes based on literature data and engineering assumptions have been generated, Step 2 of the methodology is to analyze the performance viability of these processes. In addition to performance considerations, it is also necessary to ensure optimal resource utilization. This can be achieved by the application of holistic methods like pinch analysis to optimize the proposed conceptual processes. Increased energy and mass integration enable higher utilization of raw materials and minimization of external utilities (El-Halwagi and Spriggs, 1998)(Linnhoff and Hindharsh, 1983). The minimum utility requirement for each of the candidate conceptual processes used for this case study was evaluated using Aspen HX-Net software (Aspentech, 2006).

The minimum hot and cold utility requirements were calculated based on the utilities anticipated to be available in an existing multiple user industrial facility. The minimum utility operating costs are based on the coldest cold utility and the hottest hot utility available. This cost, along with the estimated capital cost of the designed heat exchanger network for each conceptual design is used in the full performance analysis. A more detailed description of this procedure is described in Chapter 7. The normalized process performance index results per unit of product, based on the process simulation and pinch studies are reported in Figure 5.4, where the base case process, S1, is used to normalize all other calculated values.

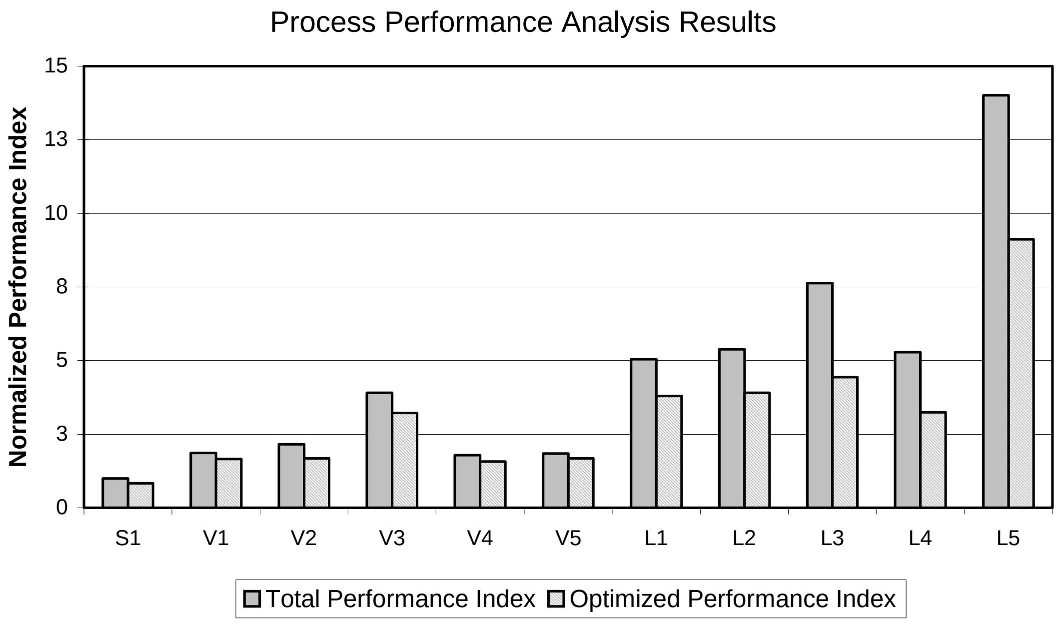

Figure 5.4. Normalized process performance index.

These results indicate that the value of the normalized process performance index of the vapor phase glycerol processes are roughly three times that of the of the standard case. Furthermore, the values of the normalized process performance index of the liquid phase glycerol processes are seven to sixteen times higher than the standard case. Although there is a significant improvement in the value of the performance index of the liquid phase processes at minimum utility, the results are still five to thirteen times higher than the standard case.

For the conditions chosen for this case study, further consideration of the liquid phase process is shown to be unnecessary. The reason for the large difference in performance between the liquid and vapor phase reaction schemes can be illustrated using the breakdown of the key contributions to the process performance index, which is presented in Figure 5.5, below.

Each simulation case is based on an equal quantity of raw material feed. This means that the absolute cost of the raw material is the same for each of the glycerol based conceptual processes. It is clear from the results shown in Figure 5.5 that the contribution of utilities in the liquid phase processes is responsible for the resulting high normalized performance index value. This increased contribution of utilities to the overall normalized process performance index value for the liquid phase processes can be attributed to several factors, i.e. the very high pressures required and the relatively low conversion of glycerol (less than 25%), which results in high recycle rates and thus large utility requirement. Therefore, for the conditions of the case study, ongoing efforts need to focus on optimization of the vapor phase processes, rather than the liquid phase processes. However, it should be noted that development of new catalysts or reaction techniques that improve the overall conversion of the liquid phase glycerol process could result in this pathway being preferred.

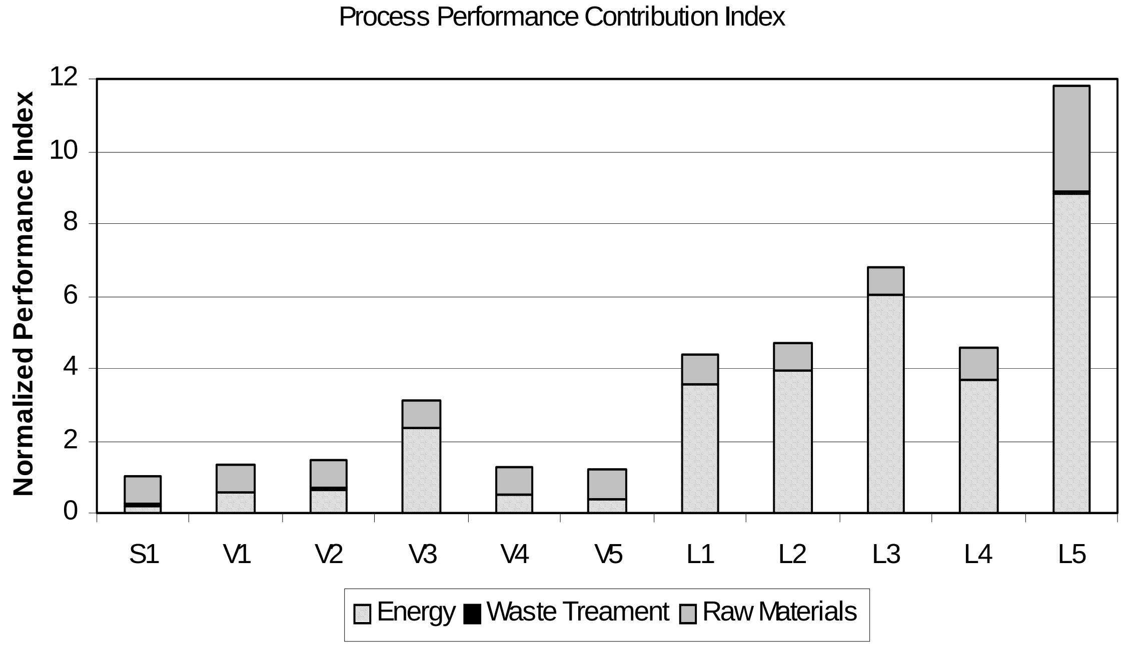

Figure 5.5. Performance index analysis breakdown.

5.5 Conclusions

Through the application of process systems engineering methods and tools, multiple candidate conceptual processes for the production of industrially important chemicals from dehydration of renewable, bio-based glycerol have been identified. Simulation models of the candidate conceptual processes were used to generate performance data which was utilized to perform a comparative performance analysis. Given the parameters considered in the case study presented in this work, current prices do not merit switching the production from crude oil derived feed stocks to a renewable bio-based raw material. However, a continued increase in crude oil prices coupled with a decrease in glycerol cost will have a major impact on the profitability of the new processes. Additionally, this analysis illustrates that developing a reaction chemistry with a product yield equivalent or better than the current technology is critical to the overall viability of the process. Otherwise, the potential impacts on performance of the downstream separation are insurmountably high. In conclusion, the developed models provide a means of estimating the overall targets that would merit the switch in feedstock. Additionally, if crude glycerol could be utilized as a feed stock as opposed to refined glycerol, the process performance of sustainable production would be greatly improved. In the case of this research case study, no dynamic modeling is required. Therefore, the next step in the simulation and optimization of the proposed conceptual processes is the assessment of process risk and the application of inherently safe design practices. This procedure is described in general in Chapter 6.

Throughout the development of more detailed designs, the environmental impact of the glycerol based production schemes is evaluated and compared with the traditional manufacturing process. The WAste Reduction (WAR) algorithm developed by US-EPA (Young and Cabezas, 1999)(Young *et al*., 2000) is used to ensure that processes with the highest potential for sustainability are chosen from the viable process options. A methodology for incorporating environmental impact assessments into conceptual development is further described in Chapter 7.

The next phase of this research involves experimental identification of the actual byproducts and the detailed reaction kinetics for the vapor phase dehydration of glycerol. The design of the laboratory equipment for conducting the vapor phase experiments is described in detail in Chapter 8. The optimization of the reactor operating conditions and the development of a scalable model of the reaction rate is described in detail in Chapters 9 and 10, respectively.

CHAPTER 6

APPLICATION OF INHERENTLY SAFE DESIGN PRACTICES

6.1 Introduction

The process design and optimization methodology introduced in Chapter 5 includes an assessment of the inherent operating risk of the proposed process. This assessment is followed by a decision based on whether the risk of operating the proposed process is acceptable. The purpose of this chapter is to present two means of addressing process risk. The first is the application of risk assessment methodology, which is used to quantify the inherent risk of a given process. The second is inherently safe design practice, which addresses the hazard of a process and addresses it in the early stages of conceptual process design. Due to the proprietary nature of the data, the risk assessment comparison of the propylene and glycerol based processes are included in Appendix A, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members.

6.2 Background

Process safety is a fundamental component of sound process design. Although the chemical industry has demonstrated an excellent safety record over the years (Sanders, 2005), the quantities and hazardous nature of many of the substances typically handled by chemical manufacturers make the potential for large scale disasters a constant concern. Because safety is so critical in industry, it is vital to introduce the concepts of safe process design practices during undergraduate chemical engineering education. From famous historic disasters such as Flixborough, England and Bhopal, India to recent events such as the Texas City BP Refinery in the United States explosion in 2005, the importance of process safety in chemical process design is abundantly clear. Gaining an appreciation of the applications of process safety during a chemical engineer's education can only enhance chemical manufacturing safety in the future.

In industry, the concept of process safety is firmly rooted in the concept of risk. From government regulatory requirements, such as those outlined by OSHA and the EPA (Nelson, 2003)(EPA, 2005)(OSHA, 2005), to industry initiatives such as Responsible Care®, the requirement of quantifying and managing risk is paramount. In addition to working within economic, performance and environmental constraints, the process design engineer is also tasked with reducing the risk of operating a chemical manufacturing process to a level acceptable to employees, regulatory authorities, insurance underwriters and the community at large.

In many classrooms today, process safety is taught from a perspective of toxicological impacts and quantifying release scenarios. These are both important topics to which students of chemical engineering should be exposed. However, in industry, the focus is much more on mitigation of upsets and prevention of release events. Therefore, a holistic approach to process safety as an integral component of sound process design is critical. An understanding of how risk is quantified in the chemical process industries will allow future process design engineers to mitigate those risks at the earliest stages of conceptual process development – at the stage where the engineer has the greatest influence on the final process design. The research presented in this chapter presents, by case study example, how the fundamental concepts of inherently safer process design can be integrated into chemical engineering education.

6.3 Risk Assessment Methodology

6.3.1 Quantifying Risk

In order to begin understanding the benefits of inherently safer process design, the chemical engineering student must first understand risk. The concept of risk is often misunderstood by both the general public, and students of chemical engineering. It is important to separate the concept of risk, from the concept of hazard. While the concept of hazard relates to the *potential* for adverse consequences, risk is rather a combination of both the *severity* of an upset scenario and the *likelihood* of that event occurring. This is an important distinction. The potential hazard associated with a substance or process is an inherent property that cannot be changed. The risk associated with handling a substance or operating a process can be high or low, depending upon the safeguards that are included in the design. Thus, for chemical engineers, the most important distinction between hazard and risk is that risk can be reduced through process design.

In order to begin to discuss risk, the process design engineer must first consider potential upset scenarios. In other words, answer the question, “What is the worst thing that can happen?” Answers to this question typically involve loss of containment of a process chemical with causes ranging from failure of control loops and operator errors to external events such as fire, among many others. It is critical to note that the answers to the aforementioned question must be considered independently of the likelihood of the worst case scenario occurring. Again, it is the combination of both the severity and the likelihood that determines the risk. In order to ensure a complete and consistent assessment of potential upset scenarios, a structured approach must be applied. The need for such an approach is the basis for a Process Hazard Analysis.

6.3.2 Process Hazard Analysis

Process Hazard Analysis (PHA) is a methodology for reviewing and assessing the potential hazards of a chemical process by utilizing a structured, facilitated team brainstorming approach. A PHA is typically facilitated by a trained team leader and attended by a wide variety of plant personnel, including engineers, managers, operators, maintenance technicians and safety, health and environmental (SHE) personnel. Although several techniques are available for performing PHAs (EPA, 2005), the goal of the PHA is always the same – to identify the potential hazards of a process and determine whether sufficient safeguards are in place to mitigate those hazards.

6.4 A Simple Example of Applying PHA Methodology

The following is a simple example that can be used to illustrate the basic concepts of a PHA. Consider a low design pressure API storage tank filled with cyclohexane. Assume that the storage tank is equipped with a “pad/de-pad” vent system to control pressure, and is located in a diked tank farm. Figure 6.1 illustrates a typical scenario that might be developed during a PHA using the “What If…?” methodology.

In Figure 6.1, it can be seen that the listed safeguards would be effective means of mitigating the personnel exposure and environmental impact consequences identified for this scenario. In addition to the cause illustrated, other causes of high pressure that might be considered by a PHA Team include the following:

- External fire in the area, leading to increased vapor pressure in the storage tank.
- Overfill via the supply pump, leading to overpressure by deadhead pump pressure.

What If…?	Initiating Cause	Consequence	Safeguards
1. There is High Pressure in the Cyclohexane Storage Tank?	1.1 Failure of the pressure regulator on nitrogen supply line to Cyclohexane Storage Tank.	1.1 Potential for pressure in tank to rise due to influx of nitrogen pad gas through failed regulator. Potential to exceed design pressure of storage tank. Potential tank leak or rupture leading to spill of a flammable liquid. Potential fire should an ignition source be present. Potential personnel injury should exposure occur. 2.1 Potential environmental release requiring reporting and remediation.	1. Conservation Vent sized to relieve overpressure due to this scenario. 2. Pressure transmitter with high alarm set to indicate high pressure in Cyclohexane Storage Tank

Figure 6.1. Example of a hazard scenario using “What If...?” methodology.

If the safeguards identified by the PHA team are not deemed adequate, recommendations are made for the implementation of additional safeguards. This technique, called Layer of Protection Analysis (LOPA), is often employed by PHA teams to quantitatively assess the risk associated with an upset scenario so that appropriate layers of protection can be applied to adequately mitigate the risk (CCPS, 2001).

Hazard assessment and layer of protection analysis are complex subjects. As such, a formal hazard analysis is typically not performed during the conceptual phase of process design. In most cases, the PHA is performed during the engineering phases of a project. However, a basic understanding of the fundamentals of risk assessment is extremely beneficial to the development of inherently safer designs during the conceptual phase of process design. The design engineering student must be aware of the types of hazard scenarios that may be identified for each piece of equipment or system in order to make inherently safer design choices during conceptual development of a process.

6.5 Inherently Safer Process Design

Inherently safe process design practices can generally be grouped into five categories (Kletz, 1998)(CCPS, 1993):

- Intensification
- Substitution
- Attenuation
- Limitation of effects
- Simplification.

Some examples of inherently safer design choices for process applications are included in Table 6.1.

Typically, however, these types of design choices are made in later stages of engineering development. Although these are important design considerations, it is very beneficial to begin evaluating inherently safer design strategies at the earliest stages of process development, when the process design engineer has the greatest opportunity to affect the safety aspects of the process. Some examples of design choices that are typically made at the onset of conceptual engineering are illustrated in Table 6.2.

Table 6.1. Inherently safer design choices for common design applications.

Hazard Scenario	Process Operation	Potential Upset Case	Inherently Safer Design
Overpressure	Filling a process vessel with a pump	Overpressure by pump deadhead due to overfill	1. Vessel design pressure greater than pump deadhead pressure 2. Static head due to vessel elevation plus vessel design pressure greater than pump deadhead pressure.
Overpressure	Operating a vessel under inert gas pressure	Failure of inlet gas regulator leading to overpressure.	1. Vessel design pressure greater that inert gas supply pressure.
Underpressure	Emptying a process vessel with a pump	Blocked vent leading to vessel collapse due to vacuum pulled during pump out.	1. Vessel designed for full vacuum
Underpressure	Draining an elevated process vessel by gravity.	Blocked vent leading to vessel collapse due to vacuum pulled during draining.	1. Vessel designed for full vacuum 2. Liquid drain lined sized to be self-venting.

Initially, inherently safer designs may seem to be more expensive than applying traditional safeguards. However when the total costs are considered, the inherently safer design is often more cost effective. Installing and maintaining multiple independent layers of protection can be expensive, however these costs are often ignored during initial cost estimates. Conceptual phase cost estimates are usually based on stand alone major equipment costs that are simply multiplied by factors to obtain the total installed cost. These factors are intended to account for instrumentation and controls, among other items needed for the complete process installation. To apply the same factors to traditional and inherently safer processes can lead to an erroneous comparison. Inherently safer processes will typically require fewer safety controls which leads to lower installation and operating costs. These factors should be considered when evaluating total project costs. Additional cost savings for inherently safer processes that are often overlooked include insurance costs and the costs associated with regulatory compliance.

Table 6.2. Opportunities for making inherently safer design choices (Kletz, 1998).

Process Design Choice	Inherently Safe Design Category	Potential Process Safety Impact
Reactor type	Intensification	Continuous reactors are typically smaller than batch reactors for a given production volume.
Feed stocks	Substitution	Less hazardous raw materials may be available to make the same products.
Process solvents	Substitution	Less hazardous and/or less volatile solvents may be available.
Reaction mechanism	Attenuation	Endothermic reactions present less potential for runaway.
Operating conditions	Attenuation	Temperatures and pressure close to ambient are typically less hazardous.
Process utilities	Attenuation	Low pressure utilities such as hot oil may be a safer choice than high pressure steam.
Alternative technology	Attenuation	Use of alternative technology, for example pervaporation instead of azeotropic distillation using a solvent entrainer.
Production rate	Limitation of effects	A continuous process making just what is required can be safer that a batch process with a large hold-up volume.
Storage volume	Limitation of effects	Minimization of volume limits the potential effects of a release.
Equipment layout	Simplification	Utilizing gravity flow minimizes the need for rotating equipment.
Cooling by natural convection	Simplification	Utilizing natural convection simplifies the process and eliminates the potential for process upsets due to loss of utilities.

6.6 Conclusions

Risk assessment and attention to inherently safe design tenets should be considered at each stage of process design. This is important because one of the responsibilities of every chemical engineer is to ensure that the excellent safety record enjoyed by the chemical process industry is maintained. Therefore it is important to apply the fundamentals of process safety during process design. Taking a holistic approach to process safety can improve the decision making procedures during conceptual process development. By applying inherently safe design choices during conceptual process development, the application of more costly independent protection layers at a later stage of process development can be avoided.

CHAPTER 7

ASSESSMENT OF POTENTIAL ENVIRONMENTAL IMPACTS

7.1 Introduction

The purpose of this chapter is to illustrate how the environmental impact analysis has been integrated into the conceptual process development by use of a simple methodology. The developed methodology is illustrated using the glycerol dehydration case study example. By integrating environmental impact analysis into the standard design heuristics used to develop and screen potential conceptual processes, the design engineer can ensure that the resulting process is not only optimized in terms of overall performance, but also is based on minimizing the environmental impact of the process.

The tool used to calculate the potential environmental impact, PEI, of the proposed conceptual processes is the Waste Reduction (WAR) algorithm, developed by the U.S. Environmental Protection Agency (Young and Cabezas, 1999)(Young *et al.*, 2000). The PEI of a given quantity of material and energy can be defined as the effect this material or energy would have if it were emitted directly to the environment (Young and Cabezas, 1999)(Young *et al.*, 2000). For the purposes of this study, only the PEI of the streams leaving the process was considered. It is assumed that each of the conceptual processes would be subject to the same regulatory environmental constraints, so the PEI after waste treatment would not provide a clear picture of the true impact of the production process itself.

There are some important limitations to using the WAR algorithm for an analysis of this type. Although the WAR algorithm provides an effective means of comparing process options with a similar basis, it cannot evaluate the impacts of switching from a crude oil to a renewable, biomass derived feed stock. Therefore one should use caution when directly comparing the PEI calculated for the glycerol cases with that calculated for processes based on utilizing crude oil derived feedstocks. The use of biomass derived feed stocks can be considered nearly carbon dioxide neutral, therefore the use of glycerol as a feed stock has a potentially significant advantage over crude oil derived feedstocks in terms of environmental impact. Since this analysis does not include a complete lifecycle assessment, any benefit gained by this switch in feed stocks will not be captured.

7.2 Background

In recent years, much attention has been focused on the impact human activities have on the global environment. The effects of using of crude oil derived fuels and feed stocks on the global climate, and the importance of pursuing the use of sustainable raw material feed stocks has been well documented (Clift, 2005)(Hoel and Kverndokk, 1996)(Vicente, 2004). In terms of energy production, biodiesel is the only alternative with an overall positive lifecycle energy balance (Buczek, 2004). Therefore use of biodiesel and its byproducts may have a positive impact on global climate change. In addition, according to the U.S. Department of Energy’s 2003 *World Energy Report*, at current rates of consumption, crude oil reserves may be depleted in 80 to 120 years

(DOE, 2003). This provides an incentive for replacing crude oil derived fuels sources with sustainable sources, such as biodiesel.

Recent estimates predict that the demand for biodiesel will grow from 6 to 9 million metric tons per year in the United States and from 5 to 14 million metric tons per year in the European Union in the next few years (Blume and Hearn, 2007). However, for every 9 kilograms of biodiesel produced, 1 kilogram of crude glycerol is formed as a byproduct (Chiu *et al.*, 2006). Due to its high viscosity, glycerol must be removed from the biodiesel product, thus reducing the carbon utilization. Therefore, the identification of novel industrial uses for this glycerol is important to the economic viability of biodiesel (USDA, 2003).

7.3 An Integrated Approach to Environmental Impact Assessment

Often the criteria used in developing conceptual options for a proposed process is based solely on its viability in terms of performance. Although the importance of performance should not be minimized, the environmental impacts of a new process should not be ignored. There are a multitude of benefits for minimizing the environmental impacts of a process:

- Potential new environmental regulations
- Emissions trading opportunities
- Potential increased costs of “after the fact” means of emissions abatement.

By taking an integrated approach, an optimized design that considers both viability in terms of performance and minimum environmental impacts can be proposed.

7.4 Environmental Assessment Methodology

The methodology for integrating environmental impact considerations with overall viability is based ensuring that the most environmentally benign process is selected from among the viable process options. This methodology is illustrated in Figure 10.1, below. This methodology is illustrated for the first phase of process development for the glycerol dehydration process. The development of the simulation options was described previously in Chapter 4.

7.4.1 Step 1: Defining Conceptual Process Options

The first step of the methodology is the definition of the potential conceptual process options. As described in Chapter 4 a review of current literature indicates that the catalytic dehydration of glycerol can be carried out in either the liquid, vapor or supercritical water phase (Neher *et al*., 1995)(Ramayya *et al*., 1987). For the development of a potential industrial process, the reaction in the supercritical water phase is eliminated due to the extremely high pressures required for this process. Therefore, only the liquid and vapor phase processes are considered for development.

7.4.2 Step 2: Process Simulation Development

Based on the results of Step 1, process simulation models are developed for the liquid and vapor phase processes. The Aspen Plus process simulation software package was used to generate the conceptual process models for each of these cases (Aspentech, 2006). Standard design heuristics are applied to develop process and recycle options. The development of these processes is described in Chapter 5.

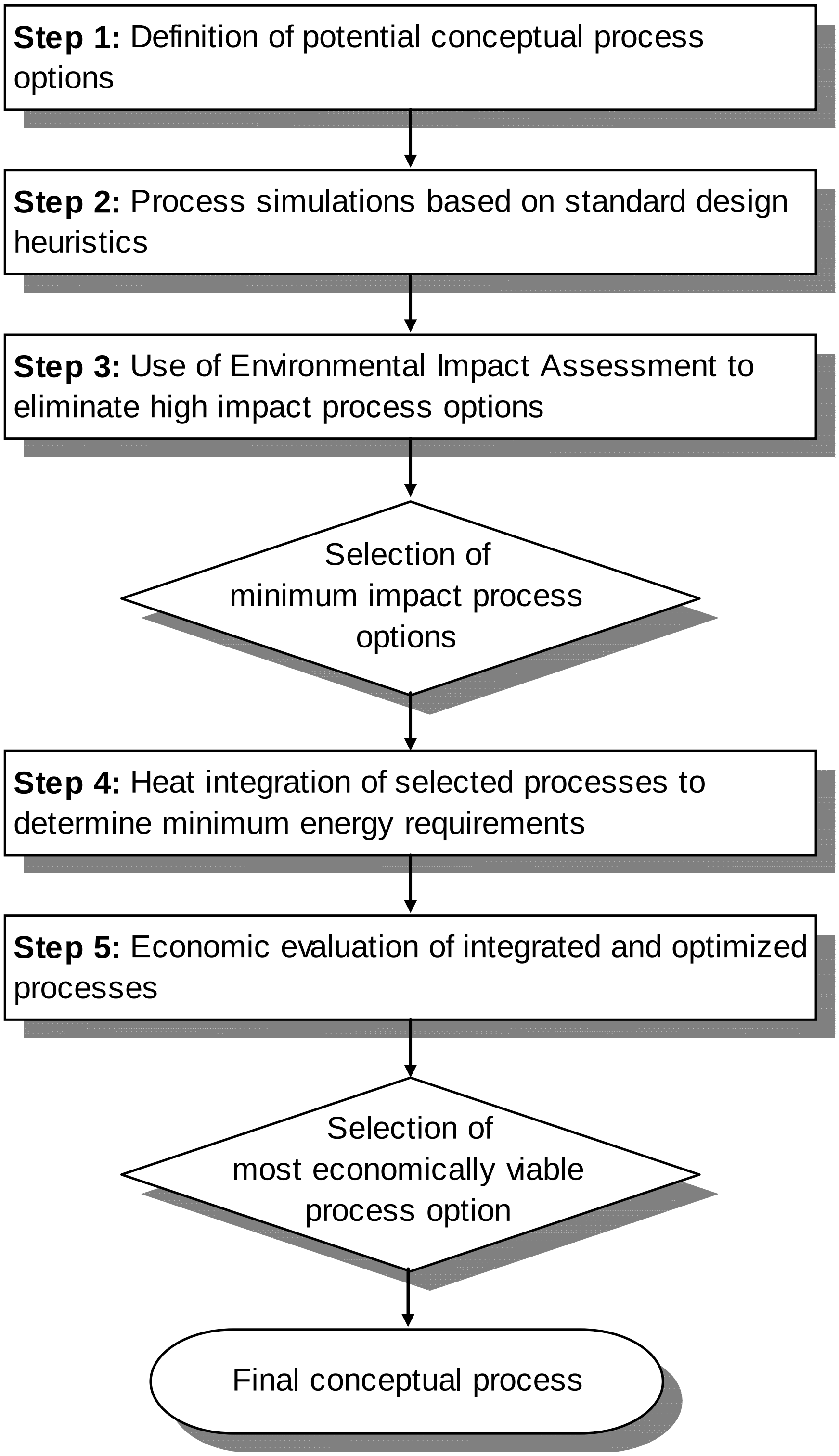

Figure 7.1. Flowchart of proposed PEI integration methodology.

7.4.3 Step 3: Environmental Impact Analysis

Once the conceptual process options have been defined and the initial simulations completed, the next step of the methodology is to calculate the Potential Environmental Impact (PEI) for each of the proposed conceptual processes. The PEI is a quantitative means of indicating the environmentally friendliness of a process (Young and Cabezas, 1999)(Young *et al*., 2000). The tool used to calculate the PEI of the proposed conceptual processes is the Waste Reduction (WAR) algorithm, developed by the U.S. Environmental Protection Agency (Young and Cabezas, 1999)(Young *et al*., 2000). The PEI of a given quantity of material and energy can be defined as the effect this material or energy would have if it were emitted directly to the environment (Young and Cabezas, 1999)(Young *et al*., 2000). The PEI for a process is made up of 8 categories of environmental impacts (Cabezas *et al.*, 1999):

- Human Toxicity: Ingestion
- Human Toxicity: Dermal/Inhalation
- Aquatic Toxicity
- Terrestrial Toxicity
- Global Warming
- Ozone Depletion
- Photochemical Oxidation
- Acidification.

The individual weighting for each of the above categories can be changed, depending on the emphasis of the study. For the purposes of this study, only the PEI of the streams leaving the process was considered, and each category will be given equal weight. It is assumed that each of the conceptual processes would be subject to the same regulatory environmental constraints, so the PEI after waste treatment would not provide a clear picture of the true impact of the production process itself. The results of the PEI analysis are illustrated in Figure 7.2, below. The contribution of the process and total energy to the total PEI is reported on a per kilogram of product basis.

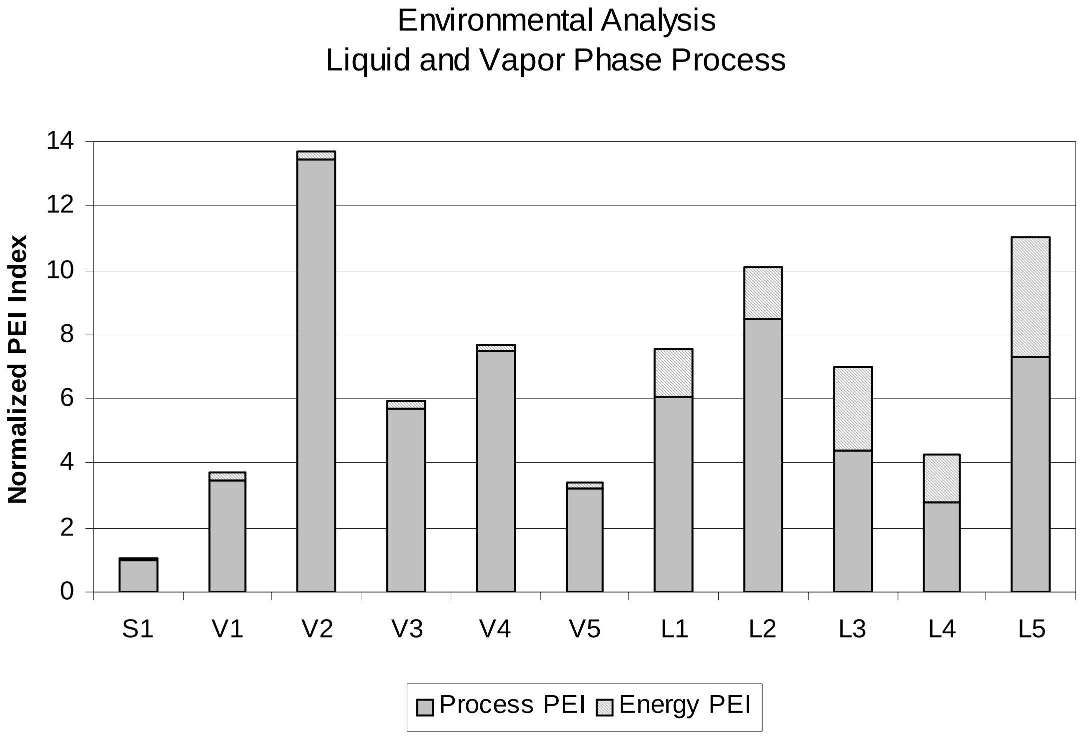

Figure 7.2. PEI analysis for liquid and vapor phase conceptual processes.

7.4.4 Step 4: Minimum Energy Analysis

In order to ensure optimal resource utilization, it is imperative to apply holistic methods like pinch analysis to optimize any proposed conceptual processes. Increased energy and mass integration enable higher utilization of raw materials and minimize the use of external utilities (El-Halwagi, 1997)(Linnhoff, 1983). The minimum utility requirement for each of the candidate conceptual processed was evaluated using the Aspen HX-Net software package (Aspentech, 2006). The development of this analysis is described in Chapter 9. The utility operating costs at minimum utility are based on the coldest cold utility and the hottest hot utility assumed to be available. The results of the energy analysis are illustrated in Figure 7.3, below. The total process energy requirement, and the process energy requirement at minimum utility is reported on a per kilogram of glycerol fed basis. Also included in this analysis is the alternative inert gas process. The development of this process will be described in Chapter 9.

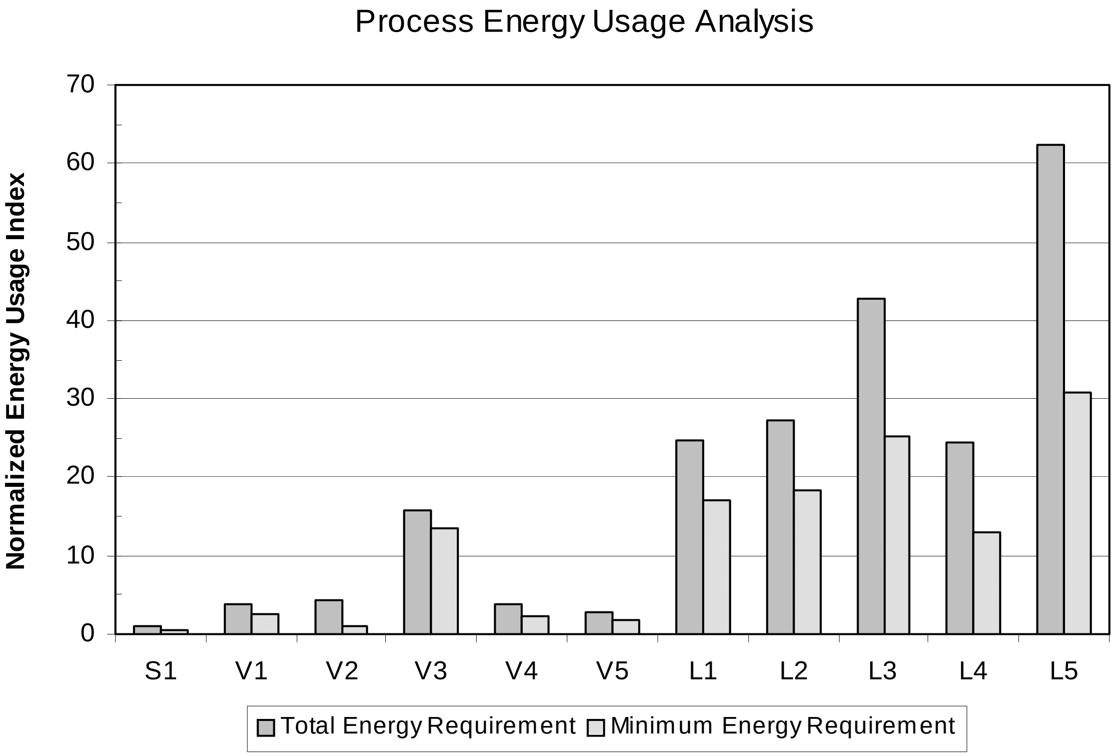

Figure 7.3. Energy usage for liquid, vapor and inert gas conceptual processes.

The results of the thermal pinch analysis indicate that there is greater potential for heat integration with the liquid phase process, however, the total utility requirements is significantly lower for the vapor phase and inert gas processes. From this analysis, the inert gas process is the most competitive with the industry standard process based on crude oil derived raw materials.

7.4.5 Step 5: Performance Analysis of Minimum PEI Processes

Based on the analysis of the results of the liquid and vapor phase processes, a new conceptual process based on the use of an inert gas to dilute the glycerol feed is generated. The development of this process is described in Chapter 9. This process represents the true minimum in terms of the process performance index, energy utilization and potential environmental impact. The result of the PEI assessment for the vapor phase, liquid phase and inert gas processes for the initial and minimum energy cases are illustrated in Figure 7.4, below.

7.5 PEI Results for Optimization Experiments

The PEI is also calculated for each of the optimization experimental cases, F1 – F21, described in Chapter 10. The results of this analysis are illustrated in Figure 7.5, below. In this figure, the product yield results are superimposed on the PEI results. From this illustration, it is seen that the PEI trends are inverse to the product yield trends. These results show that, in general, the operating conditions leading to the highest yield also lead to lower PEI values.

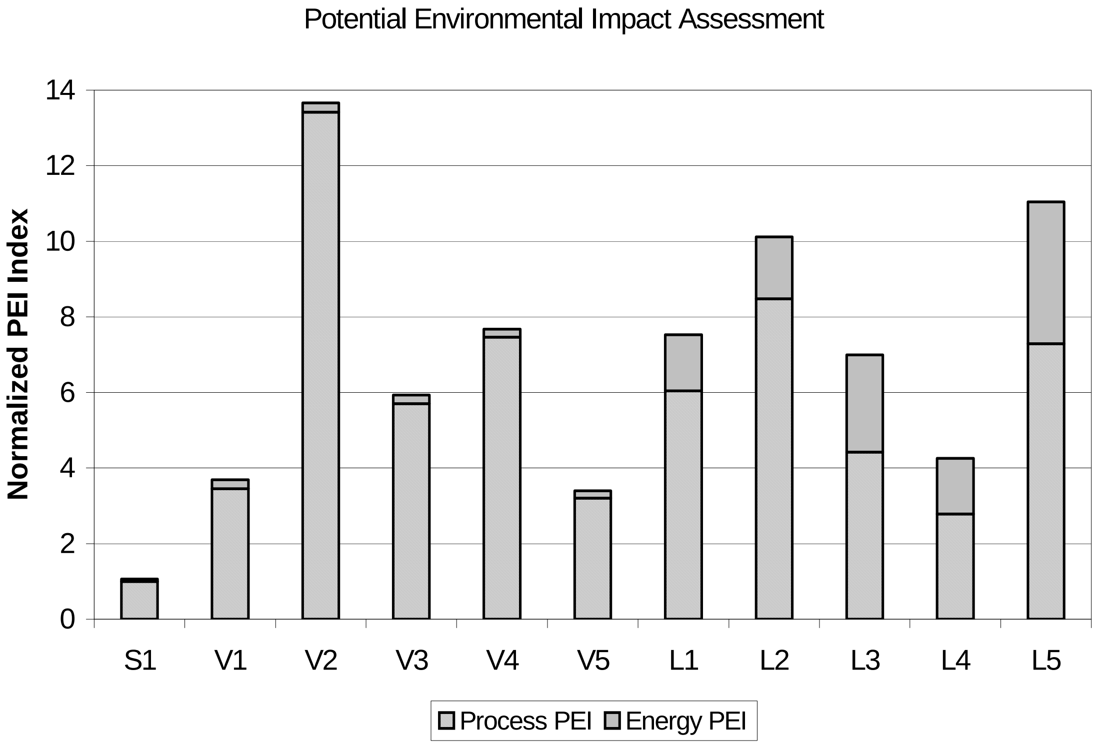

Figure 7.4. Final PEI results for vapor phase, liquid phase and inert gas processes.

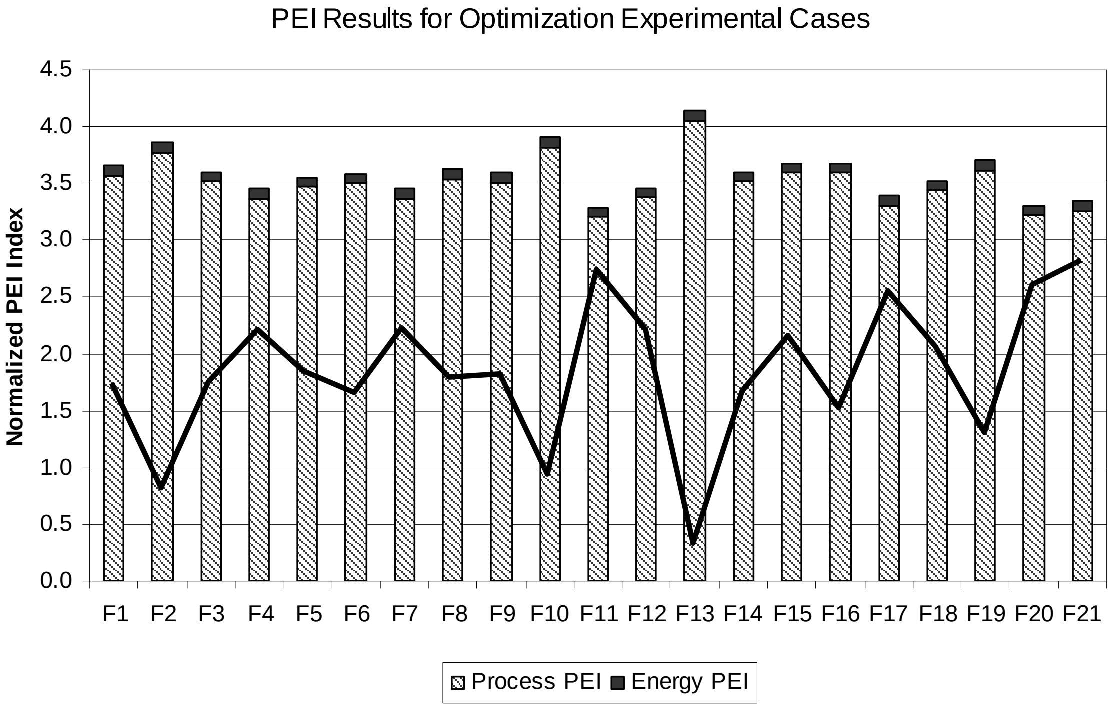

Figure 7.5. PEI results for optimization experimental cases with superimposed yield.

7.6 Conclusions

In conclusion, it should be clear that through the application of the proposed methodology for including environmental impact assessments into conceptual process design, the process with the minimum environmental impact can be identified from among the viable process options. Because of the importance of including environmental considerations into the design of industrial chemical processes, this methodology is useful because it incorporates these considerations into the early stages of process design. This allows minimization of the PEI to be achieved through process design, rather than in later stages of the process, where pollution prevention techniques are more costly.

CHAPTER 8

DESIGN AND CALIBRATION OF THE LAB SCALE MINI-PLANT

8.1 Introduction

As discussed in Chapter 5, the results of Step 1 and Step 2 of the proposed methodology showed that the initial process simulation studies indicated that the process based on vapor phase glycerol dehydration held the most promise for viability in terms of performance. To move on to Step 3 of the methodology, a lab scale mini-plant was designed based on this vapor phase process. The primary purpose of this chapter is to describe the design and function of the lab scale mini-plant for conducting experiments on the gas phase catalytic dehydration of glycerol. In this chapter, both the equipment required to model this process and the system used to control it are described. In addition, a discussion of some of the techniques required for the handling of vapor phase glycerol and its dehydration products is included.

8.2 Chemistry and Physical Property Overview

As has been previously discussed, the system being studied using this mini-plant is the catalytic vapor phase dehydration of glycerol. The physical properties of glycerol make handling it in the vapor phase challenging. The physical properties are listed in Table 8.1, below. Note that since 3-hydroxypropionaldehyde is an unstable intermediate in this system, no physical property data is included. Because of the low vapor pressure of glycerol, high temperatures are required to create and maintain a vapor phase.

The dehydration of glycerol can be catalyzed by a variety of acids, including sulfuric or phosphoric acids (Neher *et al.*, 1995)(Ramayya *et al.*, 1987). Although the acid catalyzed dehydration of glycerol can be carried out in either the liquid phase, vapor phase or in supercritical water, the focus of this research is the vapor phase reaction.

Table 8.1. Property data for glycerol and its dehydration products.

Chemical Species	**Formula**	**MW grams/mole**	**BP_{Norm} °C**	**P^{sat} @ 25°C bar**	**P^{sat} @ 300°C bar**
Formaldehyde	HCOH	30.03	N/A	5.19	536.52
Acetaldehyde	CH_3CHO	44.05	21.00	1.17	252.91
Acrolein	C_2H_3CHO	56.06	52.74	0.37	125.50
Acetone	CH_3COCH_3	58.08	56.14	0.31	105.70
Propionaldehyde	C_3H_6O	58.08	48.00	0.42	113.13
Allyl Alcohol	C_3H_4OH	58.08	96.97	3.39E-02	81.29
Acrylic Acid	C_2H_3COOH	72.06	141.19	0.01	31.66
Hydroxyacetone	$OHC_2H_2OCH_3$	74.08	145.60	4.77E-03	36.01
3-Hydroxy-propionaldehye	OHC_3H_5O	n.d.	n.d	n.d	n.d.
1,2-Propanediol	$C_3H_6(OH)_2$	76.10	187.72	1.72E-04	18.96
1,3-Propanediol	$OH(CH_2)_3OH$	76.10	214.67	3.31E-05	8.06
Glycerol	$C_3H_5(OH)_3$	92.10	288.03	0.00	1.37

In this process, the acid catalyst is supported on a porous solid support. Previous research on this process describes the use of silica or alumina as a catalyst support (Neher *et al.*, 1995). In the case of this research, the reaction is carried out in a fixed bed reactor.

Several sources report the formation of coke (solid carbon deposits) on the catalyst and in the equipment (Neher *et al.*, 1995)(Dubois *et al.*, 2006). This can cause problems with operation of the mini-plant equipment. The polymer formation can be minimized by ensuring that the system remains in the vapor phase and diluting the glycerol feed. By diluting the feed, the probability of two glycerol molecules reacting is minimized. Minimizing polymerization can also improve the product yield for the process. The coke formation is more difficult to control. Therefore the pressure loss in the mini-plant due to restricted flow area must be monitored to prevent possible plugging in the tubing or in the catalyst bed.

8.3 Mini-Plant Design Requirements

The mini-plant consists of multiple sections designed to model the front end of a glycerol dehydration process. In general, the mini-plant must contain individual unit operations to supply the raw materials, vaporize the liquid feed and carry out the dehydration reaction in a fixed bed. Additionally, because of the high temperatures, the system must be sufficiently heat traced and insulated. Finally, the mini-plant must be equipped with a means of sampling the reactor effluent in order to determine the composition. The primary control variables include temperature, inlet composition and flow rate. In addition, it is necessary to monitor the system pressure. Finally, the mini-plant must be equipped with a safety relief system to prevent personnel injury in the event of overpressure.

The individual elements of the mini-plant are connected using stainless steel tubing and stainless steel Swagelok® fittings for the heated section of the mini-plant and Teflon® tubing for the sections of the mini-plant where materials are handled at ambient temperatures. Both stainless steel and Teflon® were selected because they are inert to the glycerol dehydration chemistry. Additionally, since coking and polymer formation are known to occur, the use of Swagelok® fittings ease the opening of the tubing for cleaning or replacement. The tubing used with the mini-plant is 0.125 inch nominal diameter for the inlet streams and 0.25 inch nominal diameter for the reactor feed and discharge.

8.4 Equipment Descriptions

Based on the above requirements, appropriate equipment, instrumentation and control system were selected. The design and function of these elements are described in the following sections. Refer to Figure 8.1, the mini-plant piping and instrumentation diagram, for the location of equipment and numbered instrumentation and control elements.

8.4.1 Syringe Feed Pump

The liquid feed to the mini-plant is a liquid solution of glycerol and water. Various concentrations can be used, depending on the experiment being conducted. The solution is fed using a syringe pump. The use of a positive displacement pump allows the total mass of liquid solution supplied during an experimental run to be determined precisely. The syringe pump selected for this application allows syringes of various sizes to be used. In addition, the stepper motor that drives the pump can be operated at various speeds. The variable speed motor, in conjunction with various syringe sizes allows a wide range of possible feed flow rates.

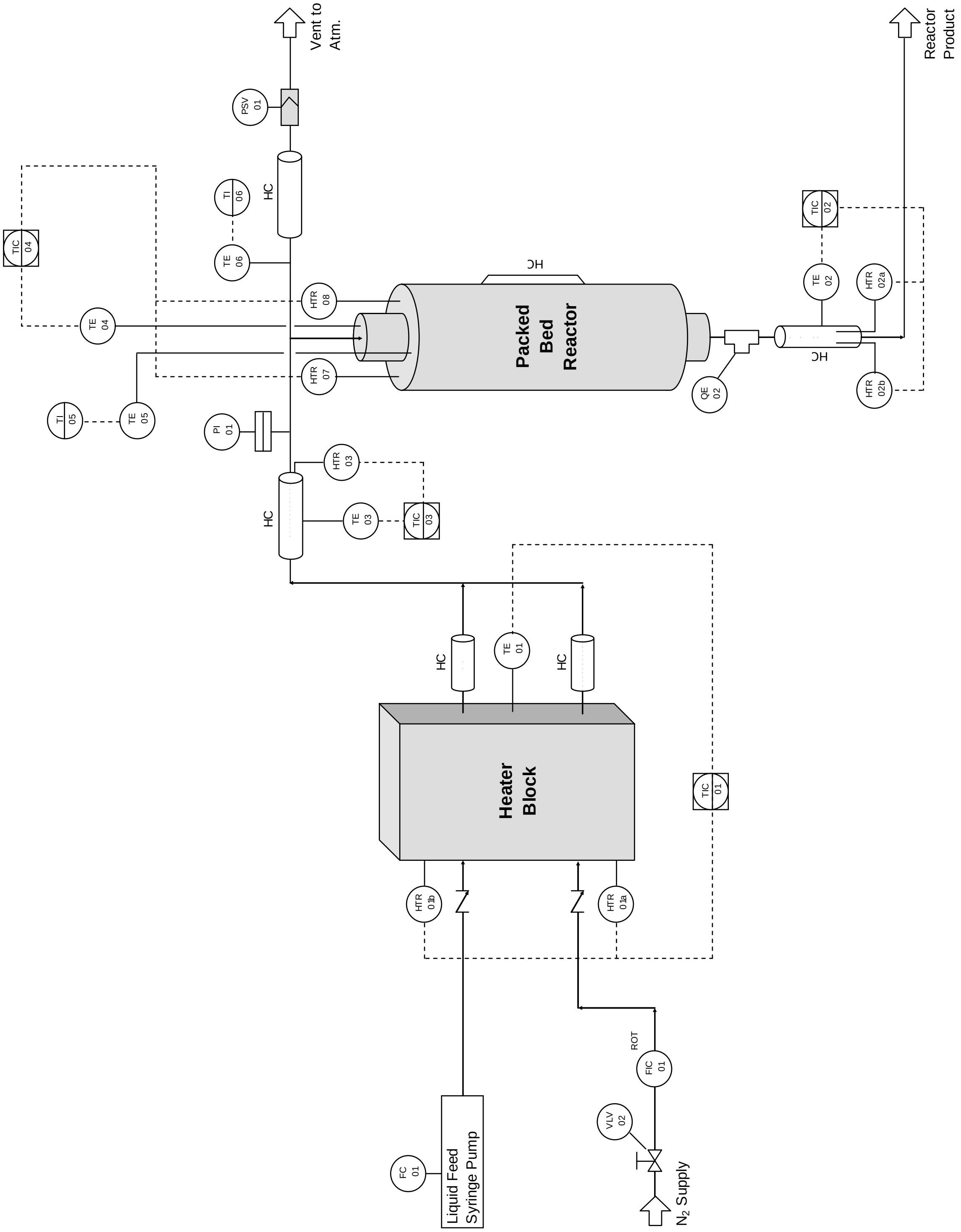

Figure 8.1. Laboratory mini-plant piping and instrumentation diagram.

8.4.2 Inert Gas Supply

In addition to the liquid feed, the mini-plant can also be supplied with an inert gas. A variety of inert gases can be used as carriers for the reactor. If nitrogen is used, supply is from the laboratory header. Other gases can also be supplied from pressurized bottles.

8.4.3 Feed Vaporizer / Preheater

The liquid feed to the system must be vaporized for conducting the vapor phase experiments. Additionally, for experiments using an inert carrier gas, the gas must be heated for mixing with the vaporized glycerol/water solution. This is achieved by passing the liquid and gas feed flows through a heater. This heater consists of a solid aluminum block with holes drilled for cartridge heaters and thermocouples. The cartridge heaters are 3-inch rods capable of supplying 200 Watts per square inch. Two heaters are used to heat the aluminum block. The control of this heater block is described in section 8.5. The liquid and inert gas feed lines are turned into 0.75 inch coils and routed through holes in the aluminum block as illustrated in Figure 8.2, below.

8.4.4 Packed Bed Reactor

The packed bed reactor is constructed from of a single piece of 0.75 inch stainless steel tubing. The reactor is fitted with a screen at the bottom to retain the solid catalyst. The packed bed reactor is surrounded by a two-piece solid cylindrical aluminum block. This block has holes drilled for two 3-inch 200 Watt cartridge heaters and a thermocouple. This block is used to maintain temperature in the Packed Bed Reactor and to provide the heat required to drive endothermic reactions. In addition to the thermocouple in the aluminum heater block, the reactor is equipped with an internal thermocouple used to monitor the temperature inside the catalyst bed.

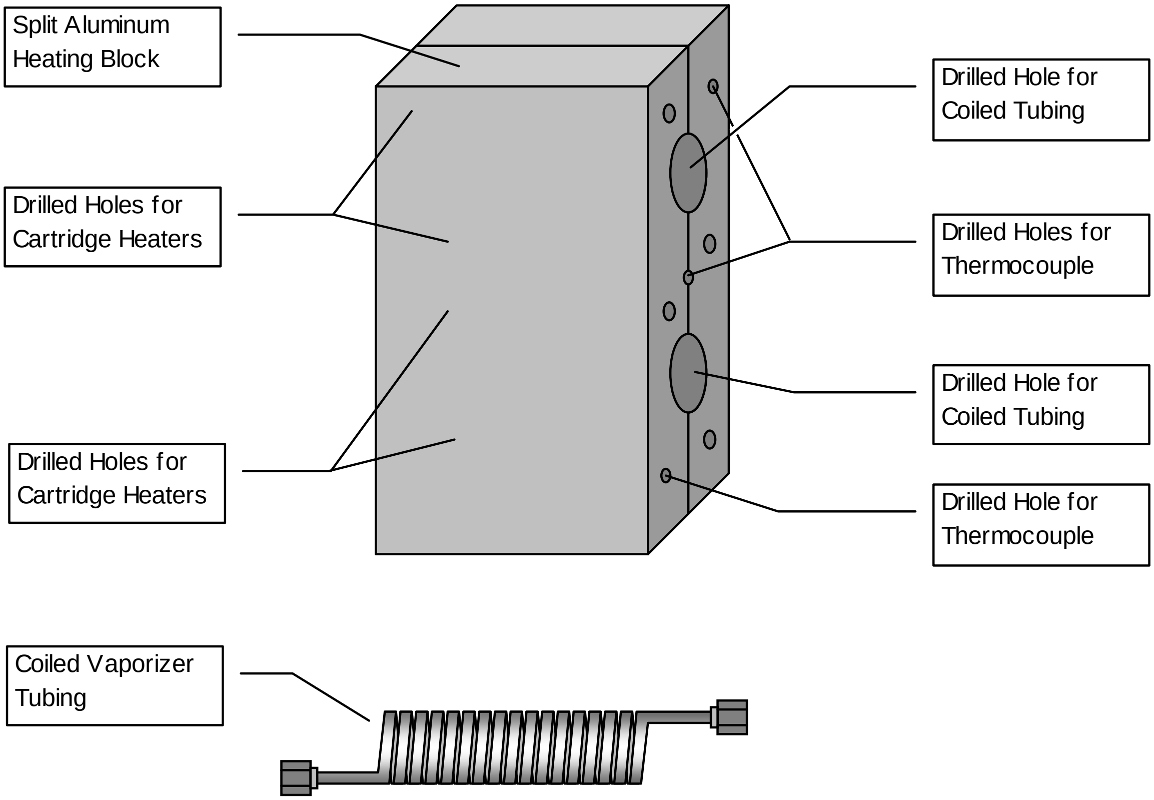

Figure 8.2. Detail of heater block for vaporizing / preheating raw material feeds.

8.5 Instrumentation and Control Systems

The primary variables of interest for the operation of the mini-plant are temperature, pressure, flow and composition. The control and instrumentation of the mini-plant are a combination of manual and automatic instrumentation and control systems. The design and function of these systems are described in the following.

8.5.1 Inert Gas Flow Indication and Control

As previously described, there are two feeds to the system, a liquid feed and inert gas feed. Although the liquid feed is controlled by a variable speed syringe pump, the inert gas feed must be controlled separately. The inert gas feed is controlled manually by a flow control rotameter, FE-01. The rotameter indicates the standard volumetric flow of inert gas into the heater block with a range of 0 – 2 cubic feet per minute.

8.5.2 Temperature Indication and Control

The temperature of the heater block, the electric tracing and the reactor heating mandrel are all automatically controlled. For this application, Omega Model CN4620 PID type controllers are utilized. These controllers are shown in Figure 8.3, below. The system is configured with three separate control loops, as illustrated in Figure 8.1. This allows each section, the heater block, the electric tracing and the fixed bed reactor to be controlled at different temperatures, if desired. Each controller is tuned independently prior to use for controlling the system. Due to the proprietary nature of the data, the process for tuning the temperature controllers is included in Appendix B, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members. The temperature range for the vapor phase glycerol dehydration reaction is 250 to 350°C (Neher *et. al*, 1995). Additionally, the thermocouples used to provide the signals must be rated for these high temperatures. Omega quick disconnect thermocouples with 304 stainless steel sheathing and type K connections are utilized for all temperature measurements in the process.

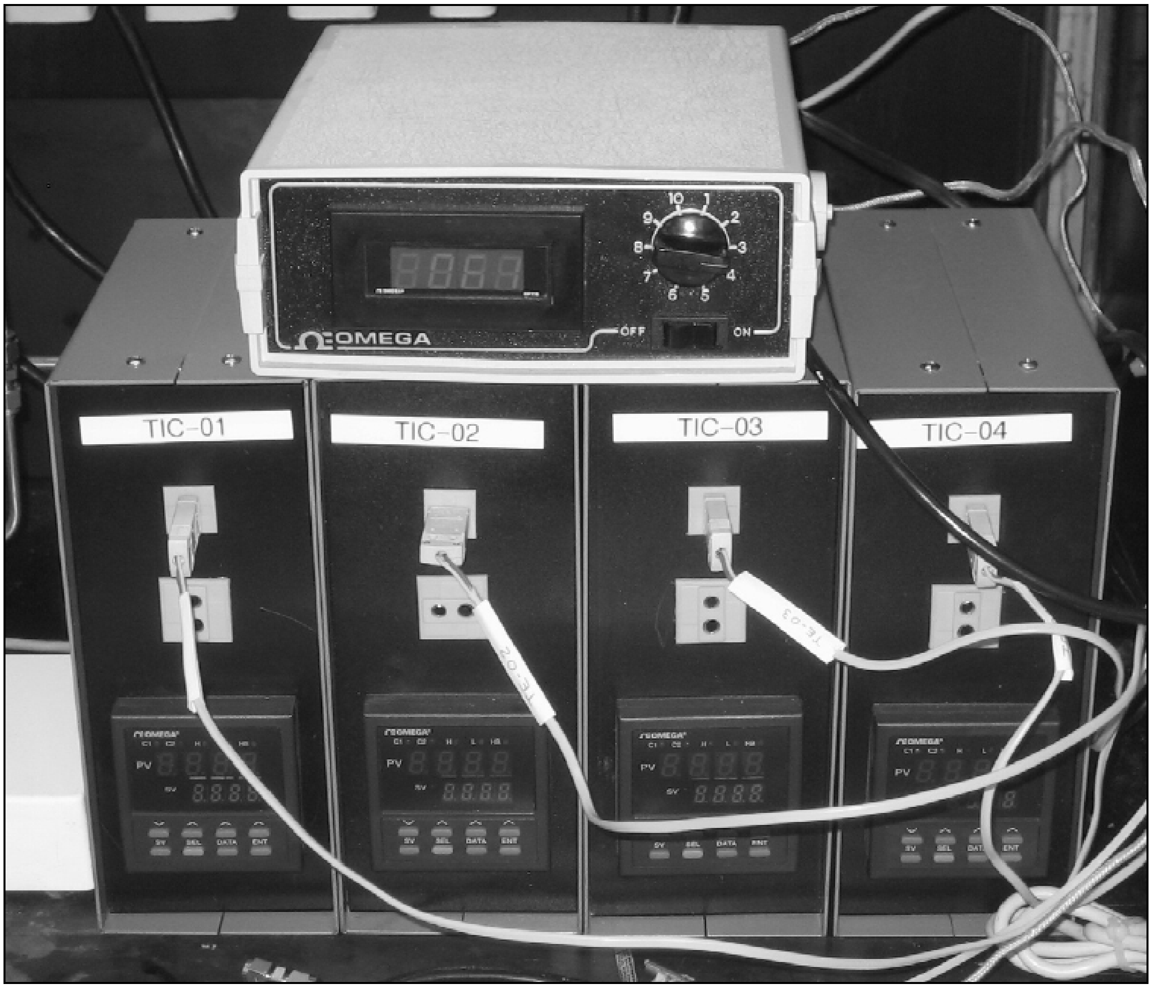

Figure 8.3. Omega temperature controllers and temperature indicator.

As previously described, the heater block is heated by two cartridge heaters, HTR 01a and HTR 01b. These two heaters are controlled together by a single PID controller, TIC-01. The temperature signal to the PID controller is via a thermocouple, TE-01. Because of the high boiling point of glycerol, the piping between the heater block and the reactor, and the reactor effluent piping is electrically traced. The electric tracing between the heater block and the reactor is a wrapped type electric strip. This tracing is controlled by PID controller TIC-03. The temperature signal is provided by thermocouple TE-03.

The electric tracing on the reactor effluent piping is provided by two cartridge heaters on a single circuit, HTR-02a and HTR-02b, controlled by TIC-02. The temperature signal is provided by thermocouple TE-02.

The final temperature control loop is the heating mandrel for the fixed bed reactor. The packed bed reactor tube is surrounded by two halves of an aluminum cylinder as illustrated in Figures 8.4 and 8.5, below.

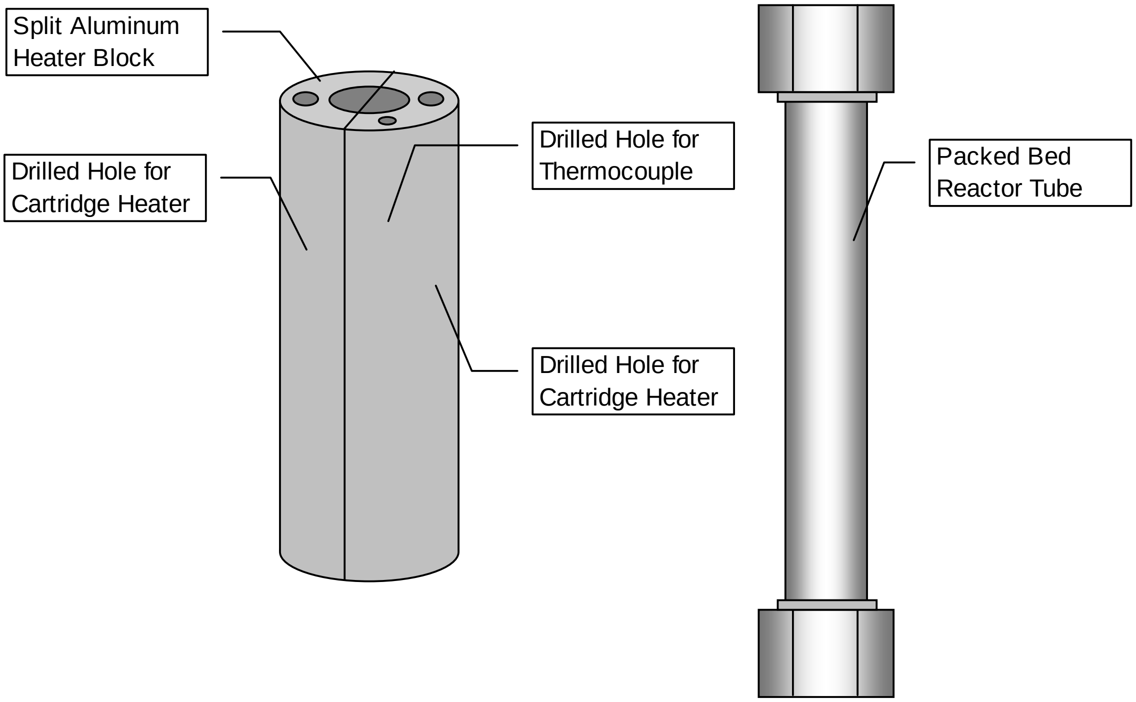

Figure 8.4. Detail sketch of split cylinder reactor heating mandrel.

The heating is provided by two cartridge heaters on a single circuit, HTR-04a and HTR-04b, controlled by TIC-04. The temperature signal however, is provided by a thermocouple inside the reactor fixed catalyst bed. This allows the temperature inside the reactor to be controlled, rather than controlling the temperature of the heating mandrel.

Although this configuration requires more careful tuning, the experimental results can be determined more accurately due to having a direct measurement of the catalyst bed temperature.

Additional thermocouples are used to provide temperature indication at other points in the mini-plant. The temperature of the heating mandrel itself is indicated by TE-05. Finally, the temperature inside the tubing connecting the heater block and the packed bed reactor is indicated by TE-06. Both of these thermocouples are wired to an electronic temperature indicator with a selector switch to view either signal.

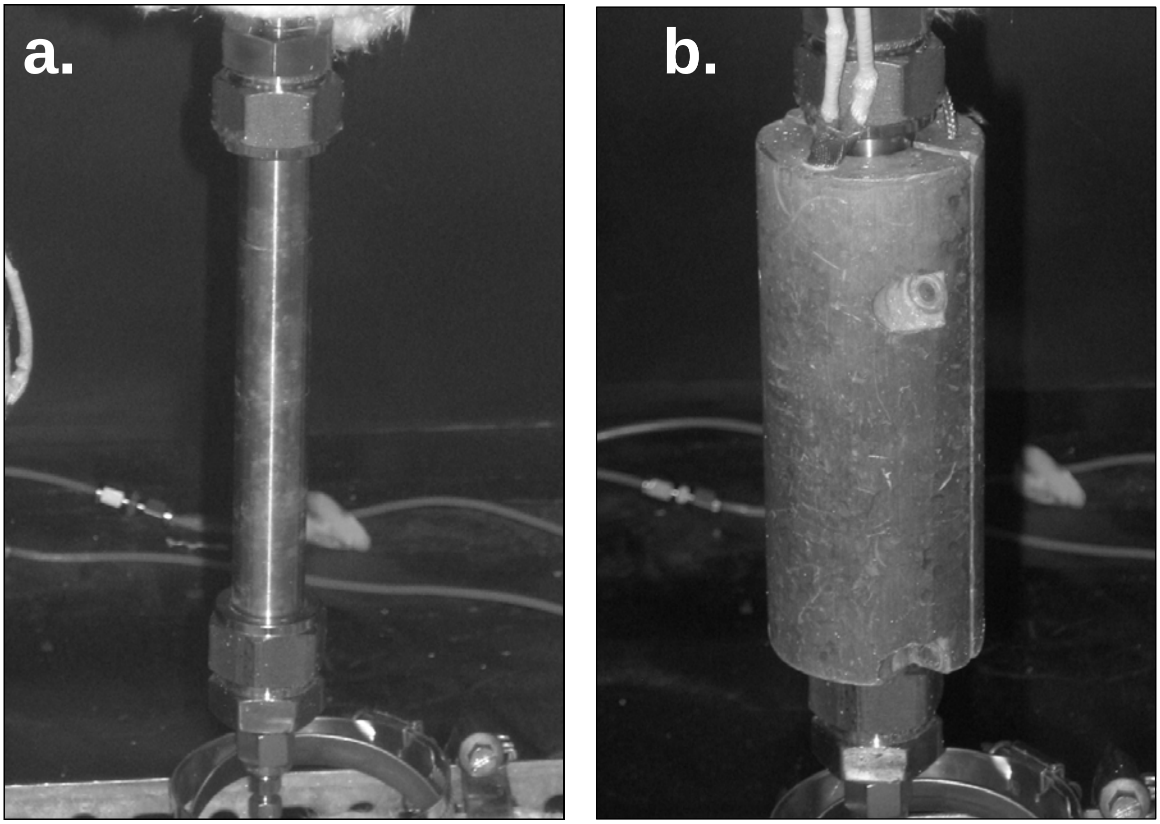

Figure 8.5. Detail photos of bare reactor tube (a) and reactor with heating mandrel (b).

8.5.3 Pressure Indication

In general, the system pressure is generated by the vapor pressure of the vaporizing liquids supplied by the feed pump. The system is open to the atmosphere and pressure is not actively controlled, therefore the pressure only increases above atmospheric pressure as a result of back pressure. As the flow is restricted, due to pluggage in equipment and piping, the system pressure rises. To monitor the system pressure, the mini-plant is equipped with a pressure gauge. Although the pressure is normally close to atmospheric pressure, any build-up of coke or polymer in the fixed bed reactor could lead to an increase in pressure. The overall system pressure is indicated by pressure gauge, PI-01, in the feed line to the reactor. This gauge has a range of 0 – 100 psig and is equipped with a diaphragm seal to prevent polymer formation in the gauge inlet. The gauge and diaphragm are filled with a high temperature silicone fill fluid. The system is protected from overpressure by a safety relief valve, described in the following.

8.5.4 Safety Systems

The system is equipped with a spring loaded pressure relief valve, PSV-01, for relieving an unsafe buildup of pressure in the system, as illustrated in Figure 6.1. Even though the Packed Bed Reactor is open to the atmosphere, plugging in the catalyst bed could be a potential cause of overpressure. Therefore, the safety relief valve is located at the top of the Packed Bed Reactor. The outlet from this valve is routed to atmosphere. The relief valve is set to open at 100 psig. This value is much higher than the normal operating pressure of the mini-plant, but far below the design pressure of the tubing and fittings used to assemble the equipment.

8.5.5 Sampling and Analysis

The reactor effluent gas is sampled using a 50 μL gas tight syringe. The piping at the outlet of the reactor contains a sampling tee, QE-01. This tee is sealed with a high temperature septum. A sample of the reactor effluent is taken by piercing the septum with the needle and drawing the gas into the syringe. The sample is then analyzed using an HP 5890 Series II gas chromatograph. The development of the method for analyzing the reactor product is described in Appendix C. Due to the proprietary nature of this procedure, Appendix C is included in Volume 2 of this dissertation. Volume 2 is not public and will only be available to the dissertation committee. A photo of the sampling port is shown in Figure 8.6, below. A photo of the complete reactor system, with the protective insulation removed for clarity, is shown in Figure 8.7, below.

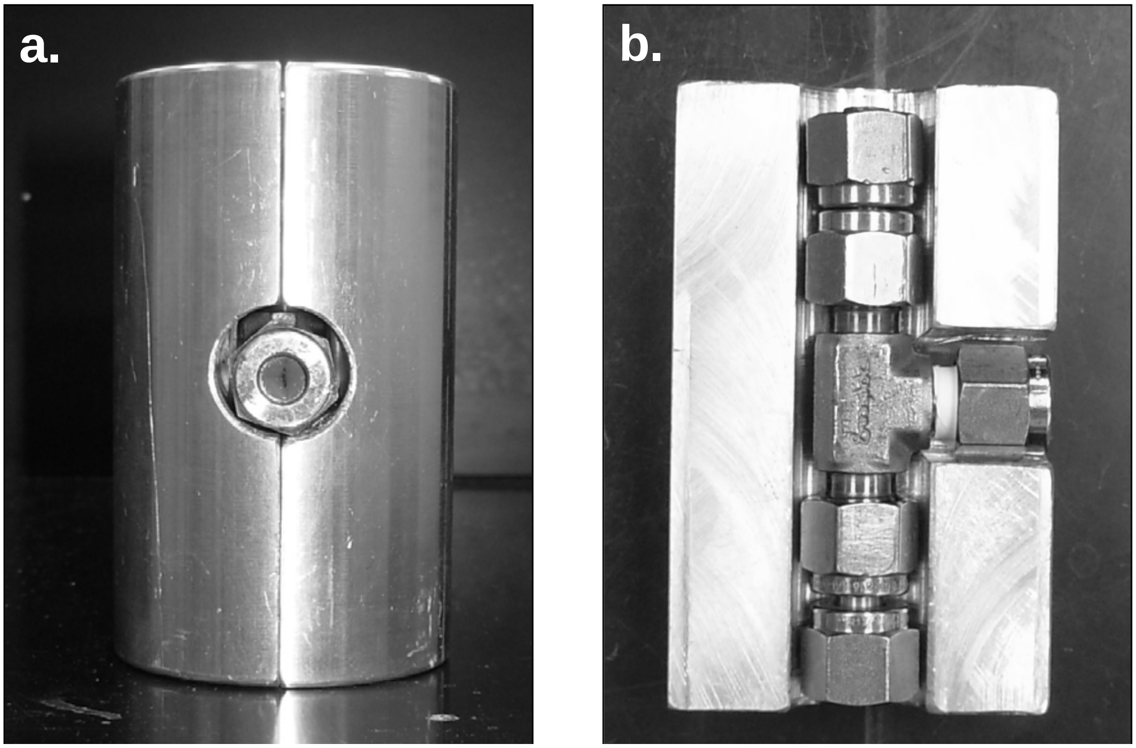

Figure 8.6. Reactor product sampling port showing jacket (a) and cutaway view (b).

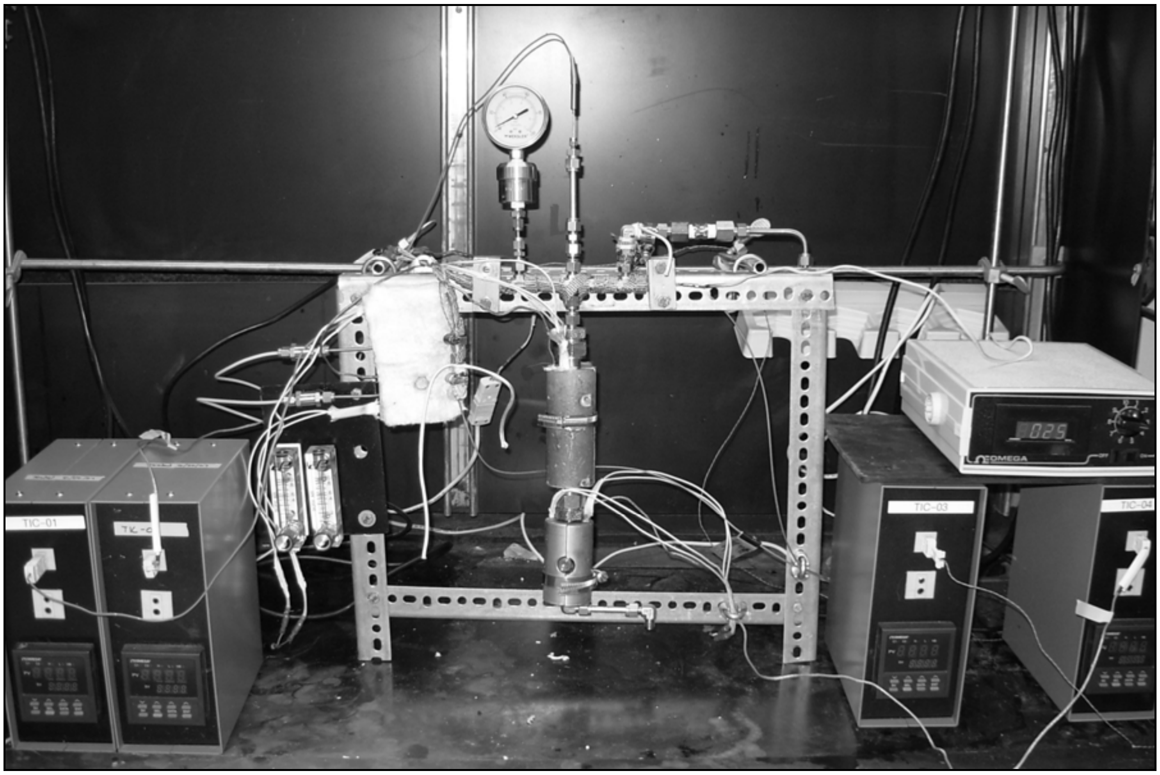

Figure 8.7. Photo of laboratory scale mini-plant (insulation removed).

CHAPTER 9

REFINED MODELS BASED ON EXPERIMENTAL RESULTS

9.1 Introduction

Step 4 of the proposed methodology is to take the initial experimental results and once again apply the simulation and optimization methodology to further refine the process. Based on the laboratory experiments, many of the assumptions required in the development of the initial process simulation models can be validated or rejected. As outlined in the conceptual process design methodology, the process simulations are to be refined based on the laboratory results. As before, an assessment of the overall performance and environmental impacts of the process options considered is incorporated into the analysis. The results of this analysis should lead to the development of new process conditions based on the revised simulation models. Finally, in Step 5 of the proposed methodology, these new process conditions are reevaluated in the laboratory to arrive at the final process design. The purpose of this chapter is to elaborate the procedure carried out in Step 4 in more detail.

9.2 Revised Simulation Cases

As previously described in Chapter 5, the initial process simulation studies have indicated that the vapor phase glycerol dehydration process was more viable in terms of overall performance than the liquid phase process. Based on this result, laboratory experiments were carried out using the apparatus described in Chapter 8. The purpose of these experiments was to determine the identity of the principle side reaction products and measure the overall glycerol conversion and product yield over the operating conditions chosen for the initial process simulation study. Based on these experimental results, the process simulation models can be revised to reflect the actual performance of the reactor. Using these new results, the minimum energy requirements, potential environmental impacts and variable operating costs can again be estimated. For this phase of the simulation analysis, four new simulation cases were generated. These cases are based on updating the three most viable and technically feasible cases from the initial process simulation study with the reaction data from the laboratory experiments. These results are reflected in cases V6 through V8. A description of these cases is listed in Table 9.1, below.

Table 9.1. List of revised vapor phase simulation cases.

Revised vapor phase processes based on laboratory chemistry	
V6	Vapor Phase Revised Base Case
V7	Revised Base Case with No Water Recycle
V8	Revised Base Case with Waste Water Stripping

These cases are based on the same process configurations as cases V1, V2 and V3 from the initial process simulation analysis, except that the reaction conversions and yield are based on experimental results. Based on the results of the laboratory analysis, the original cases, V4 and V5 have been excluded from further study due to the poor product yield.

9.3 Variable Operating Cost Analysis

For the purposes of this analysis, the variable operating costs is assumed to be comprised of three primary components:

- Raw material costs
- Waste treatment costs
- Utility costs.

Of these three components, the raw material costs are the most straightforward. For this analysis, the raw material costs are simply based on the purchase price of the glycerol and the cost of process water and/or inert gas, the feed components to the system. The contribution of raw material usage to the overall process performance is calculated and reported on a per mass of product basis. Therefore, the percentage of raw material cost for each case is a function of the overall product yield.

The waste treatment costs are a bit more difficult to quantify. Many effective waste treatment methods are available for a process such as the glycerol dehydration process. However, for this analysis, incineration of the waste product in a thermal oxidizer has been chosen. This method is a commonly used industrial application where a waste with high energy content is generated. In addition, the cost for this method can be easily calculated. For this analysis, the cost of incineration is reported as the cost of the auxiliary natural gas used for combustion and the electricity cost of the combustion air blower. In an actual industrial process, other costs may be incurred, but for the purposes of comparison, this level of detail is sufficient. The waste treatment contribution to the overall process performance are reported on a per mass of product basis.

The utility costs are based on determining the total energy requirement for each heated or cooled stream and the electricity requirement for each motor for all rotating equipment, such as pumps and compressors. Based on the required temperatures for each heated or cooled stream, a utility fluid is selected. For this conceptual development project, the utilities chosen are typical fluids assumed to be available on a large multi-user chemical production site. Supply and return conditions for cooling tower water are based on typical values for operation in the southeastern United States. The utilities used are listed in Table 7.2, below. The utility cost contribution to the overall process performance are reported on a per mass of product basis.

Table 9.2. Available utilities for process simulation models.

Utility	**Supply Temperature °C**	**Return Temperature °C**	**Supply Pressure bar(g)**	**Cost USD/GJ**
Cooling Water	30	40	5.00	3.54
Chilled Water	5	15	5.00	3.96
Hot Oil	400	350	5.00	10.00
HP Steam	216	215	20.68	12.27
MP Steam	185	184	10.34	11.60
LP Steam	147	146	3.45	10.05
Electricity	(-)	(-)	(-)	12.50
Natural Gas	amb.	amb.	5.00	8.00

Based on the methods described above, the total normalized process performance indexes for cases V6 – V9 are reported in Figure 9.1, below. The contribution of raw material, waste treatment and utility costs are included in the determination of the overall process performance. The results for the industry standard process and the initial vapor phase simulation results, cases V1 – V5, are also included for comparison purposes.

The results shown in Figure 9.1 are normalized based on the results of the standard process being given a value of 1.0. From the results shown in Figure 9.1, it should be clear that although the raw material costs per unit of product are similar, the utility costs are much higher for the vapor phase processes when compared with the industry standard process. In order to ensure that all available process energy is utilized, an analysis of the heat integration potential must be completed. This will ensure that the energy costs associated with the vapor phase processes are minimized.

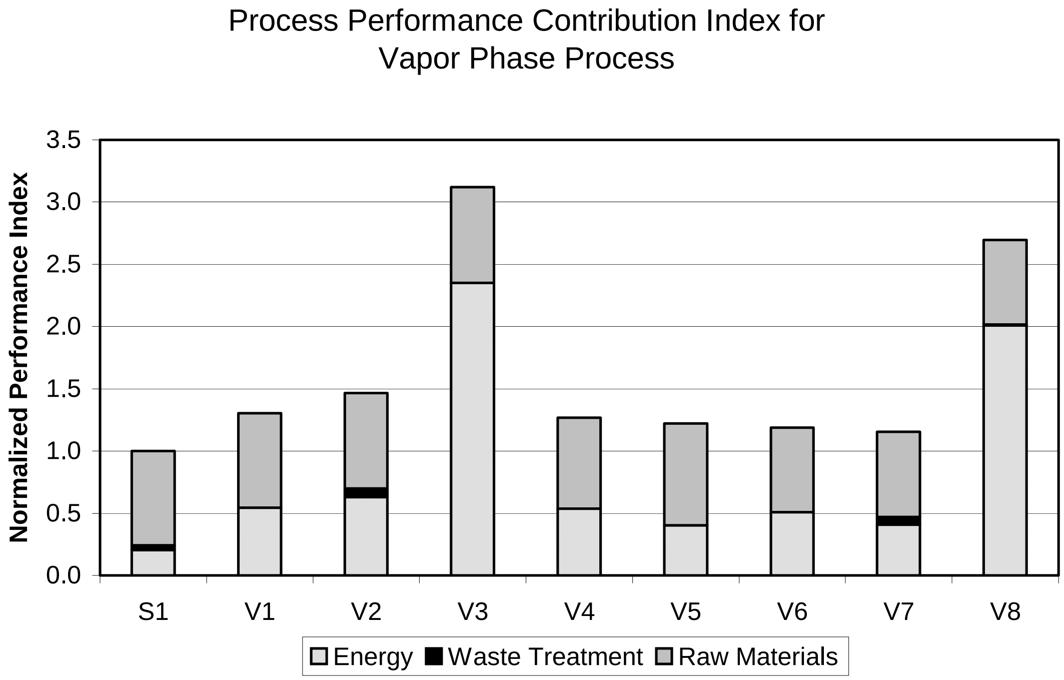

Figure 9.1. Performance index breakdown for vapor phase conceptual processes.

9.4 Heat Integration

For each of the process simulation cases, an initial thermal pinch analysis was completed to determine the minimum external utility requirements for the process. This analysis is part of Step 4 of the proposed process development methodology. At this stage of process development, the focus is still on screening potential options. Therefore, the synthesis of the heat exchanger network (HEN) and the optimization of fixed versus variable costs for the HEN will not be considered. The purpose of this analysis is simply to determine the potential for improving the overall performance for the proposed conceptual process by minimizing the external utility requirement.

9.4.1 Determining the Minimum Utility Case

The minimum utility requirement is determined using thermal pinch analysis. This value represents the theoretical minimum external utility requirement if all available process energy is exchanged. Although achieving the theoretical minimum is rarely possible in practice, it is a convenient value for comparing the energy utilization potential of various process options. Since determining the optimum heat exchanger network design is time consuming, this exercise will only be carried out for the final selected conceptual process. In this way, the minimum energy calculation is used as another screening tool for narrowing the list of potential conceptual processes.

9.4.2 Thermal Pinch Analysis

A software tool is used to automate the calculation of the minimum energy requirement for each conceptual process. The HX-Net software package developed by Aspen Tech and included in the Aspen Engineering Suite is used for this task (Aspentech, 2006). HX-Net is convenient since it is integrated with Aspen Plus, the software package used to develop the simulation models for the proposed conceptual process cases. Using the software, a template was created using the available utilities, as listed in Table 9.2.

Each process stream to be heated or cooled is then imported into HX-Net directly from Aspen Plus. The HX-Net software package is then used to calculate the thermal pinch temperature and, based on transferring all available process heat between hot and cold streams, the minimum external utility requirement is calculated. The minimum hot and minimum cold utility requirements are then reported in units of GJ/kg Product. For the purpose of this comparative analysis, the thermal pinch analysis is based only on process heat and does not include waste heat from the incinerator.

As briefly discussed previously in Chapter 5, a thermal pinch analysis was completed for all of the potential vapor phase conceptual process options. In this stage of conceptual process development, the thermal pinch analysis is completed for the new vapor phase cases, Case V6 – V9. The results of the thermal pinch analysis for the industry standard process based on using crude oil derived feedstocks and the original vapor phase cases, V1 – V5, are included for comparison. These results are illustrated in Figure 9.2, below.

The results shown in Figure 9.2 are normalized based on the results of the standard process being given a value of 1.0. These results indicate that the vapor phase glycerol process requires more energy than the industry standard process. This increased energy requirement leads to decreased process performance for the vapor phase process. In order to be competitive with the industry standard process, a more energy efficient glycerol process is needed.

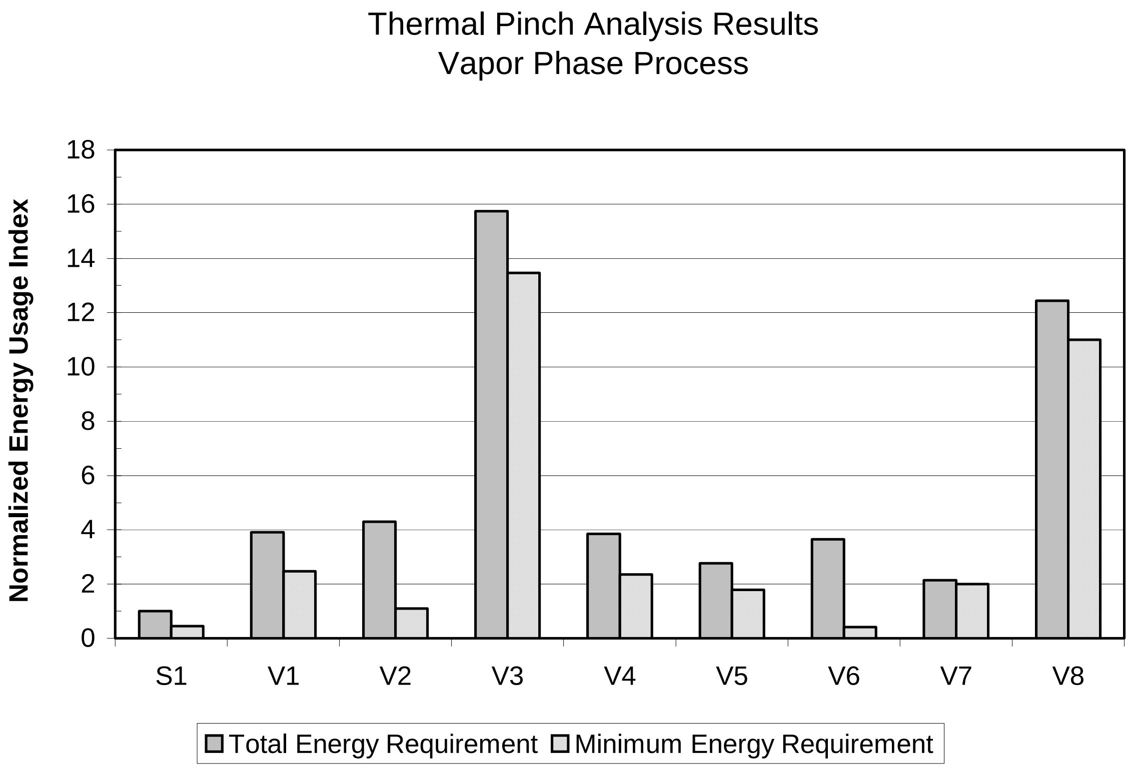

Figure 9.2. Results of thermal pinch analysis for vapor phase processes.

Although the modifications to the simulations based on the laboratory results have improved the accuracy of the models, this did not result in any significant changes in the overall performance results. However, the true power of this methodology comes from the ability to analyze the process prior to completing the experimental runs. In each case, the normalized performance index of the vapor phase glycerol process is higher than the base case industry standard process, as described in Chapter 5. Careful analysis of the sources that contribute to the normalized performance index in each case resulted in the determination that the higher contribution of energy in the vapor phase process, when compared with the crude oil based process was the reason for the poor performance, as indicated by the higher value for the overall process performance index. By analyzing the utility usage from each unit operation in the process, it was determined that the energy required to vaporize the diluent water was the primary source of the high utility cost. This discovery provides a key insight into how the overall performance of the process could be improved. Using this insight, a new process is proposed.

9.5 Development of a New Process Based on Simulation Analysis

As has been previously discussed, the glycerol feed to the reactor must be diluted in order to minimize the formation of polyglycerols. In previous studies, the chosen diluent has been water. Although this choice is effective from a process chemistry perspective, its effect on the performance of the vapor phase process is great, due to the energy required for vaporizing the water. In order to minimize this disadvantage, a new process based on using an inert gas as the diluent is proposed. Eliminating the requirement to vaporize large quantities of water is expected to reduce the variable production cost per unit mass of product. A simplified process flow diagram of a possible inert gas process is given in Figure 9.3, below.

Based on this new process, a simulation was created for the purpose of analyzing the overall process performance. The same procedure as described for the vapor phase process was utilized for the new inert gas process. Additionally, a pinch analysis was completed for this process as well. The results of this analysis are illustrated in Figure 9.4, below. The results of the industry standard process as well as the vapor phase processes are included for comparison. As before, the results are reported on a per mass of product basis.

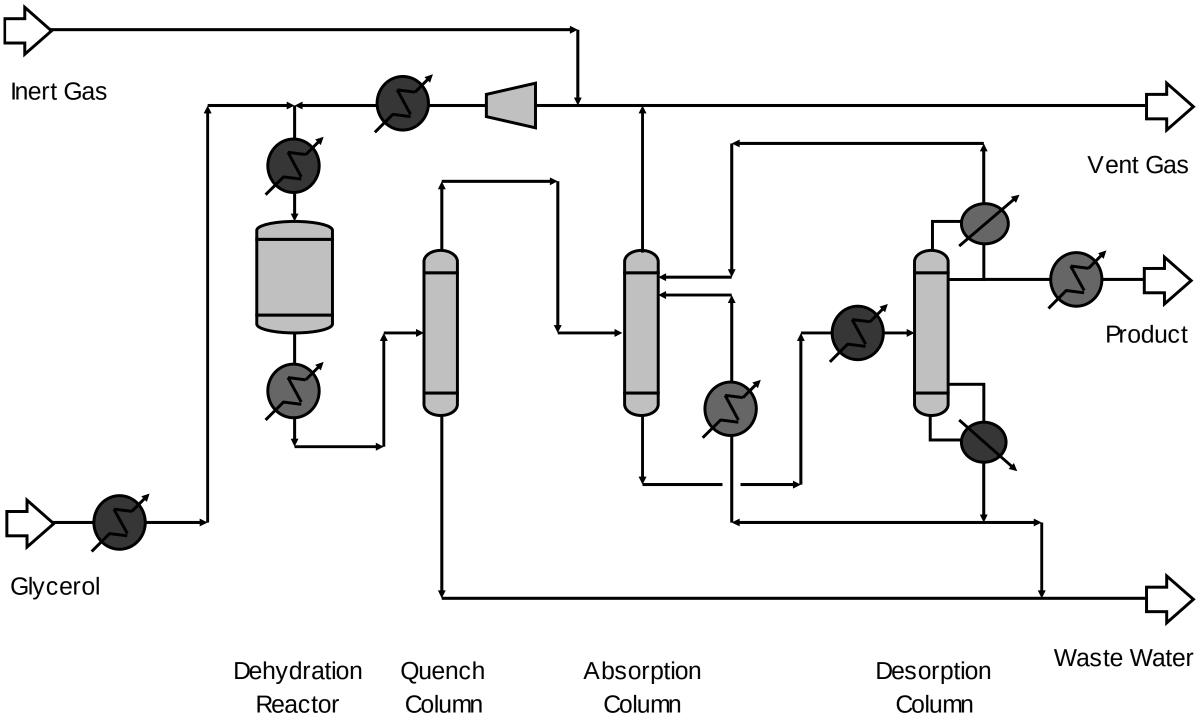

Figure 9.3. Process flow diagram of revised glycerol process using inert gas diluent.

In addition to the thermal pinch analysis, the performance index breakdown for the inert gas process can also be calculated on a per mass of product basis. These results are included in Figure 9.5, below. As before, the results of the industry standard process as well as the vapor phase processes are included for comparison.

From these results, it is clear that the performance potential for the new inert gas process is great. However, this simulation model is based on assumed reactor performance. The next step of the process design methodology is to return to the laboratory to test the assumptions made with regard to the conversion and yield of the primary product and side products for the inert gas processes. This step is step 5 of the methodology described in Chapter 4. In this step, the assumptions used to generate the process simulation are tested in the lab. This step will be repeated until the simulation results are consistent with the laboratory data. Once this data has been gathered, the simulation can be used to determine the optimum operating ranges in terms of minimizing the value of the normalized process performance index of the experimental variables controlling the conversion and yield of the reactor. This process is described in detail in Chapter 10.

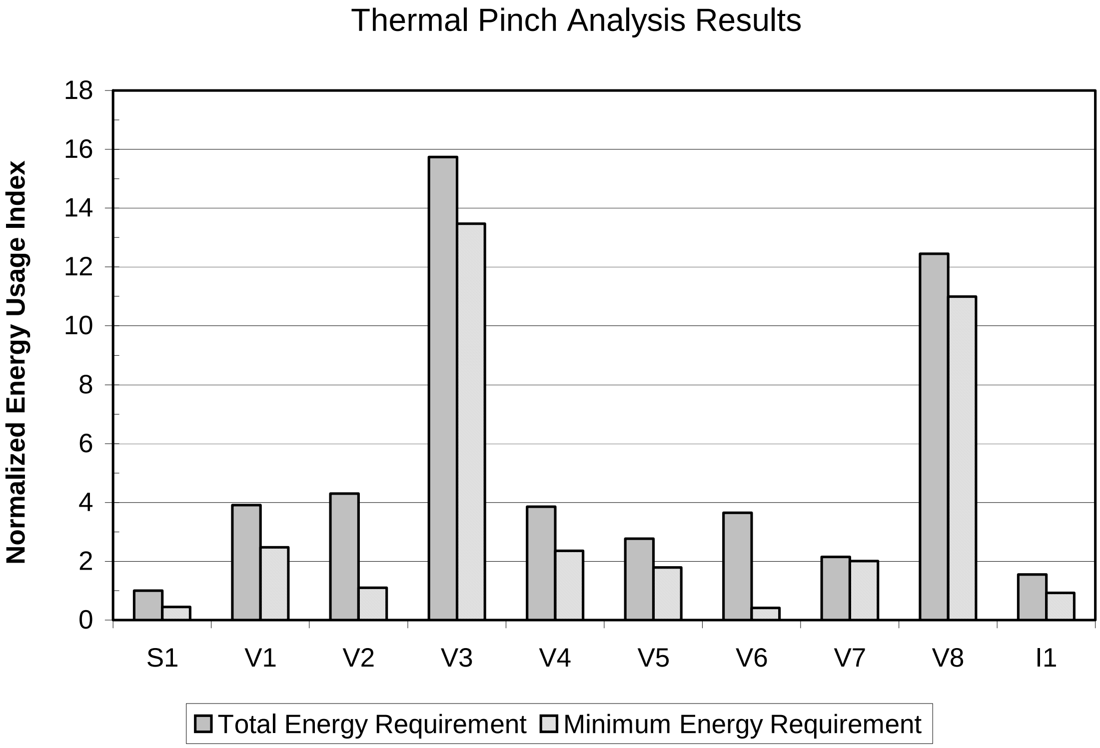

Figure 9.4. Thermal pinch analysis including inert gas process.

9.6 Simulation Analysis Results

As a result of integrating the process simulations into the laboratory experiments, a new process has been proposed. Only through the application of systems engineering methods could this innovation be developed. It is clear that the tools to analyze the entire process, the development of a glycerol based process may have been abandoned entirely.

By using heat integration, the source of the high energy requirement of the vapor phase process was easily identified. Only be identifying the source of the problem could a creative solution be found. This chapter has illustrated the true power of an integrated approach to the development of a process based on novel chemistry. The next step in the development of this process is the optimization of the chemical reactor to determine the operating conditions that lead to optimal process performance. The reactor optimization for the inert gas process is discussed in detail in Chapter 10.

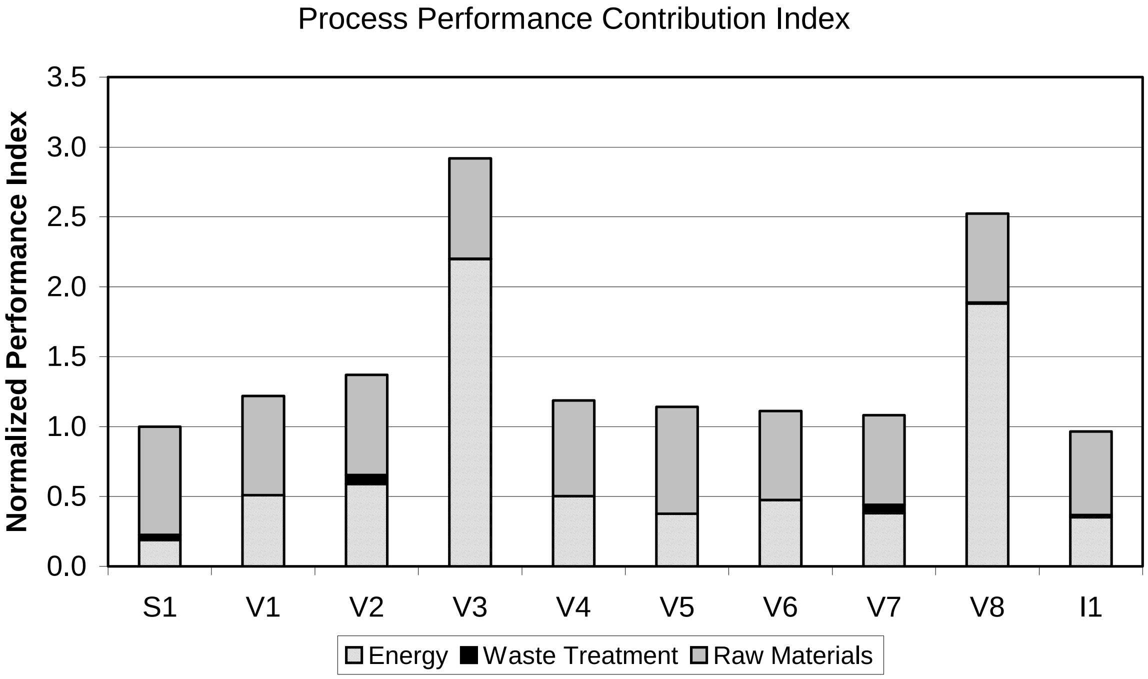

Figure 9.5. Performance index breakdown including inert gas conceptual process.

Due to the proprietary nature of the data, the simulation results are included in Appendix E, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members.

CHAPTER 10

OPTIMIZATION OF EXPERIMENTAL PARAMETERS

10.1 Introduction

To achieve the goal of ensuring that conceptual processes are based on reactor conditions that lead to optimal performance, it is proposed that process simulation and optimization be integrated into the laboratory development of chemical reaction parameters. Because the conditions that result in the highest reaction yield may not lead to optimal process performance when the downstream separation and recycle systems are included in the evaluation, a method for including process optimization with the laboratory experimentation is beneficial. By combining techniques such as statistical design of experiments (DOE) to identify the conditions that lead to optimal reaction selectivity, with process simulation and optimization, it is possible to determine the operating conditions that lead to optimum process performance.

The result of this integration is a conceptual process simulation optimized for any given set of performance indicators. For this analysis, the chosen performance index is simply an arbitrary value based on the operation of the process as a whole. Using process simulation tools to analyze how the operating conditions in the reactor affect the entire process, it is possible to ensure that the reactor parameters chosen for detailed development are the parameters that lead to an optimized process.

As described in Step 5 of the conceptual process design methodology, the assumptions made in the development of the revised process models described in Chapter 5 are optimized to complete the conceptual process design. The optimum operating temperature and feed conditions for the reactor will be determined using a statistical design of experiments approach. These results can then be incorporated into the process simulation model to arrive at the final optimized process.

10.2 Determining Ranges of Experimental Variables

The first step of this analysis is to determine which input variables have the greatest impact on the operating results. Four variables have been identified that have an appreciable impact on the performance of the process and can be evaluated using the process simulation model. These variables are:

- Reactor Temperature
- Glycerol / Water ratio in the liquid feed
- Liquid / Gas ratio in the reactor feed.
- Reactor space-velocity.

With the exception of space-velocity, which is measured experimentally as flow rate to the reactor, each of these variables can easily be evaluated using the process simulation model. Although these variables affect the process chemistry, effects on the kinetics of the reaction can only be determined in the laboratory. Therefore, the simulation models will be used to screen which sets of reactor operating conditions optimize the process performance index.

These results will be used to guide the laboratory experiments for optimizing the operating conditions. For this analysis, a “one factor at a time” (OFAT) approach will be used to determine the sensitivity of each variable on the process results. An OFAT approach is appropriate since the primary goal of this analysis is simply to determine the operating ranges for the variables in question. The simulation cases for this analysis are listed in Table 1, below. The values - -, -, +, + + indicate the four values chosen for these variables from low to high.

Table 10.1. List of process sensitivity study simulation cases.

Case	**Description**	**Case**	**Description**
1	Base Case	8	Base Case w/ LIQ/GAS = +
2	Base Case w/ GYL/WTR = - -	9	Base Case w/ LIQ/GAS = + +
3	Base Case w/ GYL/WTR = -	10	Base Case w/ Rctr Temp = - -
4	Base Case w/ GYL/WTR = +	11	Base Case w/ Rctr Temp = -
5	Base Case w/ GYL/WTR = + +	12	Base Case w/ Rctr Temp = +
6	Base Case w/ LIQ/GAS = - -	13	Base Case w/ Rctr Temp = + +
7	Base Case w/ LIQ/GAS = -		

Using the simulation model for the process, the function describing the process performance was evaluated for each of the cases listed in Table 10.1. The percent change for each case versus the base case is illustrated in Figure 10.1, below. This analysis indicates that higher glycerol to water ratios, higher liquid to gas ratios and lower reactor temperatures have a positive influence on the process performance index. For this assessment, the performance index is considered to be optimal when the function is at a minimum. It is also clear that the biggest impact on performance is due to glycerol to water ratio. It should be noted, however, that at this stage of the analysis, each of the cases are based on the same assumed overall glycerol conversion and product yield.

From Figure 10.1, it is clear that the variable with the greatest influence on the performance is the glycerol to water feed ratio. Although temperature does not appear to significantly affect the results, it is also important since it could have a significant effect on the reaction rate. Since a kinetic model of the reaction has not yet been determined, the effect of temperature on reaction rate cannot be included in the initial simulation study. The liquid to gas feed ratio also has a minor influence at high glycerol to water ratios, therefore, a fixed value will be selected for the laboratory analysis. Of the variables considered for the simulation study, those chosen for further study in the laboratory are glycerol to water feed ratio, and temperature.

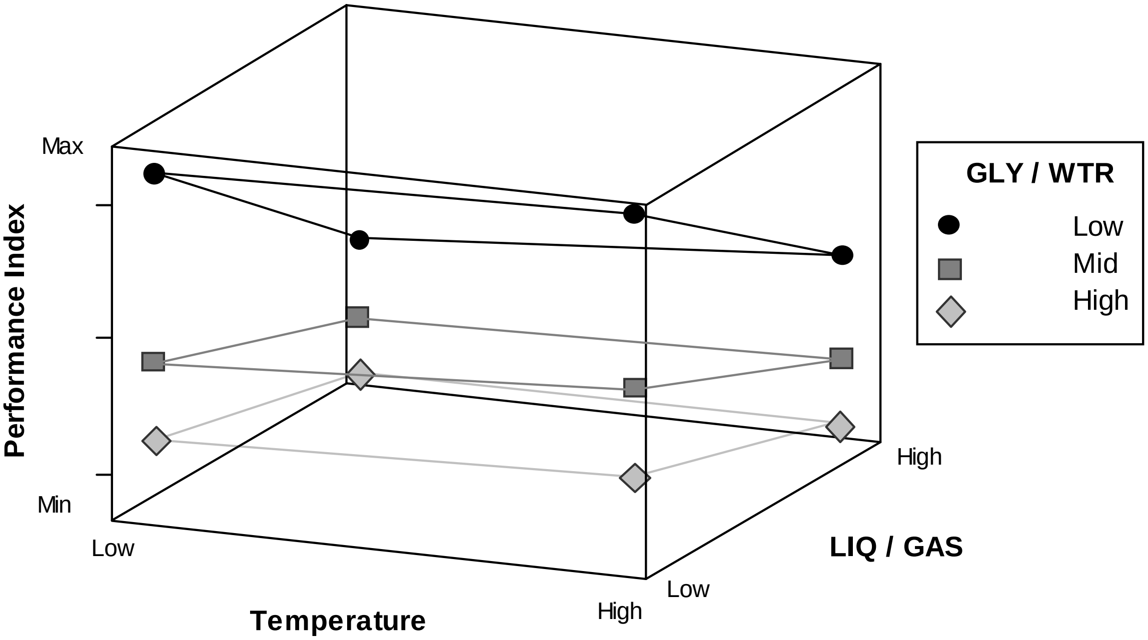

Figure 10.1. Process performance index sensitivity analysis results.

Based on this process simulation analysis, the ranges of values for the reaction variables have been determined. These ranges will serve as the basis for the laboratory experimentation to determine the optimum reactor operating conditions. Only through laboratory experimentation can the effect of the above mentioned variables on the glycerol dehydration chemistry be determined. In addition to these selected variables, an additional variable, space-velocity, will also be considered for the laboratory analysis. Again, due to the lack of a kinetic model, this variable can not be analyzed using the simulation, but is expected to have an influence on the actual reactor performance. Due to the proprietary nature of the data, the ranges for total flow rate as well as the other variables are included in Appendix D, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members.

10.3 Statistical Design of Experiments

Using the Minitab software package, a list of experiments to determine the optimum operating conditions was generated using a Bob-Behnken response surface design (Minitab, 2005). The generated list of thirteen experiments is given in Table 10.2, below. The experiments are based on the maximum (+), minimum (-) and midpoint (0) values from the range of the experimental variables described above.

The upper and lower limits of the three variables under consideration can be shown as a cube in three-dimensional space. The possible operating conditions for the reactor are all points within or on the surface of the cube. These 13 points include the middle of each edge of the cube and the center of the cube. These operating points were each run in the laboratory miniplant.

Table 10.2. List of initial optimization experimental runs.

Run No.	Temperature	Glycerol : Water	Feed Flow Rate
1	-	0	+
2	-	+	0
3	+	+	0
4	-	-	0
5	+	0	+
6	0	0	0
7	+	-	0
8	0	-	-
9	0	-	+
10	+	0	-
11	-	0	-
12	0	+	-
13	0	+	+

The Box-Behnken technique for identifying the optimum reactor operating condition is especially useful when the optimum point lies within the cube, away from a corner. The initial analysis of the experimental results indicated that this was not the case. Because of this finding, six more experimental operating points were added. These points are the face points of the cube. The operating conditions for these six points, indicated as maximum (+), minimum (-) and midpoint (0) values for each of the three variables are listed in Table 10.3, below.

Table 10.3. List of additional optimization experimental runs.

Run No.	Temperature	Glycerol : Water	Feed Flow Rate
14	-	0	0
15	0	0	-
16	0	+	0
17	0	-	0
18	0	0	+
19	+	0	0

A sketch of the cube containing the 19 experimental points is illustrated in Figure 10.2, below. The initial Box-Behnken points are shown as circles and the additional surface points are shown as diamonds.

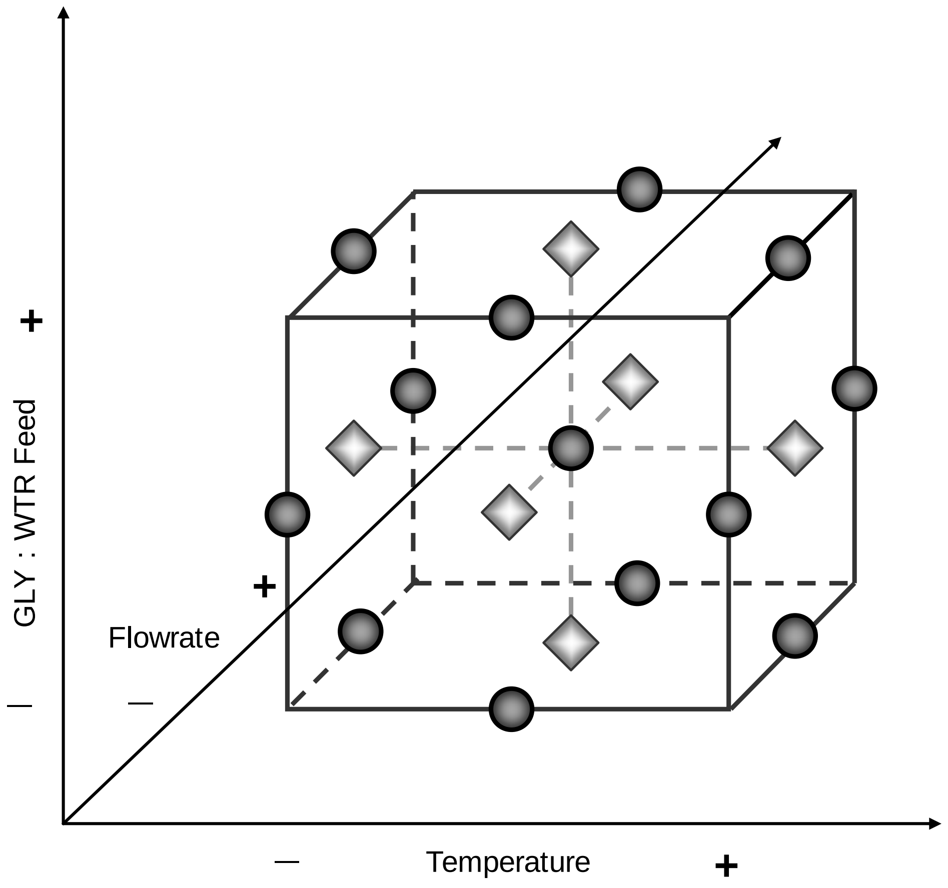

Figure 10.2. Cube plot indicating experimental design points.

10.4 Optimization of the Reactor Operating Conditions

The results of the 19 experimental cases were analyzed to determine the glycerol conversion and product yield. Glycerol conversion and product yield are defined as follows in equations 10.1 and 10.2:

$$Conversion : x = \frac{n_{\Pr oduct} + n_{Side-\Pr oduct} + n_{By-\Pr oducts}}{n_{Glycerol} + n_{\Pr oduct} + n_{Side-\Pr oduct} + n_{By-\Pr oducts}} \quad \text{(Eqn. 10.1)}$$

$$Yield : y = \frac{n_{\Pr oduct}}{n_{Glycerol} + n_{\Pr oduct} + n_{Side-\Pr oduct} + n_{By-\Pr oducts}} \quad \text{(Eqn. 10.2)}$$

Due to the relatively short catalyst life, reactor results over the first 90 minutes of operation were analyzed. Gas samples of the reactor effluent were taken at regular intervals and analyzed using a Hewlett-Packard 5890 Series II gas chromatograph. The geometric mean square average over the operating range was taken to determine the glycerol conversion and product yield for each set of operating conditions. The geometric mean, GM, is defined in equation 10.3, below.

$$GM_y = \sqrt[n]{\sum_{i=1}^{n} y_i} \quad \text{(Eqn. 10.3)}$$

The results for each run are illustrated in Figure 10.3, below. As in Figure 10.2, the operating points on the cube represented with circles indicate the Box-Behnken experimental cases and points indicated by diamonds indicate the additional cube face cases added after analyzing the initial results.

By illustrating the results in this way, the influence of all three variables on the reactor yield can be easily visualized with a single figure. Form this cube, the general trends of the experimental results can be seen. This illustration can also be used to assess the consistency of the experimental results. Any points that do not follow the general trend are suspect, and may need to be repeated in the laboratory.

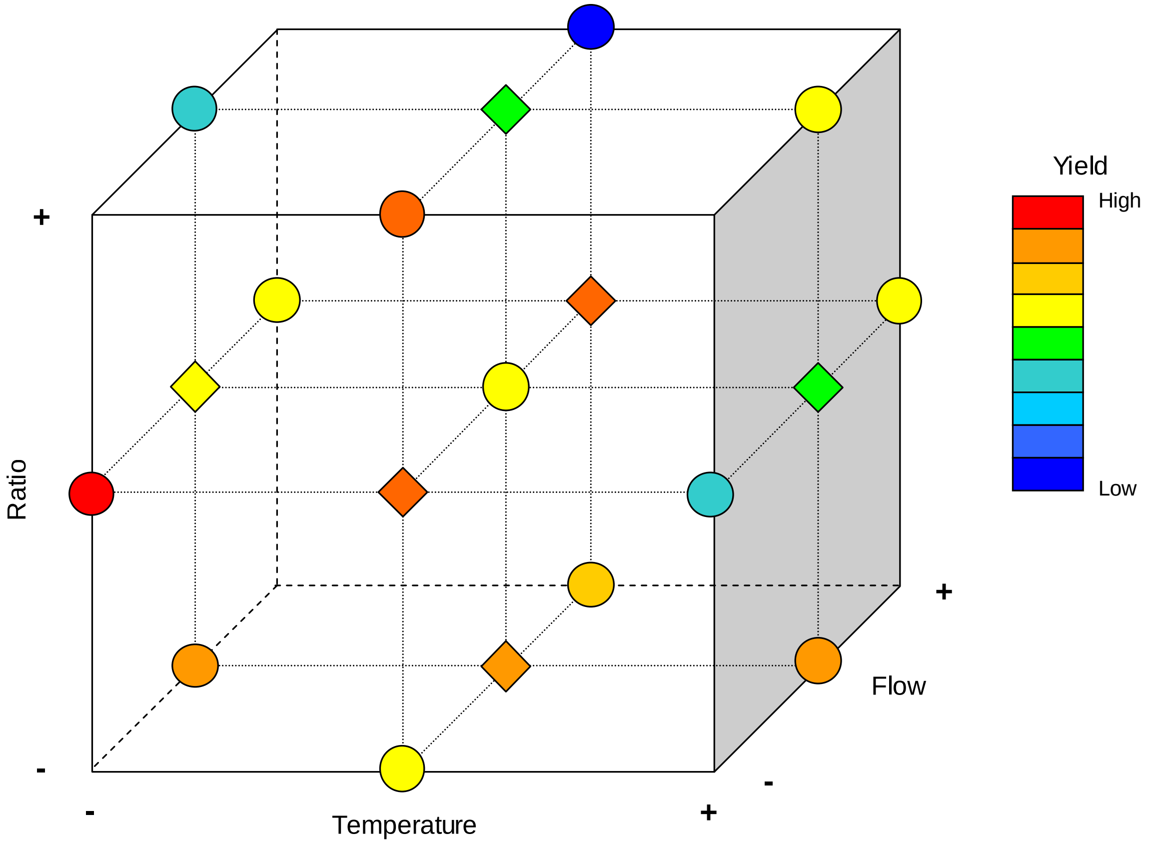

Figure 10.3. Yield results for experimental points.

From these results, certain trends become apparent. It can be seen that lower temperatures, lower flowrates and lower glycerol to water ratios result in higher product yields. Contour plots of these results, as illustrated in Figures 10.4, 10.5 and 10.6, provide a clearer picture of these trends. Due to the proprietary nature of the data, the results of these experiments are included in Appendix F, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members.

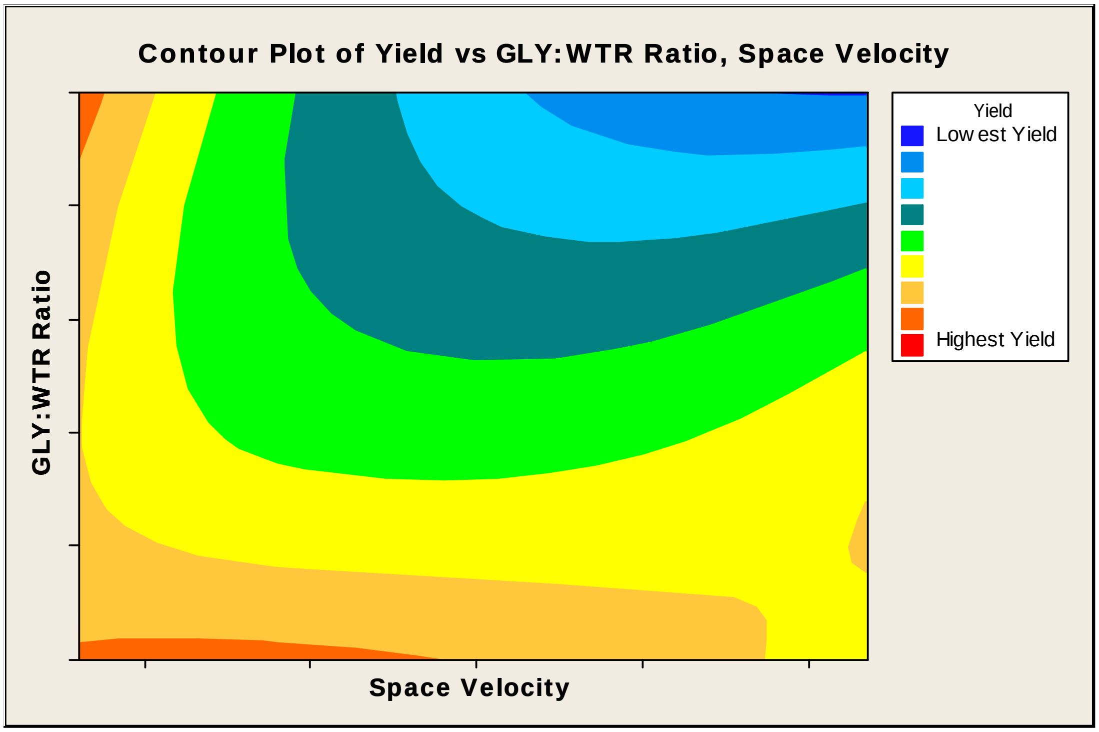

Figure 10.4. Reaction yield contour plot of GLY : WTR ratio versus space velocity.

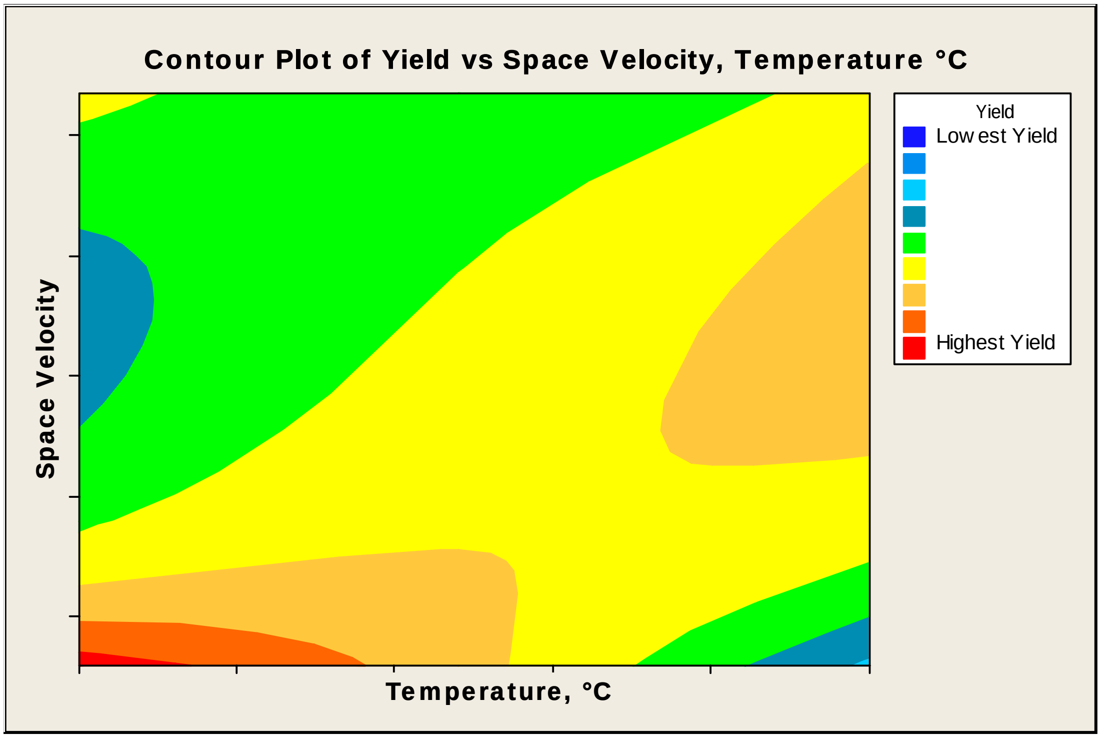

Figure 10.5. Reaction yield contour plot of space velocity versus temperature.

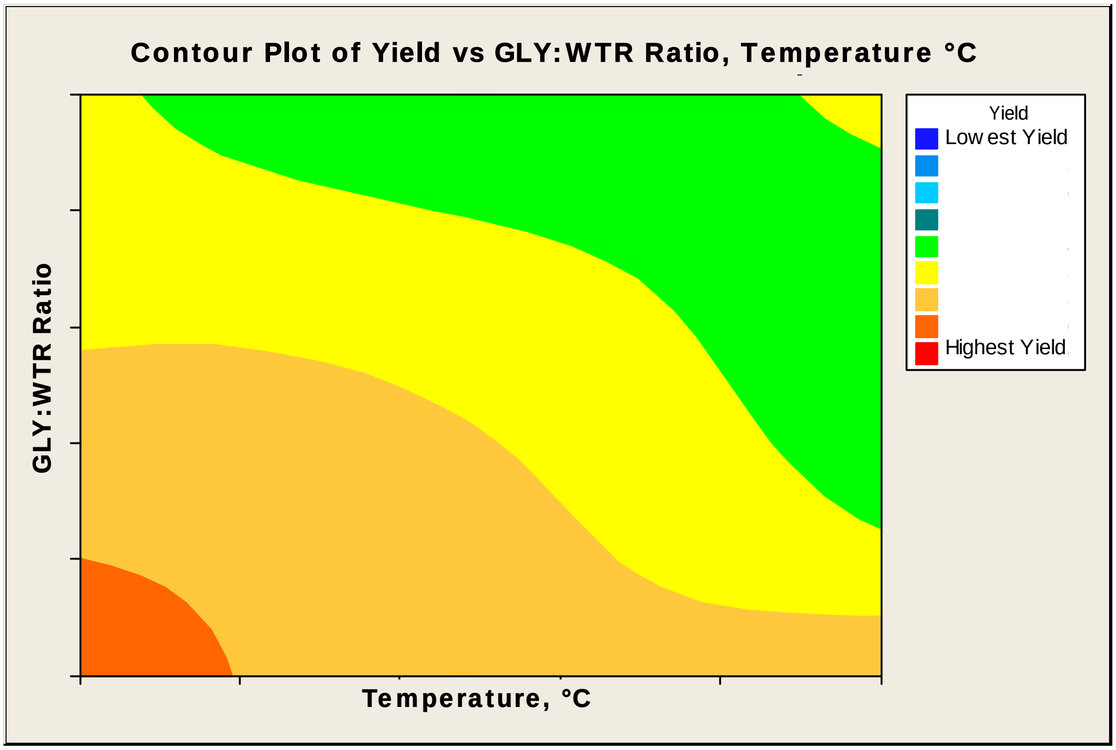

Figure 10.6. Reaction yield contour plot of GLY : WTR ratio versus temperature.

Using these three contour plots, a prediction can be made regarding the operating conditions that result in the maximum product yield. Based on these results, a new experimental point was run using the laboratory scale mini-plant. These results confirmed the prediction made using the contour plots that the highest yield occurs at the lowest values space-velocity, temperature and Glycerol : Water ratio. However, this value conflicts with the prediction from the process simulation study, as illustrated in Figure 10.1, above. In the initial process simulation assessment, the optimum performance, i.e., the point where the performance was at a minimum, occurred at the highest values of Glycerol : Water ratio. Since this initial process simulation assessment was completed without the benefit of experimental results, the next step in the optimization of the conceptual process is to update the simulations using the actual laboratory results.

10.5 Performance Analysis of the Conceptual Process Model

In order to select the final operating conditions for the glycerol dehydration process, the performance of the entire process was evaluated for each of the experimental cases. Using the process simulation to model each of the experimental cases, the overall performance index was determined. To accomplish this, each case was put on an equal basis in terms of raw material feed rate. However, putting all cases on an equal basis for raw material feed leads to a different product rate for each case. To address the discrepancy in the mass and energy balances caused by different product rates, the results for the each of the cases are reported per mass of product. The results are illustrated in Figure 10.7, below.

From the results illustrated in Figure 10.7, the trends of which conditions lead to a minimization of the performance index function become clear. The trends indicate that, as with the results of the product yield, the optimal performance occur at the lowest values of temperature and flowrate, however, unlike the yield results, the optimal performance occurs at the highest value of Glycerol : Water ratio. Contour plots of Glycerol : Water ratio versus space velocity, space velocity versus temperature and Glycerol : Water ratio versus temperature, as illustrated in Figure 10.8, 10.9 and 10.10, provide a clear picture of the performance index result trends.

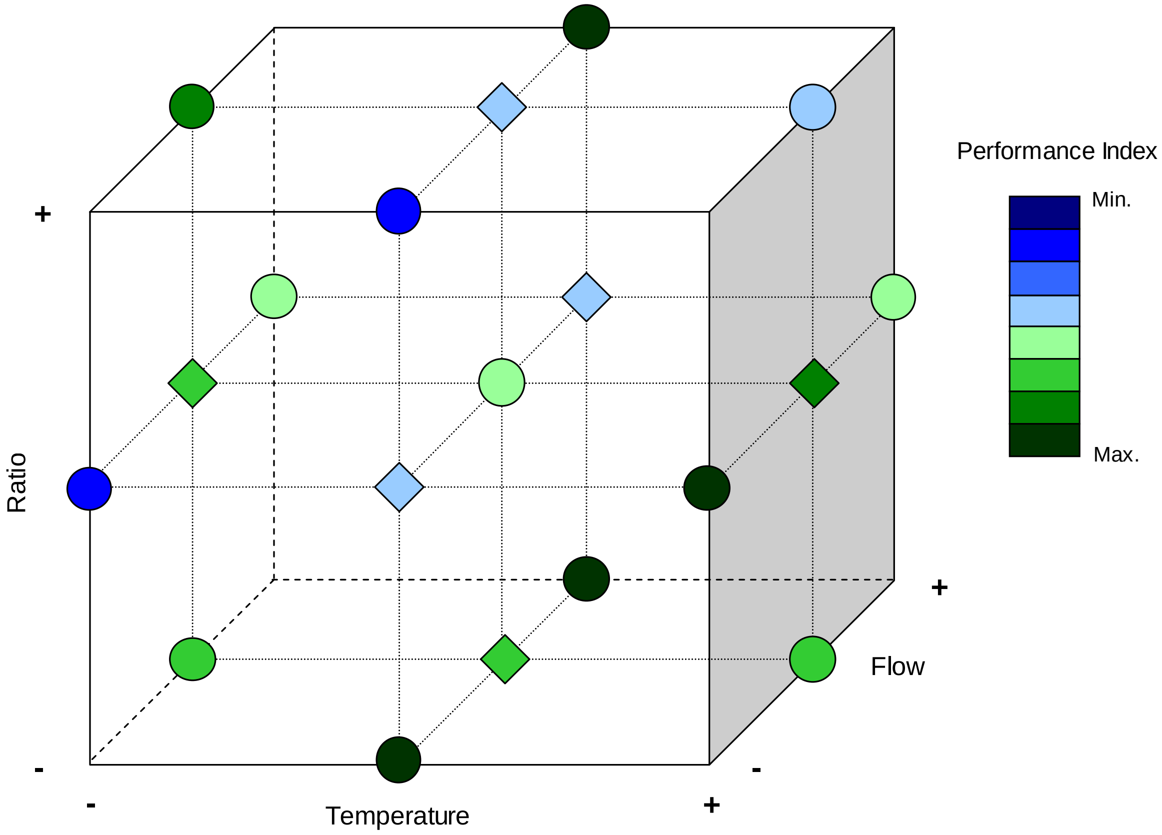

Figure 10.7. Performance index results for experimental points.

Using these three contour plots, a prediction can be made regarding the operating conditions that result in the minimization of the performance index function, i.e. the optimum process performance. These results should not be totally unexpected, due to the previously discussed results of the initial process simulation study. Due to the proprietary nature of the data, the results of the process perfromance analysis are included in Appendix F, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members.

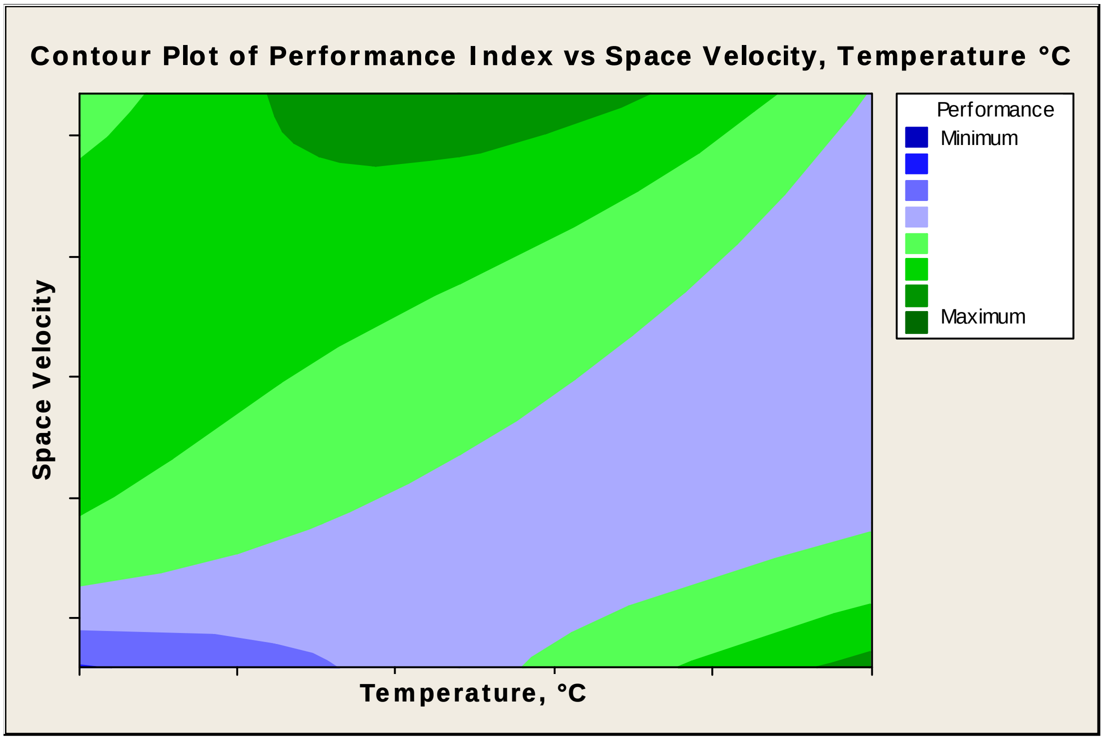

Figure 10.8. Performance index plot of GLY : WTR ratio versus space-velocity.

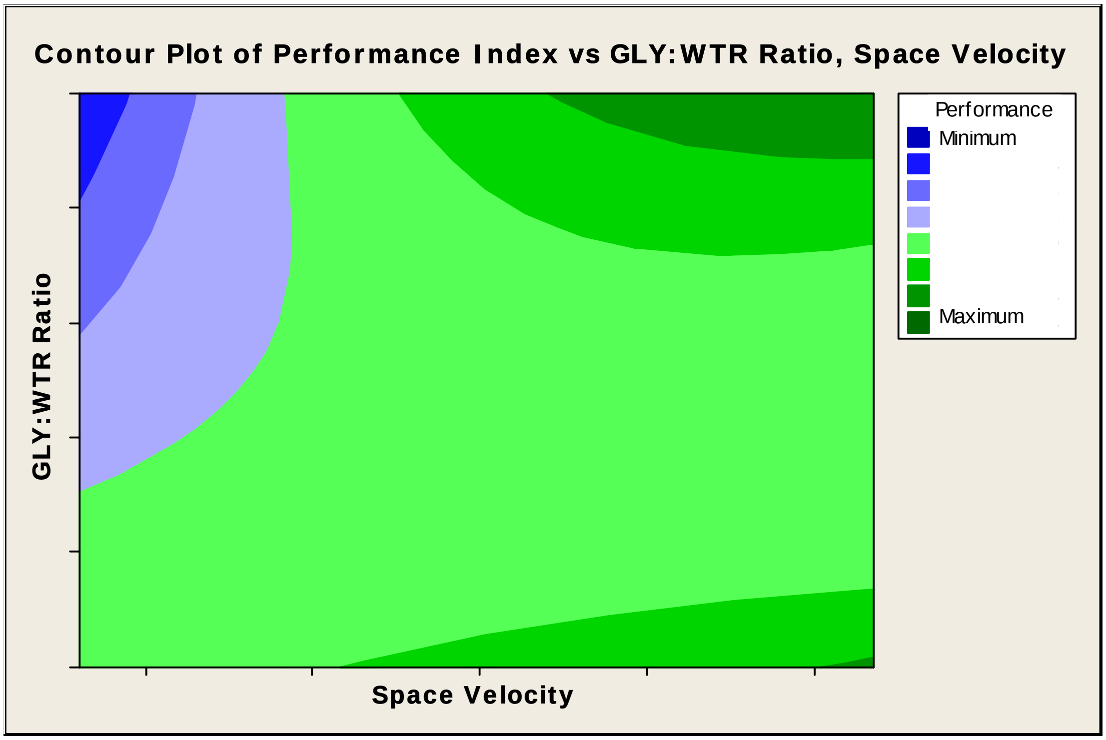

Figure 10.9. Performance index plot of space-velocity versus temperature.

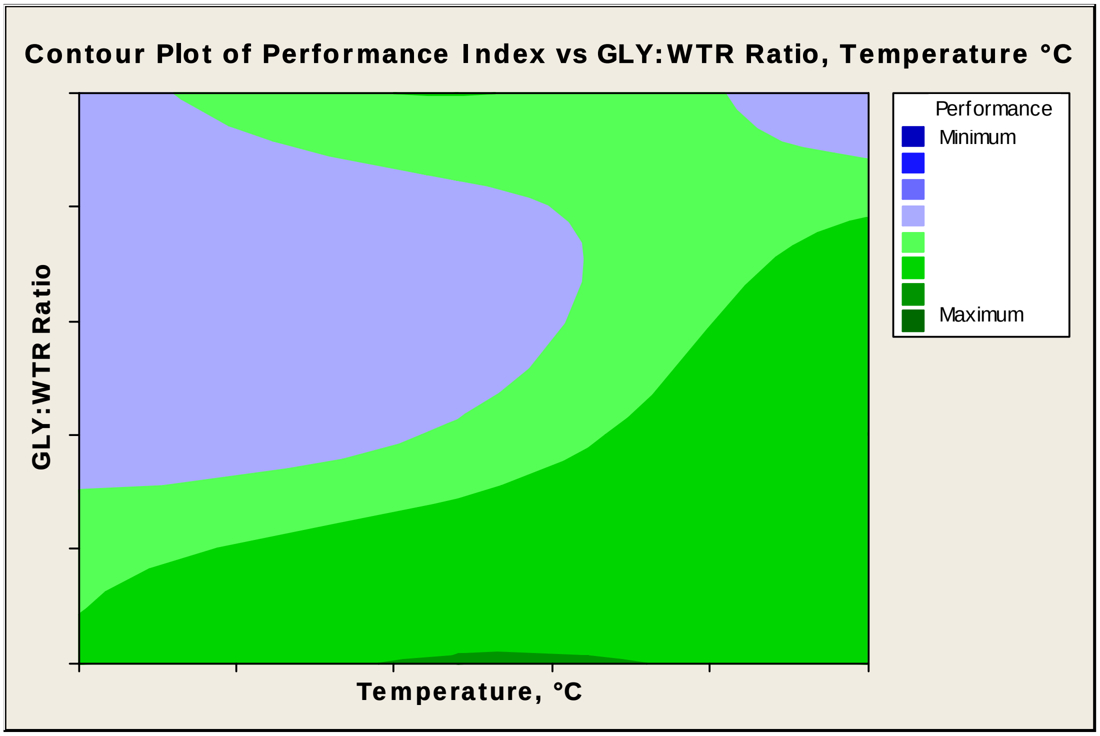

Figure 10.10. Performance index plot of GLY : WTR ratio versus temperature.

By including the process performance analysis as part of the experimental work, it can be seen that the performance benefits of operating at a higher glycerol to water ratio outweigh the higher yield achieved at a lower ratio. In fact, the operating conditions that lead to the highest yield are actually far from the performance optimum. Continuing the process development using only the higher yield operatinig conditions would have lead to a significant error in the performance of the process. This result can be clearly seen in Figure 10.11.

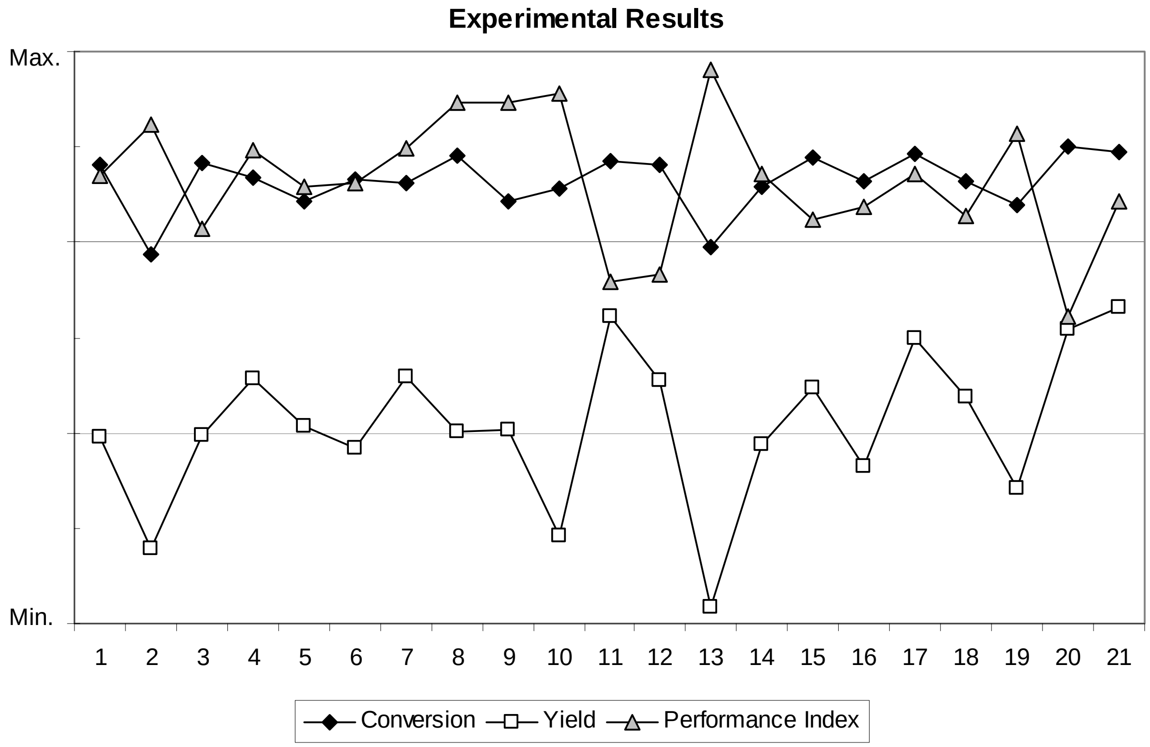

Figure 10.11. Results for experimental operating cases.

From this figure, it can be seen that at least 6 of the 21 experimental cases give a better performance result than the highest yield case. Each of these cases is at a higher Glycerol : Water ratio than the highest yield case. To complete the optimization of this process, it is necessary to apply holistic tools, like thermal pinch analysis, to ensure the optimal resource utilization. Therefore, a thermal pinch analysis was conducted for each case to ensure that the case leading to the optimal performance remains the optimum case at minimum utility usage. The results of the thermal pinch analysis are illustrated in Figure 10.12, below. The minimum utility usage is based on the hottest heating utility and coldest cooling utility assumed to be available on a large multi-user chemical site.

Based on these results, it can be seen that although there is potential for a reduction in the total energy usage due to heat integration, the effects are essentially the same for all cases. Therefore, the case originally selected as the optimally performing case is still the preferred option. This result can be seen more clearly by examining Figure 10.13, below. The minimum energy performance index values are calculated based on the minimum utility requirements. It should be noted that for this analysis, the increased equipment and infrastructure requirements for the heat exchanger network needed to achieve this minimum utility case has not been considered. Due to the proprietary nature of the data, the detailed results of this analysis for process performance are included in Appendix F, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members

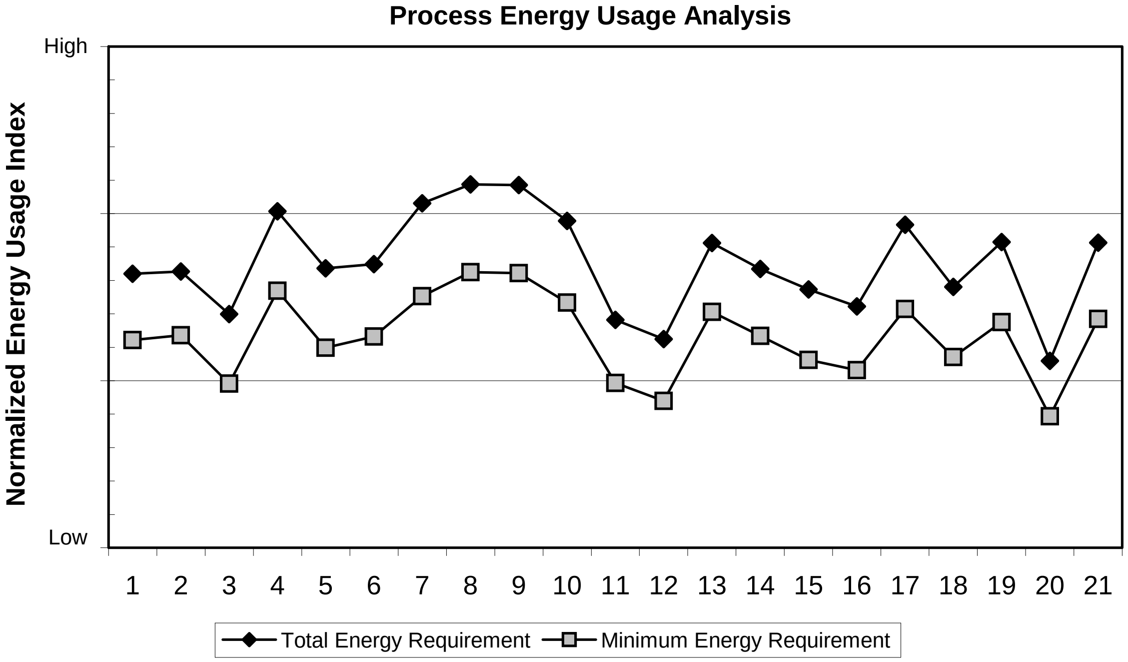

Figure 10.12. Final optimized thermal pinch analysis results.

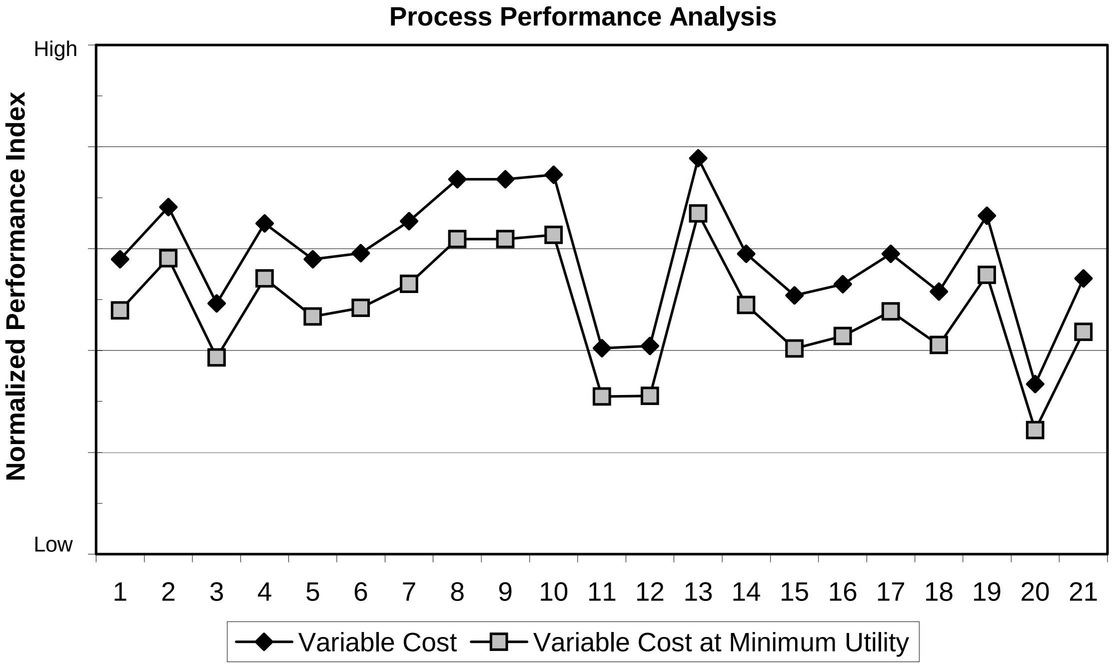

Figure 10.13. Final optimized performance index function analysis results.

10.6 Potential Environmental Impacts

As previously described in Chapter7, the U.S. Environmental Protection Agency's Waste Reduction (WAR) Algorithm can be applied to determine the potential environmental impacts (PEI) of the proposed conceptual process options. This analysis is also applied to the reactor optimization results to ensure that the conditions that lead to optimal performance also minimize the environmental impacts of the final process.

The WAR Algorithm was used to calculate the PEI for each set of reactor operating conditions. As before, contour plots of Glycerol : Water ratio versus space velocity, space velocity versus temperature and Glycerol : Water ratio versus temperature, as illustrated in Figure 10.14, 10.15 and 10.16, are used to provide a clear picture of the PEI results trends.

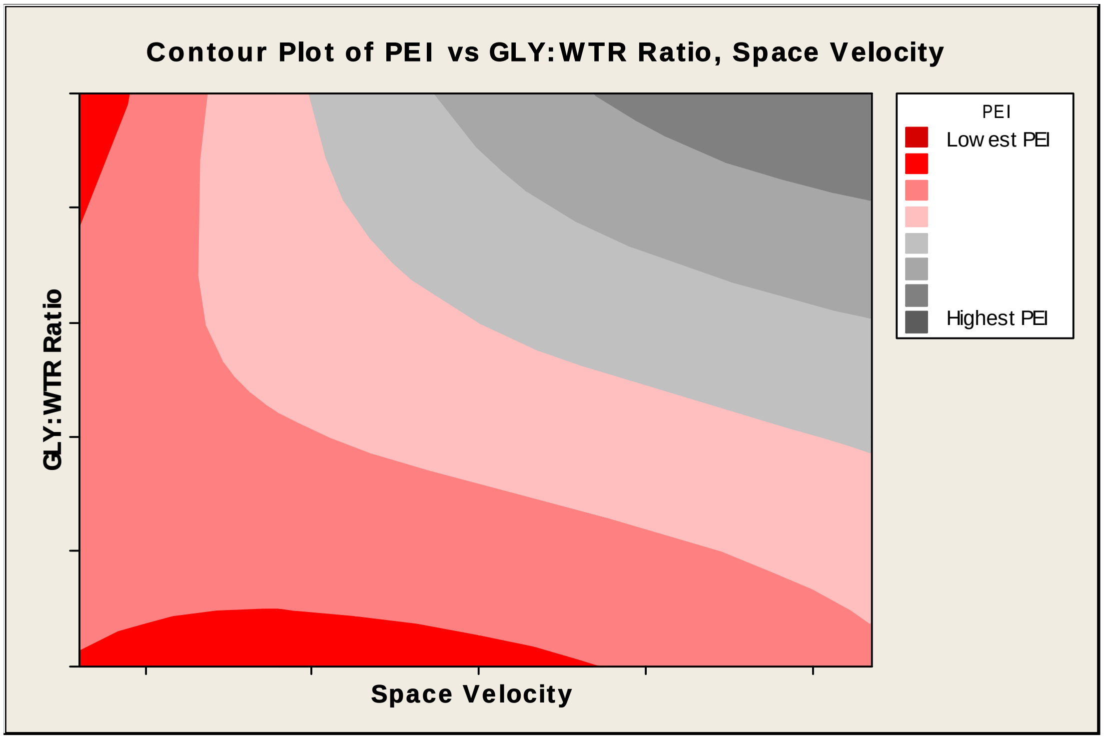

Figure 10.14. PEI plot of GLY : WTR Ratio versus space-velocity.

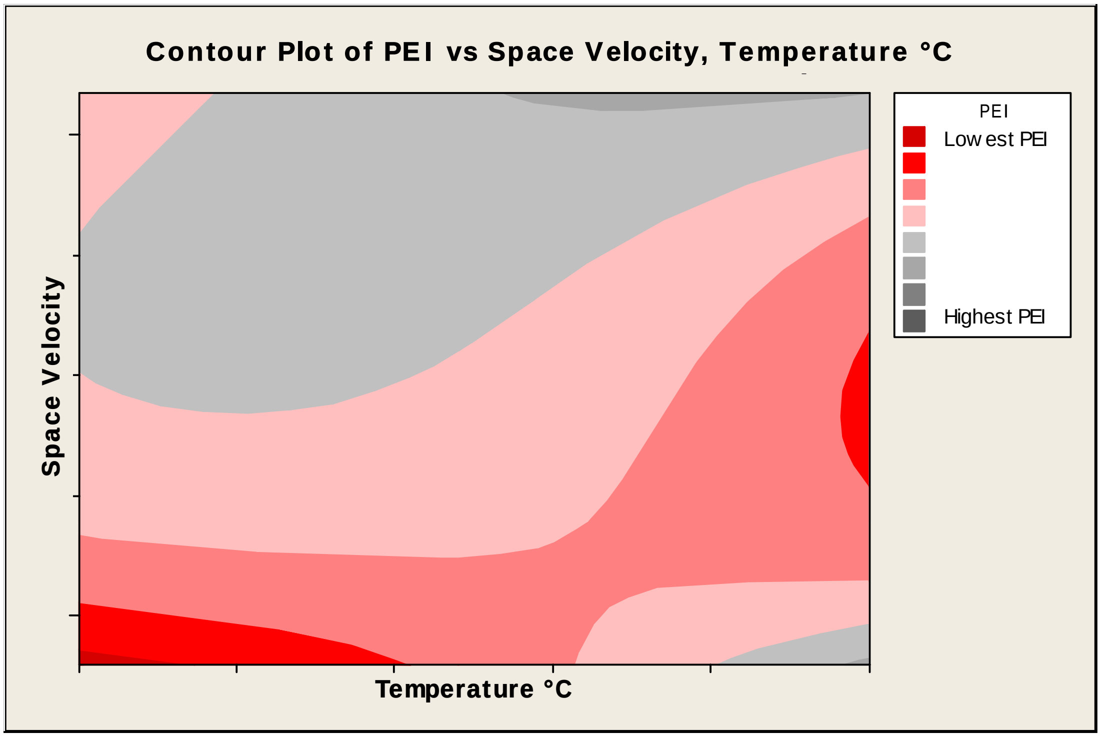

Figure 10.15. PEI plot of space-velocity versus temperature.

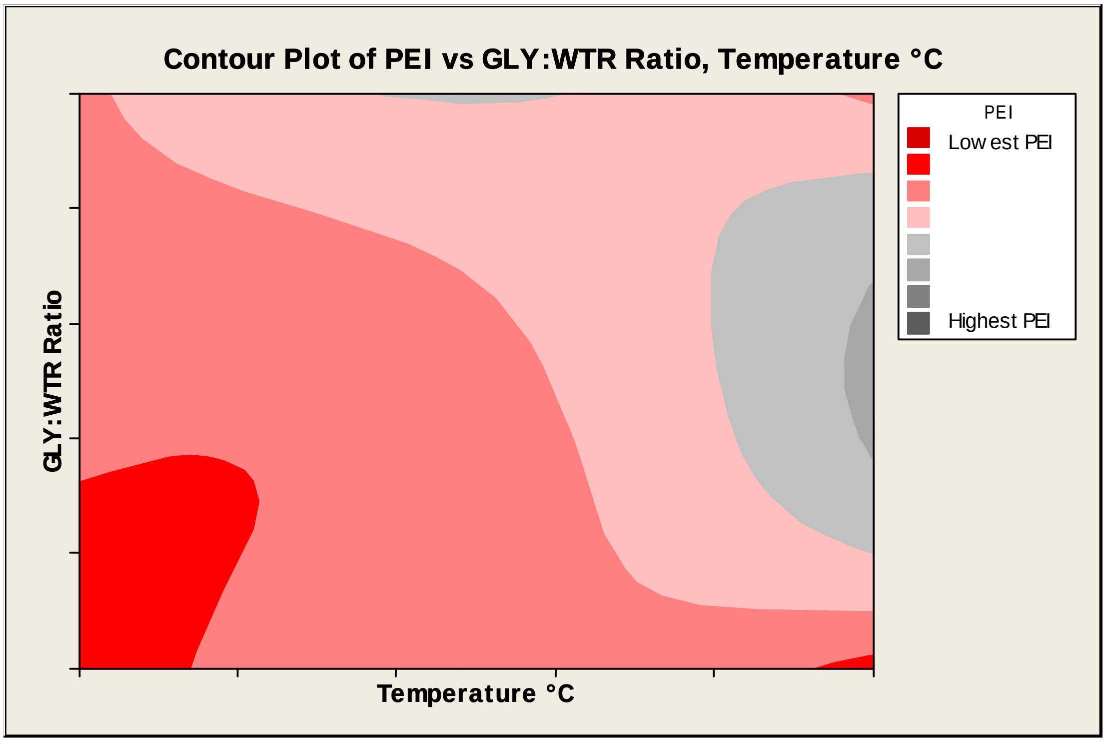

Figure 10.16. PEI plot of GLY : WTR ratio versus temperature.

These results illustrate that the region chosen as the performance optimum, i.e. the region of low temperature, low space velocity and high GLY : WTR ratio is in the region of low environmental impacts. Although the point corresponding to the performance optimum is not the minimum PEI point, it is close to the minimum. Because of the level of accuracy of the PEI calculation, this is deemed to be an acceptable result. Only if the performance optimum were far from the minimum PEI would further study be warranted.

10.7 Optimization Conclusions

In conclusion, this analysis has clearly shown the benefits of integrating process simulations with laboratory experimentation. Only when the entire process is considered does the true performance picture become clear. By applying process engineering tools along with statistical design of experiment tools in the experimental phase, the development of an optimized conceptual process can be streamlined. From the glycerol dehydration case study example, it is clear that not only does this approach improve the results, relying on a traditional approach of simply maximizing the reactor yield will lead to less than optimal results.

CHAPTER 11

PRELIMINARY REACTION MODELING AND SCALE-UP

11.1 Introduction

In order to begin moving from conceptual models to industrial equipment, the mini-plant reactor must be scaled up to production capacity. This is accomplished by developing the equations that describe the reaction rate law. These equations are based on regressions of laboratory experimental data. The software used of this regression analysis is the REX Suite by Optience Corporation. The results of the laboratory experiments and the determination of the reaction rate law expressions using the REX Suite will be discussed in this chapter.

11.2 Laboratory Experiments

In order to create a model of the reactions that makeup the glycerol dehydration system, it is necessary to conduct laboratory experiments. These experiments were conducted using the same mini-plant as described in Chapter 8. Since the reaction takes place in a packed bed reactor, the experimental data needed is conversion and yield as a function of mass of catalyst. The experimental data colleted is the composition in a fixed sample volume taken from the reactor effluent. This data serves as the input for the analysis using the REX software package.

11.3 Determining Experimental Reaction Rates

In order to collect the required data as a function of catalyst mass, nine experimental cases were defined, each with a different mass of active catalyst in the reactor. In order to ensure that the pressure profile was consistent for all runs, after the active catalyst was added, the reactor was filled the rest of the way with inert catalyst pellets. Because of its proprietary nature, the procedure for the preparation of the active catalyst is described in Appendix G which is included in the unpublished Volume 2 of this dissertation. Only dissertation committee members will have access to this volume.

Each experimental run was carried out at the optimum temperature, space velocity and glycerol to water feed ratio as described in Chapter 10. Because the optimization experiments had already been conducted, the number of experimental runs required to determine the reaction rate was greatly reduced. However, because experiments were only conducted under the previously determined optimal operating conditions, extrapolating the results to other conditions is not recommended. The nine experimental cases are listed in Table 11.1, below.

Based on the analysis of the reactor effluent, three products were identified, the desired principle product, the primary side product and an unidentified byproduct. The three formation reactions that lead to these products are described as follows:

$$Glycerol \rightarrow Principle\ Product + Water \qquad \text{(Eqn. 11.5)}$$

$$Glycerol \rightarrow Side\ Product + H_2O \qquad \text{(Eqn. 11.6)}$$

$$Glycerol \rightarrow Byproduct + Water \qquad \text{(Eqn. 11.7)}$$

Table 11.1. List of Experimental Runs.

Run No.	Mass of Active Catalyst (g)	Mass of Inert Catalyst (g)
1	1	10.5
2	2	10
3	3	9.5
4	5	8.5
5	7	7.5
6	10	6
7	13	4.5
8	16	3
9	20	1

Although the identity of the byproduct is not known, it is assumed that it is formed from the dehydration of one mole of glycerol. This assumption is a source of potential experimental error, however, the mass of the byproduct is small relative to the mass of the principle product and the side product, and therefore this error is expected to be small.

The nine experimental cases were carried out and the results are illustrated in Figure 11.1, below. The mass of the three products, principle product, side product and byproducts, as well as the mass of unreacted glycerol in each reactor sample is illustrated in this figure. The lack of scatter indicates that the experimental results are consistent. This experimental data will be used to determine the parameters for the reaction rate law expression. The glycerol conversion and principle product yield data corresponding to the measured sample composition as a function of catalyst mass is illustrated in Figure 11.2.

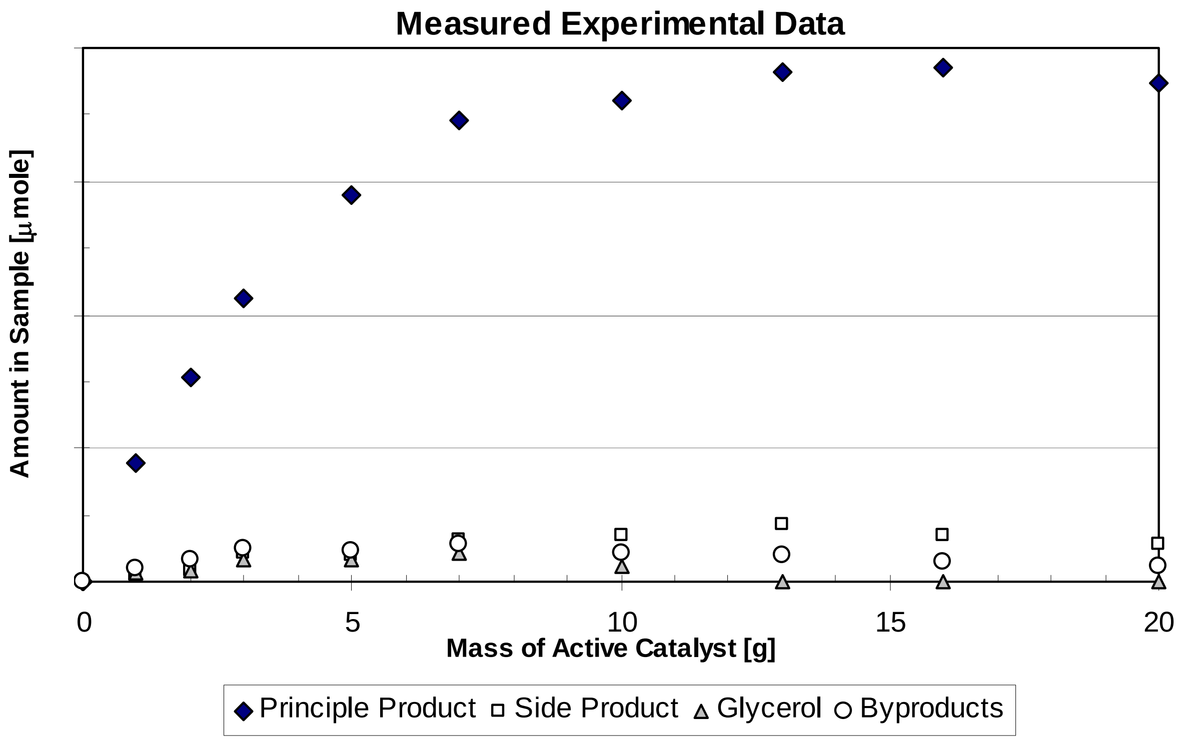

Figure 11.1. Measured data from laboratory reaction experiments.

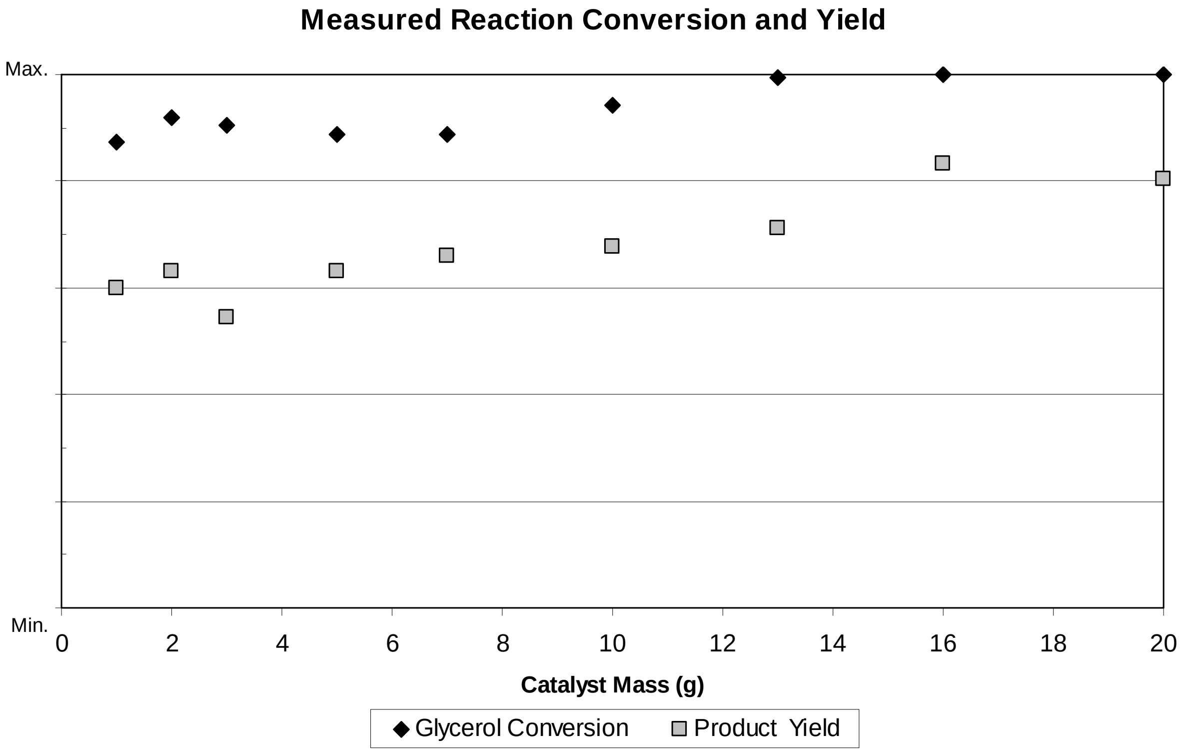

Figure 11.2. Glycerol conversion and principle product yield versus catalyst mass.

11.4 Evaluating Kinetic Models

As described above three reactions were considered for the kinetic model. Although the identity of the byproducts is undetermined, for the purposes of model development, it is assumed that the byproducts are formed by the liberation of water from glycerol. The reaction from glycerol to the products takes place on the surface of the catalyst support pellets which are covered with the phosphoric acid catalyst. Therefore the kinetic approach chosen for modeling is Langmuir-Hinshelwood-Hougen-Watson (LHHW). Since there is only one species reacting to form the two products and one byproduct, the three mechanisms end up with the same equation being used in the kinetic model.

$$r_i = k_i \frac{K * p_{GLY}}{1 + K * p_{GLY}} \qquad \text{(Eqn. 11.8)}$$

The index i indicates the reaction of interest with r_i being the reaction rate, k_i the rate constant, K the adsorption equilibrium constant and p_{GLY} the partial pressure of glycerol. The rate constants k_i are temperature-dependant following the Arrhenius law with the frequency factor k_{inf}, the activation energy E and the universal gas constant R.

$$k_i(T) = k_{\inf} * e^{-\frac{E}{RT}} \qquad \text{(Eqn. 11.9)}$$

Because of the work, described in Chapter 10, to determine the optimum operating temperature, experiments to determine the temperature dependence of the reaction rate constant were not necessary. This work to determine the rates of reaction only focuses on the kinetics at the optimum operating conditions, with the rate constants only being determined at the previously determined optimum reaction temperature.

In order to find values for the rate constants, k_i, and the adsorption equilibrium constant, K, for each of the three reactions, a parameter estimation was carried out using the REX software package. The parameter estimation is done by fitting a curve to the experimental laboratory data. The evaluation of the accuracy of the curve fit generated by the software package to the experimental data is done using a weighted least squares analysis. Due to the proprietary nature of the data, the parameter estimation results are included in Appendix H, which can be found in Volume 2 of this dissertation, which is only available to the dissertation committee members. The graphical results of the curve fitting analysis using the REX software package for the principle product, side product, by-product and glycerol feed stock are illustrated in Figures 11.3 through 11.6. The weighted least squares error for the regression analysis is also included in Appendix H.

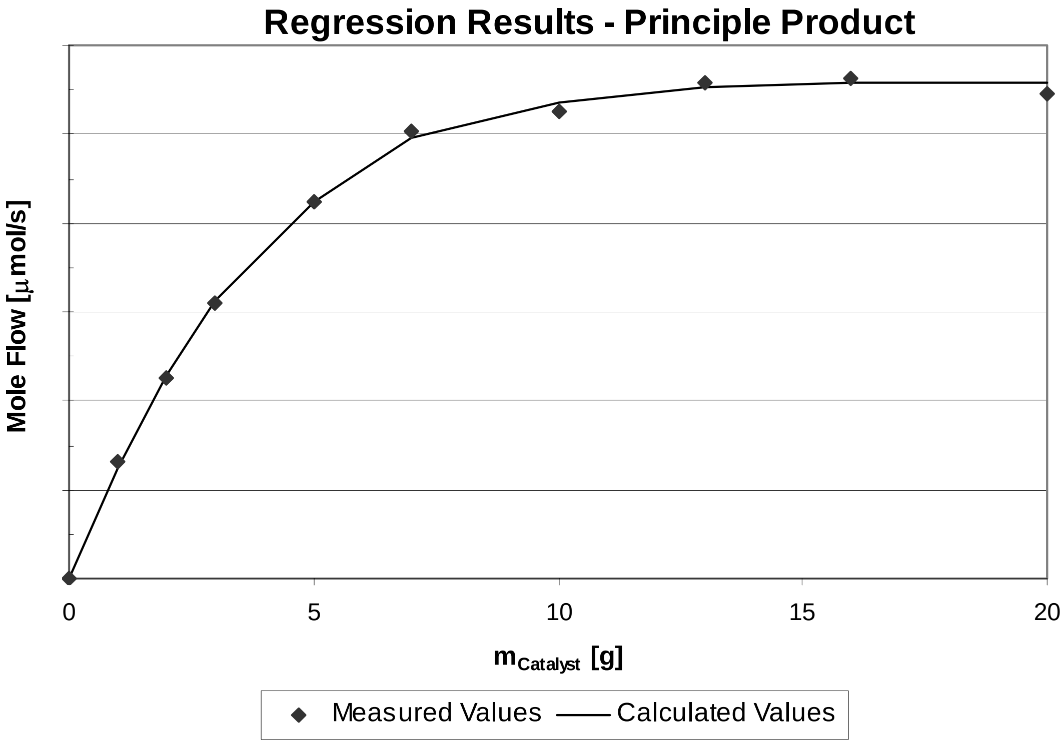

Figure 11.3. Regression results for principle reaction product.

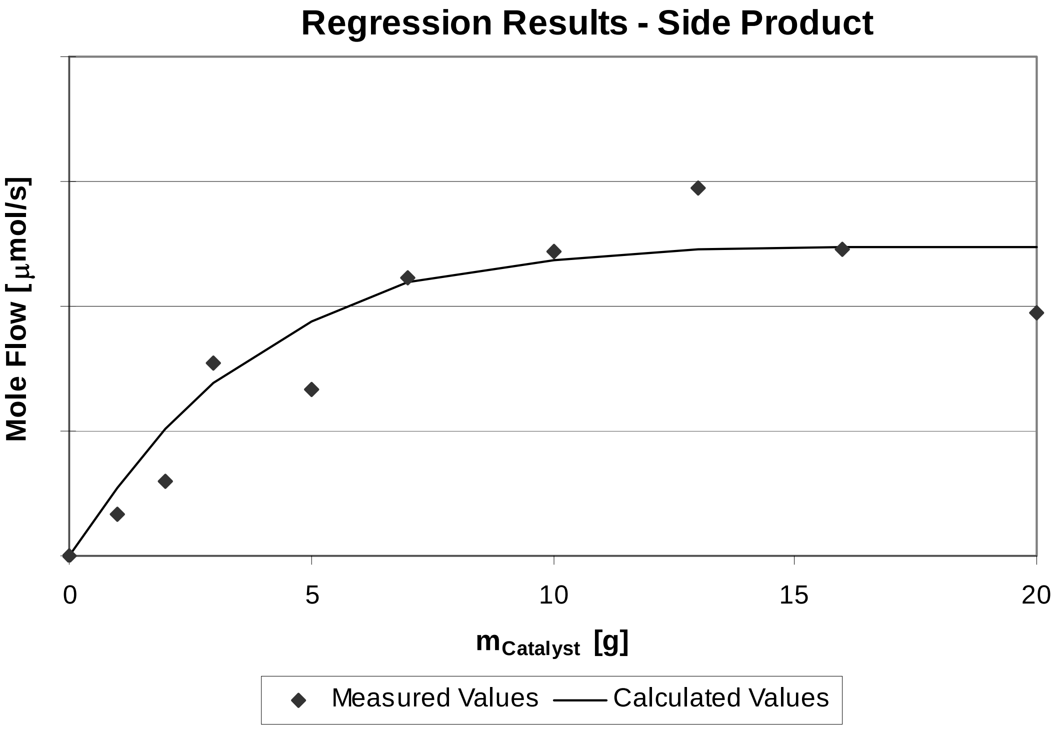

Figure 11.4. Regression results for primary side reaction product.

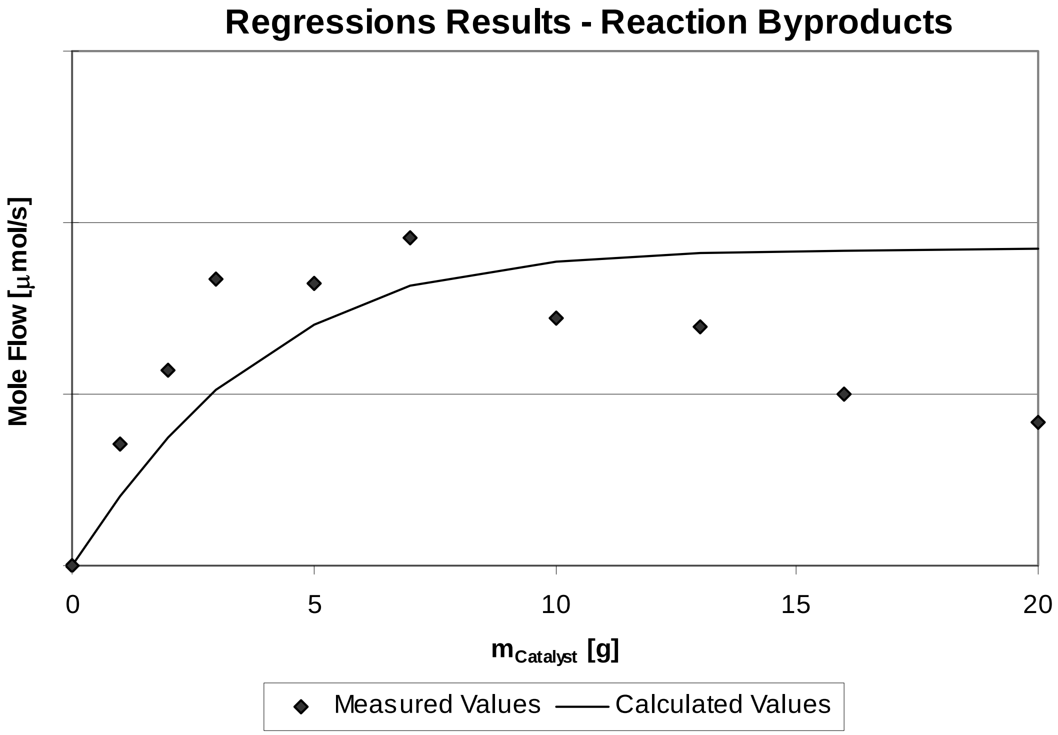

Figure 11.5. Regression results for reaction byproduct.

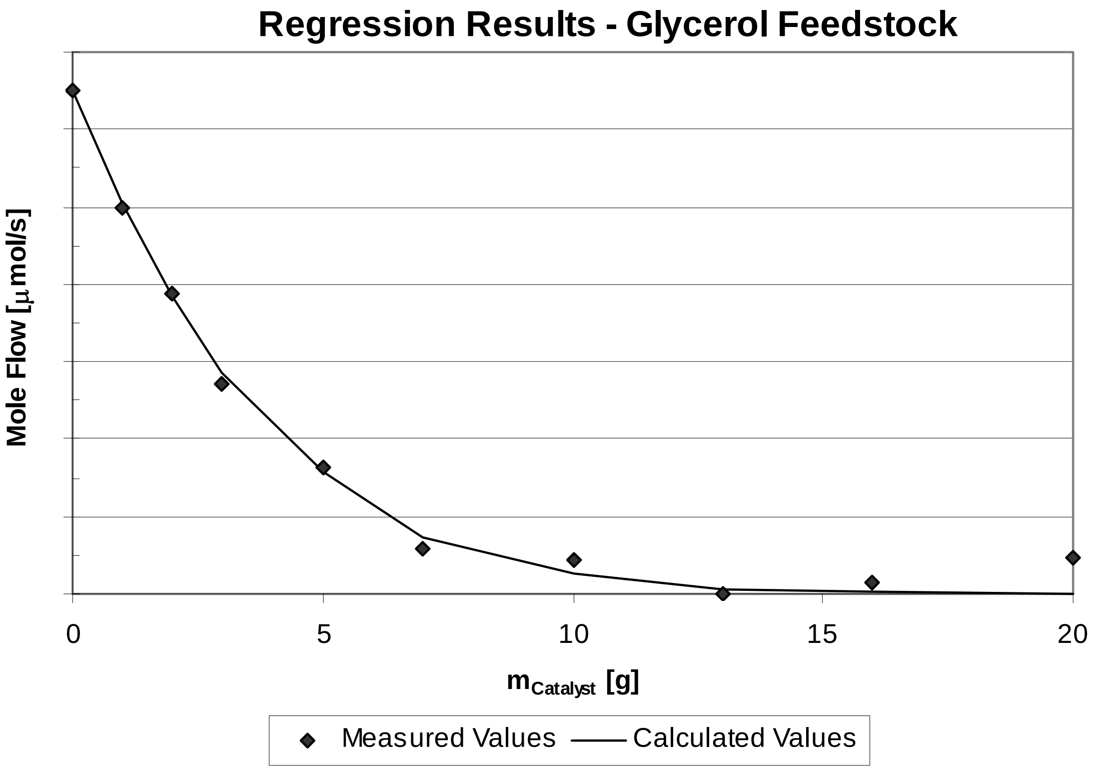

Figure 11.6. Regression results for glycerol reaction feedstock.

Based on the previous experimental results described in Chapter 10, it was observed that the catalyst activity decreases with time. After 90 to 100 minutes, the observed principle product yield drops sharply. Therefore, the adsorption equilibrium constant, K, and the rate constants for the three reactions, k_1, k_2 and k_3, were calculated using the REX software as a function of time. The results of this analysis are illustrated in Figures 11.7 through 11.10, below.

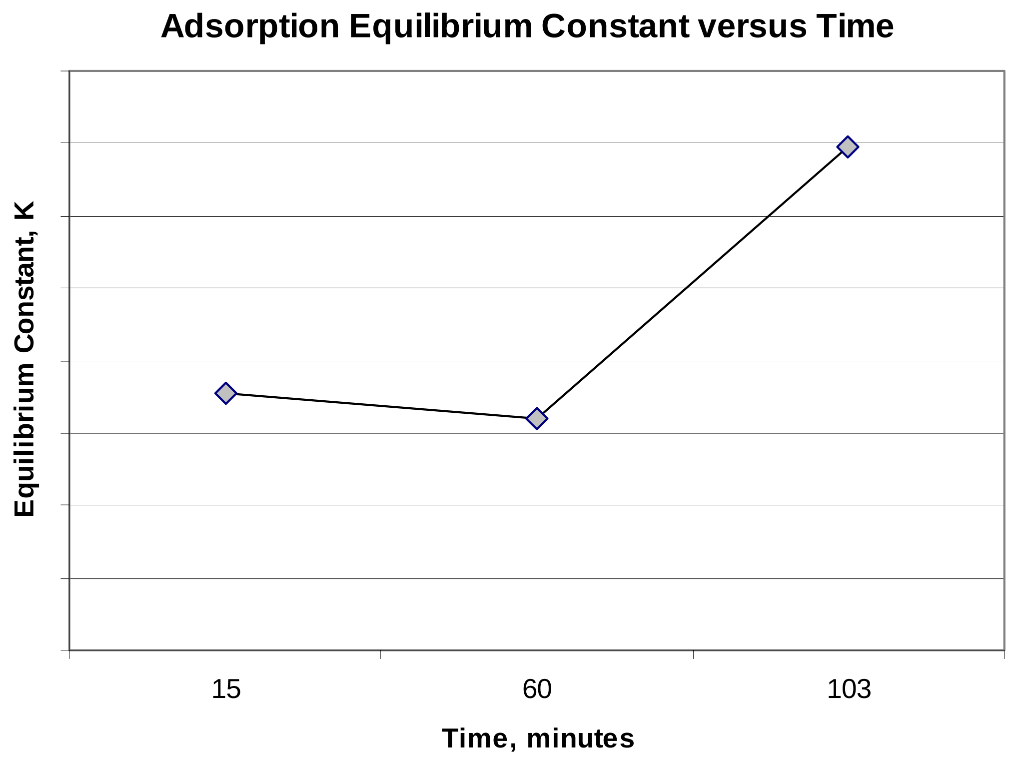

Figure 11.7. Adsorption equilibrium constant K as a function of time.

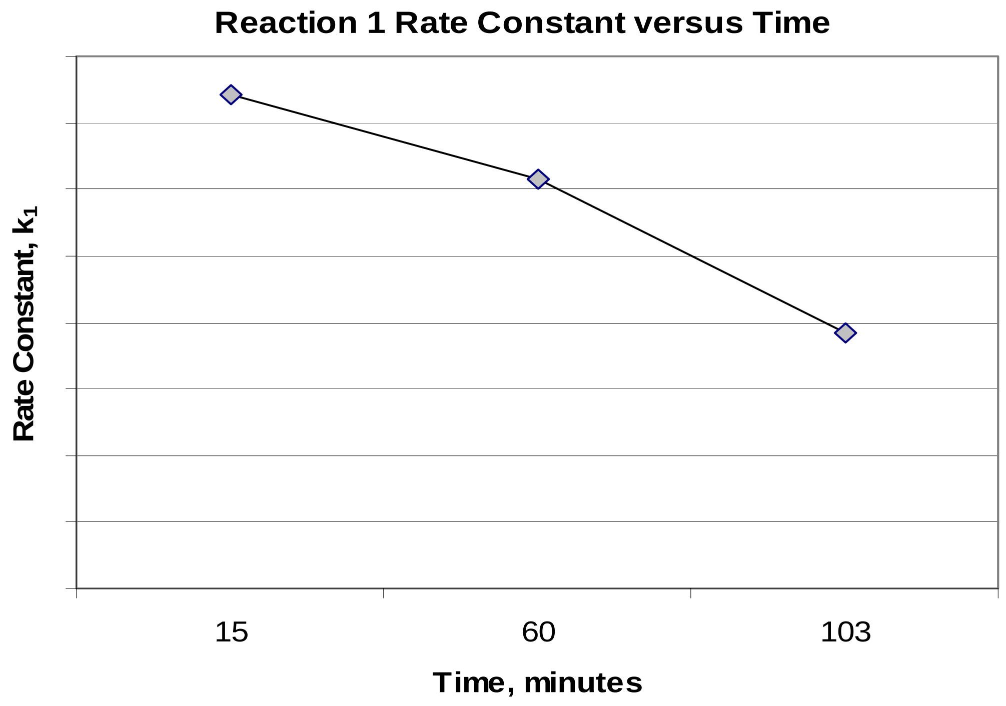

Figure 11.8. Reaction 1 rate constant, k_1, as a function of time.

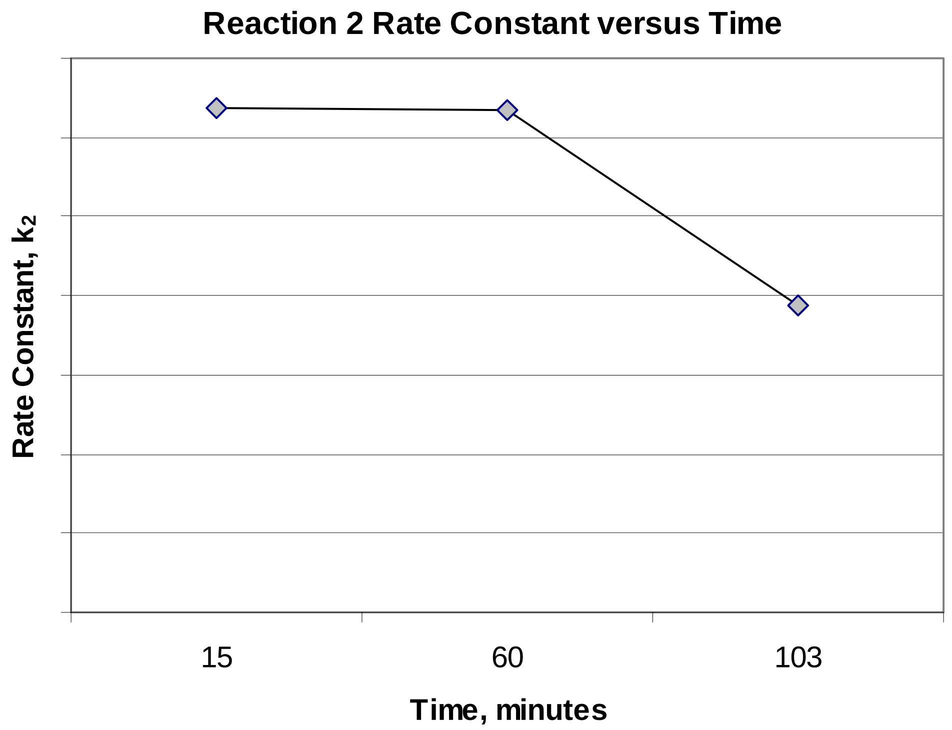

Figure 11.9. Reaction 2 rate constant, k_2, as a function of time.

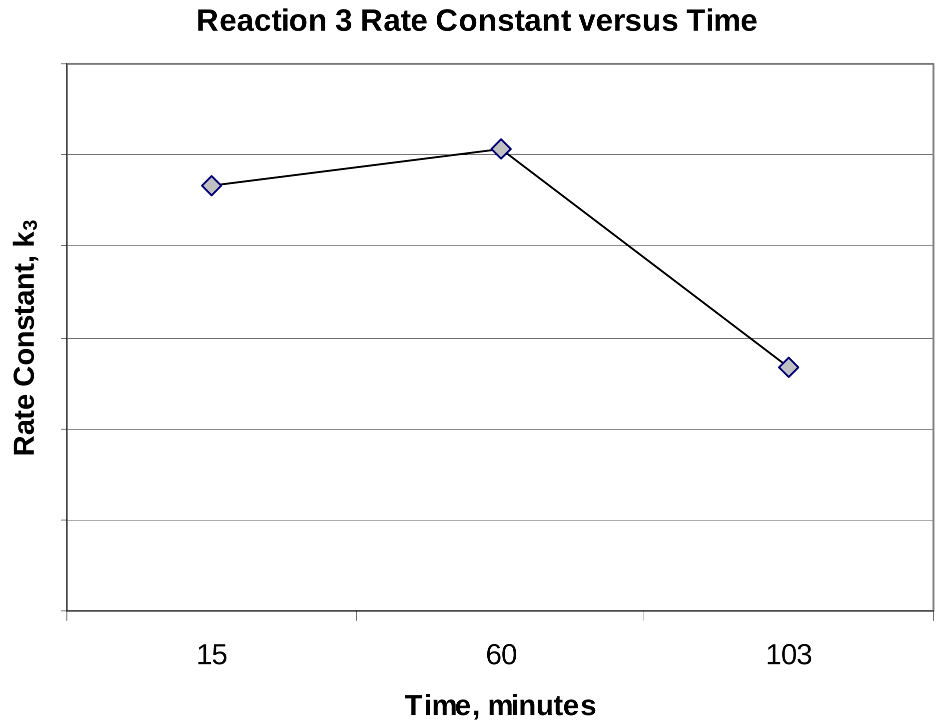

Figure 11.10. Reaction 3 rate constant, k_3, as a function of time.

From the results illustrated in Figures 11.7 through 11.10, it is clear that the reaction is effected the longer the catalyst remains in the reactor. Although it is outside the scope of this research, further research to study the mechanisms of the catalyst deactivation and how the catalyst life can be extended, would be beneficial in the development of this process.

11.5 Conclusion

The results of the analysis to determine the reaction kinetic parameters can be used to update the process simulation model described in Chapter 9. This allows the simulation to be used to determine the total mass of catalyst necessary to manufacture industrial quantities of dehydration products from glycerol. Using the technique described in this research, it should be clear that valuable experimental time can be saved by first determining the optimum operating conditions of the reactor. Although this technique does not allow for extrapolation to other temperatures, flowrates or compositions, the time saved streamlines the process development procedure while also ensuring that the proposed process will be both technically feasible and optimized regarding process performance.

CHAPTER 12

ACCOMPLISHMENTS AND CONCLUSIONS

12.1 Accomplishments

As was discussed in the introduction to this research, the activities of laboratory experimentation and conceptual process design have traditionally been considered as two independent areas of research. However, this mode of thinking can result in unnecessarily constraining the activities of the process design engineer. By limiting the operational boundaries only to those conditions originally studied in the laboratory, the true region of optimal process performance may be missed.

The research presented in this dissertation has addressed this gap between experimentation and design by focusing primarily on the development of a novel method for integrating experimental procedures into the traditional activities of conceptual process design. In particular, the primary accomplishment of this research is the development of a comprehensive approach to understanding the role that model detail and experimental design methods play in the design of chemical processes and products. This work has led to a generally applicable framework for integrating experiments with existing design tools such as process simulation and optimization to minimize the experimental runs required for finding the best process design. Furthermore, experimental analysis tools such as statistical design of experiments has been integrated into the activities of computer aided process design to further integrate these two areas of process development. Additionally, this research has laid a foundation for the further extension of the role of conceptual process design to include environmental impact assessment and risk assessment methodology. These two areas are both subjects of growing importance in the field or process design and systems engineering.

Taking a holistic view of conceptual process design is critical because it is in the conceptual stage of development that the process engineer has the greatest influence over the final industrial scale process. By applying the tools of computer aided process engineering, statistical design of experiments, environmental impact assessments, risk assessment methodology and inherently safe process design to an industrial process development project, this research has shown that the conceptual process design phase can be streamlined. By using process simulation tools to continuously to monitor the performance of the process as a whole while optimizing individual unit operations and systems, the design engineer can ensure that only conditions leading to performance optimized processes are considered. With this technique, conditions that lead to non-optimal performance can quickly and easily be screened out. Due to limited resources, methods that can be applied to shorten the time required to take a process from the initial chemistry to a final process design are always needed. By developing a method to streamline the activities of conceptual process development, the research presented in this dissertation is a significant contribution to the broad fields of process design and systems engineering.

This method of streamlining the design activities, is especially important for processes based on novel chemistry. Especially processes based on the principles of green chemistry. Since overall performance continues to drive new development, it is important to have a methodology that allows new processes to be quickly screened for performance viability. This is important to ensure that research efforts are focused on chemical processes that lead to viable manufacturing processes.

12.2 Research Conclusions

This process development methodology has been applied to an industrial case study to illustrate its general applicability. Based on the glycerol dehydration case study chosen to illustrate the methodologies developed as part of this research, many of the research accomplishments can be observed.

- From these results, it can be seen that by integrating the laboratory experiments with the process simulations, innovative process designs can be discovered.
- From the results presented, it is clear that without integrating process simulations with the laboratory experiments, the better performing Inert Gas process conditions may not have been discovered.
- Furthermore, by integrating the simulation with experimentation, the true optimum can be located. Results indicated that this was not the point with the highest yield.
- Although additional work remains to be done to complete the process development, it is clear that the glycerol dehydration process now shows potential for overall viability and warrants further study.

12.3 Path Forward and Continuing Research

The research completed for this dissertation is a first step into extending the heuristics of conceptual process design. The work presented thus far is focused on applications for continuous processes operating at steady state. The next major hurdle to address is the application of this methodology to unsteady state processes, such as batch operation. Batch operations are especially common in the area of specialty chemical manufacturing, so further developing the design methodology to include this type of process would have immediate application in industry. Further continuing research both in the area of methodology development as it applies to sustainable processes and specifically related to the glycerol dehydration case study will be discussed in the following sections.

12.3.1 Application to Sustainable Processes

Based on the recent interest in global climate change, energy independence, sustainable process development and green chemistry, it is important to have screening procedures available to assess the overall viability in terms of performance of new processes based on renewable feedstocks. Using a methodology, such as the methodology presented as part of this research, is important to ensure that development is focused on conditions that lead to viable processes.

Although the methodology presented with this research is general in nature and therefore can be applied to any chemical process, it is especially important for sustainable processes designed to replace current processes based on crude oil derived resources. This methodology can be applied to ensure that from the earliest phases of development, conceptual processes are based on conditions that lead to designs that meet the overall performance requirements of the project. Further extension of this research to include calculation of the process carbon footprint and life cycle assessment of the manufacturing process would be the next logical extension of this research.

12.3.2 Path Forward for Glycerol Dehydration Chemistry

For the specific case study based on glycerol dehydration chemistry, several tasks remain as this research continues. Continuing research, beyond the scope of this project should include moving on to the pilot scale to continuing testing and refining the reactor operating conditions. In addition, pilot scale experiments should be conducted with glycerol provided from a biodiesel refinery to determine the effect of raw material quality on the reactor conversion and product yield.

Furthermore, extending the work to include other 3-carbon industrial products that can be manufactured from glycerol should be considered. Finally, due to the relatively short catalyst life, further research to investigate in situ catalyst regeneration or the application of a fluidized bed reactor would be a logical next step. A photo of the used catalyst is shown in Figure 12.1, below. The dark catalyst indicated carbon deposits on the surface that reduce the catalyst effectiveness.

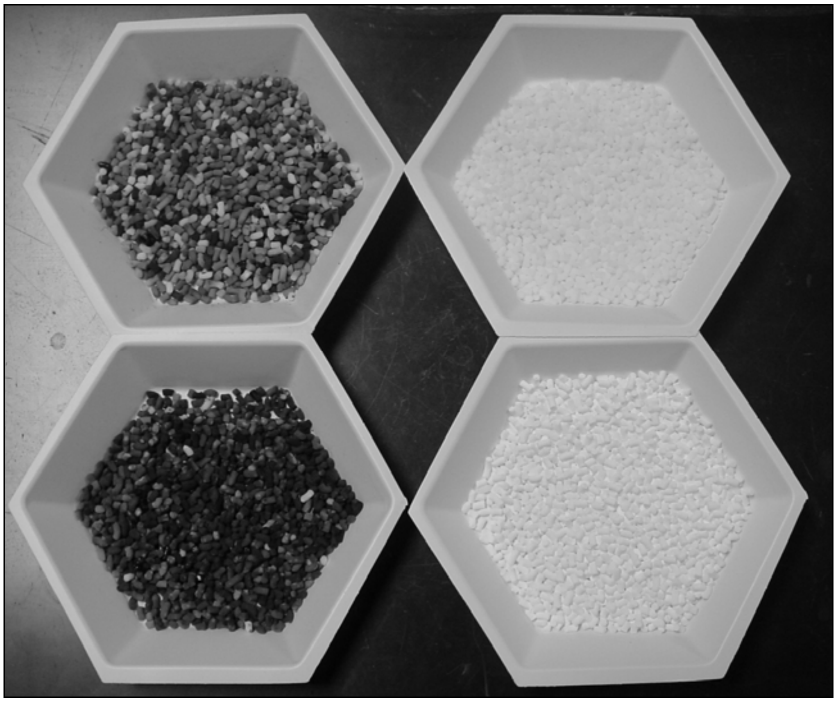

Figure 12.1. Spent and fresh catalyst samples from mini-plant operation.

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