A Comprehensive Optimization Framework for Designing Sustainable Renewable Energy Production Systems

Aryan Geraili Nejadfomeshi
Louisiana State University and Agricultural and Mechanical College

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A COMPREHENSIVE OPTIMIZATION FRAMEWORK FOR DESIGNING SUSTAINABLE RENEWABLE ENERGY PRODUCTION SYSTEMS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Cain Department of Chemical Engineering

by

Aryan Gerali Nejadfameshi
B.S., University of Tehran, 2010
M.S., Louisiana State University, 2013
May 2015
To my beloved father and mother,

Hamid and Iran

and my supportive brother

Armin
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Abstract

As the world has recognized the importance of diversifying its energy resource portfolio away from fossil resources and more towards renewable resources such as biomass, there arises a need for developing strategies which can design renewable sustainable value chains that can be scaled up efficiently and provide tangible net environmental benefits from energy utilization. The objective of this research is to develop and implement a novel decision-making framework for the optimal design of renewable energy systems.

The proposed optimization framework is based on a distributed, systematic approach which is composed of different layers including systems-based strategic optimization, detailed mechanistic modeling and operational level optimization. In the strategic optimization the model is represented by equations which describe physical flows of materials across the system nodes and financial flows that result from the system design and material movements. Market uncertainty is also incorporated into the model through stochastic programming. The output of the model includes optimal design of production capacity of the plant for the planning horizon by maximizing the net present value (NPV).

The second stage consists of three main steps including simulation of the process in the simulation software, identification of critical sources of uncertainties through global sensitivity analysis, and employing stochastic optimization methodologies to optimize the operating condition of the plant under uncertainty. To exemplify the efficacy of the proposed framework a hypothetical lignocellulosic biorefinery based on sugar conversion platform that converts biomass to value-added biofuels and biobased chemicals is utilized as a case study.
Furthermore, alternative technology options and possible process integrations in each section of the plant are analysed by exploiting the advantages of process simulation and the novel hybrid optimization framework. In conjunction with the simulation and optimization studies, the proposed framework develops quantitative metrics to associate economic values with technical barriers. The outcome of this work is a new distributed decision support framework which is intended to help economic development agencies, as well as policy makers in the renewable energy enterprises.
1. Introduction

1.1. Background

Fossil fuels have offered astounding opportunities during the 20th century and the global state of energy supply has been highly dependent on them (Figure 1.1). However, now mankind has to face the challenges arising from fossil resources exploitation. Owing to finite nature of them, volatility in their prices and concerns about their environmental impact, efforts around the world to develop and commercialize sustainable alternatives such as renewable transportation fuels and energy products have intensified (Cardona & Sanchez, 2007). Sufficient energy supply and less greenhouse gas emission are two key issues to maintain sustainable development of the global human society. Renewable energy is derived from natural resources such as wind, water, sunlight, and biomass; these resources have shorter cycles of replenishment and are provided by nature in a near-continuous basis.

![World Energy Consumption](image)

Figure 1.1: Energy consumption from different resources; Source:EIA.gov
Biomass refers to organic matters that have stored energy through photosynthesis process. Transportation fuels and chemicals can be derived from any form of biomass such as plants or organic wastes. Biomass has become one of the most commonly used renewable sources of energy in the last two decades. After a boom in the U.S. corn-based ethanol (first-generation biofuel) in the early part of the 21st century (Somma et al., 2010), the interest has gradually shifted towards more viable renewable resources such as lignocellulosic feedstocks. Negative impacts of first generation biofuels might lead to the risk of deforestation by overuse of lands, environmental risks by the widespread use of fertilizers and pesticides, and decreasing food security by the risk of creating a competition between food and fuel production.

Cellulosic ethanol is an example of such alternative fuel which is considered as a second-generation biofuel and is derived from cellulose instead of starch. The fuels and chemicals produced from lignocellulosic feedstocks are extremely attractive owing to the fact that the raw materials can be composed of “left-over” wastes of food crops and forest harvests that do not interfere with the human food chain. It also can provide new income and employment opportunities in rural areas. Further, due to the large variety of lignocellulosic materials and their abundance, these types of produced fuels and chemicals (second-generation) can overcome the challenge of limited feedstock availability that first generation biorefineries have to contend with.

Several technical challenges exist toward developing biorefineries. Biomass has a C:O ratio up to 1:1; therefore, it is significantly different in composition from crude oil. Additionally, oxygen is present in different functional forms which require different chemical steps for its removal. Crude oil and hydrocarbon fuels do not contain any oxygen. There are two main conversion platforms in a biorefinery process: (1) the biological conversion pathways based on
fermentation, and (2) thermo-chemical conversion pathways based on heat-based technologies such as gasification and pyrolysis. The main difference between these two conversion mechanisms is the primary catalysis system (Foust et al., 2009). In biological conversion pathways, biocatalysts such as enzymes and microorganisms are utilized. However, in thermochemical production routes, heat and physical catalysts are utilized to convert biomass to biofuels and chemicals.

The commercial scale production of biobased fuels and chemicals has been hampered due to the lack of capital investment, technological complexities, and product market immaturities which are driven by the nascent nature of these industries. Thus, improvement in these technologies will assist sustainable developments and provide solutions to energy related and environmental problems. In this sense, development of decision-making frameworks for renewable energy systems provides a suitable tool for analysis and investigation of these industries for potential improvements. The use of decision support to aid in decision-making process seems appropriate and in many cases it does lead more sound actions being taken by stakeholders based on a more complete picture of what is actually happening around them.

Typical decision support frameworks in renewable energy industry involve superstructure modeling, technology analysis, strategic, tactical and operational level optimization, optimization under uncertainty, and life cycle assessment. Many strategies have been proposed for designing technological flowsheets with improved performance. Some research studies focused on analysing the performance of alternative technology options for a section of biorefinery plant (Öhgren et al., 2007; Vane, 2008; Wyman et al., 2005). These studies provide a good insight for the performance and optimal operating conditions of that particular section.
Superstructure modeling is the approach that supports a systematic screening of technological options for each section of the plant and determines the optimal configuration of a process and its optimal operating conditions simultaneously from all possible alternatives (Yeomans & Grossmann, 1999). For instance, Pham and El-Halwagi (2012) developed a systematic two-stage approach for the synthesis and optimization of biorefinery configurations. Martin and Grossmann (2011) represented a superstructure optimization model which is formulated as a mixed-integer nonlinear programming problem involving short-cut models for the unit operations in the process. Sammons et al. (2007) developed a general systematic framework for optimizing product portfolio and process configuration in integrated biorefineries by including profitability measures and techno-economic metrics.

Utilization of analytical systems and mathematical models for decision-making has gained increased attention in energy industries. They can provide insights to find solutions that help businesses to remain competitive in the current fiercely competitive market environment. Nowadays, because of developments in algorithms and technologies researchers can solve real-life problems that in the past were thought to be unsolvable. As a result of this trend, several contributions have appeared over the last few years where mathematical programming techniques have been exploited by taking into account process and economic modeling. Developed frameworks assess different objectives such as environmental or techno-economic metrics.

As far as biorefining processes are concerned, optimization techniques have been implemented with the aim of optimizing the process by utilizing deterministic approaches. For instance, Karuppiah et al. (2008) and Furlan et al. (2012) developed frameworks to optimize the profitability of the biorefineries focusing on production cost reduction. Martin et al. (2011)
developed a strategy to optimize water consumption in biorefineries. Further, there are many publications which have mainly focused on identifying the optimal processing route for a biorefinery (Bao et al., 2011; Zondervan et al., 2011).

Additionally, multi-objective optimization approaches are gaining popularity and have been proposed to optimize several contradictory objective functions simultaneously such as thermo-economic and environmental impacts (El-Halwagi et al., 2013; Fazlollahi & Marechal, 2013; Giarola et al., 2011; Sharma et al., 2011; You et al., 2012). Multi-objective optimization methodologies are divided into two main categories: aggregate weight functions and Pareto-based optimization methods. Aggregating functions combine all the objectives to optimize one single objective where the relative importance of each objective is adjusted based on relative weights (Hajela & Lin, 1992). In Pareto-based optimization techniques, a relationship among solutions based on Pareto-dominance concept is established and the result will be a set of optimal solution instead of a unique result (Goldberg, 1989).

Furthermore, recent trends in process industries represent that individual businesses no longer compete as stand-alone entities, but rather as extended enterprises (also called supply chains) whose success or failure is ultimately determined in the market by the customers. Supply chain is an integrated manufacturing process wherein raw materials are converted into final products, and delivered to customers. The general schematic structure of a supply chain for a chemical value chain is represented in Figure 1.2. Nowadays, competing is not between individual organizations but between competing supply chains (Beamon, 1998). Therefore, supply chain modeling and optimization is critical to maintain economic viability in the current highly competitive marketplace (Grossmann, 2005). To accelerate the transition towards the large-scale and sustainable design of biorefineries, a significant challenge in research is to
effectively design and optimize the entire biorefinery supply chains from biomass feedstock production to customers in a cost-effective, robust, and sustainable manner. The work by Yue et al. (2014) represents the latest contributions of bioenergy supply chain modeling and discusses the challenges and key issues in detail.

Figure 1.2: Schematic structure of supply chain for chemical value chains

The aforementioned studies use deterministic modeling approaches, which assume that all the model parameters that influence the optimization task are known in advance. However, common to early stages of process design is the lack of certain information that will introduce variability into the decision-making problem. Uncertainty affects the system efficiency and may lead to either infeasible design or suboptimal performance. In terms of time horizon, short term variations can include uncertainty as a result of measurement errors and ignorance, which is to some extent inevitable and might be reduced by further studies or investing in improved technologies to acquire high quality data (Petrovic, 2001). Uncertainty can also result from long term variations such as changes in the market trend which can be controlled by employing
forecasts in renewable energy industry are currently very preliminary; understanding how uncertainties in market and technological parameters impact the design decisions is necessary for reducing the risk that limits investment and development of these technologies. Widely used methodologies developed for solving optimization problems under explicit consideration of uncertainties include chance constraint programming, stochastic programming, and robust optimization which are reviewed in detail by Sahinidis (2004). A number of contributions addressed the presence of uncertainties in optimization of biorefineries by considering various sources of uncertainties and utilizing different types of optimization methodologies (Dal-Mas et al., 2011; Gebreslassie et al., 2012; Kim et al., 2011; Tong et al., 2014).

1.2. Dissertation motivation

Although various decision support models have been developed, in most of these studies, strategic, tactical and operational decision tasks are not considered together, even though there are significant interdependencies between them. Furthermore, most of the considered decision models used for support are linear that do not take into account the inherently nonlinear mechanisms of the conversion processes (owing to complex kinetic and thermodynamic relationships). Moreover, a robust optimization framework should incorporate the uncertainty of the model parameters at different levels of decision making process and manage the financial risks associated with these uncertainties. Therefore, these complexities reveal the need for developing a comprehensive framework which can carefully support a multitude of strategic,
tactical, and operational tasks by integrating the nonlinearities involved in the process in the face of uncertainty.

The work proposed in this dissertation will incorporate solutions for the aforementioned shortcomings in order to develop a more robust framework that can mimic the actual design methodology that planners, developers, and enterprises should follow for designing sustainable renewable energy production systems. By considering the challenge of integrating process dynamics, nonlinear modeling and optimization, different software platforms are interlinked in a novel fashion to execute the framework seamlessly. Our analysis is performed by exploiting the advantages of a novel iterative framework which is composed of two layers including strategic planning and operational level optimization model. These layers will consist of several sectors that will coordinate activities within a particular division. Both layers will reciprocally interact in an effort to work towards a common and specific corporate goal.

In the first layer, strategic decision making will be formulated as a mixed integer linear programming (MILP) model which incorporates a stepwise capacity expansion strategy by defining binary variables for capacity increments at each time period in the planning horizon. Stochastic forecasts for uncertain parameters are utilized to incorporate possible market fluctuations in the strategic model. A scenario-based approach for modeling uncertainty in market parameters provides an effective way to systematically assess the impact of uncertainty on the design and operation of the enterprise. Additionally, financial risk due to uncertain market parameters is explicitly addressed in the strategic model.

In a problem like our case study, where large amounts of capital are involved, risk as well as profit is of great concern to management. In stochastic programming strategies the expected
profitability is optimized which is optimal solution on average for all the scenarios. These strategies do not allow controlling the variability of the objective function in the uncertain space. The fundamental idea in risk management is to incorporate the trade-off between financial risk and expected cost within the decision-making process by adding a criterion to control the variability of the performances associated with each specific scenario.

In operational level, the process is simulated based on the optimal results of strategic model, and then operating conditions of the plant are optimized by utilizing an evolutionary algorithm. Since many real-world optimization problems such as our case study are highly nonlinear and under various complex constraints, finding optimal solution or even sub-optimal solutions is not an easy task. Evolutionary algorithms have come to be recognized as one of the most practical approaches for solving many complex problems due to their effectiveness and applicability (Blum & Roli, 2003). Uncertainty analysis is also incorporated in the operational level model by performing a global sensitivity analysis and Monte Carlo simulation to pinpoint the most critical parameters that drive the profitability of the enterprise and reduce the model size. A commercial simulation package is employed to model the process in detail. It offers the capability to carry out rigorous energy and material balances for our complex case study (integrated biorefinery) and incorporate the non-linearities (thermodynamic relationships and complex kinetics of reactions) into the optimization framework.

Additionally, we realize that conversion technologies and process integration schemes are fraught with technical challenges that prevent commercialization. Quantification of technical challenges can help prescribe R&D and policy goals to entities in order to accelerate the path to commercialization. Therefore, in conjunction with the simulation and optimization studies, the proposed framework will develop quantitative metrics to associate economic values with
technical barriers. These values will act as thresholds that need to be breached in order to successfully commercialize a given technology. For example, a process technology can be constrained by poor product yields that can be translated into high unit production costs. Poor yields can in turn be related to operating conditions, enzymes, or raw materials.

1.3. Aims and contribution of this dissertation

The proposed research will result in a decision analysis system that will provide renewable energy entities with systematic decision support tools regarding product and process sustainability, economic analysis, strategic planning, and risk quantification. This decision support framework helps to investigate the inherent collaborative relationships between different decision layers of a renewable energy enterprise, and how these relationships can be exploited in order to improve their commercial viability and sustainability. Sensitivity analysis will help enterprises quantify technical barriers that may prevent commercialization of technologies to streamline resource allocation and R&D towards overcoming these barriers. Risk curves for each alternative will provide enterprise management with visual representations of the probabilities of losing stakeholder value by implementing a design plan. The work proposed in this dissertation has addressed the following key problems:

- A strategic linear model is developed to optimize long term decision tasks such as capacity planning for the planning horizon in renewable energy enterprises. Financial constraints are developed and blended with material and energy balances’ results to calculate the cash flows and optimize the net present value (NPV) of the enterprise. Additionally, the model gives the decision makers the flexibility to expand the capacity during the planning horizon instead of establishing the whole capacity initially.
• To overcome the mismatch between nonlinear process mechanisms, which is inherent in renewable energy processes, and LP-based strategic optimization, a lower level (operational) model is developed in which the optimized design from strategic model is utilized to simulate the process in simulation software, and update the parameter value in strategic model based on the results from simulation.

• A methodology has also been developed to investigate alternative technology options suggested in literature for each section of the plant by analyzing their energy consumption and profitability.

• The Aspen Plus model capable of performing system-wide steady-state and dynamic simulations developed for operational level modeling will have three unique features: (1) It will be for integrated large-scale and real-process dynamic simulations which will involve dozens of facilities with hundreds or thousands of units; (2) It will include capability for simulating special operations such as plant start-up, shutdown, and process; and (3) It will be an emission-embedded model that can provide both spatial (e.g., specific process, specific facility and specific equipment) and temporal (e.g., dynamic profiles from each simulation device) distributions of concerned emissions.

• This distributed strategy has the advantage of not only being able to integrate the nonlinearities to the linear strategic model, but also optimize the operating conditions (short term decisions) of the plant through utilization of metaheuristic algorithms. It also gives us the capability to impart a greater degree of realism to the actual representation of the process, by incorporating the experimentally validated kinetics of complex bio-reactions into the simulation to better estimate the nonlinear reaction dynamics.
Finally, to expand the scope our proposed framework and add more granularity into it, stochastic modeling, uncertainty analysis and global sensitivity analysis techniques are utilized to consider the variability that will be introduced into the decision-making problem by the lack of certain information in all levels of decision-making process.

The arrangement of materials in the rest of the dissertation is done in the form sections and chapters. The content of each section and chapter is mentioned briefly below.

1.4. Organization of Dissertation

This dissertation is organized into 5 sections followed by a concluding section and possible extensions to the research work. Additionally, the work that has been done for improving the convergence optimization algorithms through development of a repair strategy is presented in Appendix A. Contributions in terms of journal papers and conference presentations that have been made by the authors are also listed. The first chapter gives a brief literature background about renewable energy systems, highlights the motivation for the dissertation, and discusses the aims and contribution of this research work.

Chapter 2 introduces our proposed multi-layered decision support framework for optimal design of new and emerging renewable energy production systems by considering an iterative strategy which integrates the Net Present Value optimization along with detailed mechanistic modeling, simulation, and process optimization which yields optimal capacity plan, and operating conditions for the process. Due to the non-linear nature of process conversion mechanisms, evolutionary algorithms are implemented in the framework to optimize process operating conditions. Further, to apply complex kinetics in the process, a linkage between process simulator (Aspen Plus) and Matlab is made. To demonstrate the effectiveness of the
proposed methodology, a hypothetical case study of a lignocellulosic biorefinery is utilized. The proposed framework results reveal a deviation in optimal process yields and production capacities from initial literature estimates. These results indicate the importance of developing a multi-layered framework to optimally design a renewable energy production system.

Chapter 3 is dedicated to studying the design and modeling of fully integrated processes which utilize renewable feedstocks as raw materials by evaluating alternative technology options and possible process integrations to select the optimal configuration according to calculated process yields and economic profit criteria. The analysis is carried out by exploiting the advantages of process simulation and the proposed optimization framework in chapter 2. Additionally, an integrated software platform is developed to incorporate experimentally-derived kinetics of complex biological reactions in process simulation. To demonstrate the effectiveness of the proposed approach, an advanced biofuel production facility which has alternative technology choices for each section of the plant is utilized. The results prove the efficiency of the proposed approach, and an optimal configuration for a lignocellulosic biorefinery is obtained.

Chapter 4 focuses on expanding the scope of the proposed framework by incorporating market uncertainty in the optimization framework and studying its impact on the optimal design of enterprise. In the current formulation, a reliable optimization framework is developed by applying a distributed strategy which is composed of different layers including strategic optimization, risk management, detailed mechanistic modeling and operational level optimization. In the strategic model, a multi-objective stochastic optimization approach is utilized to incorporate the tradeoffs between the expected cost and the financial risk involved in the process. The numerical results reveal the efficacy of the proposed approach; it provides
decision makers with a quantitative analysis to determine the optimum capacity plan and operating conditions with consideration of uncertainties.

In chapter 5, the expansion of the proposed framework by incorporating uncertainty analysis in both levels (strategic and operational) is presented to add additional granularity to the decision-making strategy. Specifically, this study addresses how uncertainty in different levels of decision making process impacts uncertainty on profitability projections on emerging technologies for energy production. A structural approach is utilized for planning the production capacity, simulation of the process in detail, and optimizing the operating condition of the plant. The optimization problem was solved in a two-level approach, first stochastic linear model was developed to optimize production capacity for the desired planning horizon and then process simulation coupled with stochastic optimization algorithm was employed to optimize the operating condition of the plant. Monte-carlo based simulation and global sensitivity analysis were utilized to identify the most critical parameters and optimize the operating conditions of the plant. The global sensitivity analysis gives insight into the bottlenecks in the process and quantifies the uncertainty in the annual cash flow due to technological risks. Incorporating metrics for mitigation of financial risk in the framework (strategic model) shows that there are two important factors that influence the performance of the model in the face of market uncertainty including production capacity and allocation of feedstock between products.

Chapter 6 concludes the research work presented in this dissertation. Further, possible future work and extensions to the proposed optimization framework are suggested.
Information regarding the publications from this Dissertation is listed below:

**PUBLICATIONS:**

- “A Simulation and Techno-Economic Optimization-Based Methodology to Design Multi-Product Lignocellulosic Biorefineries”, *Chemical Engineering Transactions*, 2013, Volume 32


- “A Multi-objective optimization framework for design of integrated biorefineries under uncertainty”, under review.

**CONFERENCE PRESENTATIONS:**

• “Techno-economic analysis of multi-product biorefineries”.  
  *11th International Conference on Chemical & Process Engineering*, Milan, Italy (2013)

• “Design and Optimization of multi-product biorefineries”.  

• “A Multi-layered Optimization-Based Framework for Design and Analysis of Renewable Energy Processes”.  


• “Multi-stage Stochastic Optimization-Based Framework for Design of Integrated Biorefineries under Uncertainty”.  


• “A Framework for Optimal Design of Integrated Biorefineries under Uncertainty”.  

1.5. References


2.1. Introduction

Over the past decade, world energy consumption has increased progressively owing to the growing demand by burgeoning industrial societies in emerging markets and the rising world population. The current global state of energy supply is highly dependent on fossil fuels. Owing to finite nature of fossil fuels, rapid increase in their prices and concerns about their environmental impact, efforts around the world to develop and commercialize renewable transportation fuels and biobased chemicals have intensified (Cardona & Sanchez, 2007). As the world has recognized the importance of diversifying its energy resource portfolio away from fossil resources and more towards renewable resources, the focus has shifted from recognizing the importance of the renewable resources sector towards designing sustainable value chains that can be scaled up efficiently and provide tangible net environmental benefits from renewable energy utilization. Still, the commercialization of conversion technologies has been hampered by a multitude of endogenous and exogenous factors including unavailability of appropriate feedstock supply systems, lack of capital and investment risk appetite, and inefficient feedstock conversion systems. Out of all issues mentioned, optimizing conversion systems can have a tremendous impact on the overall profitability of renewable transportation fuels and biobased chemical value chains.

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Renewable energy in its broad sense is energy that is derived from natural resources such as sunlight, wind, water, and geothermal heat; these resources have shorter cycles of replenishment and are provided by nature on a “near-continuous” basis. Renewable energy, as a final product, comes in 2 essential forms; (1) electricity that is transported geographically using fixed transportation mediums such as utility grids and wires, and (2) transportation fuels, such as biodiesel, ethanol and butanol, whose mediums (vehicles) are mobile in nature. Once we have categorized the type of renewable energy, we can start to focus on the renewable resources that are currently utilized to produce these energies. Solar, wind, water, and hydrothermal sources in their native forms are used mostly to produce electricity. In order to democratize the use of renewable energy specifically as transportation fuels, a seamless transformation where the renewable resources are converted from their native forms to a more usable and convertible form, is necessary. Fortunately nature provides such a transformative process through the use of photosynthesis, where carbon inputs are chemically altered into organic compounds using energy from sunlight. These compounds, primarily in the form of sugars and lipids, are used to form the structure and backbone of almost all plants and trees we see around us. The question then becomes, what processes and technologies are needed to harvest this natural energy and convert them into usable forms for use as portable, transportation fuels in an economically viable and environmental and socially responsible manner.

The concept of a biobased facility had been prevalent in the United States and the world in general, for hundreds of years. Paper and sugar mills are quintessential examples of bio-facilities where renewable raw materials such as wood pulp and sugarcane are converted to value-added products. The use of composting facilities and waste digesters in farms and rural areas around the world has been a source of sustainable generation of electric power from
renewable resources for decades. In recent times, the emphasis on biobased production using renewable resources has significantly broadened its footprint to incorporate production of fuels, power and chemicals derived from a wider variety of renewable resources. Some renewable transportation fuels that are already in the commercial production phase include first generation ethanol (corn ethanol) and biodiesel (from vegetable oils and animal fats).

Recent ventures into renewable energy have been fraught with corporate failures. A driving reason for these unsuccessful ventures, in part is governed by the lack of proper planning in designing renewable energy plants and supply networks. Often exuberant forecasts of market evolution and insufficient levers in plant and supply chain design for risk mitigation have led to companies failing to maintain solvency when lab- and bench-scale innovations are commercialized for the production of renewable products. An essential part of the planning process is garnering sufficient decision support to guide long-term strategic actions in the face of process and policy uncertainty, and market and competitive risks.

Decision modeling frameworks are ubiquitously classified as decision support systems in a variety of industry verticals. In its most basic form, a decision support system is used to help value chain actors make mission-critical decisions that have an economic, social, or environmental impact on the stakeholders of the value chain. Additionally, the nature of the decisions can be (1) strategic in nature leaning towards longer term decisions that will have an extended impact on stakeholders, (2) tactical which help stakeholders develop tactics to execute the strategies that are developing through strategic planning, or (3) operational in nature where the daily or weekly management of value chain functioning is emphasized.

Within the renewable products industry, decision support systems are relatively new, somewhat driven by the nascence of the industry itself. Owing to the complex nature of supply
chains, conversion processes, and product markets, the use of decision support to aid in decision-making seems appropriate and in many cases it does lead more sound actions being taken by stakeholders based on a more complete picture of what is actually happening around them. Most decision support systems use complex mathematical formulations to model the interactions and interplay of actual physical phenomena that may go unaccounted for in case of ad-hoc decision making; consequently they are considered a valuable tool for any decision maker to compliment the “due diligence process” that they would go through before finalizing and executing critical decisions that would impact stakeholders over the short, medium, and long terms. Table 2-1 shows a list of renewable product industries and corresponding support functions for a prototypical decision support framework.

Table 2-1: Decision support functions in renewable energy production systems

<table>
<thead>
<tr>
<th>Renewable Energy Sub-industry</th>
<th>Decision Support Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar</td>
<td>Solar resource assessment; Power market analysis (supply, demand, price), load forecasting</td>
</tr>
<tr>
<td>Wind</td>
<td>Wind resource assessment, load and power forecasting, discrete parts’ inventory management</td>
</tr>
<tr>
<td>Biomass (Electricity)</td>
<td>Regional feedstock inventory analysis (GIS), feedstock logistics management, emissions management</td>
</tr>
<tr>
<td>Hydropower</td>
<td>Water resource assessment and planning, Hydropower forecasting, environmental management</td>
</tr>
</tbody>
</table>

From the perspective of new renewable product value chains, we have to be cognizant of the fact that most of these endeavors are still in their design and pre-feasibility study phase, wherein, the processes that execute the purpose of the value chain are still non-existent. For example, 2nd and 3rd generation biofuels including cellulosic ethanol and butanol, and algae oil are still in the research, development and demonstration (RD&D) phase in their commercialization cycle, where feedstock supplies, processing technology yields, and product
markets are still being studied and developed. When developing a decision support framework for such enterprises, the initial functions of the framework should therefore focus on aiding stakeholders in the intelligent design of the supply and production chains that will impact all actors and participants over strategic time horizons (10-30 years).

The inception of decision support tools and frameworks is a relatively new concept in the field of renewable energy and bio-chemicals and is gaining attention. Ramachandra et al. (2005) presented a model based decision support tool that helped solar power companies estimate the probable amount of solar energy regionally. Ouammi et al. (2012) published a model based environmental decision support system that stressed optimal technology selection and site location for wind power generation. In recent times, several analytical models have been suggested to study the effect of biomass species, technology choices, plant capacities, and process operating conditions on the production and profitability of cellulosic ethanol. The National Renewable Energy Laboratory (NREL) has developed several analytical models (Aden, 2008; Dutta & Phillips, 2009; Kazi et al., 2010) that analyze different process configurations for the production of cellulosic ethanol. A technical report by Minnesota Technical Assistance Program (2008) investigates ethanol production and introduces potential improvements in energy and water requirement as well as environmental impacts reduction. In this report a comparison of newer and older facilities in Minnesota for ethanol production is also provided. Sammons et al. (2007) developed a general systematic framework for optimizing product allocation and process configuration for a flexible biorefinery. Their methodology provides a framework for process design and product selection based on optimization. In their model, process integration methods such as pinch analysis are employed to optimize the plant. Production pathway and product portfolio are selected based on economic and environmental
criteria. Zondervan et al. (2011) proposed a model to compute the optimal processing routes in a biorefinery by considering different feedstock and products. Bao et al. (2011) developed a systematic optimization framework by integrating multiple conversion technologies. In this model the optimization problem is formulated as a linear program. Karuppiah et al. (2008) and Martin and Grossmann (2011) showed a superstructure optimization model which incorporates heat integration inside the plant. The optimization problem is formulated as a mixed-integer nonlinear programming problem involving short-cut models for all the units in the system that consist of mass and energy balances, and design equations. Pham and El-Halwagi (2012) proposed a systematic two-stage approach to the synthesis and optimization of biorefinery configurations with the available feedstocks and desired products. A “forward-backward” approach is introduced for synthesizing possible pathways. An increased emphasis on efficient supply chain management and Net Present Value optimization has yielded substantial literature concerning supply chain modeling and strategic value optimization (Lainez et al., 2009; Naraharisetti et al., 2008; Puigjaner & Lainez, 2008). Ekşioğlu et al. (2009) developed a MILP model to design the supply chain and manage the logistics of a biorefinery. In their multi-period model, the supply chain problem is described as a network design problem to determine the optimal number, size, and location of biorefineries. Mansoornejad et al. (2010) suggested and exemplified a strategy for hierarchical product, process, and network design for biorefining systems. Giarola et al. (2011) developed a multi-objective optimization model by considering financial and environmental performances simultaneously to design optimal hybrid first and second generation biorefineries. The problem is formulated as a multi-period mixed-integer linear model. Mansoornejad et al. (2013), suggested metrics to analyze the flexibility and robustness of biorefining supply chains, which evaluate their performance against volatility.
Developing an optimal biorefinery plant depends on many factors including strategic and operational level decisions. Although various decision support models have been developed, in most of these studies, strategic, tactical and operational decision tasks are not considered together, even though there is significant interdependence between them. Furthermore, most of the considered optimization problems are linear models which do not take into account the inherently nonlinear mechanism of conversion processes. The complexity of these types of processes reveals the need for developing a comprehensive framework which can support a multitude of strategic, tactical, and operational tasks by integrating the nonlinearities involved in the process.

In this paper we present the development and implementation of a novel multi-layered decision support tool for the optimal design of new and emerging renewable energy production systems which can integrate the aforementioned aspects, i.e. strategic, tactical, and operational tasks. The methodology is developed using a hypothetical case study that involves a multi-product biorefinery producing bio-ethanol, bio-succinic acid, and bio-electricity from lignocellulosic energy crops. The proposed methodology is based on an iterative framework that utilizes systems-based strategic planning and optimization in conjunction with detailed mechanistic modelling, simulation and optimization of non-linear systems. The framework builds up on our previous work (Sharma et al., 2011; Sharma et al., 2013) where a techno-economic, strategic decision optimization framework is used to select an optimal technological platform, a feedstock portfolio, and a product portfolio for the conversion of lignocellulosic resources to biofuels and value-added biochemicals. Further, an optimized long term capacity plan for the resultant configuration was also developed. In this paper, the resulting large scale
linear programming (LP) model for strategic planning is integrated into bi-layered modeling and optimization framework for designing non-linear renewable energy systems.

2.2 Design of a decision support methodology for renewable energy systems

In order to create long term value, a renewable energy enterprise has to carefully design, scale up, and operate its processing plant(s). From a modelling perspective, strategic planning models are characterized by a few salient features including inherently long planning horizons and intrinsic relationships between process variables (such as processing capacity and production rates) and economic parameters such as sales, revenue, costs, and value. In order to mathematically optimize the long term value of a renewable energy enterprise, these complex relationships have to be represented accurately without impacting the model performance significantly. While process conversion mechanisms are inherently non-linear in nature, owing to complex kinetic and thermodynamic relationships, non-linear strategic optimization models can quickly become complex to solve with solution performance suffering as more nonlinearities are added to a model. Consequently, LP models are suggested in this paper for the purpose of strategic planning. To overcome the mismatch between nonlinear process mechanisms and LP-based strategic optimization, a decomposition strategy is proposed that combines net present value (NPV) optimization for long term planning with rigorous non-linear process modelling and process-level optimization. The proposed strategy has the advantage of not only being able to integrate long term planning based on financial optimization with nonlinear process mechanisms, but also optimize process operating conditions, using metaheuristic algorithms for non-linear optimization.
Figure 2.1 shows a general schematic structure of the proposed iterative decision support strategy. The proposed framework utilizes iterative process to obtain a piecewise linear approximation of the nonlinear reaction- and thermo-dynamics; the nonlinear dynamics are simulated and their linear approximations are used during strategic planning and optimization. The following steps are performed in sequence:

1. Strategic optimization: A linear programming (LP) model is proposed to optimize the project value of a renewable energy production system with decision tasks that can include feedstock selection, product portfolio design, technological superstructure design, supply chain design, and strategic capacity planning. At this stage, linear black box models can be utilized to represent the core technologies in a renewable process system in terms of process yields, raw material inputs, and energy loads for each technology; each one of these inputs can then be used
to generate material and energy balances (linear) for the system being studied. These mass and energy balances can be integrated with financial variables through the use of cost functions (for raw material inputs), revenues (for production rates), capital investments (for capacity design), and cash balances. Readers are referred to (Sharma et al., 2011; Sharma et al., 2013) for a detailed investigation of these linkages.

2. Process simulation: The optimized design from strategic planning can then be utilized to simulate the renewable process in detail using rigorous mechanistic models. Process simulations can be carried out in standard simulation software packages (like Aspen Plus), and can be used to represent complex non-linear processes at a plant level (operational versus strategic); additional linkages can also be made between simulation software and other mathematical packages (like Matlab) in order to completely specify a non-linear plant model.

3. Operational level optimization: In the next layer of this methodology, process operating conditions are optimized using metaheuristic algorithms implemented in mathematical software packages that can solve large scale, non-linear mathematical problems. These mathematical optimization models are integrated with process simulation; the optimal operating conditions along with the simulated process yields (nonlinear) are then fed back into the strategic decision optimization model for comparison of results. Process yields are calculated based on the amount of products obtained in each unit operation from simulation results. In fact, calculated process yields from simulation results incorporate the nonlinearities of process mechanisms in strategic model and overcome the mismatch between process mechanisms and strategic planning decisions. This process is carried out iteratively until the capacity plan (from 1st Layer) and the process yields (from 2nd Layer) remain unchanged through consecutive iterations.
2.3. Application case study: lignocellulosic biorefinery

In order to demonstrate the utility of the proposed framework, the aforementioned decision support system (DSS) is applied to a hypothetical biorefinery that utilizes lignocellulosic feedstock(s) to produce biobased fuels and chemicals. Readers should note that while we are utilizing a lignocellulosic process to demonstrate the DSS, the applicability of the framework transcends just biorefineries (other processes can include algae process design, solar and wind processes, and even oil and natural gas processing plants).

Lignocellulosic Biorefinery Description: The biofuels and biochemicals produced from renewable raw materials can replace fossil-based transportation fuels like gasoline and petrochemicals and work to reduce the net carbon that is released into the atmosphere through human consumption. The CO$_2$ released during biofuel and biochemical production and consumption is biogenic carbon (derived from plant material) which is initially sequestered from the atmosphere by photosynthetic processes occurring during plant growth; this closed carbon cycle implies that, unlike fossil-based fuels and chemicals, biobased fuels and chemicals have little impact on the carbon balance in the atmosphere (Naik et al., 2010). Various sources of biomass can be utilized to produce bioproducts: cellulosic wastes like tree thinning and yard waste, forest wood and residues, agriculture residues, and dedicated energy crops (Saxena et al., 2009). Based on production technologies, the bioproduct can be classified under one of two categories: 1) first-generation bioproducts derived from food crops and forest wood, and 2) Second-generation bioproducts derived from lignocellulosic waste materials, residues and energy crops. Some concerns exist about the production of first-generation bioproducts, like corn ethanol and soy-based biodiesel, due to the impact that it has in the land use for food crop production and decreasing the ratio of food-crop-to-land area, consequently putting an upward
pressure on food pricing. Lignocellulosic feedstocks, or feedstocks derived from agriculture, forest and municipal waste material (organic waste) can be utilized to produce second-generation bioproducts (Naik et al., 2010). These bioproducts have the advantage of being derived from waste materials that do not compete with the food value chains.

The lignocellulosic materials-based fuel and chemical conversion platforms can broadly be subdivided into 2 major pathways: (1) the biological conversion pathways based on fermentation, and (2) thermo-chemical conversion pathways based on heat-based technologies like gasification and pyrolysis. Each pathway has been shown to have great promise, but each suffers from separate issues that prevent their commercial scale up (Foust et al., 2009). Thermo-chemical pathways require a large investment of capital, energy optimization and heat integration of process operations, and efficient downstream clean up and conversion processes to convert gasification/pyrolysis effluents to biobased fuels and chemicals in a profitable manner. Biological conversion pathways suffer from issues including large capital requirements for plant establishment, and inability to replicate lab-scale process yields on a commercial scale, especially yields that involve biological technologies such as enzymes and micro-organisms.

Specifically, for the sugar-based fermentation conversion pathway, there are few known commercial plants, with most demonstration scale facilities suffering from inconsistent product yields. In addition to these technical challenges, a large number of sugar platforms are essentially single-product endeavours that produce low margin fuels like ethanol (Cardona & Sanchez, 2007; D. Humbird, 2011; Kim & Dale, 2004; Sun & Cheng, 2002); with low-margin products, slight changes in input costs, process yields, or markets (prices) can have a major impact on project profitability. We believe that a truly sustainable biorefinery of the future will require a
portfolio of products whose production rates can be varied to optimize plant margins based on
input costs and product markets.

The lignocellulosic biorefinery, used in this study to validate the proposed DSS framework, is a multiproduct plant that uses a fermentation-based sugar conversion platform, with 3 products: cellulosic ethanol, biosuccinic acid, and bioelectricity. Although, a number of possible feedstocks can be used to provide lignocellulosic material for conversion, our application assumes a sample feedstock whose chemical composition resembles that of switchgrass; its composition is presented in Table 2-2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucan</td>
<td>37.00</td>
</tr>
<tr>
<td>Xylan</td>
<td>22.80</td>
</tr>
<tr>
<td>Lignin</td>
<td>15.76</td>
</tr>
<tr>
<td>Ash</td>
<td>4.93</td>
</tr>
<tr>
<td>Protein</td>
<td>3.10</td>
</tr>
<tr>
<td>Arabinan</td>
<td>3.10</td>
</tr>
<tr>
<td>Galactan</td>
<td>1.43</td>
</tr>
<tr>
<td>Mannan</td>
<td>0.30</td>
</tr>
<tr>
<td>Extractives</td>
<td>9.00</td>
</tr>
<tr>
<td>Sucrose</td>
<td>0.77</td>
</tr>
<tr>
<td>Acetate</td>
<td>1.81</td>
</tr>
</tbody>
</table>

It is also assumed that there is limited land available within a 100 mile radius of the plant which can be used for the production of switchgrass for feedstock to the plant. The production chain comprises of 6 major systems: feedstock pretreatment, sugar hydrolysis, sugar fermentation, product purification, heat and power generation, and wastewater treatment. The systems superstructure is shown in Figure 2.2. In each stage of the process system, there may be different technologies that can be investigated for finding the optimal technological
superstructure. Pretreatment technologies break down the matrix of biomass polymeric compounds to facilitate the enzymatic hydrolysis of cellulose and solubilize the hemicellulose. Among potential technologies, the two most promising candidates for cellulosic biofuel pretreatment are dilute acid and ammonia fiber explosion (AFEX). There are multiple configurations of hydrolysis and fermentation that can be considered in technology selection for hydrolyzing and fermenting lignocellulosic materials, such as separate hydrolysis and co-fermentation (SHCF), and simultaneous saccharification and co-fermentation (SSCF). The products in the fermentation effluent need to be recovered and purified; the technologies for this will depend on the type of products that are being recovered and purified.

Figure 2.2: Block diagram for the multiproduct biorefinery plant

Due to the availability of detailed process and economic data, for our case study, we will select a fixed configuration composed of:

1. Dilute Acid Pretreatment
2. Separate Hydrolysis and Co-fermentation (SHCF)
3. Ethanol recovery using a configuration with distillation columns followed by molecular sieve purification
4. Succinic acid recovery using a configuration based on cell filtration followed by crystallization.

All operational and economic data for our case study is obtained from Kazi et al. (2010), D. Humbird (2011), Li et al. (2010) and Vlysidis et al. (2011).

2.4. Framework Details

In this section each component of the proposed framework (Figure 2.1) is described in some detail with the lignocellulosic biorefinery being featured in order to apply framework design components to a case study. While the description of the framework is based on the design of the case study presented in Section 3, each component, and the framework, can readily be adapted to other process value chains also.

2.4.1. Strategic Optimization

The strategic optimization model is derived from previously published journal paper (Sharma et al., 2013); salient components of the strategic optimization model are discussed here to give the readers a feel for the model structure and decision tasks.

2.4.1.1. Process Model: All major process systems described in Figure 2.2 are represented as linear black boxes in the planning model for the technology set (fixed) considered for framework demonstration (see section 2.3). The major equations that are approximated linearly in the planning models and modelled nonlinearly during simulation and optimization include unit operations’ yield and unit operations energy balances. These equations are provided in a condensed form below:
Here, \( RM \) is the raw material of type \( r \) required during time \( t \), \( RM_{r,j}^{reqd} \) is the raw material required per unit of input \( IN_{j,t} \), where \( j \) is a process unit operation. Additionally \( P_{p,t} \) is the annual production rate of product \( p \), \( YLD_{j,p} \) is the process reaction yield, \( BM_{j=1,t} \) is the feedstock input, \( E_{j,t}^{load} \) is the energy load of unit operation \( j \), \( E_{t}^{prod} \) is the total energy produced, \( F_{f,j,t} \) is the fuel output of each unit operation, \( LHV_{f,j} \) is the heating value of the fuel from \( j \), and \( \eta \) is the heat transfer efficiency. The per unit requirements \( (RM_{r,j}^{reqd}, YLD_{j,p}^{reqd}, E_{j}^{reqd}) \) are obtained iteratively from the process simulations. Readers are directed to Sharma et al. (2013) for a complete description of the strategic optimization model. For this case study, the set of raw materials, \( r \), includes:

1. Cellulosic feedstock (Switchgrass)
2. Sulfuric Acid
3. Water
4. Corn Steep Liquor (CSL)
5. Di-ammonium Phosphate (DAP)
6. Hydrolyzing enzymes (Cellulase and Hemicellulase)
7. Ammonia
8. Fermentation Microbes

\[
RM_{r,t} = \sum_{j} RM_{r,j}^{reqd} \times IN_{j,t} \tag{2.1}
\]

\[
P_{p,t} = \left( \prod_{j=1}^{n} YLD_{j,p} \right) \times BM_{j=1,t} \tag{2.2}
\]

\[
E_{j,t}^{load} = E_{j}^{reqd} \times IN_{j,t} \tag{2.3}
\]

\[
E_{t}^{prod} = \eta \times \sum_{f,j} F_{f,j,t} \times LHV_{f,j}, \quad E_{t}^{prod} \geq \sum_{j} E_{j,t}^{load} \tag{2.4}
\]
2.4.1.2. Capacity Design Model: Additionally, the strategic planning model is utilized in this demonstration for strategic capacity planning; the following equations are used to model capacity design for each unit operation in Figure 2.2.

\[ BVCI \times CAP^{UB} \geq CapExp \]  (2.5)

\[ BVCI \times CAP^{LB} \leq CapExp \]  (2.6)

\[ Cap_t = Cap_{t-1} + CapExp_{t-CD} \]  (2.7)

\[ Cap \geq SystemInput \]  (2.8)

\[ MinUtil \times Cap \leq SystemInput \]  (2.9)

The first two equations provide bounds to capacity expansion (CapExp), where BVCI is the capacity increment binary variable that is 1 when capacity is incremented and 0 otherwise. Equation 7 is used to update the processing capacity (Cap) of each operating system, adjusting for a construction delay (CD) of 2 years. Equation 8 provides a lower bound to total established capacity based on the respective input to the operating system (SystemInput), and Equation 9 imposes minimum equipment utilization bound (MinUtil) on the established capacity. The capacity plan is then passed on to the process simulator (Aspen Plus) and the process optimizer (Matlab) in order to determine optimal operating conditions.

2.4.1.3. Financial Model: The financial model is broken into 5 salient aspects that describe the financial impact of resource procurement, technology selection, network design, production of final products, and sales:

1. Capital costs (CAPEX);
2. Financing costs of CAPEX;
3. Operating expenses and revenues;
4. Calculation of income and cash flow statement line items;
5. Calculation (optimization) of the objective function (Net Present Value)

The methodology for deriving the capital cost structure was adapted from Kazi et al. (2010) that exemplified NREL’s nth plant cost analysis. The capital expenses are broken up into six components:

1. Land acquisition charges for facility establishment
2. Equipment costs for processing,
3. Construction and Engineering costs,
4. Legal and permitting costs,
5. Contingency fund,

The operating costs for the value chain were broken into 7 parts that utilize system outputs from each node in the value chain to calculate the total cost of operation:

1. Feedstock costs including establishment, opportunity, harvesting and logistics costs
2. Water purchase and treatment costs
3. Process chemical costs for pretreatment
4. Enzyme, nutrient, and micro-organism costs for fermentation
5. Operating charges for steam and power plant operation
6. Labor costs for the entire processing facility
7. Selling, general and administrative costs for product distribution
Following the calculation of these costs, the income statement of a general enterprise was stated in equation form to calculate line items such as gross profit, earnings before interest taxes and depreciation (EBITDA), earnings before interest and taxes (EBIT), earnings before taxes (EBT), taxes, operating profit after taxes (NOPAT), and net income (NI). Additionally, the cash flow statement of an enterprise was derived (in equation form) using the outputs of the income statement along with capital investment charges. The financial model was designed to assess the impact of project operation on the enterprise’s capital structure; specifically, the cash balance of the enterprise was assumed to be composed of operating (CFO), financing (CFF), and investment cash flow (CFI). The capital structure of the enterprise was represented as the debt and equity capital that can be raised in order to fund current operations and further network capacity growth. The objective function (Net Present Value, NPV) was calculated as the sum of the discounted values (20 years) of the difference between CFO and CFI. Readers are referred to Sharma et al. (2013) for a complete description and statement of the financial model and its equations, respectively.

2.4.2. Process Simulation

Aspen Plus was utilized to simulate the multiproduct biorefinery with the optimal capacity plan obtained from strategic optimization. Additional process data for pretreatment, hydrolysis and ethanol fermentation and purification are based on the NREL reports Kazi et al. (2010) and D. Humbird (2011), and for succinic acid fermentation and purification the data are obtained from Li et al. (2010) and Vlysidis et al. (2011). To better estimate the nonlinear reaction dynamics of enzymatic hydrolysis and fermentation, experimentally-derived kinetic models are utilized to simulate the reactions in enzymatic hydrolysis, ethanol fermentation and succinic acid fermentation. Each kinetic model is briefly explained below:
2.4.2.1. Enzymatic Hydrolysis: A multi-reaction kinetic model (Kadam et al., 2004) is implemented to describe the enzymatic hydrolysis of switchgrass. The mathematical representation of the kinetics is presented in Appendix A, Table A.1. This model includes reactions for:

1. Substrate reactivity (Equation A.1) which considers the reduction in the rate of hydrolysis as saccharification progresses because of the change in crystalline structure of cellulose or substrate accessibility.

2. Decomposition of cellulose to cellobiose (Equation A.2) and glucose (Equation A.3) which happen on the surface of cellulose.

3. Cellobiose hydrolysis to glucose (Equation A.4) which occurs in the solution and is a homogenous reaction which follows Michaelis-Menton kinetics.

4. Enzyme adsorption (Equation A.5) which follows the Langmuir type isotherms

5. Temperature effects on hydrolysis (Equation A.6) based on Arrhenius model which is valid in a limited range of temperature where the enzyme is active.

Cellulose is hydrolysed to glucose and cellobiose by utilizing the combination of endo-β-1, 4-glucanase (EG), exo-β-1, 4-cellobiohydrolase (CBH), and cellobiose is hydrolysed to glucose by the action of β-glucosidase. Langmuir isotherms are used to explain the adsorption of cellulose enzyme and the model distinguishes between the CBH/EG and β-glucosidase enzymes. Sugar inhibitions considered in this model assumes that the hydrolysed sugars can bind to the active site of the substrate and decrease the formation rate of enzyme-substrate complex which is a competitive mode of inhibition.

2.4.2.2. Ethanol Fermentation: The kinetic model implemented in this study for ethanol production (via sugar fermentation) is based on the two-substrate developed model of
Leksawasdi et al. (2001), by consuming a recombinant bacteria *Z.mobilis ZM4* (pZB5), which is capable of fermenting glucose and xylose simultaneously (co-fermentation). The mathematical representation of the fermentation kinetics is presented in Appendix A, Table A.2. The model is based on the following reactions:

1. Cell growth on glucose (Equation A.7) and xylose (Equation A.8) which incorporates the Monod kinetic model for substrate limitation and product inhibition.

2. Glucose and xylose consumption (Equation A.10 and Equation A.11) which are considered in separate equations by incorporating the inhibition effects.

3. Ethanol production (Equation A.14) which incorporates the production from glucose (Equation A.12) and xylose (Equation A.13) by considering the weighting factor ($\alpha$).

Due to simultaneous cell growth on both of the substrates (glucose and xylose), there is competition to contribute (via cell growth) to produce ethanol. The weighting factor ($\alpha$) represents the relative consumption rates of the two sugars (Equation A.9 and Equation A.14). The best value for the weighting factor ($\alpha$) was determined to be $\alpha = 0.65$ (Leksawasdi et al., 2001).

2.4.2.3. Succinic Acid Fermentation: A kinetic model developed by Song et al. (2008) which models the conversion of glucose to succinic acid using *M.succiniciproducens* MBEL55E is implemented in this study. While the main product of this model is succinic acid, the other acids such as acetic, formic and lactic acids are also produced as by-products of the fermentation process. The mathematical representation of the fermentation kinetics for succinic acid is presented in Appendix A, Table A.3. The model is based on the following reactions:
1. Cell growth on glucose (Equation A.15) which is based on a modified Monod equation model that incorporates excess substrate inhibition on the growth of bacteria. Product concentration and critical product concentrations are sum of the amount of succinic and other acids produced in the process (Equation A.22).

2. Cell death model (Equation A.16); which is based on the equation suggested by Levenspiel (1980) to model the cell death caused by produced organic acids accumulated during fermentation in the culture broth and cause cell death after reaching a predetermined concentration of the total acid ($P_{\text{crit,g}}$).

3. Organic acid formation (Equations A.17 to A.20) which are based on the Luedeking and Piret (1959) model by incorporating growth-associated and non-growth-associated formation of acids.

4. Glucose consumption (Equation A.21) based on the carbon mass balance in the fermentation process.

The proposed model considers the conversion of glucose to organic acids; additionally we assume that 10% of xylose is also converted to succinic acid based on the following chemical reaction:

$$3 \text{ Xylose} + 5 \, \text{CO}_2 \rightarrow 5 \, \text{Succinic Acid} + 2.5 \, \text{O}_2$$

2.4.3. Process Optimization

The simulated process (Aspen Plus) with optimized capacity plan from strategic planning is linked to a metaheuristic optimization model that is implemented in Matlab to optimize the process operating conditions. A simplified version of the financial model presented in section
2.4.1 is used to design the objective function that is optimized here. The objective function used for optimization is the annual cash flow, CF, which takes into account the revenue generated from the sale of products, \( P_p \), (where \( p \) represents the type of product produced including ethanol, succinic acid, and excess electricity), the direct costs of raw materials, \( RM_{r,p} \), (where \( r \) represents the type of raw materials including feedstock, enzymes, nutrients, chemicals, make-up water), and the labour, maintenance and transportation costs (annual fixed costs, FC). Additionally, tax credits (\( Tax^{\text{credits}} \)) and liabilities (\( Tax^{\text{Liability}} \)) are also modelled to yield the after tax cash flow, Equation 2.14 (objective function). The costing data are obtained from Kazi et al. (2010), Vlysidis et al. (2011) and Laser et al. (2009). Ethanol price is assumed to be $2 per gallon, succinic acid price is assumed to be $6000 per ton and electricity prices are set at $0.05 per kilowatt-hour. Production capacities obtained from strategic planning are incorporated during process optimization as constraints (Equation 2.15) to control the switchgrass throughput and production rates. The following equations represent the objective function calculations.

\[
CF^{\text{Before Tax}} = \sum_p P_p \times Price_p - \sum_{r,p} RM_{r,p} \times Cost_r - FC \tag{2.10}
\]

\[
Tax^{\text{Liability}} = CF^{\text{Before Tax}} \times tax^{\text{rate}} \tag{2.11}
\]

\[
Tax^{\text{credits}} = \sum_p P_p \times Credit_p \tag{2.12}
\]

\[
Tax^{\text{net}} = \max(0, Tax^{\text{Liability}} - Tax^{\text{credits}}) \tag{2.13}
\]

\[
CF^{\text{After Tax}} = CF^{\text{Before Tax}} - Tax^{\text{net}} \tag{2.14}
\]

\[
P_p^{\text{simulation}} \leq P_p^{\text{strategic optimization}} \tag{2.15}
\]

For solving optimization problems deterministically, analytical properties of the problem such as convexity of the objective function should be utilized to generate a deterministic
sequence of points in the search space. Additionally, in many real-world problems such as biorefinery processes, complex mass and energy constraints are involved in the optimization problem. To solve these large scale nonlinear problems deterministically, constraint equations should be incorporated into the objective function (Lagrangian relaxation). However, in our study, the process simulator (Aspen Plus) is utilized to model the biorefinery. All the mass and energy balances are embedded in the simulation and constraints are satisfied when simulation is converged. Furthermore, since the process model is comprised of non-convex functions, many deterministic optimization methods will fail to find global optima. To overcome these problems, metaheuristic approaches are implemented for process optimization as they do not require manipulation of the mathematical structure of the objective function and the constraints (Mariano et al., 2011). In fact, the optimizer treats the process simulations in Aspen Plus as a black box. The optimized decision variable values from Matlab are sent to Aspen Plus where the process is simulated for these values. The simulated results are then passed back to the optimizer to re-solve the objective function. Two alternative metaheuristic algorithms were implemented and tested for efficiency in the optimization of the selected biorefining process: 1) Differential Evolution, and 2) Simulated Annealing. These algorithms are discussed in detail in the next 2 sections.

2.4.3.1. Differential Evolution Algorithm: Differential evolution method (DE) was first proposed by Storn and Price (1997); this method is a parallel direct search method and is often considered as an evolution based method. The initial population of n vectors, which are the decision variables, is randomly selected and covers the entire parameter space. Each vector serves as the target vector alternatively. For each vector in generation $G$, $x^G$, DE generates a new parameter vector, $x^{G+1}$, by adding the randomly selected vector, $x^G_{r1}$, to the weighted difference
between two other randomly chosen vectors (Equation 2.16), \( x_{r2}^G, x_{r3}^G \), (mutation operation). The mutated vector’s parameters are then mixed with the parameters of another predetermined vector, to yield the trial vector (Equation 2.17, \( u^{G+1} \)); this operation is called the **crossover operation**. If the trial vector yields a higher objective function than the target vector, the trial vector replaces the target vector; this is called the **selection operation**. The vector population is updated in each iteration according to the target vectors. This iterative process is carried out until the convergence criteria are satisfied. In this study, the DE algorithm is terminated when (1) there is no significant improvement in the best value of the objective function after a predetermined number of iterations is reached, or (2) the maximum number of function evaluations, \( nfe \), is reached. A flow chart of the utilized DE algorithm is presented in Figure 2.3.

\[
\nu^{G+1} = x_{r1}^G + F \cdot (x_{r2}^G - x_{r3}^G) \tag{2.16}
\]

\[
\begin{align*}
\nu^{G+1} & = \nu^{G+1} & \text{if } \text{rand} (i) \leq CR \\
\nu^{G} & = \nu^{G} & \text{if } \text{rand} (i) > CR
\end{align*}
\]

2.4.3.2. Simulated Annealing Algorithm: General Simulated Annealing is a stochastic local search algorithm initially proposed by Kirkpatrick et al. (1983). The key feature of simulated annealing is its ability to escape local optima by allowing hill-climbing moves that worsen the objective function value in hopes of finding global optima. This optimization algorithm is based on Metropolis acceptance criteria, which governs how a thermodynamic system moves from its current state to a new state where its internal energy content is being minimized.
The candidate solution ($Y$) is accepted based on the acceptance probability (Equation 2.18). In this equation $T_k$ is the temperature at iteration $k$ (outer loop). Based on this equation, a worse solution, in maximization problem, might be accepted with some probability, as a hill climbing move in order to escape a local maximum. The $T_k$ value is determined by a cooling schedule; in this study we utilized a geometric law to describe the temperature reduction (Equation 19); as $T_k$ decreases the probability to accept a worse solution also decreases.
$P(\text{accept } Y \text{ as next solution}) = \begin{cases} 
\exp \left[ -\frac{f(Y) - f(X)}{T_k} \right] & \text{if } f(Y) - f(X) < 0 \\
1 & \text{else}
\end{cases} \quad (2.18)$

$T_{k+1} = \alpha T_k \quad (2.19)$

A flow chart of the utilized simulated annealing algorithm is presented in Figure 2.4.

![Flow Chart](image-url)

Figure 2.4: Flow chart for simulated Annealing algorithm

Simulated annealing starts with an initial solution vector, $X$, that is randomly generated in the solution space and evaluated to find the objective function ($f(X)$) value. A neighbouring solution is then generated ($Y$) as a new candidate, by choosing a random point in the search that defines the random direction and the step size, $\Delta r$. We used an adaptive step size change which implies that as the number of iterations increase in inner loop, the new selected candidate’s deviation from the previous point decreases. This iterative process is carried out until the
convergence criteria are satisfied. In this study the SA algorithm is terminated when (1) there is no significant improvement in the best found solution after a predetermined number of iterations, or (2) the calculated temperature in the outer loop reaches the predetermined \( T_{\text{min}} \).

2.4.3.3. Penalty Function: For both of these algorithms the inequality constraints, which are the production capacities that obtained from strategic planning, are handled by utilizing the penalty function method. In this approach for handling inequality constraints, the modified objective function \( F(\bar{x}) \) is defined as sum of original objective function \( f(\bar{x}) \) and a penalty term \( g_j(\bar{x}) \) which depends on the constraint violation.

\[
F(\bar{x}) = f(\bar{x}) + \sum_{j=1}^{J} R_j(g_j(\bar{x}))
\] (2.20)

The parameter \( R_j \) is the penalty parameter of the jth inequality constraint to make the constraint of the same order of magnitude as the original objective function value.

2.5. Results and Discussion

To demonstrate the proposed methodology, the assumed process technology superstructure (Dilute Acid-SHCF-Distillation-Sieves-Crystallization) is used for strategic design of processing and product recovery capacities (Results provided later). During strategic planning, data utilized for process yields and costing parameters for each technology is based on National Renewable Energy Laboratory reports and literature data (D. Humbird, 2011; Kazi et al., 2010; Li et al., 2010; Vlysidis et al., 2011).

Dilute acid pretreatment breaks down the cellulose structure of biomass and converts the xylose polymer to xylose sugar. Enzymatic hydrolysis then converts cellulose to glucose by
utilizing cellulase enzyme which is a mixture of enzymes that work together to break down complex cellulosic polymers to simpler sugars like glucose. The sugars produced from hydrolysis and pretreatment are then fermented to ethanol and succinic acid. We utilized a process configuration where hydrolysis and fermentation are carried out in separate tanks; when hydrolysis and fermentation occur separately, the sugar stream sent to enzymatic hydrolysis reaction can be at an elevated temperature allowing for faster and more efficient conversion of cellulose (due to higher activity of enzymes at higher temperatures). Ethanol production occurs by simultaneous fermentation of two sugars, glucose and xylose. The microorganism proposed by Leksawasdi et al. (2001), recombinant Z. mobilis, is capable of fermenting both of the sugars to produce ethanol. Additionally, M. succiniciproducens, an organism which utilizes glucose to produce succinic acid is assumed to be added to fermentation reactor to produce succinic acid. In this study, we additionally assume that 10% of xylose is also converted to succinic acid. A beer column followed by a rectification column is designed to purify ethanol up to its azeotropic boiling point, followed by sieve-based purification to reach fuel grade purity (99.5% by mass). For succinic acid purification, a one-step crystallization recovery model, developed by Li et al. (2010), which is based on the variation of succinic acid solubility at different PHs, is selected.

The entire process is simulated in Aspen Plus for the capacities that are designed during strategic optimization. The process conditions for dilute acid pretreatment, and ethanol purification are based on the process design data obtained from National Renewable Energy Laboratory (NREL) report (D. Humbird, 2011). For simulating enzymatic hydrolysis, and ethanol- and succinic acid fermentation, kinetic models described in section 4.2 are implemented in Matlab and linked with Aspen Plus to obtain precise conversions of each reaction by solving a system of differential equations in Matlab.
For succinic acid purification, cellular debris is separated from the fermentation effluent by centrifugation, which is followed by an evaporator that vaporizes most of the water and organic acids that have lower boiling points than succinic acid. The concentrated stream obtained from bottom of the evaporator is sent to a crystallizer that separates succinic acid from other organic acids and trace water based on differential solubilities. While formic, acetic and lactic acids are water-miscible at pH from 1-14 at temperatures above 0°C, succinic acid solubility decreases sharply when the temperature decreases (Li et al., 2010). Therefore, succinic acid can be selectively separated from other acids using solubility-driven crystallization. Pure succinic acid crystals are obtained via another centrifugation operation, and finally a dryer is used to reduce the moisture in the crystals to purify it to acceptable end use purity (> 90% by mass).

Process integration suggested by Zeikus et al. (1999) and Nghiem et al. (2010) is utilized in this work to capture the carbon dioxide produced during ethanol fermentation and use it in succinic acid fermentation (as a carbon source). We assumed that CO\textsubscript{2} produced from ethanol fermentation has a high purity and is siphoned from the ethanol fermentation tank to succinic acid fermentation tank. This can have a 2-fold benefit on plant economics and emissions – (1) it reduces the carbon footprint of the biorefinery as it permanently sequesters ethanol-derived CO\textsubscript{2} into succinic acid molecules, and also (2) it reduces the amount of carbon dioxide that is required as a purchased input for succinic acid production. The process flowsheet for succinic acid production is shown in Figure 2.5.
During process optimization, the following operating variables are manipulated in order to optimize annual operating cash flows for the biorefinery: (1) temperature in enzymatic hydrolysis, (2) sugar allocation (from hydrolysis) between ethanol and succinic acid fermentation, and (3) enzyme (cellulase) loading during hydrolysis.

Enzyme activity is correlated with reaction temperature, through the Arrhenius model (Equation A.6); temperature plays an important role in increasing or decreasing the rate of enzymatic reactions, and thus impacts the overall cellulose (to glucose) conversion yield. Decreasing reaction temperature below a certain threshold can also result in a dramatically reduced rate of reaction, while increasing it above a threshold can result in protein denaturation; consequently the search space for optimal temperature determination is limited between a range (D. Humbird, 2011). In this study we assumed that the acceptable range for temperature (T) is between 40°C and 50°C. The hydrolyzed sugar stream, mainly glucose and xylose, is split 2
before fermentation; one stream is sent to ethanol fermentation reactors while the other is used for succinic acid fermentation. These allocated sugar streams impact the fermentation reaction kinetics and consequently the product yields in the fermentation effluent. The manipulated decision variable during optimization is the fraction of total sugar that is used for ethanol fermentation (X). The amount of enzyme used in hydrolysis is determined by a ratio based on the amount of cellulose present in the sugar stream to hydrolysis reactor and the specific activity of the enzyme. Based on the kinetic models implemented in Matlab for hydrolysis and fermentation, sugar yield and ethanol production generally increase with higher enzyme loading (Figs. 2.6a and 2.6b). However, additional enzyme increases direct costs and furthermore, as shown in Figure 2.6c, there is an optimal enzyme loading rate for succinic acid production beyond which product yield decreases with increasing enzyme concentration. The initial glucose concentration in succinic acid fermentation depends on the amount of sugar allocated to its production and also the amount of sugar that is produced during hydrolysis; therefore, enzyme loading, sugar allocation and temperature have a complex set of impacts on process yields and consequently, on process economics.

The lower bound and upper bound of the optimization variables are set as shown in Table 2-3.

<table>
<thead>
<tr>
<th>Optimization Variable</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis Temperature (°C)</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Sugar allocation ratio (sugar to ethanol)</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Enzyme load (g enzyme/ kg Cellulose)</td>
<td>5</td>
<td>50</td>
</tr>
</tbody>
</table>

As described before, simulated annealing (SA) and differential evolution (DE) optimization algorithms are implemented separately in Matlab and linked to the simulations in Aspen Plus.
Figure 2.6: a) Glucose concentration in hydolysate for different enzyme ratios b) Ethanol concentration in fermentation broth for different enzyme ratios c) Succinic acid concentration in fermentation
The parameter settings for DE and SA are shown in Table 2-4.

Table 2-4: Differential evolution and simulated annealing parameters

<table>
<thead>
<tr>
<th>Parameters/operators</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Simulated annealing</strong></td>
<td></td>
</tr>
<tr>
<td>Iteration per temperature</td>
<td>40</td>
</tr>
<tr>
<td>$T_{max}$</td>
<td>400</td>
</tr>
<tr>
<td>$T_{min}$</td>
<td>0.01($T_{max}$)</td>
</tr>
<tr>
<td>Cooling rate ($\alpha$)</td>
<td>0.8</td>
</tr>
<tr>
<td>Initial step size</td>
<td>0.3($upper\ bound - lower\ bound$)</td>
</tr>
<tr>
<td>Penalty coefficient ($R_j$)</td>
<td>100000</td>
</tr>
<tr>
<td><strong>Differential evolution</strong></td>
<td></td>
</tr>
<tr>
<td>Maximum number of function evaluation</td>
<td>500 (MAXNFE)</td>
</tr>
<tr>
<td>Population size (NP)</td>
<td>30</td>
</tr>
<tr>
<td>Weighing coefficient (F)</td>
<td>0.5</td>
</tr>
<tr>
<td>Crossover rate (CR)</td>
<td>0.95</td>
</tr>
<tr>
<td>Penalty coefficient ($R_j$)</td>
<td>100000</td>
</tr>
</tbody>
</table>

The average number of function evaluations required to find the optimal values for decision variables are 200 (DE algorithm) and 300 times (SA algorithm). In our case, DE algorithm is also able to find a better objective function value (average). The comparison between the results is shown in Table 2-5. These results show that DE has better performance characteristics compared to the SA algorithm for this specific application. Therefore, DE is chosen to implement the iterative optimization framework (Figure 2.1). The convergence behavior of the DE algorithm is plotted in Figure 2.7. It can be seen that the convergence is steady and stable. The iteration results are presented in Table 2-6.
Table 2-5: Optimal values for decision variables and objective function

<table>
<thead>
<tr>
<th></th>
<th>DE</th>
<th>SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>44.00 °C</td>
<td>47.00 °C</td>
</tr>
<tr>
<td>Sugar allocation</td>
<td>0.40 (ethanol), 0.60 (succinic acid)</td>
<td>0.40 (ethanol), 0.60 (succinic acid)</td>
</tr>
<tr>
<td>Enzyme loading ratio</td>
<td>20 (g enzyme/ Kg Cellulose)</td>
<td>24 (g enzyme/ Kg Cellulose)</td>
</tr>
<tr>
<td>Cash flow</td>
<td>$70 million per year</td>
<td>$69 million per year</td>
</tr>
</tbody>
</table>

Table 2-6 shows that during the first iteration, yield data obtained from literature (step 1) is utilized for strategic capacity planning (LP). The optimal plant capacities (step 2) are passed to the process simulation and optimization steps in order to find the optimal operating conditions by using non-linear optimization technique.

Figure 2.7: Convergence history for DE algorithm
Table 2-6: Iteration results in optimization strategy

<table>
<thead>
<tr>
<th>Parameters and Variables</th>
<th>Iteration1</th>
<th>Iteration2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Step 1</td>
<td>Step 2</td>
</tr>
<tr>
<td><strong>Capacity Constraints</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feedstock (1000 ton/yr)</td>
<td>--</td>
<td>333.3</td>
</tr>
<tr>
<td>Ethanol (MM gal/yr)</td>
<td>--</td>
<td>11.082</td>
</tr>
<tr>
<td>Succinic Acid (1000 ton/yr)</td>
<td>--</td>
<td>15.6</td>
</tr>
<tr>
<td><strong>Process Variables</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugar Allocation</td>
<td>--</td>
<td>0.52</td>
</tr>
<tr>
<td><strong>Yield Parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugar (kg/kg)</td>
<td>0.87</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Fermentation</td>
<td>0.85</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Fermentation</td>
<td>0.25</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Purification</td>
<td>0.99</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Purification</td>
<td>0.78</td>
<td>--</td>
</tr>
</tbody>
</table>

Yields calculated from the results of optimal simulation are passed to strategic model (step 3). To check the convergence, these yields are compared with the ones used in step 1-iteration 1. As the difference between the values is greater than the threshold, the strategic optimization solves the LP model again, based on new yield values (step 1–iteration 2). The new capacity plan is again sent to process simulation and optimization module to find the optimal operating conditions and calculate process yields accordingly (step2-iteration2). Major changes from the literature derived yield values (Step 1, Iteration 1) are noticed in Table 2-6, as non-linear kinetic models are utilized as opposed to linear yield equations, in order to estimate the dynamics of the reactions (Step 3-Iteration 1, Step 2-Iteration 2). This demonstrates the utility of the proposed methodology to reconcile nonlinear process models with LP-based economic optimization (strategic planning). While feedstock capacities remain the same throughout the
framework demo, the optimal product recovery capacities are reduced successively as the actual process yields (obtained from our ASPEN simulations) are shown to be much lower than assumed (linear) conversion yields in literature (also utilized during initial strategic optimization). Figure 2.8 presents the optimal process configuration and the main process specifications.

Figure 2.8: Optimal process configuration

This Figure shows that the main sections requiring energy are the fractionation and recovery; during co-generation, by burning combustible by-products from the biorefinery, such as lignin and biogas, the steam and electricity demand for the plant is supplied internally. Furthermore, additional revenues are generated by selling excess electricity as a by-product. Figure 2.9 shows the final simulated concentration profiles of the reactants and products in enzymatic hydrolysis and ethanol and succinic acid fermentations obtained by solving the system
of differential equations for the kinetic models implemented in Matlab. Final configuration of the proposed framework for the biorefinery process is shown in Table 2-7 which represents the optimized variables in strategic planning and process modeling and optimization sections and final yields calculated for each section of the plant accordingly.

Figure 2.9: Concentration profiles: a) glucose(solid line), cellulose( dashed line) in enzymatic hydrolysis, b) glucose(solid line), xylose( dotted line), ethanol(dashed line) in ethanol fermentation c) glucose( dashed line) , succinic acid(solid line) in succini
Table 2-7: Optimal Framework results

<table>
<thead>
<tr>
<th>Variable</th>
<th>Optimal Value</th>
<th>Framework section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock Capacity (100 ton/yr)</td>
<td>333.3</td>
<td>Strategic planning</td>
</tr>
<tr>
<td>Ethanol production Capacity ( MM gal/yr)</td>
<td>10.00</td>
<td>Strategic planning</td>
</tr>
<tr>
<td>Succinic acid production Capacity ( 100 ton/yr)</td>
<td>13.30</td>
<td>Strategic planning</td>
</tr>
<tr>
<td>Net present value ( $ MM/yr)</td>
<td>68.00</td>
<td>Strategic planning</td>
</tr>
<tr>
<td>Sugar yield ( kg/ kg)</td>
<td>0.81</td>
<td>Process simulation</td>
</tr>
<tr>
<td>Ethanol Fermentation yield (kg/ kg)</td>
<td>0.71</td>
<td>Process simulation</td>
</tr>
<tr>
<td>Succinic Acid Fermentation yield (kg/kg)</td>
<td>0.15</td>
<td>Process simulation</td>
</tr>
<tr>
<td>Ethanol Purification yield (kg/ kg)</td>
<td>0.98</td>
<td>Process simulation</td>
</tr>
<tr>
<td>Succinic Acid Purification yield (kg/kg)</td>
<td>0.78</td>
<td>Process simulation</td>
</tr>
<tr>
<td>Hydrolysis Temperature ( °C )</td>
<td>44.00</td>
<td>Process optimization</td>
</tr>
<tr>
<td>Enzyme loading (g enzyme/ Kg Cellulose)</td>
<td>20.00</td>
<td>Process optimization</td>
</tr>
<tr>
<td>Sugar allocation ratio ( sugar to ethanol )</td>
<td>0.40</td>
<td>Process optimization</td>
</tr>
<tr>
<td>Cash flow after tax ( $ MM/yr)</td>
<td>70</td>
<td>Process optimization</td>
</tr>
</tbody>
</table>

2.6. Conclusion

We developed a framework to optimally design renewable energy production systems that are governed by nonlinear process dynamics. The framework focuses on integrating strategic planning tasks with operational tasks such as plant operations and the optimization of process conditions. Our methodology focuses on integrating simulation and optimization of nonlinear processes with LP-based optimization of strategic planning decisions. The framework takes a distributed modeling approach, wherein, strategic planning decisions are optimized separately from process optimization, and the nonlinear process dynamics (during strategic planning) are represented using an iterative algorithm. Standard simulation and mathematical software packages are utilized to represent nonlinear processes and optimize their operating conditions; the optimized results are passed back and forth between the LP and the nonlinear simulation/optimization until optimal results do not change through consecutive iterations.

The strategic planning LP focuses on optimizing the long term value (NPV) of a renewable energy enterprise by manipulating decisions such as technology selection, feedstock and product portfolio design, strategic capacity planning, and supply chain design. In this paper,
we presented a detailed development of the operational simulation and optimization component of the framework. We utilized a hypothetical case study of a lignocellulosic biorefinery that produces bioethanol, bio-succinic acid, and bioelectricity from switchgrass. For the sake of demonstration, the technology superstructure for the biorefinery was assumed to be fixed and the LP was used to optimize strategic capacity plans for the plant. Further, the operational modeling and optimization of the plant utilized Aspen Plus for nonlinear simulations and Matlab for nonlinear process optimization. Kinetic process models were implemented in Matlab to impart greater fidelity to the simulation in Aspen Plus. Metaheuristic optimization algorithms were employed in order to optimize process conditions including temperature (hydrolysis), raw material loading (enzymes for hydrolysis), and flow rates (sugar allocation). The final results included an optimal capacity plan for the biorefinery, the optimal NPV, and the optimal operating conditions for the hydrolysis reactor. The framework shows a deviation in process yields, and a deviation in the production capacities and operating conditions, from initial literature estimates. This is attributed to the framework’s use of nonlinear modeling and optimization strategies, which served to impart a greater degree of realism to the representation of the actual biorefining process.

Future work will include incorporating more nonlinear process variables within the proposed framework, incorporating uncertainty analysis in the framework by analyzing different scenarios based on changes in the market condition, strategically designing the supply chain and technology superstructures, modeling environmental and social characteristics of a system during design, and applying the methodology to different renewable energy systems.
2.7. References


3. Technology Analysis of Integrated Biorefineries through Process Simulation and Hybrid Optimization

3.1. Introduction

As the world has recognized the importance of diversifying its energy resource portfolio away from fossil resources and more towards renewable resources such as biomass, there arises a need for developing strategies which can design renewable sustainable value chains that can be scaled up efficiently and provide tangible net environmental benefits from energy utilization (Grossmann & Guillén-Gosálbez, 2010; Iniyan & Sumathy, 2000; Henrik Lund, 2007; H. Lund & Mathiesen, 2009; Ostergaard, 2009). Biobased fuels and chemicals can be derived from any form of biomass such as plants or organic wastes. After a boom in the U.S. corn-based ethanol (first-generation biofuel) in the early part of the 21st century (Somma et al., 2010), the interest has gradually shifted towards more viable renewable resources such as lignocellulosic feedstocks since the viability and sustainability of first generation biofuels are uncertain and questionable (Naik et al., 2010; Rathmann et al., 2010). Negative impacts of first generation biofuels might lead to the risk of deforestation by overuse of lands, environmental risks by the widespread use of fertilizers and pesticides, and decreasing food security by the risk of creating a competition between food and fuel production.

Cellulosic ethanol is an example of such alternative fuel which is considered as a second-generation biofuel and is derived from cellulose instead of starch. The fuels and chemicals produced from lignocellulosic feedstocks are extremely attractive owing to the fact that the raw materials can be composed of “left-over” wastes of food crops and forest harvests that do not interfere with the human food chain.

1 Reprinted by permission of Energy (See Appendix C)
It also can provide new income and employment opportunities in rural areas. Further, due to the large variety of lignocellulosic materials and their abundance, these types of produced fuels and chemicals (second-generation) can overcome the challenge of limited feedstock availability that first generation biorefineries have to contend with.

There are two main conversion platforms in a biorefinery process: (1) the biological conversion pathways based on fermentation, and (2) thermo-chemical conversion pathways based on heat-based technologies such as gasification and pyrolysis. The main difference between these two conversion mechanisms is the primary catalysis system (Foust et al., 2009). In biological conversion pathways, biocatalysts such as enzymes and microorganisms are utilized. However, in thermochemical production routes, heat and physical catalysts are utilized to convert biomass to biofuels and chemicals.

By considering the fact that conversion technologies in second generation biorefineries are relatively immature and recalcitrance of lignocellulosic materials can cause major barriers to the economical production of biofuels (Cardona & Sanchez, 2007; Kim & Kim, 2013), process synthesis by analysing alternative technology options, considering possible process integrations, and developing mathematical optimization methodologies can be useful for designing more cost-effective configurations with improved techno-economic and environmental characteristics. Many frameworks have been proposed for designing technological flowsheets with improved performance. Some research studies focused on analysing the performance of alternative technology options for a section of biorefinery plant (Öhgren et al., 2007; Vane, 2008; Wyman et al., 2005). These studies provide a good insight for the performance and optimal operating conditions of that particular section. However, conversion of biomass to biofuels and biochemicals is a complex process which includes different processing steps; for example in
biochemical route, pretreatment, hydrolysis, fermentation and purification are required to produce fuels and chemicals from biomass; there are many tradeoffs in the commercial scale design of these sections owing to their interdependency, which are often overlooked when each section is analysed independently.

Additionally, several research studies considered single-product endeavours that produce low margin fuels like ethanol (Cardonaalzate & Sanchetoro, 2006; Humbird et al., 2011; Martín & Grossmann, 2012; Quintero et al., 2008; R. Wooley et al., 1999); with low-margin products, slight changes in input costs, process yields, or markets (prices) can have a major impact on project profitability. With this in mind, it is important to analyse a mix of high and low margin products and optimize the production volume of them to maximize the long term value of a biorefinery.

Finally, several approaches have been developed for selecting optimal feedstocks, technological superstructures and product portfolios in the biorefinery process (Bao et al., 2011; Mansoornejad et al., 2010; Martín & Grossmann, 2012; Sammons et al., 2007; Zondervan et al., 2011). Most of these studies have focused on using single values for process parameters (including reaction conversion rates) that may or may not be true in real operations of the plant. Further, most of these studies considered linear methods or shortcut equations for modeling the integrated biorefinery process to allow for large model development with relatively short computational times. However, conversion mechanisms in biorefinery processes are inherently non-linear in nature.

In this study, we incorporate solutions for the aforementioned shortcomings in order to develop a more robust framework that can mimic the actual design methodology that planners, developers, and enterprises should follow for designing sustainable biorefineries of the future:
1. To achieve a cost-effective design of commercial-scale biorefineries, it is crucial to understand the entire integrated biorefining process and how one stage of the process can impact the performance of the others. Therefore, these tradeoffs should be incorporated in the process by developing detailed fully integrated models which include all the process units from feedstock to products.

2. Ethanol as a fuel and succinic acid as a high value chemical are the main products of the biorefinery in our current study and their production rates can be varied to optimize plant margins based on input costs and product markets.

3. To impart a greater degree of realism to biorefinery design, true estimates of process parameters are crucial. Consequently, nonlinear process dynamics that are inherent in complex bioprocesses should be incorporated while modeling the plant.

4. Operational level optimization should be included in the optimization framework to design a comprehensive optimization strategy which considers the impact of- and the tradeoffs between long and short term decisions into a single framework.

   By considering the challenge of integrating process dynamics, nonlinear optimization and strategic planning, different software platforms need to be interlinked in a novel fashion to execute the framework seamlessly. Our analysis is performed by exploiting the advantages of a novel hybrid optimization framework which incorporates a two layer optimization strategy including strategic planning and operational optimization using rigorous nonlinear process simulations as well as metaheuristic optimization. At this stage of model development, the focus of our current study is analyzing the profitability of the process based on production yields, operating costs, and energy consumptions. Detailed cost estimation of all the unit operation at different capacities will be done as the next step to expand our proposed framework and add
more flexibility into it. The case study considered in this work is an advanced biorefinery which has different technology options for each section of the process, and the ability to produce multiple products from lignocellulosic raw materials.

3.2. Hybrid optimization methodology

The proper choice of optimization methodology depends on the complexity of the problem. To design an optimal biorefinery different aspects including strategic and operational level decisions should be considered. Strategic decisions are the longer term decisions which have an extended impact on the economic, environmental and social value of an enterprise, while operational level decisions focus on daily/weekly management of plant operation. In a previous publication (Geraili et al., 2014) a framework was proposed to maximize the economic value of renewable energy systems with decision tasks that included feedstock selection, product portfolio design, technology superstructure design, strategic capacity planning, and optimization of operating conditions.

Following is the brief description of the hybrid optimization algorithm, with considering some modifications to the previously proposed framework. LP models are suggested for the purpose of strategic capacity planning. However, there will be a mismatch between the real (nonlinear) mechanism of the plant and the LP-based optimization model. To overcome the mismatch and also for incorporation of nonlinear operational level optimization in one framework, a two-level approach is proposed as shown in Figure 3.1. This two level approach combines net present value (NPV) optimization for long term planning with rigorous nonlinear operational level simulation and optimization. In the upper level, the capacity is designed strategically by maximizing the NPV of the plant. Then this capacity is sent to the lower level of the optimization algorithm. First the process is simulated in the simulation software (Aspen Plus)
based on the optimal capacity plan and results are utilized in the process optimization model in MATLAB to optimize the decision variables by maximizing the annual cash flow of the process. Process simulation and optimization will be performed iteratively until the convergence criteria are met. In the final stage, process yields obtained from the results of simulation are compared with the yields which were used in strategic model to check the convergence criteria of the hybrid algorithm. If the process yields are different from the ones which were used in the strategic model, these new values should be updated in the strategic model and this procedure continues until the algorithm converges. Each component of the proposed algorithm (Figure 3.1) is briefly described in the following section.

![Figure 3.1: Structure of the proposed hybrid methodology](image-url)
3.2.1. Strategic capacity optimization

Strategic optimization is carried out by a linear programming (LP) model developed and implemented in GAMS to optimize the net present value (NPV) of the process by manipulating its capacity. Process yields, raw material inputs, and energy loads of each unit operation are utilized as inputs to develop linear black box models of mass and energy balances that dictate core technologies in the biorefinery. These balances are integrated with cost and revenue functions through a techno-economic model. For details on the model structure, readers are referred to Sharma et al. (2011) and Sharma et al. (2013).

3.2.2. Operational level optimization

Due to the complexities involved in biorefining processes including inherently nonlinear conversion mechanism, mathematical modeling of the process will comprise of non-convex functions. Although deterministic methods are relatively fast, they might get trapped in local optima since such problems might have many local solutions. Metaheuristic methods are more suitable for solving these types of problems, since a wide range of values for parameters would be searched and probability of getting trapped into local optima would be decreased. Furthermore, for solving large scale nonlinear optimization problems deterministically, constraints should be incorporated into the objective function. However, in many practical large-scale applications, models in simulation environments are used to mimic complex processes behavior (Robertson et al., 2014). Therefore, the modeling equations are embedded in simulation software and cannot easily be extracted. In our case study the whole biorefinery process is simulated in simulation software (Aspen Plus). Consequently, all the mass and energy balances are embedded in the simulation and constraints are satisfied when the simulation is converged.
Metaheuristic approaches can overcome this problem as they do not require the manipulation of the mathematical structure of the objective function and constraints (Mariano et al., 2011).

Differential evolution (DE) algorithm, which is a metaheuristic approach, was selected as an efficient optimization method for biorefinery processes in the previously published paper (Geraili et al., 2014); this algorithm is utilized here to optimize operating conditions. This optimization algorithm is written in MATLAB and directly linked with the Aspen Plus simulator to facilitate the automation of process simulation and optimization. In fact, the optimizer treats the process simulations in Aspen Plus as a black box. The optimized decision variable values from Matlab are sent to Aspen Plus where the process is simulated for these values. The simulated results are then passed back to the optimizer to re-solve the objective function.

### 3.3. Process description and Technology Options

In this study, we consider a biorefinery that has the option to produce multiple products (ethanol and succinic acid) using lignocellulosic feedstock. We consider a sugar-based fermentation platform (biochemical pathway) as the production route to analyse different technology options and possible process integrations. Overall, biofuel and biochemical production from lignocellulosic biomass consists of different sections to convert biomass to final products. The basic steps in these processes are: pretreatment, hydrolysis, fermentation, product purification, heat and power generation, and waste water treatment.

In our previously published paper (Sharma et al., 2013), a detailed strategic planning model was presented where financial modeling was integrated with equation-oriented (linear) mass and energy balances to design optimal feedstock and product portfolios for a biomass-based refinery. The selected product portfolio included ethanol as a biofuel and succinic acid as
a high value biochemical. Additionally, switchgrass which is an energy crop was selected as the optimal feedstock. Since the main goal of the current study is to expand our developed decision support framework, which was proposed in the previous papers (Geraili et al., 2014; Sharma et al., 2013), and adding more flexibility into it by analyzing alternative technologies and possible process integrations, the optimal portfolios obtained in Sharma et al. (2013) are utilized in the current study for development of alternative technology scenarios. Readers are directed to Sharma et al. (2013) and Geraili et al. (2014) for a complete description of the multi-layered optimization framework. The composition of switchgrass is shown in Table 3-1. The physical-property data for the components were obtained either from Aspen plus databank or from NREL’s databank on biomass for wood components such as cellulose and hemicellulose (R. J. Wooley & Putsche, 1996).

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucan</td>
<td>37.00</td>
</tr>
<tr>
<td>Xylan</td>
<td>22.80</td>
</tr>
<tr>
<td>Lignin</td>
<td>15.76</td>
</tr>
<tr>
<td>Ash</td>
<td>4.93</td>
</tr>
<tr>
<td>Protein</td>
<td>3.10</td>
</tr>
<tr>
<td>Arabinan</td>
<td>3.10</td>
</tr>
<tr>
<td>Galactan</td>
<td>1.43</td>
</tr>
<tr>
<td>Mannan</td>
<td>0.30</td>
</tr>
<tr>
<td>Extractives</td>
<td>9.00</td>
</tr>
<tr>
<td>Sucrose</td>
<td>0.77</td>
</tr>
<tr>
<td>Acetate</td>
<td>1.81</td>
</tr>
</tbody>
</table>

The superstructure of the lignocellulosic biorefinery that we consider, along with the alternative technology options, is shown in Figure 3.2.
In the following part each of these sections are explained in more detail and alternative options are suggested as the operating routes.

3.3.1. Pretreatment

Pretreatment of biomass is always required to remove or modify the complex matrix of lignin and hemicellulose in order to make simple sugars accessible for efficient fermentation to final products. Pretreatment has been viewed as one of the most expensive and key processing steps within the conversion of biomass to fermentable sugars (Zheng et al., 2009) as all
downstream operations are affected by its effectiveness (Da Costa Sousa et al., 2009). Therefore, proper technology selection for pretreatment can significantly improve the overall efficiency of converting biomass to bioproducts, and reduce production and capital costs.

In this study, acid pretreatment is utilized which is one of the viable technologies and have been explored extensively in recent years (Mosier et al., 2005; Wyman, 1999). The acid is used to hydrolyse the feedstock chemically. Dilute acid pretreatments typically use sulphuric acid as a catalyst to solubilize hemicellulose and lignin at low acid concentration (0.05-5%), and increase the digestibility of cellulose in enzymatic hydrolysis (Da Costa Sousa et al., 2009). This pretreatment method is a fast and easy technology to perform but it is hampered by by-product formation. During this process, degradation products such as furfural, 5-hydroxymethylfurfural, inhibitors such as acetic acid, and corrosion products are produced (Yang & Wyman, 2008). To reduce the toxicity of hydrolysates generated from acid pretreatment, detoxification is necessary as the by-products can have negative impact on downstream process sections such as enzymatic hydrolysis and fermentation (Ranatunga et al., 1997). Two technology options are considered for detoxification process in our study: (1) ammonia conditioning, and (2) overliming.

3.3.1.1 Overliming: This process is most widely used for hydrolysate conditioning (Martinez et al., 2001). In this conditioning technology, as shown in Figure 3.3, the hydrolysate slurry obtained from pretreatment reactor is sent to a pressure filter to separate the solid and the liquid portions to facilitate the conditioning of liquid. After the separation step, material is overlimed to raise the pH. The pH of overliming process is the key factor for improving the hydrolysate fermentability. In this study, selected pH for detoxification model is 10 based on the optimal value obtained by Mohagheghi et al. (2006). They showed that conditioning at pH 10
enabled the highest ethanol yield. This yield was achieved at a compromise condition in between the conditions that maximized fermentability and minimized sugar loss. The liquid is re-acidified to adjust to a value appropriate for fermentation by adding sulfuric acid. Produced gypsum (Calcium sulfate) is precipitated and removed in the second solid-liquid separation step. The hydrolysate is recombined with the solids and passed to the enzymatic hydrolysis reaction. All the produced gypsum is assumed to be removed by filtration.

Figure 3.3: Overliming conditioning

3.3.1.2. Ammonia conditioning: An alternative technology for detoxification is ammonia (NH₄OH) conditioning which is based on the work of Alriksson et al. (2005). The process flowsheet for this technology is represented in Figure 3.4. The hydrolysate slurry is cooled in the conditioning reactor, where a mixture of ammonia and water is used to raise the pH from 1 to 5-6 and dilute the slurry to 20 wt% total solids. Due to the high miscibility of ammonia in the pretreated mixture, there is no requirement to separate the solid and liquid fractions for conditioning process. Then, the detoxified slurry is passed to the enzymatic hydrolysis reactor. The operating conditions of these technologies are obtained from Humbird et al. (2011) and
Jennings and Schell (2011). The process data for both of these technology options are shown in Table 3-2.

<table>
<thead>
<tr>
<th>Table 3-2: Ammonia condition and overliming process data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agent</strong></td>
</tr>
<tr>
<td>Lime, Sulfuric Acid</td>
</tr>
<tr>
<td>Ammonia (To raise the pH to 5)</td>
</tr>
<tr>
<td>Lime (To raise the pH to 10)</td>
</tr>
<tr>
<td>Sulfuric acid (To adjust pH)</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Water (To control the solid for hydrolysate to 20 wt%)</td>
</tr>
<tr>
<td>Solid-liquid separation</td>
</tr>
</tbody>
</table>

Figure 3.4: Ammonia conditioning

3.3.2. Enzymatic hydrolysis and ethanol fermentation

Enzymatic hydrolysis of cellulose is carried out by cellulase enzymes which are usually a mixture of several enzymes. In hydrolysis, cellulose chains are broken down in order to produce monomeric sugars (glucose) for fermentation. Substrate, cellulase activity, and reaction conditions (temperature, pH) are the factors that affect enzymatic hydrolysis efficiency.
The monomeric sugars produced in enzymatic hydrolysis and pretreatment are fermented to final products in a fermentation tank. In recent years, a considerable amount of research has been done to develop yeasts which can utilize the sugars with reasonable yields and rates (Olsson et al., 1995; Zhang et al., 1995). Recombinant strains, which are developed by genetically engineered yeasts, are able to ferment glucose and xylose simultaneously, co-fermentation, such as the strain developed by Zhang et al. (1995). However, the rates of glucose and xylose fermentation are different.

When enzymatic hydrolysis and fermentation are performed sequentially, the process is called separate hydrolysis and co-fermentation (SHCF). Since hydrolysis and fermentation have relatively similar process conditions, one of the main integration possibilities in bioethanol production process is the simultaneous occurrence of hydrolysis and ethanol co-fermentation (SSCF) (Sun & Cheng, 2002). In previous study by Geraili et al. (2014), separate hydrolysis and co-fermentation (SHCF) of ethanol was simulated in a multiproduct biorefinery by considering experimentally-derived kinetic models. In SHCF, enzyme activity is inhibited by cellobiose and also produced sugars. Several methods have been developed to reduce the inhibition including: increasing the concentration of enzymes, removal of sugars during hydrolysis, and simultaneous saccharification and co-fermentation (Sun & Cheng, 2002). In this study, by utilizing the mathematical model developed by Morales-Rodriguez et al. (2011), simultaneous saccharification and co-fermentation (SSCF) technology option is investigated. Produced sugars are simultaneously fermented to ethanol to reduce the inhibition of sugars in hydrolysis. Calculated optimal temperatures for hydrolysis (44°C) and fermentation (32°C) in SHCF based on the study of Geraili et al. (2014) and Humbird et al. (2011) indicate that the conditions used in SSCF cannot be optimal for both the enzymes and the yeast. Although an increase in
temperature can speed up the hydrolysis, loss of cell viability counters these gains. Temperature for SSCF of ethanol should be selected by considering the fact that enzymes and microorganisms can be practical in a limited range of temperature. The optimal temperature for SSCF is around 38°C (Philippidis, 1996; Philippidis & Hatzis, 1997; Sun & Cheng, 2002) which is a compromise between the optimal temperature for hydrolysis and ethanol fermentation. The SSCF technology is described in more detail based on the developed kinetic model in Section 3.3.4.

3.3.2.1. Solid/liquid (SL) separation: Another alternative technology option considered here is for SL separation, which is used to extract the residual solids after enzymatic hydrolysis as shown in Fig. 2. In most of the developed biorefinery processes all of non-fermentable solids are carried through the whole process and are separated in the purification section. In one of our proposed configurations, solid-liquid separation equipment is utilized after hydrolysis and before fermentation. Since all of the fermentable components of the biomass are converted to monomeric sugars before fermentation, there might be no benefit to pass them to the fermentation tank. Additionally, there is a possibility that removal of non-fermentable solids can enhance the subsequent fermentation and also reduce the energy consumption in distillation columns. In our proposed scenario, residual solids recovered from the process such as lignin, and unconverted cellulose and hemicellulose, are passed directly to the combined heat and power section to be burnt for producing the required steam and electricity in the plant. It is assumed that solid-liquid separators remove all the solid particles successfully from the liquid and produce solid streams with specified moisture content of 20%.
3.3.3. Succinic acid fermentation

One of the considered possible process integrations in this study is to develop configurations which integrate production of ethanol and succinic acid based on the developed models by Zeikus et al. (1999) and Nghiem et al. (2010). Succinate was suggested as a promising co-product to improve the economics of industrial ethanol fermentation (Lynd et al., 2002). Succinic acid as a fermentation product has distinct environmental advantages over ethanol fermentation. In ethanol fermentation CO$_2$ is formed as a waste, whereas in succinic acid production CO$_2$ is consumed.

The fermentation of these two main products occurs in separate tanks but in the same facility. For succinic acid fermentation, *Mannheimia succiniciproducens* MBEL55E which is the genetically engineered strain developed by Song et al. (2008) is considered as the microorganism. Two scenarios are developed for succinic acid production: (1) SHCF of ethanol and succinic acid fermentation, and (2) SSCF of ethanol and succinic acid production. In scenario with SHCF for ethanol, the hydrolysed stream (including mainly pretreated and hydrolysed sugars) is split in two (Figure 3.5a); for the other scenario with SSCF of ethanol, the pretreated feedstock (including mainly produced sugar in pretreatment and unconverted cellulose) is split in two (Figure 3.5b); one stream is sent to ethanol production while the other is used for cellulose hydrolysis and succinic acid fermentation. The allocation ratio is an important factor which impacts the fermentation kinetics and production yields.
To better estimate the nonlinear reaction dynamics of enzymatic hydrolysis and fermentation, experimentally derived kinetic models are utilized in process simulation. Each kinetic model is briefly explained in the following section:

3.3.4. Kinetic Models

A multi-reaction kinetic model developed and validated with experimental data by Kadam et al. (2004) is used here for enzymatic hydrolysis of polymeric sugars. Inhibitions considered in this model assume that the hydrolysed sugars can bind to the active site of the substrate and decrease the formation rate of enzyme-substrate complex which is a competitive mode of inhibition. The mathematical representation of the hydrolysis kinetics is presented in Appendix A, Table A-1.
For ethanol fermentation the two-substrate developed kinetic model by Leksawasdi et al. (2001) which is capable of fermenting glucose and xylose simultaneously (co-fermentation) is utilized. The mathematical representation of the fermentation kinetics is presented in Appendix A, Table A-2. Due to simultaneous cell growth on both of the substrates (glucose and xylose), there is competition to contribute (via cell growth) to produce ethanol. The weighting factor ($\alpha$) represents the relative consumption rates of the two sugars (Equation A.9 and Equation A.14). The best value for the weighting factor ($\alpha$) was determined to be $\alpha = 0.65$ (Leksawasdi et al., 2001). It is assumed that the value for ($\alpha$) is constant during the process and for all the considered alternative technology scenarios.

Since hydrolysis and fermentation have relatively similar process conditions, these two separate models for hydrolysis and co-fermentation are combined to develop a new mathematical model for simultaneous saccharification and co-fermentation (SSCF). In the study by Morales-Rodriguez et al. (2011), a mathematical model for SSCF was proposed and verified. It was shown that by considering proper inhibition functions, a new model can be proposed which illustrates a good prediction of complex reactions in SSCF of ethanol production. Based on this model and the results obtained by Bezerra and Dias (2005) and Philippidis et al. (1993) an additional ethanol inhibition factor, ($C_{Et}/K_{1IEt}$) is added in cellulose hydrolysis (Eq. B2, Appendix B) to build a new kinetic model for SSCF of ethanol. The value for inhibition coefficient of ethanol on cellulose hydrolysis ($K_{1IEt}$) is assumed to be 10 times higher than the inhibition coefficient of cellobiose on cellulose conversion ($K_{1IC2}$). The following equation shows the modified cellulose hydrolysis:
\[ r'_1 = \frac{K_{1Y} C_{G1B} R_S C_S}{1 + \frac{C_{G2}}{K_{2G2}} + \frac{C_{G}}{K_{1G}} + \frac{C_{XY}}{K_{1XY}} + \frac{C_{EL}}{K_{1LET}}} \]

For succinic acid fermentation a kinetic model developed by Song et al. (2008) which models the conversion of glucose to succinic acid is used. While the main product of this model is succinic acid, the other acids such as acetic, formic and lactic acids are also produced as by-products of the fermentation process. The mathematical representation of this fermentation kinetics is presented in Appendix A, Table A-3. Implementation of these experimentally-derived kinetic models in process simulation is explained in section 3.4.

3.3.5. Purification and concentration

The product stream from fermentation, also called beer, is a mixture of desired and undesired products, cell mass, and water that needs to be purified and concentrated. Technology selection for purification depends on the type of products that need to be recovered. All the purification technologies use differences in the chemical and physical properties of the desired product from undesired ones as a driving force for separation. For instance, in cases where fermentation products are more volatile than water, such as ethanol, recovery by distillation is the technology of choice. In our study, distillation columns are employed for ethanol recovery. First, in a beer column ethanol is recovered, where most of the water remains with the solids part. Then the recovered ethanol is concentrated in rectifying column up to its azeotropic boiling point. Finally it is dehydrated by sieve-based purification to obtain ethanol with fuel grade purity (99.5% by mass).

In fermentation-based succinic acid production processes, considerable cost is associated with purification, in some cases reaching more than 60% of the total production costs (Bechthold
Contaminated organic acids including acetic, formic, and lactic acids adversely affect the recovery of succinic acid as well as its yield in the fermenter. In our study, the developed model by Vlysidis et al. (2011) for succinic acid recovery is utilized. Firstly cellular debris is separated from the fermentation effluent by centrifugation, which is followed by an evaporator that vaporizes most of the water and organic acids that have lower boiling points than succinic acid. The concentrated stream obtained from bottom of the evaporator is sent to a crystallizer that operates at 4°C. While formic, acetic and lactic acids are water-miscible at pH from 1-14 at temperatures above 0°C, succinic acid solubility decreases sharply when the temperature decreases (Li et al., 2010). Therefore, succinic acid can be selectively separated from other acids using solubility-driven crystallization. Finally a centrifuge and a dryer are required to separate the pure succinic acid crystals and reduce its moisture to acceptable end use purity (> 90% by mass). In Figure 3.6, the process flowsheet for succinic acid fermentation followed by purification of the final product is represented.

Figure 3.6: Process flowsheet for succinic acid production
3.3.6. Waste water treatment and power generation

Treating the waste water streams generated in the biorefinery is necessary to meet water quality regulations and provide purified water for reuse to reduce the plant makeup water. The recycled water is a combination of water coming from different sections; this water is initially screened to remove large particles. Screening is followed by anaerobic and aerobic digestions to digest the organic matters in the recycled water stream. Anaerobic digestion is a complex biochemical reaction. In this process, a gas that is mainly composed of methane and carbon dioxide, also referred to as biogas, is produced and is considered as a fuel source in combustion section. Amount of biogas produced varies with the amount of organic waste fed to the digester. Then the water is treated further by aerobic digestion to produce relatively clean water which can be used again in the process. Aerobic digestion is a natural biological degradation process in which bacteria that thrive in oxygen-rich environments break down the waste. In addition to purified water, sludge which is mainly composed of cell mass is also produced in aerobic digestion and is burned in the combustor. The concentration of sludge is adjusted in the simulation to obtain 44% moisture in the combined solid feed to the combustor. Process and economic data for the waste water treatment of biorefinery are obtained from Humbird et al. (2011).

The combined system of combustor, boiler, and turbogenerator is considered for steam and electricity production. Extracted residual solids (mainly lignin), biogas and sludge are utilized as the combined solid feed to the combustor. This combined feed to the combustor has a lower heating value (LHV) of 2300 kcal/kg. A fan moves air into the combustor chamber. Produced flue gas from combustor preheats the entering combustion air and exits to the baghouse to remove particulate ash which is assumed to be landfilled; the treated water is then entered to
the heat exchanger circuit and is evaporated and superheated to high pressure steam. A multistage turbine and generator is implemented in the simulation to produce electricity. Superheat steam leaving the boiler is extracted from turbine at different extraction ports (low-pressure steam for distillation and high-pressure steam for pretreatment). The advantages of including combined heat and power generation section in the process include energy self-sufficiency, reduction in waste disposal cost, and additional revenue through sale of excess electricity to the grid and providing a co-product credit. Process and economic data for the steam and electricity production section are obtained from Humbird et al. (2011) and Kazi et al. (2010). The next section discusses the software architecture that is used to simulate the proposed process superstructure.

3.4. Software Architecture

One of the main characteristics of our approach is the incorporation of experimentally validated kinetic models with process simulations. Due to the dynamic nature of such kinetic models, proper software architecture needs to be formulated and implemented. The complex kinetics of bio-reactions from literature are modeled in Matlab and linked with process simulation. The communication between Aspen Plus and Matlab is based on dynamic data exchange by using Aspen Plus ActiveX Automation technology which enables the user to transfer data to and from other Windows applications. Active links are created between Aspen Plus result fields to the kinetic models in Matlab. Additionally, active links are created from Matlab kinetic models to input fields in Aspen Plus. In each iteration of the proposed strategy (see Figure 3.7), conversion rate of biological reactions (hydrolysis and fermentation) in process simulation (Aspen Plus) are modified based on the solution of differential equations for the kinetic models. Since many recycle streams are defined in the process configuration of the plant,
the inlet concentrations of the reactants change when the conversion rate values (result of Matlab model) are modified. Therefore, this integrated method needs to be carried out iteratively until the change in concentration of reactants through consecutive iteration become less than a defined threshold. Our method shows an efficient real-time data exchange model for imparting a greater degree of realism to the simulations.

![Diagram](https://via.placeholder.com/150)

Figure 3.7: Simplified diagram for implementation of complex kinetics in process simulation

### 3.5. Process simulation

Suggested alternative technology options in each section of the plant are utilized to build different scenarios. These scenarios are simulated using Aspen Plus. Table 3-3 provides a matrix of the technology scenarios that are simulated.

In complex processes such as our developed scenarios, there are numerous operating conditions which can significantly affect the annual revenue and production yields of the process. Here, we have used the optimal parametric values obtained from literature for scenarios
1 to 5. In scenario 6, the allocation of produced sugars for the purpose of coproduction of ethanol and succinic acid, and the inhibition impact of sugars and enzymes on fermentation lead to a problem that merits further optimization to maximize the annual revenue of this scenario.

For simulation of the developed process configurations, the main input data in bioethanol production are obtained from Humbird et al. (2011), Kazi et al. (2010), and Aden et al. (2002), and for succinic acid fermentation and purification the process data are based on the developed models of Vlysidis et al. (2011) and Li et al. (2010).

3.6. Results and discussion

In this section, the results of analyzing different scenarios based on their annual operating cash flows and production yields are presented. Annual cash flow, which takes into account the sale of products and the costs of raw materials and utilities, is calculated by utilizing the simulation results for mass and energy of the process streams. The costing data are obtained from Kazi et al. (2010), Vlysidis et al. (2011), and Laser et al. (2009). Ethanol price is assumed
to be $2 per gallon, succinic acid price is assumed to be $6000 per ton, and electricity price is set at $0.05 per kilowatt-hour.

3.6.1. Detoxification technology options

In scenario 1 and 2, all the technology options in the process are equal except the detoxification section. Both of the proposed scenarios have the total capacity of processing 40 ton/h of biomass feedstock. Simulation results of these configurations are represented in Table 4 and Figure 3.8.

In overliming, sugar can be lost to side reactions due to the conversion to unfermentable compounds in conditioning reactor. Additionally, some part of sugar is also lost during the solid-liquid separation process which precipitates the produced gypsum in reacidification. Sugar losses and gypsum disposal cost are eliminated by replacing the overliming with ammonia conditioning. Due to higher sugar loss in overliming process, as the results show in Table 3-4 and Figure 3.8, hydrolyzate stream which enters the fermentation reactor has lower amount of sugar. Therefore, sugar fermentation occurs at a lower extent in comparison to ammonia conditioning and produced ethanol yield is lower. On the other hand, due to higher cost of ammonia in comparison to lime, the utility cost of the scenario with overliming conditioning is lower. Furthermore, the implementation of overliming process as the detoxification technology allows a reduction in energy cost of the plant since part of the solids are separated in solid-liquid separation equipment and smaller load of solid are sent to distillation column. Consequently, a lower amount of steam is required to purify the product, see energy cost in Table 3-4. The energy and chemical prices are obtained from National Renewable Energy Laboratory report by Humbird et al. (2011). Table 3-5 presents the prices used in the economic analysis.
Table 3-4: Comparison of alternative technologies for conditioning

<table>
<thead>
<tr>
<th>Conditioning technology</th>
<th>Ethanol yield (gal/dry ton feedstock)</th>
<th>Energy cost (GJ/h)</th>
<th>Annual cash flow ($ MM/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overliming</td>
<td>55.00</td>
<td>12.45</td>
<td>6.50</td>
</tr>
<tr>
<td>Ammonia conditioning</td>
<td>58.00</td>
<td>12.72</td>
<td>7.10</td>
</tr>
</tbody>
</table>

Table 3-5: Unit price of Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Price</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid</td>
<td>0.089</td>
<td>$/kg</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.45</td>
<td>$/kg</td>
</tr>
<tr>
<td>Lime</td>
<td>0.077</td>
<td>$/kg</td>
</tr>
<tr>
<td>Enzyme</td>
<td>0.121</td>
<td>$/kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.05</td>
<td>$/kWh</td>
</tr>
</tbody>
</table>

Figure 3.8: Sugar and solid recovery for alternative conditioning technologies
Annual cash flow results, Table 3-4, show that although the utility and energy costs in the scenario with overliming conditioning are lower, the higher ethanol yield in ammonia conditioning will result in higher profitability. Therefore, ammonia conditioning has a better performance and can be considered as an effective detoxification technology that improves conversion of sugars.

3.6.2. Solid liquid separation process

The results for the configurations 1 and 3, which have alternative options for solid separation in ethanol production, are shown in Table 3-6 and Figure 3.9. Energy produced in combustion of solid streams sent to the combined heat and power section for scenario 1 and 3 are roughly similar since the composition of these streams is comparable. As the results show in Table 3-6, solid separation before fermentation, scenario 3, has the advantage of reducing the energy cost in distillation column owing to higher initial ethanol concentration and lower load of solid in the column. However, the drawbacks for solid separation before fermentation are:

- Sugar loss: part of the sugars produced in pretreatment and hydrolysis are separated with the solids and are not utilized in the fermentation.
- Inhibition effect of sugars in fermentation: by separating the solids after hydrolysis, glucose and xylose concentrations will increase in the inlet stream to fermentation tank. Based on the implemented kinetic model for fermentation, shown in previous section, glucose and xylose have inhibitory effect on ethanol fermentation. Therefore, sugars are converted to ethanol in a lower extent in comparison to scenario 1, Fig. 9.

Results obtained from simulation of these two configurations show that although energy consumption in scenario 3 is reduced, lower ethanol yield due to sugar loss and inhibitory effect
of sugars in fermentation will result in lower annual cash flow. Therefore, solid separation in purification section, scenario 1, is the preferred technology. It is worth noting that the implemented kinetic model reveals the negative impact of high sugar concentration in ethanol production and imparts a greater degree of realism to the actual representation of the biorefining process.

Table 3-6: Comparison of alternative technologies for solid separation

<table>
<thead>
<tr>
<th>Lignin separation</th>
<th>Unit energy cost for distillation step (MJ/gal ethanol)</th>
<th>Sugar loss (% wt)</th>
<th>Ethanol yield (gal/dry U.S. ton feedstock)</th>
<th>Annual cash flow ($ MM/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>35.20</td>
<td>0</td>
<td>58.00</td>
<td>7.10</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>30.00</td>
<td>5.00</td>
<td>55.00</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Figure 3.9: Sugar conversion in ethanol fermentation for two alternative solid separation technologies
3.6.3. SHCF and SSCF

In scenario 6 which considers the coproduction of ethanol and succinic acid, the pretreated biomass is divided in two streams. One part is allocated in ethanol production and the other is used in the production of succinic acid. For succinic acid production, first the pretreated biomass is hydrolyzed and then is passed to the fermentation tank. The initial glucose concentration in product fermentation depends on the amount of pretreated biomass allocated to its production and also the amount of sugar that is produced during hydrolysis; therefore, enzyme loading and allocation of pretreated biomass have a complex set of impacts on process yields and economics, and need to be selected optimally.

A sensitivity analysis is carried out to observe the impact of enzyme loading in production of sugars and final products. Figure 3.10 shows that by increasing the enzyme loading, sugars and ethanol production will increase. However, there is an optimal enzyme loading rate for succinic acid production beyond which production rate decreases with increasing enzyme concentration as a result of sugar inhibition and also cell death due to presence of high concentrations of acids in culture broth (Kong et al., 2006). Further, adding more enzymes also increases the direct cost of the plant. Additionally, Arrhenius equation in the kinetic model indicates that enzyme activity is correlated with reaction temperature. Consequently, temperature plays an important role in changing the rate of enzymatic reactions and thus impacts the overall cellulose conversion. In our developed process optimization model, the following operating variables are manipulated in order to optimize annual operating cash flows for the biorefinery: (1) temperature in enzymatic hydrolysis for succinic acid production, (2) pretreated biomass allocation ratio between ethanol and succinic acid production, and (3) total enzyme (cellulase) loading for hydrolysis of sugars.
As explained before, differential evolution (DE) optimization algorithm is implemented in Matlab and linked to the simulations in Aspen Plus. The parameter setting for DE is shown in Table 3-7.

![Figure 3.10: Effect of enzyme loading on sugar, ethanol, and succinic acid production](image)

<table>
<thead>
<tr>
<th>Parameters/operators</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum number of function evaluation (MAXNFE)</td>
<td>700</td>
</tr>
<tr>
<td>Population size (NP)</td>
<td>30</td>
</tr>
<tr>
<td>Weighing coefficient (F)</td>
<td>0.8</td>
</tr>
<tr>
<td>Crossover rate (CR)</td>
<td>0.9</td>
</tr>
<tr>
<td>Penalty coefficient (R_f)</td>
<td>100000</td>
</tr>
</tbody>
</table>
Iterative results of the hybrid optimization methodology are presented in Table 3-8 which shows that in two iterations the model is converged. Initial process yields are obtained from literature (step1); then these yields are utilized in strategic model to optimize the capacity of the process (step2); the optimal values for the capacity are passed to the process level simulation and optimization to find the optimal process conditions and calculate the process yields based on the results of simulation (step3). These calculated yields are compared with the initial values used in the strategic model to check the convergence. Since the difference between calculated yields and initial yield values is greater than the threshold, this hybrid optimization needs to be carried out again based on the new yield values. Final results reveal a deviation in optimal process yields and production capacities from initial literature estimates. Optimal values of the decision variables obtained from optimization model are shown in Table 3-9. The convergence behavior of the implemented optimization algorithm is also plotted in Figure 3.11. It can be seen that the convergence is steady and stable.

### Table 3-8: Iteration results in hybrid optimization strategy

<table>
<thead>
<tr>
<th>Parameters and Variables</th>
<th>Iteration1</th>
<th>Iteration2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Step 1</td>
<td>Step 2</td>
</tr>
<tr>
<td><strong>Capacity Constraints</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feedstock (1000 ton/yr)</td>
<td>--</td>
<td>333</td>
</tr>
<tr>
<td>Ethanol (MM gal/yr)</td>
<td>--</td>
<td>11.0</td>
</tr>
<tr>
<td>Succinic Acid (1000 ton/yr)</td>
<td>--</td>
<td>15.0</td>
</tr>
<tr>
<td><strong>Yield Parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugar (kg / kg)</td>
<td>0.87</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Fermentation</td>
<td>0.85</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Fermentation</td>
<td>0.25</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Purification</td>
<td>0.99</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Purification</td>
<td>0.78</td>
<td>--</td>
</tr>
</tbody>
</table>
Due to the simultaneous glucose production and sugar (glucose & xylose) consumption in SSCF, sugar concentration in the bioreactor is kept below the inhibition threshold. Additionally, since sugar is consumed in fermentation reactions, a sugar sink is created which helps to convert
the cellulose (to glucose) in a higher extent. Simulation results (for scenario 1 and 4) based on the optimal operating conditions show that SSCF have a 12% higher overall ethanol yield in comparison to SHCF process. Table 3-10, presents the calculated annual cash flow for four different process configurations. There is a huge improvement in the profitability of the process by incorporating succinic acid as a co-product of the plant. Therefore, it shows that for having a truly sustainable biorefinery process, a portfolio of products which comprise biofuels and value added biochemicals is required whose production rates can be varied to optimize plant margins based on input costs and product markets. The results for the scenario which utilizes SSCF technology and produces succinic acid as a co-product of the plant reveals that the annual cash flow of the process has improved 11% in comparison to scenario 5 (SHCF for ethanol and succinic acid as a co-product). The corresponding annual ethanol and succinic acid productions are 11.40 (MM gal/yr) and 15540 (ton/yr), respectively.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Annual cash flow (MM$/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>7.1</td>
</tr>
<tr>
<td>Scenario 4</td>
<td>8.5</td>
</tr>
<tr>
<td>Scenario 5</td>
<td>70.0</td>
</tr>
<tr>
<td>Scenario 6</td>
<td>77.6</td>
</tr>
</tbody>
</table>

Calculated concentration profiles for SSCF are shown in Figure 3.12. The concentration profiles illustrate that glucose is converted faster to ethanol in comparison to xylose which is in agreement with the experimental results obtained by Kang et al. (2010) and Leksawasdi et al. (2001). Figure 3.13 and Figure 3.14 show the calculated concentration profiles in enzymatic hydrolysis and fermentation for succinic acid production, respectively.
Figure 3.12: Concentration profiles in simultaneous hydrolysis and co-fermentation for ethanol production

Figure 3.13: Concentration profiles in enzymatic hydrolysis for succinic acid production
In addition to analyzing the impact of varying enzyme load on production yields (Figure 3.10), further sensitivity analysis was performed to elucidate the impact of price fluctuations of important materials (including raw materials and products) on the profitability of the optimized process configuration. Results from the sensitivity analysis are presented in Figure 3.15 and Table 3-11. The reference prices (Table 3-11) that have been used for the economic analysis correspond to price sensitivity equal to 1 in Figure 3.15. Material prices are changed according to these reference prices and the corresponding annual cash flows of the plant are calculated.
Results from the slopes of the lines show that succinic acid price variation has the highest effect on the profitability of the process. Additionally, it is shown that for raw materials, which have negative slopes, switchgrass price variations have a greater influence on the profitability than enzyme price changes.
3.7. Conclusions

In this paper a procedure was proposed to analyze flowsheet configurations of integrated biorefinery processes to develop an optimal process configuration by investigating several options in each process step and utilizing a hybrid optimization algorithm. The proposed hybrid algorithm has the advantage of integrating long term planning with operational level decisions. Additionally, integrated software architecture is developed for comprehensive modeling of the biorefinery process. In this integrated software platform, experimentally-derived complex kinetics of bio-reactions from literature are modeled in Matlab and linked with process simulation in Aspen Plus to impart a greater degree of realism to the modeling of actual biorefinery process. In this study, we presented a detailed development of the operational simulation and optimization component of the framework by designing integrated biorefineries, and analyzing the profitability of the process based on production yields, operating costs, and energy consumptions. Furthermore, by simulating the entire model in Aspen Plus, the implicit correlations between upstream and downstream stages of the process are taken into consideration. To demonstrate the utility of the proposed procedure a hypothetical lignocellulosic biorefinery was analyzed.

Different scenarios were synthesized by considering alternative technologies to analyze fully-integrated biorefinery processes. The results show that ammonia conditioning is the preferred technology for detoxification since it had a higher ethanol yield and lower sugar loss in comparison to overliming. Although the process configuration with solid separation before fermentation had a lower energy cost, extracting the residual solids in purification section was selected as the preferred technology for solid separation due to the higher ethanol yield and
annual cash flow. Additionally, the reaction-reaction integration possibility of hydrolysis and fermentation, SSCF, in ethanol production was investigated based on the modified kinetic model. SSCF technology had a better performance in comparison to separate hydrolysis and fermentation in terms of sugar conversion and product yields. Furthermore, optimization results showed that considering succinic acid as a co-product of the plant makes a huge difference in the profitability of the process.

For a comprehensive profitability assessment of a biorefinery, detailed capital cost calculations should also be included as one of the main criteria for decision making process. Future work will include expanding our proposed decision support framework by incorporating detailed cost estimation of all the unit operations at different capacities, and incorporating uncertainty analysis into the proposed methodology by considering various sources of uncertainties such as change in market and operational parameters.

3.8. References


4.1. Introduction

Currently, chemical and energy industries are heavily reliant on fossil fuels such as petroleum, coal and natural gas. As fossil fuel supplies are expected to be less available, more expensive, and a leading source of air and water pollution, the needs for alternative production chains in energy and chemical sectors become more urgent. Renewable energy sources are expected to play an important role in the supply of the future energy demand. In the quest for sustainable alternatives, the industry is experiencing a steady growth in the production of biobased fuels and chemicals that are developing the emerging concept of biorefining (Demirbas, 2007). Biorefineries appear to be a promising avenue for energy and chemical production from biomass as part of the solution to climate change, and the heavy dependence on fossil fuels (Jefferson, 2006); this emerging industry can also enhance energy security and create job opportunities.

From the perspective of new renewable product value chains, we have to be cognizant of the fact that most of these endeavors are still in their pre-feasibility study phase, wherein, the processes that execute the purpose of the value chain are still non-existent. When developing a decision support framework for such enterprises, the initial functions of the framework should therefore focus on aiding stakeholders in the intelligent design of the supply and production chains that impact all actors and participants over strategic time horizons (10-30 years). Value chain actors should make mission-critical decisions that have economic, social, and environmental impacts on the stakeholders of the value chain. The nature of these decision tasks can be strategic, tactical, or operational. Hence, there is a need for development of efficient
strategies to analyze these emerging technologies and yield optimal trade-offs between performances of different criteria.

In order to manage the complexity of the decision-making process for designing renewable energy production systems, several contributions have appeared over the last few years where mathematical programming techniques have been exploited by taking into account process and economic modeling. The National Renewable Energy Laboratory (NREL) has developed detailed analytical models to analyze different process configurations for cellulosic ethanol production (Aden, 2008; Dutta & Phillips, 2009; Kazi et al., 2010). Furthermore, many multi-echelon and multi-period models for biorefinery design and planning have been employed (Akgul et al., 2011; Avami, 2013; Ekşioğlu et al., 2009; Elia et al., 2011; Karuppiah et al., 2008; Mansoornejad et al., 2010; Martin & Grossmann, 2011; Martín & Grossmann, 2012; Pham & El-Halwagi, 2012; Sammons et al., 2007; Zondervan et al., 2011). Additionally, multi-objective approaches have also been proposed to optimize several conflicting objectives simultaneously (El-Halwagi et al., 2013; Fazlollahi & Marechal, 2013; Giarola et al., 2011; Sharma et al., 2011; You et al., 2012). Since algorithms still struggle with the size and non-convexity of the resulting models for complex chemical processes such as integrated biorefineries, optimization problems usually incorporate simplified process descriptions and shortcut methods. Detailed overview of recent advances in the optimization of energy systems are reviewed by Connolly et al. (2010) and Shabani et al. (2013).

The aforementioned studies use deterministic modeling approaches, which assume that all the model parameters that influence the optimization task are known in advance. However, common to early stages of process design is the lack of certain information that will introduce variability into the decision-making problem. Uncertainty affects the system efficiency and may
lead to either infeasible design or suboptimal performance. Product prices and demands are exogenous parameters set in the open market, which propose a great challenge for the management to control their evolution during the planning horizon of the plant. These factors have hampered investment capital formation in the renewable sector and have deterred prospective entities from undertaking commercialization of lab- and demonstration scale projects. Thus, market uncertainty is a significant factor which should be incorporated into the optimization framework to add additional value and granularity to the decision-making process. Widely used methodologies developed for solving optimization problems under explicit consideration of uncertainties are reviewed by Sahinidis (2004), which includes chance constraint programming, stochastic programming, and robust optimization.

A number of contributions addressed the presence of uncertainties in optimization of biorefineries. For example, Kim et al. (2011) proposed a two stage mixed integer stochastic programming model to determine the number, location, and size of production units by maximizing the overall expected profit while incorporating the uncertainty of parameters. In this model, global sensitivity analysis is utilized to understand the influence of various uncertain parameters and identify the parameters that have the greatest impact on the optimization problem. Dal-Mas et al. (2011) proposed a mixed integer linear programming (MILP) optimization model for corn-based ethanol supply chain design which considers the market value fluctuation of corn and ethanol. This optimization model considers the maximization of economic performance and minimization of financial risk in the biofuel supply chain. Gebreslassie et al. (2012) developed a bi-criterion, multi-period MILP model for optimal design of hydrocarbon biorefinery supply chains under supply and demand uncertainties that simultaneously minimizes the expected annualized cost and financial risk. Tong et al. (2014)
presented a two-stage stochastic MILP model for optimal design and strategic planning of an advanced hydrocarbon biofuel supply chain integrated with existing petroleum refineries based on scenario generation for uncertain parameters. In this model, biomass availability, production and capital costs, crude oil price, and government incentives are introduced as uncertain parameters.

Although several decision-making frameworks have been developed for optimal design and operations of biorefineries, in most of the studies mentioned above, strategic, tactical and operational decision tasks are not addressed within a single optimization model, even though there is a significant interdependence between them. Furthermore, the aforementioned studies consider linearization assumptions and simplifications for modeling the process in order to keep the model tractable and allow large model development with relatively short computational time. However, conversion mechanisms in biorefinery processes are inherently nonlinear in nature. Moreover, the risks associated with the uncertainties potentially involved in biorefineries may significantly affect the optimal performance of the plant and cause extra expenses to accommodate unexpected events (Pistikopoulos, 1995). Therefore, this work aims to fill these research gaps by proposing a novel decision support tool that seamlessly integrates the optimization of long and short term decisions in the face of uncertainties and incorporates the nonlinearities involved in the conversion mechanisms of the process into the optimization framework.

A previous paper by the authors (Geraili et al., 2014a) proposed a methodology to generate and identify optimal configuration and operating conditions for a biorefining enterprise with very promising results in terms of energy consumption and production cost. In this study we expand the scope of the framework by incorporating market uncertainty through stochastic
programming in strategic model. This iterative framework is based on a distributed, systematic approach, which is composed of different layers including systems-based strategic optimization, detailed mechanistic modeling, and operational level optimization. In the stochastic optimization model, scenario-based formulation is utilized to transform the original strategic optimization problem under uncertainty into a deterministic approximation by discretizing the uncertain market parameters (Grossmann & Sargent, 1978). In conjunction with the simulation and optimization studies, the proposed framework will develop quantitative metrics to associate economic values with technical barriers. Furthermore, explicit risk measure is added to the model as a new objective to allow the management of financial risk according to the decision maker’s attitude; risk management formulation is introduced to the model to reduce the economic losses due to unfavorable scenarios and to simultaneously improve the economic performance, thus leading to a multi-objective optimization problem. A hypothetical case study, multi-product lignocellulosic biorefinery that converts biomass to value-added biofuels (cellulosic ethanol) and biobased chemicals (succinic acid), is presented to exemplify the efficacy of the proposed framework. This paper is organized as follows. The proposed optimization framework is presented in section 2. After a general description of the integrated biorefining case study, details of the proposed strategy and its application to biorefinery are presented. The optimization results are then presented and discussed to demonstrate the effectiveness of the proposed framework as a decision-making strategy. Lastly, concluding remarks and future directions are presented and discussed in the conclusion section.
4.2. Decision support framework

The proposed framework aims to develop an innovative, model-based decision support system in order to investigate the inherent collaborative relationships between different decision layers of a renewable energy enterprise, and how these relationships can be exploited in order to improve their commercial viability and sustainability. The proposed framework utilizes a distributed architecture to model decision making for renewable energy operations with several key features. The renewable energy enterprise will be represented as a real entity with different interdependent and functional layers in its decision hierarchy—the Corporate Planning (Strategic) Layer and the Production Planning Layer (Operational). The strategic and operational layers will consist of several sectors that will coordinate activities within a particular division. Both layers will reciprocally interact in an effort to work towards a common and specific corporate goal. A general schematic structure of the proposed iterative decision support strategy is presented in Figure 4.1.

The layered decomposition does not necessarily imply a hierarchy; each layer is functionally dependent on the others for information to complete its model. This information can be used in the form of constraints or parameters by other models, the idea being that the optimized solutions from one layer should not violate physical constraints in other layers. A major component of any decision support system is a forecasting module that estimates the future parameters that will impact the enterprise performance. In our study, product supplies, demands and prices are deemed uncertain parameters; once the requisite parameters are forecasted over the desired time scales these parameters are inserted into the decision analysis framework. During the first stage, strategic decision making will be formulated as an MILP model which incorporates a stepwise capacity expansion strategy by defining binary variables for
capacity increments at each time period in the planning horizon. The model is represented by linear equations for mass and energy balances to describe physical flow of materials across the system nodes, and financial flows that result from the system design and material movements. These mass and energy balances that dictate core technologies in the energy production system are integrated with cost and revenue functions through a techno-economic model. Different scenarios are developed based on stochastic forecasts for uncertain market parameters. The strategic model will determine the optimal design of production capacity of the plant for the planning horizon by maximizing the expected net present value (NPV). Management of risk due to uncertain parameters is explicitly addressed in the strategic model by adding a criterion to control the variability of the performances associated with each specific scenario; in fact, the tradeoff between risk and profitability of the plant will be incorporated to strategic decision making process.

The capacity plan is then sent to the lower level of the optimization algorithm, which optimizes the operating conditions of the plant. The production layer will contain an iterative strategy to integrate detailed process simulation of production facilities in the network with plant-wide optimization models. Process simulation will enhance our understanding of the complex process, help identify potential improvements that can be made in the configuration and operation, and incorporate much realism to the computer representation of the process (including nonlinear thermodynamics and biological kinetics). For the purpose of nonlinear plant-wide optimization, a stochastic algorithm will be integrated with simulations; these novel algorithms are especially robust in solving nonlinear optimization problems such as the optimization of a renewable energy process.
Economic optimization and risk analysis will provide users with visual tools that merge decision-making intuition with mathematical rigor; using an iterative framework implementation and real-time information exchange between each decision layer, we may potentially overcome the mismatch between nonlinear process mechanisms and linear estimations used during linear programming (LP) optimization of strategic decisions. Each component of the proposed algorithm (Figure 1) is described in greater detail within Section 4.4.

4.3. Process description

In order to demonstrate the utility of the proposed framework, the aforementioned optimization strategy is applied to a hypothetical biorefinery that utilizes lignocellulosic feedstock(s) to produce biobased fuels and chemicals. Readers should note that while we are...
utilizing a lignocellulosic process, the applicability of the framework transcends just
biorefineries (other processes can include algae process design, and even oil and natural gas
processing plants).

4.3.1. Lignocellulosic Biorefinery

The conversion platforms of lignocellulosic biorefinery can broadly be subdivided into 2
major pathways: (1) the biological conversion pathways based on fermentation, and (2) thermo-
chemical conversion pathways based on heat-based technologies like gasification. The
lignocellulosic biorefinery used in this study is a multiproduct plant that uses a fermentation-
based sugar conversion platform with 3 products: cellulosic ethanol, biosuccinic acid, and
bioelectricity. We assume that the prospective biorefinery is located in the southwest region of
Louisiana and utilizes biomass crops sourced from limited land available within a 100 mile
radius of the plant.

Switchgrass serves as the selected feedstock for the biorefining process. The production
chain comprises of 6 major systems: feedstock pretreatment, sugar hydrolysis, sugar
fermentation, product purification, heat and power generation, and wastewater treatment. The
systems superstructure is shown in Figure 4.2. Pretreatment technologies break down the matrix
of biomass polymeric compounds to facilitate the enzymatic hydrolysis of cellulose and
solubilize the hemicellulose. Biomass is exposed to dilute sulfuric acid (0.05-5 wt%) at a high
temperature (140-190°C) and moderate solids concentration (30 wt%) for a short time to
solubilize hemicellulose and lignin and increase the digestibility of cellulose in enzymatic
hydrolysis. During this process, xylose degradation products such as furfural, inhibitors such as
acetic acid, and corrosion products are produced. Ammonia (NH_4OH) conditioning technology is
selected for detoxification of pretreated biomass based on the work of (Alriksson et al., 2005;
Jennings & Schell, 2011). In the conditioning reactor, mixture of ammonia and water is used to raise the pH from 1 to 5-6 and dilute the slurry to 20 wt% total solids. The resulting pretreated slurry is split into two streams: One stream that is allocated for the production of ethanol and the other stream that is sent to succinic acid production. In ethanol production, sugars produced in saccharification are simultaneously co-fermented to ethanol. Purchased cellulase enzyme and nutrients for co-fermentation of sugars are added to the reactor at a compromise temperature for hydrolysis and ethanol fermentation. This process is known as simultaneous saccharification and co-fermentation (SSCF) which has been shown to help to reduce the inhibition impact of sugars in hydrolysis (Sun & Cheng, 2002). The pretreated slurry allocated to succinic acid production is first hydrolyzed by utilizing the purchased enzymes and the produced sugar is fermented to succinic acid and other acids such as acetic, formic and lactic acid as by-products of fermentation by utilizing genetically engineered strain Mannheimia succiniciproducens MBEL55E developed by Song et al. (2008).

The products in the fermentation effluent need to be recovered and purified; the purification technologies will depend on the type of products that are being recovered. Ethanol recovery is accomplished with employing two distillation columns and a sieve-based purification to obtain ethanol with fuel grade purity (99.5 wt%). In succinic acid purification, most of the water and organic acid with boiling points lower than succinic acid are vaporized in the evaporator. The concentrated stream is sent to a crystallizer which selectively separates succinic acid based on its solubility behavior. Finally, to purify succinic acid crystals to an acceptable end use purity (> 90 wt%) a centrifuge and a dryer are utilized.

To reduce make-up water requirement, a sequence of anaerobic and aerobic digesters are considered in process modeling to digest organic materials contained in the waste waters coming
from different sections of the plant. Anaerobic digestion produces a biogas which is rich in methane and is considered as a fuel source in combustion section. Aerobic digestion is carried out in lagoons to produce a clean water stream that is recycled to the plant. Additionally, sludge which is primarily composed of cell mass is also produced in aerobic digestion that is used to produce steam and power in combustion section. Recycled water is introduced into different areas of the plant such as pretreatment to minimize the purchased fresh water consumption. Solids from recovery sections (mainly lignin), biogas from anaerobic digestion, and sludge from aerobic digestion are considered as the combined solid feed in the combustion section to produce high pressure steam, electricity and process heat. Combustion section is composed of combustor, boiler, and turbogenerator.

Figure 4.2: Process flow diagram
To better estimate the nonlinear reaction dynamics of enzymatic hydrolysis and fermentation, experimentally derived kinetic models are utilized in process simulation. All operational and economic data for our case study is obtained from Kazi et al. (2010), D. Humbird (2011), Li et al. (2010) and Vlysidis et al. (2011).

4.4. Framework details

Our proposed systematic framework consists of three main steps which guide the user in solving the stochastic optimization problem (Figure 4.1). This iterative framework includes the methods and tools such as linear modeling of the process, uncertainty analysis, risk management, process simulation (nonlinear modeling), and stochastic optimization. In this section each component of the proposed framework is described in some detail with the lignocellulosic biorefinery being featured in order to apply the framework design components to a case study.

4.4.1. Strategic model

This section presents the model that is used to describe the capacity design problem. The model is formulated as a stochastic mixed integer based linear program (MILP) with a 14-year planning horizon and bi-annual time steps, yielding a total of 7 time steps. Special emphasis is laid on the strategic capacity planning leading to a long-term planning horizon. Bi-annual time steps were chosen to represent a full business cycle so that shorter term fluctuations in market conditions are averaged out. The mathematical formulation of the strategic planning model is broken into sub-models for ease of description, which include a production model, flexible capacity design model, financial model and a risk management model.

Production model: All major process systems are represented as linear black boxes in the planning model for the technology set considered for the framework demonstration. The major equations that are approximated linearly in the planning model and modelled nonlinearly during
process simulation and optimization include unit operations’ yield and unit operations’ energy balances. These equations are given in the following form:

**Biomass feedstock production:** The biomass production formulation is developed to model plant’s decisions for calculating the acreage of land harvested and the total amount of produced biomass to be utilized as the feedstock.

\[
BM_{t,s}^{\text{hyst}} = land_{t,s}^{\text{hyst}} \times BYLD_{t} \times HVST^{\text{loss}}
\]  

\[
land_{t,s}^{\text{hyst}} = land_{t-1,s}^{\text{hyst}} + land_{t-GD,s}^{\text{new}} - land_{t,s}^{\text{release}}
\]  

\[
land_{t,s}^{\text{release}} = land_{t-GC,s}^{\text{new}}
\]  

\[
land_{t,s}^{\text{hyst}} \leq Maxland_{t}
\]

The mass balance for biomass production in Equation 4.1 takes into account the harvest losses \((HVST^{\text{loss}})\), where \(BM_{t,s}^{\text{hyst}}\) is the amount of produced biomass in time period \(t\) for scenario \(s\) based on total harvested land \(land_{t,s}^{\text{hyst}}\) and the expected biomass yield \(BYLD_{t}\) from harvesting operation. Equation 4.2 is the area balance on land which ensures that steady feedstock is supplied to the plant at each time period \(t\) by contracting new lands, \(land_{t-GD,s}^{\text{new}}\). Additionally, the growth delay of harvesting \(GD\) is introduced to the model by considering the availability of new contracted land \(land_{t-GD,s}^{\text{new}}\), after the defined growth delay. To model the
growth cycle of the biomass, GC, Equation 4.3 is introduced which mandates the release of the land when it has run the course of its production cycle. Harvested land is also constrained by the total amount of available land $Maxland_t$ at each time period $t$ for each scenario $s$ based on Equation 4.4 to ensure that it does not exceed its available amount.

Integrated biorefining process model: The mass balance is performed for each node in the conversion chain of the integrated biorefinery; these nodes include pretreatment, hydrolysis, fermentation, product recovery, and product sales in end-use markets. These material balances should take into account the theoretical yield and the actual yield to adjust the theoretical amount to an actual yield which can be obtained from each of unit operations. The material balance is given by:

$$\text{SystemInput}_{eqp,t,s} \times YLD_{eqp,t}^{theoretical} \times YLD_{eqp,t}^{actual} = \text{SystemOutput}_{eqp,t,s} \quad (4.5)$$

Here, $\text{SystemInput}_{eqp,t,s}$ is the input to the unit operation $eqp$ (nodes in the conversion chain) at time period $t$ for scenario $s$, $YLD_{eqp,t}^{theoretical}$ is the theoretical amount of product that is expected from unit operation $eqp$ at time period $t$, and $YLD_{eqp,t}^{actual}$ is utilized to adjust the amount of product from each unit operation $eqp$ to an actual recoverable amount at time $t$, and $\text{SystemOutput}_{eqp,t,s}$ represents the amount of product of node $eqp$ during time $t$ for scenario $s$. Actual yield, $YLD_{eqp,t}^{actual}$, is the parameter which is used to incorporate the nonlinearities of the process to the MILP formulation of the proposed strategic optimization model by updating its value iteratively based on the results from process simulation in Aspen Plus.
Demand constraints are introduced by the following equations to model the sale levels for each product.

\[ Sales_{p,t,s} + PL_{p,t,s} = Product_{p,t,s} + PL_{p,t-1,s} \times (1 - loss_p) \]  

(4.6)

\[ Sales_{p,t,s} \geq CSL \times Demand_{p,t,s} \]  

(4.7)

\[ Sales_{p,t,s} \leq Demand_{p,t,s} \]  

(4.8)

Equation 4.6 is the material balance for the flow of final products to end-use markets. Where \( Sales_{p,t,s} \) is the amount of product \( p \) sold to the market during time \( t \) for scenario \( s \), \( PL_{p,t,s} \) represents the inventory of product \( p \) at time \( t \) for scenario \( s \) which is maintained on site, losses during product inventories are considered by defining the term \( loss_p \). It is assumed that at each time period, a certain percentage of demand \( Demand_{p,t,s} \) has to be satisfied based on the customer service level \( CSL \) (Equation 4.7). Sales are further constrained by the maximum demand that is available to be fulfilled at each time period \( t \) and scenario \( s \) (Equation 4.8).

Flexible design of capacity: Flexible designs can add great improvements in overall expected benefits by enabling the managers to adjust to new circumstances and flexible adaption to a long-term market development. They can avoid bad circumstances for unfavorable future and when the future offers new opportunities, flexibility in design will enable them to take advantage and benefit from those possibilities. In the proposed framework a flexible capacity design is incorporated based on the following equations.
Equation 4.9 provides bounds to capacity expansion ($Cap_{eqpt,s}$) of each operating system ($eqp$) at time period $t$ and scenario $s$, where $BVCl_{eqpt,s}$ is the capacity increment binary variable of operating system $eqp$ at time period $t$ for scenario $s$ which is 1 when capacity is incremented and 0 otherwise. Constraint in Equation 4.10 ensures that total established capacity of each operating system $Cap_{eqpt,s}$ for each time period and each scenario is sufficiently large to satisfy the input to that operating system $SystemInput_{eqpt,s}$. Equation 4.11 is used to update the processing capacity $Cap_{eqpt,s}$ of each operating system, adjusting for a construction delay ($CD$) of 2 years. Construction delay term is utilized to force the optimizer that no production can occur while the facility is under construction. Optimized capacity plan is then passed on to the process simulator (Aspen Plus) and the process optimizer (Matlab) in order to determine optimal operating conditions.

Financial model: The financial model is broken into 3 salient aspects that describe the financial impact of network design, production of final products, and sales:

6. Market model
7. Calculation of capital costs, operating expenses and revenues
8. Calculation (optimization) of the objective function (Net Present Value)

**Market model:** Market model describes price and demand evolution of the products in the integrated biorefinery. We assume that market of bioproducts is impacted primarily by oil prices since oil is the primary determinant of alternative transportation fuel markets. The price of crude oil is represented as a stochastic input following Geometric Brownian Motion (GBM), based upon which the bioproduct market parameters are derived, yielding stochastic price-demand sets. GBM assumption implies a high degree of volatility in predicted prices and embeds a high level of uncertainty. Since stochastic variables following GBM are log-normally distributed, oil prices can be represented by a continuous lognormal distribution characterized by the expected value and standard deviation at any time. Natural logarithm of the oil price has the standard deviation of $\sqrt{\Delta T}$. Where $\sigma$ indicates the constant volatility in the GBM representation of oil price and $\Delta T$ shows the time interval considered in discretization of the stochastic model.

**Scenario generation:** The most widely employed approach for optimization under uncertainty is the stochastic programming method. A stochastic program is a mathematical program in which some of the parameters defining a problem instance are random. The uncertain parameters are commonly assumed to follow discrete probability distributions and a planning horizon consisting of a fixed number of decision points. Therefore, the stochastic process can be represented with scenario trees. Scenario-based stochastic programming is an approximation approach to transform the intractable stochastic problem into a tractable one. This strategy avoids high-dimensional numerical integration in the solution of the problem, since the expected net present value (objective function) can be calculated as finite sums and each constraint can be duplicated for each scenario. The main idea is to address only a finite number of selected realizations of
uncertainty in the optimization. Each realization is regarded as one scenario and is assigned with a probability. In the proposed framework, average bi-annual crude oil prices can move up or down with a given probability from the current time period to the next, yielding a Markov chain based decision tree. Each node in the decision tree is represented as a price scenario for crude oil (and consequently for bioproduct markets) and over the 7 time periods this yields a total of 64 oil price scenarios.

Binomial lattice generation approach which was suggested by Cox et al. (1979) is utilized to discretise the continuous stochastic model of oil price. A binomial lattice can be thought of as a time-varying probability tree. The stochastic variables are assumed to move up or down sequentially over time with estimated probabilities \( p^{up} \) and \( p^{down} \) obtained by the following equations:

\[
\begin{align*}
    u &= e^{\sigma \sqrt{T}}, \quad d = \frac{1}{u} \\
    p^{up} &= \frac{e^{r \sqrt{T}} - d}{u - d}, \quad p^{down} = 1 - p^{up}
\end{align*}
\]

Here, \( u \) and \( d \) represent up and down movements in oil price and \( r \) is the risk-free discount rate equal to the yield on a 10-year treasury bond. The process for discretizing the stochastic variable is presented in Figure 4.3.
Calculation of the price and the demand of products (ethanol and succinic acid) is derived from the hypothetical market model proposed in the previously published journal paper (Sharma, Romagnoli, et al., 2013); a simplified diagram of this model is presented in Figure 4.4 and its salient components are discussed here to give the readers a feel for the model structure.

Figure 4.4: Simplified market model for evolution of price and demand in product
GDP growth and inflation rates are derived by using stochastic oil price model as a proxy for the state of the economy in macroeconomic model. Liquid ethanol commodity market is determined by different market forces including oil price, RFS mandates, and macroeconomic factors such as GDP growth, interest rates, and inflation rates (Luchansky & Monks, 2009; Rask, 1998). For forecasting long term trends in the proposed biobased succinic acid market, certain qualitative assumptions are considered. It assumes that succinic acid will serve markets that are currently served by petroleum derivatives. Furthermore, marginal cost of production, environmental premium, and supply-demand balance are the other factors which have significant impact in determination of the dynamic market trend in the future. It should be noted that the utilization of the hypothetical market model proposed by Sharma, Romagnoli, et al. (2013) is purely with demonstrative motive to incorporate a fundamentally derived predictive model for value estimation of uncertain parameters in dynamic market to the development of our comprehensive optimization framework.

Capital cost, operating expenses and revenue calculation: Capital cost (Capex) calculation during each time period for each scenario includes land establishment cost for biomass production, equipment cost for processing biomass, construction and engineering cost, legal and permitting cost, contingency cost, and working capital investment as shown in Equation 4.14. The methodology for capital cost structure is adapted from Kazi et al. (2010) that exemplifies NREL’s nth plant cost analysis.

\[
\text{Capex}_{t,s} = \text{Capex}^{\text{land}}_{t,s} + \text{Capex}^{\text{tot,eqp}}_{t-1,s} + \text{Capex}^{\text{C&E}}_{t-CD,s} + \text{Capex}^{\text{Cont}}_{t,s} + \text{Capex}^{\text{LP}}_{t,s} + \text{Capex}^{\text{WC}}_{t,s}
\]  (4.14)
Since Net Present Value calculation (objective function) gives explicit consideration to the time value of money, charges considered in the capital cost calculation are distributed over the construction period \((CD)\) instead of being charged all at once so as to minimize the present value of costs. Construction, engineering, contingency, and working capital costs are calculated as a percentage of total equipment and established land costs at each time period \(t\). Cost of each equipment is calculated based on the linear approximated equation represented in Equation 4.15 (Sharma, Vlosky, et al., 2013). It is worth mentioning that \(Capex_{eqp}^{t,s}\) equals to zero if the binary variable for the capacity expansion of that equipment, \(BVCI_{eqp,t,s}\), is zero because of constraints 4.9 and 4.15 which means that capacity is not expanded at that specific time period.

\[
Capex_{eqp}^{t,s} = BVCI_{eqp,t,s} \times FC_{eqp} + CapExp_{eqp,t,s} \times VC_{eqp}
\]  \hspace{1cm} (4.15)

Operating cost \((Opex)\) at time period \(t\) for scenario \(s\) is the summation of feedstock harvesting cost, process chemical costs, utility cost, other ancillary raw materials, labor costs, and selling, general and administrative costs. These costs are described by the following equation:

\[
Opex_{t,s} = C_{t,s}^{HVST} + C_{t,s}^{chemical} + C_{t,s}^{utility} + C_{t,s}^{other} + C_{t,s}^{labor} + C_{t,s}^{SGA}
\]  \hspace{1cm} (4.16)

Revenues are generated from the sale of products at forecasted product prices as shown in Equation 4.17.

\[
Revenue_{t,s} = \sum_p (Sales_{p,t,s} \times Price_{p,t,s})
\]  \hspace{1cm} (4.17)
Objective function: Following the calculation of costs and revenues, free cash flow ($FCF$) of the enterprise which is a measure for financial performance is calculated as the difference between operating cash flows and capital expenditures. Net present value of the enterprise is calculated as the sum of a time series of free cash flows that have been discounted back to the present for the whole planning horizon as shown in the following equations.

$$NPV_s = \sum_{t=1}^{T_L} \frac{FCF_{t,s}}{(1+ir)^t}$$

Here $ir$ represents the discount rate (or annual rate of return), and $T_L$ is the project lifetime. Since we are dealing with uncertain future, the value of the process is not a fixed number but an expectation over a range of possible futures that follows a discrete probability function. We can think of it as an average value over a range of good and bad outcomes. The expected NPV (Equation 4.19) is considered as the objective of our strategic optimization model to be maximized.

$$E[NPV] = \sum_s (P_s \times NPV_s)$$

Where, $NPV_s$ is the net present value corresponding to the realization of each scenario $s$, and $P_s$ is the probability of occurrence of such scenario.

Risk management model: In the stochastic programming model, optimal solution is obtained by maximizing the total expected net present value which is optimal on average for all the scenarios. The expected value of NPV is a risk-neutral objective and does not reflect the variability of performances associated with each specific scenario. Therefore, there is no guarantee that the process will perform at a certain level over all the uncertain parameter space.
The only guarantee is that the average value of objective function is optimized. However, in any decision under risk, expected profit is not the only objective. Management is also concerned about the risk involved in the model. The trade-off between financial risk and profitability of the plant should be incorporated to the stochastic programming formulation. Therefore, a two criteria approach is considered which profitability (NPV) and a specific risk metric are the objectives to be optimized. Different criteria for assessing the variability of performance (risk measures) have been proposed in the literature (Eppen et al., 1989; Gebreslassie et al., 2012; You et al., 2009). In this study, downside risk method proposed by Eppen et al. (1989) is introduced to the model as the risk management strategy.

**Downside Risk management:** In this approach the risk associated with scenarios whose profits are not desirable is minimized. As shown in Figure 4.5, downside risk is calculated based on the area underneath the curve of probability function which has lower profitability than the defined threshold ($\pi$). To introduce the risk in the framework, a positive variable $\delta_s$ which is the deviation between the NPV of each scenario and the defined threshold is considered based on the following constraint.

$$\delta_s \geq \pi - \text{NPV}_s, \quad \delta_s \geq 0$$  \hspace{1cm} (4.20)

These inequalities indicate that when the NPV of a scenario is higher than the target value $\pi$, $\delta_s$ equals to zero, and when NPV is lower than the target value, it equals to their difference. Therefore, downside risk is calculated as the expected value of positive deviations from the defined target $\pi$ based on the following equation:
Addition of downside risk management in the framework results in a multi-objective problem including two conflicting objective functions (maximizing expected NPV and minimizing the financial risk). The ε-Constraint method is utilized in our formulation for solving the multi-objective optimization model. This optimization method is based on formulating an auxiliary model by transferring one of the objectives of the original problem to the constraint (Mavrotas, 2009). One of the advantages of the downside risk management strategy is avoiding...
the need to define binary variables since a continuous linear measure as shown in Equation 4.20 is utilized to quantify the risk.

4.4.2 Operational level modelling and optimization

After obtaining the capacity plan which is designed strategically by maximizing the expected NPV of the plant, this capacity is utilized in the operational level model for rigorous nonlinear process simulation and optimization. First the process is simulated in the simulation software (Aspen Plus) and results from simulation are utilized in the optimization model implemented in MATLAB to maximize the profitability of the process. This strategy will be performed iteratively until the convergence criterion is met.

Process simulation: Simulation of the technological configuration was carried out using Aspen Plus with the optimal capacity plan obtained from strategic optimization. Main input data utilized for process simulation in bioethanol production are obtained from Humbird et al. (2011), Kazi et al. (2010), and Aden et al. (2002), and for succinic acid fermentation and purification the process data are based on the developed models of Vlysidis et al. (2011) and Li et al. (2010). Part of the physical property data of the components required for simulation were obtained from Wooley and Putsche (1996). One of the characteristics of our approach is the incorporation of the complex kinetics of bio-reactions in our simulation model. Due to the complexity of energy production process networks, modification to one unit operation at one location may propagate through the network and its feedback loops which will result in unforeseen consequences in the plant. An iterative dynamic data exchange between process simulation model in Aspen Plus and developed kinetic models in Matlab (Geraili et al., 2014b) is embedded as part of the process simulation. Developed mathematical formulations for the kinetics are based on the validated models by Kadam et al. (2004) for enzymatic hydrolysis, model by Morales-Rodriguez et al.
(2011) for simultaneous hydrolysis and co-fermentation of ethanol, and the developed model by Song et al. (2008) for succinic acid fermentation.

Process optimization: Due to the complexities involved in biorefining processes including inherently nonlinear conversion mechanism, mathematical modeling of the process will comprise of non-convex functions. Although deterministic methods are relatively fast, they might get trapped in local optima. Stochastic methods are more suitable for solving these types of problems, since a wide range of values for parameters would be searched. Furthermore, for solving large scale nonlinear optimization problems deterministically, constraints should be incorporated into the objective function. However, in many practical large-scale applications, models embedded in the simulation environments are used to mimic complex processes behavior (Robertson et al., 2014). In our case study all the mass and energy balances are embedded in the simulation and constraints are satisfied when the simulation is converged. Stochastic approaches can overcome this problem as they do not require the manipulation of the mathematical structure of the objective function and constraints (Mariano et al., 2011).

There are numerous operating conditions which can affect the production cost and profitability of the biorefinery. The parameters which have significant effect on the plant’s profitability were identified in our previously published paper (Geraili et al., 2014b), which are related to the hydrolysis of feedstock and fermentation of sugars. Enzyme loading, pretreated biomass allocation and hydrolysis temperature have a complex set of impacts and can considerably affect the process yields as well as production costs and revenues of the plant. The optimization objective used here is to maximize the annual cash flow of the process (Equation 4.22), which takes into account the revenues generated from the sale of products, the direct cost of raw materials and the annual fixed costs.
Here, \( P_p \) represents the production of each product \( p \) including ethanol, succinic acid, and excess electricity, and \( RM_{r,p} \) is the amount of raw material type \( r \) utilized for the production of product \( p \), and annual fixed costs, \( FC \), includes the labor, maintenance and transportation costs. Selected production capacity plan in strategic optimization is incorporated as constraints during process optimization to control the production rates, Equation 4.23. These inequality constraints are handled by exploiting the penalty function approach. In this approach, modified objective function (penalized objective), \( OBJ(\bar{x}) \), is defined as sum of the original objective, \( \text{obj}(\bar{x}) \), and a penalty term, \( g_j(\bar{x}) \), which depends on the constraint violation (Equation 4.24). Here, \( R_j \) is the penalty coefficient of the \( j \)th inequality constraint to make it of the same order of magnitude as the original objective function.

\[
P_p^{\text{strategic planning}} \leq P_p^{\text{strategic planning}} \tag{4.23}
\]

\[
OBJ(\bar{x}) = \text{obj}(\bar{x}) + \sum_{j=1}^{l_p}(R_j \times g_j(\bar{x})) \tag{4.24}
\]

To solve the operational level optimization problem, differential evolution algorithm (DE), which is a stochastic optimization method, is selected and written in MATLAB. This algorithm is simple in concept and can be easily implemented. Table 4.1 provides the DE parameters utilized in this study. To facilitate the automation of process simulation and optimization, DE algorithm in MATLAB is linked with the simulation in Aspen Plus simulator.
In this section, the results for optimal strategic and operational level decisions of the multiproduct biorefinery are discussed based on the proposed decision making framework. The decision variables considered in the framework are composed of the optimal capacity plan for long term production in biorefinery, optimal temperature for enzymatic hydrolysis, optimal enzyme amount utilized in hydrolysis reaction and optimal allocation of pretreated biomass for production of final products. To illustrate the effectiveness of the proposed strategy, different case studies are considered including: Base case, stochastic model, and stochastic model coupled with risk management model.

Base case is considered as a deterministic model and all the economic parameters are fixed through the planning horizon. The economic parameters used for this case study are the same with those in Sharma, Vlosky, et al. (2013) and Geraili et al. (2014a). Stochastic model considers the variability in the market that is inherent in real world; thus, stochastic formulation based on scenario generation is developed for strategic optimization. Finally, the third case study is an extension of the stochastic model by incorporating financial risk through downside risk

<table>
<thead>
<tr>
<th>Parameters/operators</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum number of function evaluation</td>
<td>1000</td>
</tr>
<tr>
<td>Population size</td>
<td>30</td>
</tr>
<tr>
<td>Weighing coefficient</td>
<td>0.8</td>
</tr>
<tr>
<td>Crossover rate</td>
<td>0.9</td>
</tr>
<tr>
<td>Penalty coefficient (R_f)</td>
<td>100000</td>
</tr>
</tbody>
</table>

4.5. Results and Discussion

In this section, the results for optimal strategic and operational level decisions of the multiproduct biorefinery are discussed based on the proposed decision making framework. The decision variables considered in the framework are composed of the optimal capacity plan for long term production in biorefinery, optimal temperature for enzymatic hydrolysis, optimal enzyme amount utilized in hydrolysis reaction and optimal allocation of pretreated biomass for production of final products. To illustrate the effectiveness of the proposed strategy, different case studies are considered including: Base case, stochastic model, and stochastic model coupled with risk management model.
management. A multi-objective optimization model is implemented to establish the tradeoffs between cost and risk. Plant life time considered for all the case studies is 14 years with an annual discount rate of 10%.

Figure 4.6: Histogram of the NPVs for the stochastic programming model

Base on the results of the MILP model for the strategic optimization which is implemented in the modeling system GAMS and solved with a CPLEX linear solver, optimal values of the decision variables are calculated. Since the main focus of this work is to expand the scope of our proposed framework by incorporating uncertainty into the model, results for the deterministic model (base case) are presented in Table 4-2 for the comparison purposes, and detailed analysis of the results for stochastic programming model are presented as follows.

The expected NPV of the stochastic solution is 62.8 $MM which indicates that value is created through enterprise activities and it is a profitable project investment. Figure 4.6 illustrates a wide range of values for calculated NPVs of different scenarios considered in the model which represent the influence of market variability in the optimization of strategic model. Results in
Table 4-2 show that a higher profitability (NPV) is obtained by the stochastic model which is 44% higher than deterministic solution. We can also see that feedstock processing capacity of the plant also increases 40% in comparison to the deterministic model and more sugar is allocated to succinic acid production. Currently, the market volume of succinic acid is relatively small due to the nascent stage of its market. However, with its high-value applications, product acceptance and diffusion, application market of bio-based succinic acid has the potential to improve fast over the planning horizon and this market growth is taken into account in the stochastic model.

Table 4-2: Comparison of base case and stochastic model

<table>
<thead>
<tr>
<th></th>
<th>Feedstock capacity (1000 ton/yr)</th>
<th>Sugar allocation ratio (for ethanol production)</th>
<th>Ethanol production (MM gal)</th>
<th>Succinic acid production (1000 ton)</th>
<th>Net present value ($MM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base case</strong></td>
<td>155.0</td>
<td>0.66</td>
<td>7.1</td>
<td>4.00</td>
<td>45.0</td>
</tr>
<tr>
<td><strong>Stochastic case</strong></td>
<td>218.0</td>
<td>0.62</td>
<td>11.1</td>
<td>6.00</td>
<td>62.8</td>
</tr>
</tbody>
</table>

Expected amount of biomass utilized in each time period is illustrated in Figure 4.7. As is shown in this figure, in the first time period there is no production due to the introduced growth delay functionality in the mathematical formulation (\(GD = 2\) years) of biomass harvesting, and there is a growth in the expected amount of harvested biomass due to the additional capacities established in the plant and also the developments in the market parameters during the planning horizon which are explained in more detail as follows.
Figure 4.7: Biomass utilization

Figure 4.8 depicts the allocation of pretreated biomass to ethanol and succinic acid production that is obtained as a result of model optimization. Additionally, the expected production trends of ethanol and succinic acid over the planning horizon are represented in this figure. Demand, production rates, and sugar allocation are presented based on the expected values of all the considered scenarios in each time period.

Succinic acid sales follow the demand growth while ethanol market share decreases with increase in demand. It is apparent that succinic acid market provides the greatest opportunity for profitability and it can be enhanced if larger volumes of succinic acid can be sold into the market. In fact, ethanol is considered as the high-volume fuel that maintains healthy bottom-line while succinic acid is considered as a high margin chemical to improve overall margins. Furthermore, allocation of pretreated biomass to ethanol production increased over the planning horizon possibly because of additional capacity installed for ethanol production.
Figure 4.8: Ethanol and succinic acid production

To illustrate the expansion in capacity of ethanol production, scenario 36 is taken as the reference scenario which has the closest NPV to the expected total NPV among all scenarios. Figure 4.9 shows that based on the strategic optimization model which utilizes binary variables for capacity expansion constraint in Equation 4.9 to select a setup allowing the best compromise between cost and flexibility, additional capacity for ethanol production is installed during 4th and
5th periods in the planning period before the maximum capacity for ethanol production is reached.

Figure 4.9: Capacity expansion in ethanol recovery section for scenario 36

Figure 4.10 represents the forecasted free cash flow (and its components) that are generated from the operation of the optimal design and the evolution of the cumulative expected NPV of the enterprise. The expected NPV is broken up into two major components: the discounted value of expected operating cash flow (ECFO) which is calculated based on the value of plant operation, and the discounted value of expected capital investment made in the plant (ECAPEX). We notice that the project payback period is 10 years which is not desirable for investment. One of the financial strategies that can be investigated to shorten the payback period for biorefinery project investments is to incorporate more profitable product portfolio comprising of higher margin, lower volume specialty products such as pharmaceuticals. Techno-economic modeling and analysis of different product portfolios is an area we are actively pursuing at the PSE group at LSU.
The major biomass capacity investments are made during the first period; however, as mentioned earlier, the charges are distributed over the planning horizon to mitigate the present value of the costs. Succinic acid production capacity is established at the beginning while two increments are made for ethanol recovery capacity in the 4th and 5th time periods and additional capital costs are incurred due to the capacity investments.

![Figure 4.10: Free cash flow components and the evolution of the optimal expected NPV](image)

Iterative results of the hybrid optimization methodology are presented in Table 4-3 which shows that in two iterations the model is converged. Initial process yields are obtained from literature (step1); then these yields are utilized in strategic model to calculate the production capacity plan (step2); the optimal values for the capacity are passed to the process level simulation and optimization to find the optimal process conditions and calculate the process yields based on the results of simulation (step3). These calculated yields are compared with the
initial values used in the strategic model to check the convergence. Since the difference between calculated yields and initial yield values is greater than the threshold, this hybrid optimization needs to be carried out again based on the new yield values.

Table 4-3: Iteration results in hybrid optimization strategy

<table>
<thead>
<tr>
<th>Parameters and Variables</th>
<th>Iteration 1</th>
<th>Iteration 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Step 1</td>
<td>Step 2</td>
</tr>
<tr>
<td>Feedstock (1000 ton/yr)</td>
<td>--</td>
<td>222.2</td>
</tr>
<tr>
<td>Ethanol (MM gal/yr)</td>
<td>--</td>
<td>15.3</td>
</tr>
<tr>
<td>Succinic Acid (1000 ton/yr)</td>
<td>--</td>
<td>6.0</td>
</tr>
<tr>
<td>Sugar (kg / kg)</td>
<td>0.87</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Fermentation</td>
<td>0.85</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Fermentation</td>
<td>0.25</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Purification</td>
<td>0.99</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Purification</td>
<td>0.78</td>
<td>--</td>
</tr>
</tbody>
</table>

Values of the decision variables obtained from the hybrid optimization model are shown in Table 4-4. The convergence behavior of the proposed optimization algorithm is also plotted in Figure 4.11. It can be seen that the convergence is steady and stable.

Table 4-4: Optimal values for decision variables and objective function

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>33.55 °C</td>
</tr>
<tr>
<td>Sugar allocation</td>
<td>0.62 (ethanol), 0.38 (succinic acid)</td>
</tr>
<tr>
<td>Enzyme loading ratio</td>
<td>34.8  (g enzyme/ Kg Cellulose)</td>
</tr>
<tr>
<td>Cash flow</td>
<td>$71 million per year</td>
</tr>
</tbody>
</table>
Results for managing the downside risk: The impact of the proposed risk management procedure is presented in Figure 4.12 and Table 4-5. In the calculation of the downside risk, the target level $\pi$ is set to 51 $\text{SMM}$. We can see that how the risk management approach reconstructed the NPV distribution of the scenarios to reduce the risk of occurrence of unfavorable scenarios while maintaining an acceptable expected revenue. As expected, the results from multi-objective optimization model reveal that there is a conflict between the two objectives, economic performance and financial risk. As shown in Table 4-5, a reduction of the downside risk can be attained at the expense of a reduction in the expected net present value (economic objective) of the process.

Another interesting result as can be observed in Table 4-5 is that the minimization of the downside risk leads to allocation of more sugar to succinic acid production. Note that succinic
acid is considered as a promising co-product to improve the economics of industrial fermentation; consequently, allocation of more sugar to succinic acid production will make the optimal solution less sensitive to the fluctuations in the price and demand of the products. Additionally, reduction in the financial risk of the process leads to a reduction in the expected biomass processing capacity of the plant as shown in Table 4-5. Incorporation of the risk in the optimization framework will tend to give more conservative design which means although the capacity of the plant has decreased, net present value of scenarios have much higher chances to be between the desired target. This leads to a more robust behavior of the framework in the face of uncertainty.

Figure 4.12: Comparison of cost distribution before and after risk management

Table 4-5: Comparison of feedstock and production capacities before and after risk management

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Expected NPV ($MM)</th>
<th>Downside risk</th>
<th>Feedstock Capacity (1000 tons/yr)</th>
<th>Sugar allocation ratio (for ethanol production)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stochastic case</td>
<td>62.8</td>
<td>10%</td>
<td>218</td>
<td>0.62</td>
</tr>
<tr>
<td>Risk management case</td>
<td>60.0</td>
<td>3%</td>
<td>152</td>
<td>0.59</td>
</tr>
</tbody>
</table>

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4.6. Conclusion

The methodology proposed in this article provides a comprehensive and flexible framework within which different aspects of sustainability are considered to yield a full-fledged decision support and analysis system. This algorithm has the advantage of integrating long term planning with operational level decisions. Furthermore, scenario analysis is conducted to incorporate uncertainty of market parameters in the framework and downside risk management is appended to the strategic model to control the variability of performance and incorporate the tradeoff between risk and profitability of the plant within the decision making process. An integrated multi-product lignocellulosic biorefinery producing value-added biofuels (ethanol) and biobased chemicals (succinic acid) has been presented to show the capabilities of the proposed approach.

The analysis of the results from stochastic formulation reveal that considering uncertainty will provide results that reflect the variation of market parameters and behave better than the deterministic model (yielding better expected NPV). Additionally, incorporating metrics for financial risk mitigation in the framework shows that there are two important factors that influence the performance of the model in the face of uncertainty including production capacity and allocation of pretreated biomass between ethanol and succinic acid production. The outcome of this work is a new distributed decision support framework which is intended to help economic development agencies, as well as policy makers in the renewable energy enterprises to carefully evaluate and plan investment and operating decisions before execution.
4.7. References


5.1. Introduction

Driven by the increase in industrialization and population, the global demand for energy is steadily growing. Since the world primary sources for energy and chemicals are fossil fuels, this growth raises important issues at environmental, economic, and social levels. In recent years there has been a marked surge in the search for alternative sources of energy that wean the world off of dependence on fossil fuels and reduce the carbon foot-print. As the world has recognized the importance of diversifying its energy resource portfolio away from fossil resources and more towards renewable resources such as biomass, there arises a need for developing strategies which can design renewable sustainable value chains that can be scaled up efficiently and provide tangible net environmental benefits from energy utilization.

The improvement of renewable energy technologies will assist sustainable development and provide a solution to several energy related environmental problems. The biorefinery concept embraces a wide range of technologies able to separate biomass resources (wood, grasses, corn, corn stover, etc.) into their building blocks which can be converted to value-added products. After a boom in U.S. corn-based ethanol in the early part of the 21st century, the interest has gradually shifted towards more viable sources for production of biofuels and biochemicals. Second generation biofuels are examples of such fuels that are extremely attractive owing to the fact that the raw materials can be composed completely of “left-over” wastes of food crops and forest harvests that don't interfere with the human food chain and the natural ecosystem. It also can provide new income and employment opportunities in rural areas (Naik et al., 2010).
Several contributions have appeared over the last few years in order to manage the complexity of decision making process for designing profitable renewable energy production systems. Painuly (2001) developed a multi-phase, stakeholder-based approach to identify the barriers to renewable energy penetration and suggested measures to overcome these identified barriers. Banos et al. (2011) presented a review of computational optimization strategies that have been applied to renewable energy production systems. Many of the proposed studies in the literature use deterministic modeling approaches which assume that all the parameters are known in advance (Leduc et al., 2010; Zhang et al., 2013; Zondervan et al., 2011). However, common to early stages of process design is the lack of certain information that will introduce variability and significant risk into the decision-making problem. It is important to provide the decision-maker with as much guidance as possible to support their difficult task of making critical decisions.

Uncertainties are introduced in process design in many ways. Insufficient knowledge about reaction pathways and kinetics contributes to uncertainty just like limited thermodynamic data for chemical components does; lack of experience when performing a scale-up with novel process equipment presents another source of uncertainty; fluctuations in product demand; volatility in prices of feedstock and product, and potential economic risk are also critical and should be taken into account. Some of the decisions that need to be made in the face of uncertainty are related to strategic planning and the others are made during the process design and optimization. Failure to consider these uncertainties may lead to nonoptimal designs and cause significant extra expenses to accommodate unexpected events. Literature reviews have highlighted some of the key uncertainties inherent in integrated biorefining processes (Awudu & Zhang, 2012; Kou & Zhao, 2011).
The significance of uncertainty has prompted a number of researchers to address optimal design of biorefineries in the face of uncertainty. Most of the preliminary work on stochastic optimization of biorefineries only considers one type of uncertainty (such as uncertain product demand or sale price of products) (Dal-Mas et al., 2011; Kostin et al., 2012). However, development of a comprehensive framework which can link these decision-making processes under uncertainty is of critical importance, and interaction and integration between them is required for successful process implementation. A very common measure to account for risk stemming from uncertainty is overdesign. It may be simple solution, but it is a costly one too. Several methods exist for incorporating uncertainty into the decision analysis process which can be classified as either qualitative or quantitative methods.

An example of a qualitative risk analysis method is the SWOT (strengths, weaknesses, opportunities, and threats) approach which is commonly used in strategic planning. It quantifies verbally each aspect of uncertainty under a set of generic, qualitative conditions. On the other hand, quantitative risk analysis uses different numeric scales to categorize the input parameters or the system’s behaviour under certain conditions. It can be divided to deterministic and stochastic methods.

Simplest deterministic method for evaluating the impact of uncertainty is sensitivity analysis. In this approach ranges are used to represent uncertain model parameters. Stochastic risk analysis method is based on the idea of assigning a probability distribution to each uncertain model parameter. Uncertain parameters are represented as random variables. The challenge is to choose good probabilistic distributions. A good knowledge of the process and availability of historical data helps the decision maker to define accurate distributions. There are also other
approaches in uncertainty modelling which are reviewed in the work by Sahinidis (2004) and fundamental differences of them are explained in detail.

In previous chapter, the development of systematic optimization framework for biorefining processes under uncertainty was explained which focused on one type of uncertainty (market uncertainty). In this study we present an extension to the proposed framework by developing a multi-layered decision support tool that can be utilized by energy entrepreneurs, resource and technology investors in the renewable energy industry to carefully design and optimize the business value of their energy endeavors considering all types of uncertainties including uncertainties in strategic and operational levels. A structural approach is utilized for planning the production capacity, simulation of the process in detail, and optimizing the operating condition of the plant. First stochastic linear model is developed to optimize production capacity for the desired planning horizon and then process simulation coupled with stochastic optimization algorithm is employed to optimize the operating condition of the plant. Monte-carlo based simulation and global sensitivity analysis are utilized to identify the most critical parameters and optimize the operating conditions of the plant. Global sensitivity analysis gives insight into the bottlenecks in the process and quantifies the uncertainty due to technological risks. Product demand and price uncertainties are taken into account at the strategic planning level, and uncertainties related to parameters characterizing the processing technologies are addressed in operational level optimization. To demonstrate the effectiveness of the proposed methodology, a hypothetical case study of a multiproduct lignocellulosic biorefinery based on sugar conversion platform is utilized.
5.2. Design of decision support framework

Linear programming (LP) models are suggested for the purpose of strategic planning. To overcome the mismatch between nonlinear process mechanisms (due to complex kinetic and thermodynamic models in energy systems) and LP-based strategic optimization, a decomposition strategy is proposed that combines net present value (NPV) optimization for long term planning with rigorous non-linear process simulation and process-level optimization. In the strategic layer, different scenarios are developed based on stochastic forecasts for uncertain market parameters including price and demand of bioproducts. The process is formulated as a stochastic mixed integer linear programming (MILP) model which incorporates stepwise capacity expansion by defining binary variables in the formulation of the model. To control and manage the financial risk associated with uncertain market parameters at the optimal design of production capacity, downside risk management proposed by (Eppen et al., 1989) is introduced to the model. Downside risk approach is adopted because it is a consistent measure of risk with good mathematical properties which enable efficient optimization by means of linear programming techniques. The output of the model includes optimal design of production capacity of the plant for the planning horizon by maximizing the expected net present value (NPV) and minimizing the financial risk.

The results are then fed to the second stage of the optimization algorithm. The second stage, which optimizes the operating conditions of the plant, consists of three main steps including simulation of the process in the simulation software (nonlinear modeling), identification of critical sources of uncertainties through global sensitivity analysis affecting selected performance criteria, and employing stochastic optimization methodologies to optimize the operating condition of the plant under uncertainty. Figure 5.1 shows a general schematic
structure of the proposed iterative decision support strategy. The iterative process is used to obtain a piecewise linear approximation of the nonlinear reaction- and thermo-dynamics; the nonlinear dynamics are simulated and their linear approximations are used during strategic planning and optimization. Each component of the proposed algorithm is described in more detail in section 5.3.

Figure 5.1: Framework for operational level optimization under uncertainty
5.3. Framework details

In this section each component of the proposed framework (Figure 5.1) is described in some detail. While the description of the framework is based on the design of the case study presented in Section 5.4, each component, and the framework, can readily be adapted to other energy value chains.

5.3.1. Strategic model

Strategic model is formulated as a mixed integer stochastic linear programming model with a 14-year planning horizon and bi-annual time steps. The mathematical formulation is broken into sub-models for ease of description which include a production model, financial model, uncertainty characterization and risk management model.

Figure 5.2: The structure of the proposed strategic decision-making model under uncertainty
Mathematical formulation and detailed explanation of each sub-model in strategic planning has been presented in the previous chapter (chapter 4, section 4.4.1). A schematic representation of the strategic planning layer is given in Figure 5.2.

5.3.2. Operational level model

After obtaining the capacity plan which is designed strategically, this optimal capacity is utilized in the operational level model for rigorous nonlinear process simulation and optimization. Process simulation and optimization will be performed iteratively until the convergence criteria are met. The systematic operational layer optimization model consists of several sub-steps which guide the user in solving a stochastic optimization problem in the face of uncertainty. The framework includes a number of methods and tools such as process simulation in Aspen Plus, global sensitivity analysis and Monte Carlo based stochastic optimization. Figure 5.3 represents the proposed strategy for the operational level optimization.

![Figure 5.3: Operational level optimization strategy](image-url)
5.3.2.1. Process simulation and modeling: By simulating the entire model in Aspen Plus, the implicit correlations between upstream and downstream stages of the process are taken into consideration. Additionally, based on the architecture that was developed in previous chapters, complex kinetics of bio-reactions is also incorporated in the simulation model that imparts a greater degree of realism to the actual representation of the process. The incorporation of kinetics in simulation is based on dynamic data exchange between Aspen Plus and complex kinetic models of biological reactions implemented in Matlab (Geraili et al., 2014).

5.3.2.2. Sensitivity analysis: Then, the Sobol global sensitivity method (Sobol, 2001), a variance–based Monte-Carlo technique, is used to reduce the complexity of the stochastic optimization problem in operational level by focusing only on the parameters which are most influential on the output of the process model. Sensitivity analysis is a general concept which aims to quantify the variations of an output parameter of a system with respect to changes to some input parameters. The global sensitivity analysis focuses on the pattern of change in model output due to change in model input parameters over a potential variation range of parameter value rather than a single parameter value. Consequently, this analysis is able to show the relative importance of individual model input parameters more reasonably as compared with the local sensitivity analysis.

The sobol sensitivity analysis model can be represented in the form of

\[ Y = f(x_1, x_2, \ldots, x_k) \]

where \( x_1, x_2, \ldots, x_k \) are input factors and \( Y \) is the model output. The total variance of \( Y \) is calculated as follows:
\[ V(Y) = \sum_{i=1}^{k} V_i + \sum_{1 \leq i < j \leq k} V_{ij} + \cdots + V_{1,2\ldots k} \]  

(5.1)

\[ V(Y) \] is the total variance of the output variable \( Y \), \( V_i \) measures the main effect of the parameter \( x_i \), and the other terms measure the interaction effects. Decomposition of Eq.(1) yields two types of sensitivity indices are:

\[ S_i = \frac{V_i}{V(Y)} \]  

(5.2)

\[ S_{T_i} = 1 - \frac{V_{-i}}{V(Y)} \]  

(5.3)

\( S_i \) is the first order sensitivity index for the \( i \)th parameter. This index represents the main effect of parameter \( x_i \) on the output variable \( Y \) and measures the variance reduction that would be achieved by fixing that parameter. The values calculated for first order sensitivity can be used to rank individual parameters importance on the basis of contribution to the variance of \( Y \). This is called Factor Prioritization (FP) setting (Saltelli et al., 2000).

\( S_{T_i} \) is the total sensitivity index for the \( i \)th parameter and is the sum of all the effects involving parameter \( x_i \). The parameter \( V_{-i} \) is the sum of all variance terms that do not include the index \( i \). The index \( S_{T_i} \) takes into account the interactions between the \( i \)th parameter and the other parameters. The total sensitivity index can be thought as the expected fraction of variance that would be left if only the parameter \( x_i \) were to stay undetermined. \( S_{T_i} \) can be used for model reduction purposes; this is called Factor Fixing (FF) setting (Saltelli et al., 2000).

The sensitivity indices can be computed using a Monte Carlo method by generating random samples of parameters within the defined range for each of them followed by estimation of \( V(Y), V_i, V_{-i} \) based on the following procedure:
1) Select the sample dimension \((N)\).

2) Generate two random sample matrices \(M_1\) and \(M_2\) of dimension \(N \times K\).

3) Define a matrix \(N_i\) formed by all columns of \(M_2\) except the \(i\)th column which is taken from \(M_1\), and a matrix \(N_{Ti}\) complementary to \(N_i\) formed with \(i\)th column of \(M_1\) and with all the remaining columns of \(M_2\).

4) Compute the model outputs which will be column vectors \((N \times 1)\) for the sample matrices \(M_1, N_i, N_{Ti}\); resulting column vectors are:
\[
Y = f(M_1), \quad Y' = f(N_i), \quad Y''_i = f(N_{Ti})
\]

5) Then the sensitivity indices are calculated based on the scalar products of the above vectors:
\[
f_0 = \frac{1}{N} \sum_{j=1}^{N} Y^j \quad (5.4)
\]
\[
V = \frac{1}{N} \sum_{j=1}^{N} (Y'^j)^2 - f_0^2 \quad (5.5)
\]
\[
V_i = \frac{1}{N} \sum_{j=1}^{N} Y^{(j)} Y'^{(j)} - f_0^2 \quad (5.6)
\]
\[
V_i = \frac{1}{N} \sum_{j=1}^{N} Y^{(j)} Y''_i^{(j)} - f_0^2 \quad (5.7)
\]

To apply the Sobol sensitivity analysis method to the proposed case study, the complete set of kinetic parameters characterizing the biological reactions in hydrolysis and fermentation are selected in the list of potential sources of uncertainties. These uncertainties may come from
experimental procedures used to estimate parameter values, measurement accuracy, changes in enzyme and microorganism activities. Table A1 represents the parameters analyzed in this study.

5.3.2.3. Stochastic optimization model: Once sensitivity measures have identified the significant sources of uncertainties in the process, a stochastic optimization algorithm is used to find out the optimal operating conditions with the aim of maximizing the annual cash flow in the plant. The generic mathematical form of the optimization problem is represented in Equation (5.8):

\[
\min Z(x) = c^T x + E_x[f(x, \theta_i)]
\]

Constraints:

\[
h(x) = 0
\] (5.9)

\[
g(x) \leq d_i
\] (5.10)

\[
\theta^L_i \leq \theta_i \leq \theta^U_i
\] (5.11)

The objective function is composed of a deterministic term \(c^T x\), where \(c^T\) represents a constant vector and \(x\) is the vector of decision variables, and an uncertain term \(f(x, \theta_i)\) which is the expected value to represent the uncertainty as a function of the decision variables, \(x\), and uncertain parameters, \(\theta_i\). \(h(x)\) is the vector of quality constraints and \(g(x)\) is the set of inequality constraints.

The proper choice of optimization methodology depends on the complexity of the problem. Although deterministic methods are relatively fast, they might get trapped in local
optima due to the complexities involved in biorefining processes including inherently nonlinear conversion mechanism. Monte Carlo based optimization strategy has the advantage of reducing the tendency to be entrapped in a local optima since the sampling is global rather than local and it avoids the dependency on an assumed set of initial conditions (Gallagher & Sambridge, 1994). Furthermore, for solving large scale nonlinear optimization problems deterministically, constraints should be incorporated into the objective function. However, in many practical large-scale applications, models in simulation environments are used to mimic complex processes behavior (Robertson et al., 2014). Therefore, the modeling equations are embedded in the simulation software and cannot easily be extracted. In our case study the whole biorefinery process is simulated in the simulation software (Aspen Plus). Consequently, all the constraints are satisfied when the simulation is converged. Monte Carlo based optimization strategy can overcome this problem as they do not require the manipulation of the mathematical structure of the objective function and constraints.

The first step in this optimization method is performed by sampling from operating conditions which is formed by a matrix of operating variables. Then a Monte-Carlo simulation is performed using sampling from the important uncertain parameters (identified in sensitivity analysis) space to estimate the uncertainty of model outputs used in the objective function calculation. The results from Monte-Carlo simulation are then evaluated based on statistical techniques (95% confidence interval) in order to identify the optimal operating scenario with high confidence levels. This optimization algorithm is written in MATLAB and directly linked with the Aspen Plus simulator to facilitate the automation of process simulation and optimization.
5.4. Application case study: Lignocellulosic biorefinery

In order to demonstrate the utility of the proposed framework, the aforementioned decision support system is applied to a hypothetical biorefinery that utilizes lignocellulosic feedstock(s) to produce biobased fuels and chemicals. The lignocellulosic biorefinery used in this study is a multiproduct plant that uses a sugar-based fermentation platform (biochemical pathway) as the production route, with 3 products: cellulosic ethanol, biosuccinic acid, and bioelectricity. Switchgrass serves as the selected feedstock for the biorefining process. Although, a number of possible feedstocks can be used to provide lignocellulosic material for conversion, our application assumes a sample feedstock whose chemical composition resembles that of switchgrass. It is also assumed that there is limited land available within a 100 mile radius of the plant which can be used for the production of switchgrass for feedstock to the plant.

The production chain comprises of 6 major processing steps (Figure 5.4): feedstock pretreatment, sugar hydrolysis, sugar fermentation, product purification, heat and power generation, and wastewater treatment. In chapter 3, a procedure to analyse flowsheet configuration of integrated biorefineries was developed and an optimal configuration was obtained by investigating several options in each processing step. In the current study this optimal configuration is fixed and considered as a case study which is composed of:

1. Dilute acid pretreatment to solubilize hemicellulose and lignin and increase the digestibility of cellulose
2. Ammonia conditioning for detoxification of pretreated biomass
3. Simultaneous enzymatic hydrolysis and co-fermentation for ethanol production (SHCF)
4. Separate hydrolysis and fermentation for succinic acid production
5. Ethanol purification using a configuration with distillation columns followed by molecular sieve
6. Solid separation in purification to extract the residual solids
7. Succinic acid recovery using a configuration based on cell filtration followed by crystallization
8. A sequence of anaerobic and aerobic digesters to digest organic materials contained in the waste water from the biorefining process
9. Combined system of combustor, boiler, and turbogenerator for steam and electricity production

Figure 5.4: Block diagram for the multiproduct biorefinery plant

One of the characteristics of our approach is the incorporation of the complex kinetics of bio-reactions in the simulation model. An iterative dynamic data exchange between simulation model in Aspen Plus and developed kinetic models in Matlab (Geraili et al., 2014) is embedded as part of the process simulation. Developed mathematical formulations for the kinetics are based
on the validated models from literature (Kadam et al., 2004; Morales-Rodriguez et al., 2011; Song et al., 2008)

Technological configurations along with capital and operational cost, yield, and energy data for bioethanol production section are obtained from Humbird et al. (2011) and Kazi et al. (2010). For succinic acid production, operational and economic data are obtained from Vlysidis et al. (2011); these are used as starting estimates to begin the iterative optimization process.

5.5. Results and discussion

In this section, the results for optimal strategic and operational level decisions of the multiproduct biorefinery are discussed. The decision variables considered in the framework are composed of the optimal capacity plan for long term production in biorefinery, optimal temperature for enzymatic hydrolysis, optimal enzyme amount utilized in hydrolysis reaction and optimal allocation of pretreated biomass for production of final products. Additionally, uncertain parameters in operation of the plant are analysed through global sensitivity analysis to find the most influential ones and reduce the complexity of stochastic optimization model. Plant life time considered in this study is 14 years with an annual discount rate of 10%.

Results of the stochastic MILP model for the strategic optimization which is implemented in the modeling system GAMS and solved with a CPLEX linear solver are shown in Table 5-1. Two different cases are considered to illustrate the impact of the proposed risk management procedure. In one case, the stochastic model is solved just by maximizing the expected NPV (single objective, risk-neutral) and for the other case the stochastic model is solved by introducing financial risk management model and considering the tradeoff between financial risk and profitability of the plant (Multi-objective). As expected, the results from multi-objective
optimization model reveal that there is a conflict between the two objectives, economic performance and financial risk.

As shown in Table 5-1, a reduction of the downside risk can be attained in the expense of a reduction in the expected net present value (economic objective) of the process. Figure 5.5 illustrates a wide range of values for the calculated NPVs of these two considered scenarios which represent the influence of market variability in the optimization of strategic model. Furthermore, results show that minimization of downside risk leads to allocation of more sugar to succinic acid production and reduction in expected biomass processing capacity. Hence, although introducing financial risk management in our proposed decision making framework yields in more conservative design by reducing the production capacity, profitability (net present value) of scenarios have much higher chances to be between the desired target that leads to a more robust behaviour of the framework in the face of uncertainty.

Table 5-1: Comparison of feedstock and production capacities before and after risk management

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Expected NPV ($MM)</th>
<th>Downside risk</th>
<th>Feedstock Capacity (1000tons/yr)</th>
<th>Sugar allocation ratio (for ethanol production)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stochastic case</td>
<td>62.8</td>
<td>10%</td>
<td>218</td>
<td>0.62</td>
</tr>
<tr>
<td>Risk managed case</td>
<td>60.0</td>
<td>3%</td>
<td>152</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Kinetic parameters in biological reactions are considered as potential uncertainty sources in operational level model (technological risks) which resulted in a total of 65 parameters. A complete list of all the kinetic parameters and their description is represented in Table 5-5. Sobol global sensitivity analysis is performed to assess the relative sensitivity of these model parameters.
Through extensive Monte Carlo simulations, it is found that some parameters are rather insensitive. If the values of these insensitive parameters are fixed, a simplified model which reduces the complexity of the search space is obtained. Calculated sensitivity indices for model input parameters are shown in Figure 5.6 and Figure 5.7. It is found that 20 of the kinetic parameters are significantly affecting the uncertainty on annual cash flow of the process and the other uncertain parameters can be fixed at a value in their variation ranges without resulting significant fluctuations in the calculation of the objective function.

Based on our previous studies, Hydrolysis temperature, sugar allocation, and enzyme loading are selected as important operating variables to be optimized (Geraili et al., 2014). Then a sample of selected operating variables and also a sample for the shortlist of uncertain parameters were created to perform a Monte Carlo stochastic optimization.
Figure 5.6: First order sensitivity indices of annual cash flow

Figure 5.7: Second order sensitivity indices of annual cash flow
Table 5-2 represents the results of scenarios from Monte Carlo simulation; these optimal scenarios are ranked based on the mean value and 95% confidence interval that they have. The scenarios which have higher mean value than the base case and also the lowest confidence interval are the most feasible designs which can increase the profitability of the plant. The reason that 95% confidence interval is considered as a performance criteria in addition to mean value is that by ranking the scenarios based on only the mean value, the optimization model does not reflect the variability associated with the uncertainty of parameters in the process, and there will be no guarantee that the process will perform at a certain level over all the uncertain parameter space. Consequently, consideration of high mean value and 95% confidence interval together as a performance criteria will result in the selection of the scenarios which will correspond to high average cash flow and narrow uncertainty range. Optimal values of the decision variables obtained from Monte Carlo stochastic optimization model are shown in Table 5-3.

Table 5-2: Monte Carlo simulation results for annual cash flow maximization

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Mean</th>
<th>95% Confidence interval</th>
<th>% saving (95% confidence interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>8700</td>
<td>120</td>
<td>--</td>
</tr>
<tr>
<td>Sample 14</td>
<td>9570</td>
<td>83</td>
<td>30.8</td>
</tr>
<tr>
<td>Sample 47</td>
<td>9153</td>
<td>104.3</td>
<td>13.1</td>
</tr>
</tbody>
</table>

Table 5-3: Base case and optimal operating conditions

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Hydrolysis Temperature (°C)</th>
<th>Sugar allocation (ethanol)</th>
<th>Enzyme loading ratio (g enzyme/ Kg Cellulose)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>33.45</td>
<td>0.44</td>
<td>25</td>
</tr>
<tr>
<td>Optimal</td>
<td>39.3</td>
<td>0.37</td>
<td>13.1</td>
</tr>
</tbody>
</table>
Iterative results of the hybrid optimization methodology are presented in Table 5-4 which shows that in two iterations the model is converged. Initial process yields are obtained from literature (step1); then these yields are utilized in strategic model to calculate the production capacity plan (step2); the optimal values for the capacity are passed to the process level simulation and optimization to find the optimal process conditions and calculate the process yields based on the results of simulation (step3). These calculated yields are compared with the initial values used in the strategic model to check the convergence. Since the difference between calculated yields and initial yield values is greater than the threshold, this hybrid optimization needs to be carried out again based on the new yield values.

Table 5-4: Iteration results in hybrid optimization strategy

<table>
<thead>
<tr>
<th>Parameters and Variables</th>
<th>Iteration1</th>
<th>Iteration2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Step 1</td>
<td>Step 2</td>
</tr>
<tr>
<td>Feedstock (1000 ton/yr)</td>
<td>--</td>
<td>222.2</td>
</tr>
<tr>
<td>Ethanol (MM gal/yr)</td>
<td>--</td>
<td>15.3</td>
</tr>
<tr>
<td>Succinic Acid (1000 ton/yr)</td>
<td>--</td>
<td>6.0</td>
</tr>
<tr>
<td>Sugar (kg / kg)</td>
<td>0.87</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Fermentation</td>
<td>0.85</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Fermentation</td>
<td>0.25</td>
<td>--</td>
</tr>
<tr>
<td>Ethanol Purification</td>
<td>0.99</td>
<td>--</td>
</tr>
<tr>
<td>Succinic Acid Purification</td>
<td>0.78</td>
<td>--</td>
</tr>
</tbody>
</table>
5.6. Conclusions

In this study a new hybrid optimization methodology to determine the optimal production capacity plan and operating conditions for an integrated multi-product biorefinery in the face of stochastic inputs and outputs was presented. The optimization problem was solved in a two-level approach, first stochastic linear model was developed to optimize production capacity for the desired planning horizon and then process simulation coupled with stochastic optimization algorithm was employed to optimize the operating condition of the plant. Monte-carlo based simulation and global sensitivity analysis were utilized to identify the most critical parameters and optimize the operating conditions of the plant. The global sensitivity analysis gives insight into the bottlenecks in the process and quantifies the uncertainty in the annual cash flow due to technological risks.

Incorporating metrics for mitigation of financial risk in the framework (strategic model) shows that there are two important factors that influence the performance of the model in the face of market uncertainty including production capacity and allocation of pretreated biomass between ethanol and succinic acid production. The results indicate that taking uncertainties into consideration is a fundamental step in decision-making processes.

Table 5-5: Input uncertainty of kinetic parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Default value</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>relating substrate reactivity with degree of hydrolysis, dimensionless</td>
<td>1</td>
<td>0.75</td>
<td>1.25</td>
</tr>
<tr>
<td>$K_{fr}$</td>
<td>reaction rate constant 1,g/mg.h</td>
<td>22.3</td>
<td>16.73</td>
<td>27.88</td>
</tr>
<tr>
<td>$K_{1IG2}$</td>
<td>inhibition constant for cellobiose 1,g/kg</td>
<td>0.015</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>$K_{2IG}$</td>
<td>inhibition constant for glucose 1,g/kg</td>
<td>0.1</td>
<td>0.08</td>
<td>0.13</td>
</tr>
<tr>
<td>$K_{1IXy}$</td>
<td>inhibition constant for xylose 1,g/kg</td>
<td>0.1</td>
<td>0.08</td>
<td>0.13</td>
</tr>
<tr>
<td>$K_{2IG2}$</td>
<td>inhibition constant for cellobiose 2,g/kg</td>
<td>132</td>
<td>99</td>
<td>165</td>
</tr>
<tr>
<td>$K_{2IG}$</td>
<td>inhibition constant for glucose 2,g/kg</td>
<td>0.04</td>
<td>0.03</td>
<td>0.05</td>
</tr>
</tbody>
</table>
### Table 5-5 continued

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Glucose (g/kg)</th>
<th>Xylose (g/kg)</th>
<th>Glucose (g/kg)</th>
<th>Xylose (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{2XY}$</td>
<td>inhibition constant for xylose</td>
<td>0.2</td>
<td>0.15</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>$K_{3r}$</td>
<td>reaction rate constant $r$, h$^{-1}$</td>
<td>285.5</td>
<td>214.13</td>
<td>356.88</td>
<td>356.88</td>
</tr>
<tr>
<td>$K_{3M}$</td>
<td>substrate (cellulose) saturation constant</td>
<td>24.3</td>
<td>18.23</td>
<td>30.38</td>
<td>30.38</td>
</tr>
<tr>
<td>$K_{3IG}$</td>
<td>inhibition constant for glucose</td>
<td>3.9</td>
<td>2.93</td>
<td>4.88</td>
<td>4.88</td>
</tr>
<tr>
<td>$K_{3IXY}$</td>
<td>inhibition constant for xylose</td>
<td>201.0</td>
<td>150.75</td>
<td>251.25</td>
<td>251.25</td>
</tr>
<tr>
<td>$E_{1max}$</td>
<td>maximum enzyme 1 that can be adsorbed on substrate</td>
<td>0.06</td>
<td>0.05</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>$K_{2ad}$</td>
<td>dissociation constant for enzyme</td>
<td>0.4</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$K_{2ad}$</td>
<td>dissociation constant for enzyme</td>
<td>0.1</td>
<td>0.08</td>
<td>0.13</td>
<td>0.13</td>
</tr>
</tbody>
</table>

**Ethanol fermentation**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Glucose (g/kg)</th>
<th>Xylose (g/kg)</th>
<th>Glucose (g/kg)</th>
<th>Xylose (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{m,g}$</td>
<td>maximum specific growth rate in cell growth</td>
<td>0.31</td>
<td>0.2945</td>
<td>0.3255</td>
<td>0.3255</td>
</tr>
<tr>
<td>$K_{4g}$</td>
<td>monod constant for growth on glucose</td>
<td>1.45</td>
<td>1.3775</td>
<td>1.5225</td>
<td>1.5225</td>
</tr>
<tr>
<td>$C_{Etmax,g}$</td>
<td>maximum ethanol concentration in cell growth</td>
<td>28.9</td>
<td>27.455</td>
<td>30.345</td>
<td>30.345</td>
</tr>
<tr>
<td>$K_{4g}$</td>
<td>inhibition constant for growth on glucose</td>
<td>200</td>
<td>190</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>$\mu_{m,xy}$</td>
<td>maximum specific growth rate in cell growth</td>
<td>0.1</td>
<td>0.095</td>
<td>0.105</td>
<td>0.105</td>
</tr>
<tr>
<td>$K_{5xy}$</td>
<td>monod constant for growth on xylose</td>
<td>4.91</td>
<td>4.6645</td>
<td>5.1555</td>
<td>5.1555</td>
</tr>
<tr>
<td>$C_{Etmax,xy}$</td>
<td>maximum ethanol concentration in cell growth</td>
<td>26.6</td>
<td>25.27</td>
<td>27.93</td>
<td>27.93</td>
</tr>
<tr>
<td>$K_{5xy}$</td>
<td>inhibition constant for growth on xylose</td>
<td>600</td>
<td>570</td>
<td>630</td>
<td>630</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>weighing factor for glucose consumption, dimensionless</td>
<td>0.65</td>
<td>0.6175</td>
<td>0.6825</td>
<td>0.6825</td>
</tr>
<tr>
<td>$q_{smax,g}$</td>
<td>overall maximum specific glucose utilization, g/hr</td>
<td>10.9</td>
<td>10.355</td>
<td>11.445</td>
<td>11.445</td>
</tr>
<tr>
<td>$K_{7g}$</td>
<td>substrate limitation constant in glucose consumption, g/kg</td>
<td>6.32</td>
<td>6.004</td>
<td>6.636</td>
<td>6.636</td>
</tr>
<tr>
<td>$C_{Etmax,g}$</td>
<td>maximum ethanol concentration in glucose consumption, g/kg</td>
<td>42.6</td>
<td>40.47</td>
<td>44.73</td>
<td>44.73</td>
</tr>
<tr>
<td>$C_{Etmax,xy}$</td>
<td>maximum ethanol concentration in xylose consumption, g/kg</td>
<td>56.3</td>
<td>53.485</td>
<td>59.115</td>
<td>59.115</td>
</tr>
<tr>
<td>$K_{7g}$</td>
<td>substrate inhibition constant in glucose consumption, g/kg</td>
<td>600</td>
<td>570</td>
<td>630</td>
<td>630</td>
</tr>
<tr>
<td>$q_{smax,xy}$</td>
<td>overall maximum specific xylose utilization, g/hr</td>
<td>186</td>
<td>176.7</td>
<td>195.3</td>
<td>195.3</td>
</tr>
<tr>
<td>$K_{8xy}$</td>
<td>substrate limitation constant in xylose consumption, g/kg</td>
<td>3.27</td>
<td>3.1065</td>
<td>3.4335</td>
<td>3.4335</td>
</tr>
<tr>
<td>$C_{Etmax,xy}$</td>
<td>maximum ethanol concentration in xylose consumption, g/kg</td>
<td>53.1</td>
<td>50.445</td>
<td>55.755</td>
<td>55.755</td>
</tr>
<tr>
<td>$C_{Etmax,xy}$</td>
<td>maximum ethanol concentration in xylose consumption, g/kg</td>
<td>81.2</td>
<td>77.14</td>
<td>85.26</td>
<td>85.26</td>
</tr>
<tr>
<td>$K_{8xy}$</td>
<td>substrate inhibition constant in xylose consumption, g/kg</td>
<td>600</td>
<td>570</td>
<td>630</td>
<td>630</td>
</tr>
<tr>
<td>$q_{pmax,g}$</td>
<td>overall maximum specific ethanol production by glucose fermentation, g/hr</td>
<td>5.12</td>
<td>4.864</td>
<td>5.376</td>
<td>5.376</td>
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<tr>
<td>$K_{9g}$</td>
<td>substrate limitation constant in glucose fermentation, g/kg</td>
<td>6.32</td>
<td>6.004</td>
<td>6.636</td>
<td>6.636</td>
</tr>
<tr>
<td>$C_{Etmax,g}$</td>
<td>maximum ethanol concentration in glucose fermentation, g/kg</td>
<td>42.6</td>
<td>40.47</td>
<td>44.73</td>
<td>44.73</td>
</tr>
<tr>
<td>$C_{Etmax,xy}$</td>
<td>maximum ethanol concentration in xylose fermentation, g/kg</td>
<td>75.4</td>
<td>71.63</td>
<td>79.17</td>
<td>79.17</td>
</tr>
<tr>
<td>$K_{9g}$</td>
<td>substrate inhibition constant in glucose fermentation, g/kg</td>
<td>186</td>
<td>176.7</td>
<td>195.3</td>
<td>195.3</td>
</tr>
<tr>
<td>$q_{pmax,xy}$</td>
<td>overall maximum specific ethanol production by xylose fermentation, g/hr</td>
<td>1.59</td>
<td>1.5105</td>
<td>1.6695</td>
<td>1.6695</td>
</tr>
<tr>
<td>$K_{10xy}$</td>
<td>substrate limitation constant in xylose fermentation, g/kg</td>
<td>0.03</td>
<td>0.0285</td>
<td>0.0315</td>
<td>0.0315</td>
</tr>
<tr>
<td>$C_{Etmax,xy}$</td>
<td>maximum ethanol concentration in xylose fermentation, g/kg</td>
<td>53.1</td>
<td>50.445</td>
<td>55.755</td>
<td>55.755</td>
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</tbody>
</table>
Table 5-5 continued

<table>
<thead>
<tr>
<th>(K_{I_{xy}})</th>
<th>substrate Inhibition constant in xylose fermentation, g/kg</th>
<th>600</th>
<th>570</th>
<th>630</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{I_{xy}})</td>
<td>maximum specific growth rate in glucose fermentation, 1/h</td>
<td>1.324</td>
<td>1.2578</td>
<td>1.3902</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>inhibition constant for growth on glucose, g/kg</td>
<td>88.35</td>
<td>83.9325</td>
<td>92.7675</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>specific death rate, 1/h</td>
<td>0.010</td>
<td>0.0095</td>
<td>0.0105</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>growth-associated parameter for succinic acid formation, dimensionless</td>
<td>0.626</td>
<td>0.5947</td>
<td>0.6573</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>non-growth-associated parameter for succinic acid formation, 1/h</td>
<td>0.355</td>
<td>0.33725</td>
<td>0.37275</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>growth-associated parameter for acetic acid formation, dimensionless</td>
<td>0.626</td>
<td>0.5947</td>
<td>0.6573</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>non-growth-associated parameter for acetic acid formation, 1/h</td>
<td>0.124</td>
<td>0.1178</td>
<td>0.1302</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>growth-associated parameter for formic acid formation, dimensionless</td>
<td>0.665</td>
<td>0.63175</td>
<td>0.69825</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>non-growth-associated parameter for formic acid formation, 1/h</td>
<td>0.105</td>
<td>0.09975</td>
<td>0.11025</td>
</tr>
<tr>
<td>(K_{I_{xy}})</td>
<td>non-growth-associated parameter for lactic acid formation, 1/h</td>
<td>0.210</td>
<td>0.1995</td>
<td>0.2205</td>
</tr>
<tr>
<td>(Y_{i})</td>
<td>stoichiometric yield coefficient of cell on glucose</td>
<td>0.765</td>
<td>0.72675</td>
<td>0.80325</td>
</tr>
<tr>
<td>(Y_{SA})</td>
<td>stoichiometric yield coefficient of succinic acid on glucose</td>
<td>1.31</td>
<td>1.24445</td>
<td>1.3755</td>
</tr>
<tr>
<td>(Y_{AA})</td>
<td>stoichiometric yield coefficient of acetic acid on glucose</td>
<td>0.999</td>
<td>0.94905</td>
<td>1.04895</td>
</tr>
<tr>
<td>(Y_{FA})</td>
<td>stoichiometric yield coefficient of formic acid on glucose</td>
<td>1.532</td>
<td>1.4554</td>
<td>1.6086</td>
</tr>
<tr>
<td>(Y_{LA})</td>
<td>stoichiometric yield coefficient of lactic acid on glucose</td>
<td>0.999</td>
<td>0.94905</td>
<td>1.04895</td>
</tr>
<tr>
<td>(msg)</td>
<td>specific maintenance coefficient, 1/h</td>
<td>0.061</td>
<td>0.05795</td>
<td>0.06405</td>
</tr>
</tbody>
</table>

5.7. References


6. Conclusion and Future Directions

This dissertation has focused on the development of a comprehensive decision-making framework for optimal design of emerging technologies in renewable energy production systems. The present work systematically addressed the problems of modelling the process, analysis of alternative technologies, optimizing strategic and operational level decisions, evaluating the impact of different sources of uncertainties (parameters in strategic and operational level) that introduce variability into the decision-making problem and management of the risk due to these uncertain parameters. A summary and conclusions of the proposed optimization framework is as follows:

- A novel robust decision support framework for design of sustainable renewable energy production systems is developed that can mimic the actual design methodology that planners, developers, and enterprises should follow. This framework focuses on integrating strategic planning tasks with operational tasks. Owing to complex kinetic and thermodynamic relationships of conversion mechanisms in energy production systems, these processes are inherently non-linear in nature. Non-linear strategic optimization models can quickly become complex to solve with solution performance suffering as more nonlinearity is added to a model. Consequently, linear programming (LP) models are suggested in this framework for the purpose of strategic planning.

- To overcome the mismatch between nonlinear process mechanisms and LP-based strategic optimization, a decomposition strategy is proposed that combines strategic optimization for long term planning with rigorous non-linear process modelling and process-level optimization. The proposed strategy has the advantage of not only being able to integrate long term planning based on financial optimization with nonlinear
process mechanisms in simulation software, but also optimizes process operating conditions by utilizing stochastic optimization methods (Metaheuristics).

- Standard simulation and mathematical software packages are utilized to represent the process and execute the framework seamlessly. Process dynamics, nonlinear optimization and strategic planning are interlinked in a novel fashion that gives the flexibility to decision makers to add more granularities to the framework by incorporating more rigorous data and more rigorous modeling calculations when they are available.

- Experimentally validated kinetic models for complex biological reactions derived from literature are incorporated with process simulation. The complex kinetic models are modeled in MATLAB and linked with process simulation in Aspen Plus. Conversion rate of biological reactions in process simulation are modified based on the solution of differential equations for the kinetic models. This software architecture that we developed for implementation of complex kinetics imparts a greater degree of realism to the simulation.

- Flexibility in design can help the enterprise to avoid bad circumstances for unfavorable future and when the future offers new opportunities, flexibility will help to take advantage of those possibilities. Thus, to incorporate this flexibility in our strategic model for designing the capacity of the plant, a stepwise capacity expansion strategy is utilized by defining binary variables for capacity increments at each time period in the planning horizon. Therefore, since some of the variables are constrained to be integers (binary variables), the model for strategic planning will be a mixed integer linear programming (MILP).
The framework that is developed up to chapter 4, all the model parameters are assumed to be perfectly known in advance (i.e., they are deterministic). However, common to early stages of process design is the lack of certain information. To tackle this problem, we expand the scope of our proposed framework by incorporating uncertainty analysis to the model. In chapter 4, long-term uncertainties over the lifespan of the integrated biorefinery such as price and demand of the products are included in optimization framework based on a hypothetical market model. Scenario-based stochastic programming model is developed to transform the original strategic optimization model under uncertainty into a deterministic approximation by discretizing the uncertain parameters.

In the stochastic programming model, optimal solution is obtained by maximizing the total expected value of the objective function which is optimal on average for all the scenarios. The expected value is a risk-neutral objective and does not reflect the variability of performances associated with each specific scenario. To manage the risk associated with uncertain parameters and control the variability of performance, downside risk management method is introduced to the strategic model to incorporate the trade-off between financial risk and profitability of the plant in the optimization process. Addition of downside risk management in the framework results in a multi-objective problem including two conflicting objective functions (maximizing economic profitability and minimizing the financial risk).

The model proposed in chapter 4 is expanded to develop a comprehensive systematic optimization framework in chapter 5 which incorporates various sources of uncertainty including market uncertainties and uncertainty in parameters that characterize the
processing technologies in energy production. In the first layer of the framework (strategic model), the same strategy as explained in chapter 4 will be utilized. Results from strategic model are then used to optimize the operating condition of the plant under uncertainty in the second layer. Operational layer is composed of process simulation, global sensitivity analysis and a stochastic optimization algorithm based on Monte-Carlo simulation.

A hypothetical case study, multi-product lignocellulosic biorefinery that converts biomass to value-added biofuels (cellulosic ethanol) and biobased chemicals (succinic acid), is presented to exemplify the efficacy of the proposed framework. A summary and conclusion of the main results for the optimal strategic and operational level decisions is as follows:

- Results from analysing alternative technologies in configurations of integrated biorefineries through simulation and hybrid optimization show that:
  - Ammonia conditioning is the preferred technology for detoxification since it has a higher ethanol yield and lower sugar loss in comparison to overliming.
  - Extracting the residual solids in purification is selected due to the resulting higher ethanol yield and annual cash flow. It is worth noting that the implemented kinetic model reveals the negative impact of high sugar concentration in ethanol production and imparts a greater degree of realism to the actual representation of the process.
  - Based on the modified kinetic model for simultaneous saccharification and fermentation (SSCF) of ethanol, simulation results show that simultaneous glucose production and sugar (glucose & xylose) consumption in SSCF will
keep the sugar concentration below the inhibition threshold. Additionally, since sugar is consumed in fermentation reactions, a sugar sink is created which helps to convert the cellulose (to glucose) in a higher extent.

- Furthermore, optimization results showed that considering succinic acid as a co-product makes a huge difference in the profitability of the enterprise. Therefore, it shows that for having a truly sustainable biorefinery process, a portfolio of products which comprise biofuels and value added biochemicals is required whose production rates can be varied to optimize plant margins based on input costs and product markets.

- During hydrolysis and fermentation, results from simulation show that enzyme loading, sugar allocation and temperature of the reactors have a complex set of impacts on process yields and consequently, on process economics. Therefore, the following operating variables are manipulated in order to optimize annual operating cash flows: (1) temperature in enzymatic hydrolysis, (2) sugar allocation (from hydrolysis) between ethanol and succinic acid fermentation, and (3) enzyme (cellulase) loading during hydrolysis.

- The framework shows a deviation in process yields, and a deviation in the production capacities and operating conditions, from initial literature estimates. This is attributed to the framework’s use of nonlinear modeling and optimization strategies, which served to impart a greater degree of realism to the representation of the actual biorefining process.

- Additionally, analysis of the results from simulation and optimization show that the main sections requiring energy are the fractionation and recovery. During co-
generation, by burning combustible by-products from the biorefinery, such as lignin and biogas, the steam and electricity demand for the plant is supplied internally. Furthermore, additional revenues are generated by selling excess electricity as a by-product.

- Results from stochastic formulation (for modeling market uncertainty) reveal that considering uncertainty will provide results that reflect the variation of market parameters and behave better than the deterministic model (yielding better expected NPV).

- Additionally, incorporating metrics for financial risk mitigation in the framework shows that there are two important factors that influence the performance of the model in the face of uncertainty: 1) production capacity and 2) allocation of pretreated biomass between ethanol and succinic acid production.

- Results from global sensitivity analysis for evaluating the impact of potential uncertainty sources in operating condition of the plant reveal that some parameters are rather insensitive. If the values of these insensitive parameters are fixed, a simplified model which reduces the complexity of the search space is obtained.

6.1. Recommendations for future works

This dissertation emphasized on development of the proposed optimization framework and its application for design and optimization of a biorefining process. However, this methodology is general and applicable to different energy production systems. There are several ways that future research can extend this dissertation research:

- Measuring the environmental and social dimensions of sustainability for the system during design and incorporate these measures into the optimization framework through
establishing a tradeoff between different dimensions of sustainability (economic, environmental and social); expanding the proposed decision support framework by incorporating detailed cost estimation of all the unit operations at different capacities through utilization of Aspen Process Economic Analyzer software; incorporating more nonlinear process variables within the proposed framework; evaluating different product portfolios including those involve production of value added chemicals; extending the applicability of the framework to other renewable energy systems including energy production systems wind, sun and other agricultural resources.

- Another possible line of future research is the design and optimization of shale oil and gas production systems fitted with the proposed framework. Shale gas is one of the alternative energy sources drawn momentous investment and discussion as a cleaner and more sustainable energy. The research directions can include development of a superstructure optimization approach for strategic planning of a shale gas production process by selecting the number of wells to drill, selecting the location of them and optimizing the water utilization for well drilling and fracturing. Additionally, an important impact of shale gas on the chemical industry is the production of value-added chemicals from natural gas liquids. Therefore, simulating and analyzing alternative technology options for downstream processing of shale gas is an important issue which we are currently working on at the PSE group at LSU. Moreover, a superstructure optimization model can be developed to integrate fuel production from biomass, developed in this dissertation, and shale gas to enhance the production capacity of biorefineries and improve the profitability.
Appendix A: Parameters Utilized in the Framework

Experimentally-derived kinetic models and definition of parameters are represented in the following tables:

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<tr>
<th>Enzymatic hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
</tr>
<tr>
<td>$\alpha$</td>
</tr>
<tr>
<td>$C_j$</td>
</tr>
<tr>
<td>$S_0$</td>
</tr>
<tr>
<td>$r_1$</td>
</tr>
<tr>
<td>$K_{ir}$</td>
</tr>
<tr>
<td>$C_{EiR}$</td>
</tr>
<tr>
<td>$C_{G2}$</td>
</tr>
<tr>
<td>$C_G$</td>
</tr>
<tr>
<td>$C_{xy}$</td>
</tr>
<tr>
<td>$K_{1IG2}$</td>
</tr>
<tr>
<td>$K_{1IG}$</td>
</tr>
<tr>
<td>$K_{1IXy}$</td>
</tr>
<tr>
<td>$K_{1IEt}$</td>
</tr>
<tr>
<td>$r_2$</td>
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<tr>
<td>$K_{2r}$</td>
</tr>
<tr>
<td>$K_{2IG2}$</td>
</tr>
<tr>
<td>$K_{2IG}$</td>
</tr>
<tr>
<td>$K_{2IXy}$</td>
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<td>$K_{3r}$</td>
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<td>$K_{IM}$</td>
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**Succinic acid fermentation**

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<td>cell dry weight in glucose fermentation, g/kg</td>
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Table A-1: Kinetic model for enzymatic hydrolysis

1. $R_s = \alpha \frac{C_s}{S_0}$

2. $r_1 = \frac{K_{1r} C_{EIB} R_s C_s}{1 + \frac{C_{G2}}{K_{11G2}} + \frac{C_G}{K_{11G}} + \frac{C_{XY}}{K_{11XY}}}$

3. $r_2 = \frac{K_{2r}(C_{EIB} + C_{E2B}) R_s C_s}{1 + \frac{C_{G2}}{K_{21G2}} + \frac{C_G}{K_{21G}} + \frac{C_{XY}}{K_{21XY}}}$

4. $r_3 = \frac{K_{3r} C_{E2F} C_{G2}}{K_{3M} \left( 1 + \frac{C_G}{K_{31G}} + \frac{C_{XY}}{K_{31XY}} \right) + C_{G2}}$

5. $C_{EIB} = \frac{E_{imax} K_{iad} C_{EIF} C_S}{1 + K_{iad} C_{EIF}}$

6. $K_{lb}(T2) = K_{lb}(T1) e^{\frac{-E_{lb}}{RT + 1 \left( \frac{1}{T2} - \frac{1}{T} \right)}}$
Table A-2: Kinetic model for ethanol fermentation

\[ r_4 = \frac{\mu_{m.g} C_G}{K_{1g} + C_G} \left( 1 - \frac{C_{Et} - C_{EtIs.g}}{C_{Etmax.g} - C_{EtIs.g}} \right) \left( \frac{K_{41g}}{K_{41g} + C_G} \right) \]

\[ r_5 = \frac{\mu_{m.xy} C_{xy}}{K_{Sxy} + C_{xy}} \left( 1 - \frac{C_{Et} - C_{EtIs.xy}}{C_{Etmax.xy} - C_{EtIs.xy}} \right) \left( \frac{K_{5Sxy}}{K_{5Sxy} + C_{xy}} \right) \]

\[ r_6 = \frac{dC_X}{dt} = \alpha \cdot r_4 \cdot C_X + (1 - \alpha) \cdot r_5 \cdot C_X \]

\[ r_7 = -\alpha \cdot q_{smax, g} \frac{C_X C_G}{K_{7g} + C_G} \left( 1 - \frac{C_{Et} - C_{EtIs,g}}{C_{Etmax,g} - C_{EtIs,g}} \right) \left( \frac{K_{71sg}}{K_{71sg} + C_G} \right) \]

\[ r_8 = -(1 - \alpha) \cdot q_{smax, xy} \frac{C_X C_{xy}}{K_{Bxy} + C_{xy}} \left( 1 - \frac{C_{Et} - C_{EtIs,xy}}{C_{Etmax,xy} - C_{EtIs,xy}} \right) \left( \frac{K_{B1sxy}}{K_{B1sxy} + C_{xy}} \right) \]

\[ r_9 = q_{pmax, g} \frac{C_G}{K_{9g} + C_G} \left( 1 - \frac{C_{Et} - C_{Etip,g}}{C_{Etmax,g} - C_{Etip,g}} \right) \left( \frac{K_{9ipg}}{K_{9ipg} + C_G} \right) \]

\[ r_{10} = q_{pmax, xy} \frac{C_{xy}}{K_{10xy} + C_{xy}} \left( 1 - \frac{C_{Et} - C_{Etip,xy}}{C_{Etmax,xy} - C_{Etip,xy}} \right) \left( \frac{K_{10ipxy}}{K_{10ipxy} + C_{xy}} \right) \]

\[ r_{11} = \frac{dC_{Et}}{dt} = \alpha \cdot r_9 \cdot C_X + (1 - \alpha) \cdot r_{10} \cdot C_X \]

Table A-3: Kinetic model for succinic acid fermentation

\[ r_X = \frac{dC_{SGXg}}{dt} = \frac{\mu_{m,gs} C_{SG} C_{SGXg}}{K_{SG} + C_{SG} + C_{SG}^2 / K_{SLg}} \left( 1 - \left( \frac{p_g}{P_{Crit,g}} \right)^i \right) \]

\[ r_X = \frac{dC_{SGXg}}{dt} = -K_d C_{SGXg} \]

\[ r_{SA} = \frac{dC_{SA}}{dt} = \alpha_{SA} r_X + \beta_{SA} X \]

\[ r_{AA} = \frac{dC_{AA}}{dt} = \alpha_{AA} r_X + \beta_{AA} X \]

\[ r_{FA} = \frac{dC_{FA}}{dt} = \alpha_{FA} r_X + \beta_{FA} X \]

\[ r_{LA} = \frac{dC_{LA}}{dt} = \alpha_{LA} r_X + \beta_{LA} X \]

\[ r_{C_{SG}} = -\frac{dC_{SG}}{dt} = \frac{1}{Y_X} r_X + \frac{1}{Y_{SA}} r_{SA} + \frac{1}{Y_{AA}} r_{AA} + \frac{1}{Y_{FA}} r_{FA} + \frac{1}{Y_{LA}} r_{LA} + m s g C_{SGXg} \]

\[ P_g = C_{SA} + C_{AA} + C_{FA} + C_{LA} \]
Appendix B: An Improved Hybrid Optimization Approach through Utilization of Active Specification Switching Strategy

B.1. Introduction

Simulations are increasingly important in the field of optimization as software becomes more specialized at accurately describing particular processes. In a competitive and evolving modeling software landscape, software can have superior benefits in different areas. This makes optimization of simulations better suitable for an environment where multiple software types are specialized and communicate with one another; tasks are specialized as well. The unit engineers can update simulations to incorporate process changes and long-term dynamics using the same software configuration.

Stochastic optimization is suitable for a real-world environment where modeling and optimization tasks are specialized and multiple software types are integrated. However, stochastic optimization methods can exacerbate simulation convergence issues. A converged solution is a solution in which all equations in the model are satisfied. A set of decision variables generated by an optimizer can violate a constraint within the model when chosen stochastically since the optimizer does not consider modeling constraints. If the values of a set of decision variables are outside the convergence space, the model’s solver will not converge. Also, the solver may not converge if the optimizer makes large jumps in the solution space. Despite advances of non-linear equation solvers, the solver’s initial condition strongly affects convergence. Typically, the modeling solver’s initial condition is the value of the previous point solved. Therefore, increasing the solution space can help find global optima; however, taking larger steps increases occurrences of non-converging solutions by worsening the solver’s initial condition.
In this work, a method to aid in convergence of nonlinear equations by relocating the solver is introduced. Deactivating known values and activating intelligently chosen unknown variables at predicted values efficiently formulate initial conditions. This repair strategy is integrated into an optimization problem to demonstrate the improvement in robustness of the optimization algorithm. This repair strategy has the ability to:

1. Relocate the solver for non-converged models caused by poor initial conditions,
2. Utilize points formulated in relocating non-converged models as a perturbation phase.

The performance of the hybrid metaheuristic algorithm with repair is compared to the algorithm without the repair technique. Results indicate that the repair strategy is able to improve the convergence of the model.

In the following section a repair strategy and its integration with metaheuristic optimization algorithms which improves their application when optimizers and simulators are separate entities by repairing non-converged simulations due to poor I.C. and infeasibilities is discussed. Having the ability to repair non-converged simulations improves the robustness of the optimizer.

### B.2. Repair strategy

Modeling complex problems typically involves solving sets of nonlinear equations. Setting the problem up as an optimization problem and minimizing the error of the equations through an iterative procedure such as Newton Raphson best solves sets of non-linear equations. Many variations of these procedures have been researched in order to improve the algorithms computational performance and reduce the sensitivity to initial conditions (such as the Inside-Out algorithm). Although there have been improvements in the sensitivity to techniques which solve sets of nonlinear equations, sensitivity to initial conditions are still an issue (Biegler et al., 1985).
In many cases the nonlinear set of equations has more variables than equations and the modeler is interested in the model conditions at a specific set of variables. The modeling equations are solved by setting (giving values to) variables known as active specifications. The set of active specifications are the same size as the degrees of freedom of the problem. The active specification of interest to the modeler, \( X \), may not be the easiest way of solving the set of equations. For example, calculating fluid properties at particular temperatures usually takes one calculation; however, calculating the temperature at a vapor pressure is an iterative process (Antoine’s equation). There may be multiple different sets of active specifications, \( Y \), which are easier to solve than \( X \). Our approach will formulate new I.C.s, which can help attain convergence at non-converged specified values of set \( X \), by using values obtained at solutions of the easier-to-converge sets \( Y \). The variables of all sets \( Y_i \)'s which are not included in set \( X \) are denoted by set \( Z \). The values in set \( Z \) must be predicted before beginning the repair algorithm. Figure B.1 illustrates the algorithm block diagram for the proposed repair strategy.

**B.3. Integration of repair strategy with metaheuristic algorithms**

In the case of optimization, the variables of interest, set \( X \), must include the set of decision variables. The remaining DOF are chosen to meet constraints and ease of convergence criterion. Different sets of active specifications, which are easier to solve than \( X \), may not be composed of the original decision variables of the optimization problem. These sets can be used to bring the non-converged points in \( X \) back to the solution space at the highest objective function value found during active specification switching. However when evaluating a point to use as new I.C., we may serendipitously find that it has a higher objective function.
Figure B.1: Repair strategy

Figure B.2 illustrates an integration of a general metaheuristic optimization procedure and the repair strategy for optimizing a nonlinear set of equality constraints. The method begins by defining an inner and outer loop counter, $I$ and $R$. We generate new random points, $X_{\text{new}}$, similar to the metaheuristic strategy and then send them to the model to solve for values necessary to calculate the objective function. The method differentiates from the other optimization methodologies where the models do not converge. Instead of ignoring the point or simply only repairing it and returning to the counter, the repair strategy is initiated. The easier-to-converge sets ($Y_i$s) are evaluated, and if a set $Y_i$ has a better optimal value than the current optimal, then the solver immediately moves to the new point (serendipitous outcome). This outcome is the perturbation phase of the optimization algorithm. A new neighborhood is immediately chosen around this point.
B.4. Application case study: distillation optimization

Distillation is an energy intensive process, and improvement can have substantial benefits. The heat integration of a distillation train is such an example of a problem that is difficult to formulate precise feasibility constraints. Simulations of distillation processes are used for optimizing the energy integration problem. A simulation of a distillation column solves the heat, mass, and thermodynamic equations at a particular set of active specifications. During the
optimization algorithm, the active variables must include the decision variables of the optimization problem such as pump around flow rates, steam flow rates, and constraints of the problem such as cut point temperature values. It is assumed in our problem that cut points are constant constraints. The robustness of temperature variables leads us to choose as many temperatures as possible for the active specs such as overhead, boiler, and PA return temperatures for rapid convergence and model robustness.

Optimizing a simulation of a process containing distillation units by stochastic algorithms leads to issues of convergence. The thermodynamic, energy, and mass balances of the column are embedded into the simulation. There are multiple nonlinearities, especially in the thermodynamic equations. Randomly selected points without considering the modelling equations are not guaranteed to be feasible. Therefore, distillation optimization with a stochastic algorithm can benefit greatly from an embedded repair strategy.

The specifications required are equal to the degrees of freedom. In our case, some of the active specs used are pump around flow rates, temperatures, and product flow rates. Easier-to-converge sets constructing a set $Z$ composed of variables that can be interchanged with the decision-variable-inclusive set $X$ as active specifications creates $Y$’s. Manipulating the heat removed with the pump around flow rates at constant return temperatures can be infeasible by conflicting with the heat added by steam and furnace duties at the cut point constraints, causing the distillation columns in the model to not converge. However, there is a set of active specifications that will more easily converge; the product flow rates corresponding to the cuts will commonly cause the solver to return to a converging solution. This is because the product flow rates are stronger functions of the composition of the feed rather than the degree of separation or unit conditions. The product flow rates can then be used as new variables, $Z$, to
create easier-to-converge sets $Y$. When a point does not converge, the specification on the heat removal is relaxed by removing a PA stream flow rate. A product flow rate (PF) corresponding to one of the cut point constraints is then activated. If switching a PA to a PF brings the solver back into the converging region, then an I.C. is discovered where only one variable value differs. This is the strategy to create repairing-potential new initial conditions equal to the product of the number of pump around and the number of product flow rates.

Variables in the $Z$ set, which are used to create $Y$ sets for I.C.’s, must be assigned predicted values. Each incoming crude has about the same cut fraction, $x_{\text{cut}}$, depending on its composition, however it can change slightly due to operating conditions. The cuts are a strong function of feed composition, but product flow rates can be adjusted slightly and within the constraints; therefore, the product-cut flow rate values, $PF_{\text{cut}}$, are calculated each time a neighborhood is constructed. At the operating condition of the center point of the neighborhood, the flow rate of each incoming crude oil, $FR_{\text{Crude}}$, is perturbed. Regressed values for the cut fractions are obtained from using GRG method. Predicted values for each cut are then formulated by summing each incoming crude oil by the formulated cut fraction, $PF_{\text{cut}} = \sum_{\text{CrudeFeeds}} FR_{\text{Crude}} \times x_{\text{cut}}$.

The initial conditions used in the repair strategy are incorporated into the optimization routine. If the model converges with this new set of variables, the objective function is noted. If an objective function is serendipitously found to be higher than the current best of the algorithm, a neighborhood is constructed around the new point’s current value of the inactive DV. Otherwise, the algorithm checks to see if there is still PA’s left to switch on in order to check for more set $Y$’s to evaluate. Then, the active variables are switched back to set $X$ so as to once again
have the active variable include the DV’s. We then check to see if we have run out of set Z. If we have not, we move the product flow index, j, up one and switch again. If there are no more remaining in that set Z, the Z index is reset to one and checked the next pump around decision variable. Figure B.3 represents the implementation of the repair strategy in optimization of distillation columns.

Figure B.3: Repair strategy for optimization integration block diagram

The repair strategy exits in three basic ways. The first two are desirable and terminate the repair strategy immediately. If the model is solved at a different set of active specifications and upon switching back to the DV specification converges, then the repair strategy is terminated immediately (1). This is an example of when an appropriate initial condition was not given to the solver causing the model to not converge. Second, if the model converges on a new set of specifications with a higher objective function (or one within the current objectives $TA_i$ value)
the repair strategy will update deactivated decision variable’s values and create a neighborhood around this new point. In this case we have serendipitously found a good solution to search around (2). In a situation where the algorithm evaluates an infeasible point and no set $Y$ converges, the algorithm refers to the optimization optimal solution (3).

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Vita

Aryan Geraili was born in Tehran, Iran. He graduated from Kamal high school, Tehran. In 2010, he obtained his Bachelor degree in Chemical Engineering from University of Tehran. After which he proceeded to Louisiana State University, Louisiana, U.S.A., for graduate studies in chemical Engineering. There he joined Professor Jose Romagnoli’s Process Systems Engineering Group in December 2010. In December 2013 he received a Master of Science degree in Chemical Engineering from Louisiana State University. He expects to receive the Doctor of Philosophy degree in Chemical Engineering with a minor in Industrial Engineering in May 2015. To date he is the author of ten peer-reviewed journal articles, and conference proceedings. His research has also been presented at four major national and international conferences.