Synthesis and design of optimal biorefinery

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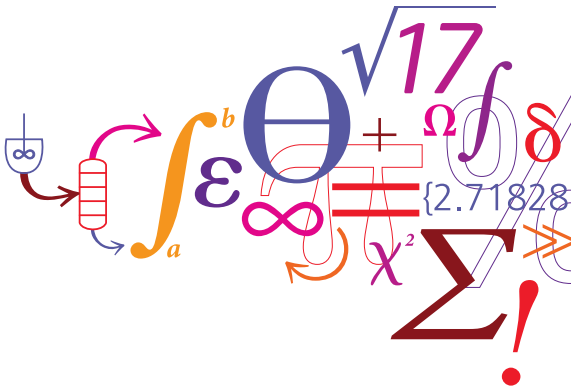

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Ph.D. Thesis
April, 2015

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Synthesis and design of optimal biorefinery

PhD Thesis

Peam Cheali

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Preface

This thesis is submitted as partial fulfillment of the requirements for the Doctor of Philosophy (PhD) degree at the Technical University of Denmark. The PhD project was carried out at the CAPEC-PROCESS Research Center, at the Department of Chemical and Biochemical Engineering, from May 2012 to April 2015, under the supervision of Associate Professor Gürkan Sin as main supervisor, and Professor Krist V. Gernaey as co-supervisor. This project has been conducted in close collaboration with Dr. Alberto Quaglia, former PhD at DTU and Dr. John A. Posada from Energy & Resources, Utrecht University and Department of Biotechnology, Delft University of Technology. I would like to thank them all for their valuable support, training, criticism, and guidance which have resulted in a rewarding work, professional and personal development.

I am grateful to my parents: Mrs.Cholticha and Mr.Mongkol; my aunts: Ms.Boonmee and Mrs.Porntip for their love and support. Moreover, I also feel grateful for all beautiful things I received within these wonderful three years from wonderful people whom I called my "Danish family": (i) my Danish landlords: Marie-anne, Arne and Per; (ii) Thai people in Denmark: Pee Yui & Pee Mhoo, Pee Lamoon & Pee Mon, Pee Lamai who have treated me as their family member; Pee Orn, Pee Kate, Pee Joy, Pee Tuk, Pee Nam, Pee Kob, Pee Dang, Pee Puu, Pee Jai, Panthong and more who have supported me since my first day in Denmark; (iii) All other wondeful people: Alberto, Katrine, Miguel, Jakob, Albert & Natalia, Michele & Elena, Thomas, Nacho, Tuong-Van, Esben, Carolina, Dasha, Felipe, Silvia, Hande, Albert Camos, Marina & Manolis, Andreas, Larissa, Alafiza & Imran, Fazli, Zainatul, Ali, Seyed & Tannaz, Stefano & Elena, Catarina & Joao, Laura, Lisa, Alessandra, Anthony, Florian, Estelle-Teresa-Mafalda, Carina, Riccardo, Mariona, Rebecca, Jerome, Eva & Gitte, Amata, Pichayapan, Anjan, Alberte and many more. Looking back, there are many people who have also taught me, and also shared their valuable experiences professionally and personally with me, whom I need to thank and give credit: Assoc. Prof. Phavanee, Dr. Piyapong at King Mongkut's University of Technology North Bangkok (KMUTNB), Thailand; Ms. Thapakorn, Mrs. Orawan at Linde (Thailand); and Ms. Suphattarin for all special supports. I also feel grateful for all invaluable lessons and examples from the King of Thailand. There are still a number of wonderful people to who I feel grateful, and that I cannot name here. They will always be remembered, thank you.

Peam Cheali
Kgs. Lyngby, April, 2015

Abstract

Chemical manufacturing, transportation fuels production and power plants among other sectors have strongly depended on fossil-based resources. To support sustained economic growth, additional fossil-based resources are required, but, inevitably, this also has a major impact on the global environment. These challenges motivate the development of sustainable technologies for processing renewable feedstock for the production of fuels, chemicals and materials in what is commonly known as a biorefinery. The biorefinery concept is a term to describe one or more processes which produce various products from bio-based feedstock. Since there are several bio-based feedstock sources, this has motivated development of different conversion concepts producing various desired products. This results in a number of challenges for the synthesis and design of the optimal biorefinery concept at the early-stage of process development: (i) Combinatorial challenge: a large number of potential processing paths resulting from the combination of many potential feedstocks, and many available conversion technologies to produce a number of desired products; (ii) Data challenge: the data typically used for early stage process feasibility analysis is of a multidisciplinary nature, often limited and uncertain; (iii) Complexity challenge: this problem is complex requiring multi-criteria evaluation (technical, economic, sustainability).

This PhD project aims to develop a decision support tool for identifying optimal biorefinery concepts at the early-stage of product-process development. To this end, a systematic framework has been developed, including a superstructure-based optimization approach, a comprehensive database of processing and conversion technologies, and model libraries to allow generation and comparison of a large number of alternatives at their optimality. The result is the identification of the optimal raw material, the product (single vs multi) portfolio and the corresponding process technology selection for a given market scenario. The economic risk of investment due to market uncertainties is further analysed to enable risk-aware decision making. The application of the developed analysis and decision support toolbox is highlighted through relevant biorefinery case studies: bioethanol, biogasoline or biodiesel production; algal biorefinery; and bioethanol-upgrading concepts are presented. This development and analysis provides a robust guidance to support the development of sustainable and future biorefineries.

Resumé på dansk

Sektorer vedrørende kemikaliefremstilling, brændstofproduktion og kraftværker m.fl. er stærkt afhængige af fossile ressourcer. For at understøtte en vedvarende økonomisk vækst er flere fossile ressourcer nødvendige, hvilket, uundgåeligt, leder til alvorlige virkninger på det globale miljø. Disse udfordringer motiverer udviklingen af bæredygtige teknologier til bearbejdning af vedvarende råvarer til produktion af brændstoffer, kemikalier og materialer, i det der almindeligvis betragtes som et bioraffinaderi. Bioraffinaderikonceptet dækker over de en eller flere processer, der producerer forskellige produkter fra biobaseret råmateriale. Da der er flere biobaserede råvarer, giver dette anledning til udvikling af forskellige konverteringskoncepter til at producere forskellige ønskede produkter. Dette resulterer i en række udfordringer til syntese og design af det optimale bioraffinaderikoncept i det tidlige stadie af procesudvikling: (i) Kombinatorisk udfordring: et stort antal potentielle behandlingsveje som følge af en kombination af mange potentielle råmaterialer, mange konverteringsteknologier og produkter; (ii) Dataindsamlingsudfordring: data, der typisk anvendes til tidlig procesgennemførelighedsanalyse er af tværfaglig karakter og ofte begrænset og usikker; (iii) Kompleksitetsudfordring: dette problem er komplekst, som kræver adskillige evalueringskriterier (teknisk, økonomisk, bæredygtighed).

Dette ph.d.-projekt har til formål at udvikle et beslutningsværktøj til at til at identificere optimale bioraffinaderikoncepter i den tidlige produkt/procesudviklingsfase. Til dette formål er en systematisk ramme blevet udviklet, der inkluderer en superstrukturbaseret optimeringstilgang, en omfattende database af bearbejdnings- og omdannelsesteknologier, og modelbiblioteker til at tillade generering og sammenligning af et stort antal alternativer for i sidste ende at identificere optimale løsninger. Resultatet er identificering af den optimale råvare, produktportefølje (enkelt eller adskillige) og de tilsvarende procesteknologivalg for et givet markedsscenario. Den økonomiske investeringsrisiko som følge af markedets usikkerhed er yderligere analyseret for at give anledning til risikobevidst beslutningstagning. Anvendelsen af den udviklede analyse og beslutningsværktøjskasse er fremhævet gennem relevante bioraffinaderi case studier: bioethanol, biobenzin eller biodieselproduktion; algebioraffinaderi; og bioethanol-opgraderingskoncepter er præsenteret. Denne udvikling og analyse giver en robust vejledning til at støtte udviklingen af bæredygtige og fremtidige bioraffinaderier.

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1. Introduction

The first chapter, *Introduction*, constitutes a general overview of the PhD project. A brief background and the challenges of early-stage product-process design of biorefinery are given. The motivation of the study together with the overall structure of the thesis document is presented here as well. Finally, dissemination activities related to the project and the main achievements of this thesis are briefly outlined.

1.1 Introduction

The chemical industries including chemical manufacturing, fuels production and power plants have traditionally strongly depended on fossil-based feedstock (crude oil, natural gas, coal, chemicals, etc.). Continued economic growth still leads to the development of activities that are highly energy dependent and intensive. However, the use of fossil fuels as the main energy resource is associated with many issues and impacts including long-term availability, supply security, price volatility, and especially, environmental impacts such as the emissions of greenhouse gases and the resulting climate change effects (King et al., 2010). These challenges motivate the development of sustainable technologies for processing renewable feedstock for fuel, chemical and material production, and biorefineries are an example of such technologies. The biorefinery concept refers to the process which uses biomass as a renewable feedstock to partially substitute fossil fuels for both production of energy, fuels and chemicals.

Process-product design framework

Chemical product-process design is an open problem which involves many activities (process creation, development of basic concept, experimental studies, detailed design, etc.), and decision-making at different levels as presented in Figure 1.1.

Chemical product-process design typically consists of 5 main stages (Seiden et al., 2009). The *concept stage* is the earliest stage where a number of ideas and concepts are generated. Preliminary process synthesis, which is the decision-making approach at the early-stage, is used to screen among the possible alternatives and to identify the promising ones in order to move further to the next stage. The *feasibility stage* is the step where the ideas and concepts are further developed by performing the feasibility study, simulation study, and an experimental study for selected alternatives. The detailed process synthesis is used to rank and compare the feasible concepts that have been developed before moving to the detailed design stage. At the *detailed design stage*, one alternative is selected and everything is then ready to perform the detailed design, equipment sizing, detailed capital cost estimation, procurement, and detailed economic analysis. Consequently, the complete design (plant design and layout) including

construction work, commissioning and operation is performed in the *Manufacturing stage*. Sales and marketing is then involved in the last stage, the *Product introduction*, in order to plan and maximize the product sales.

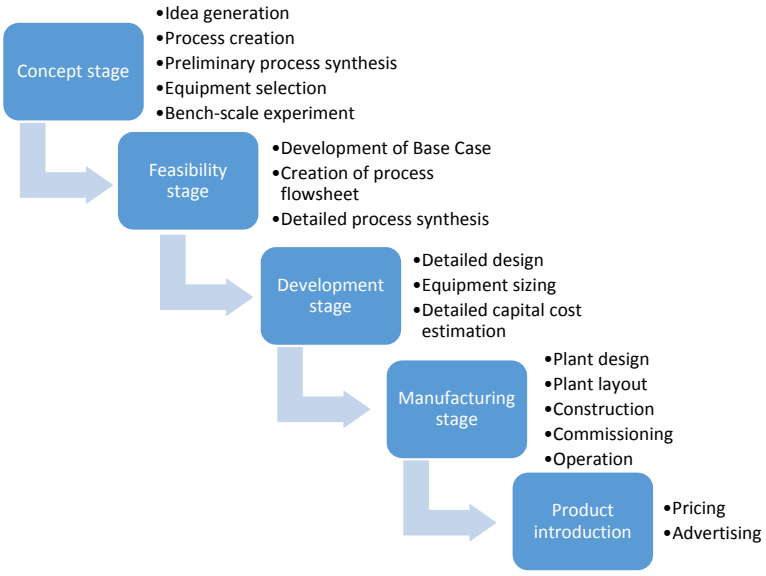

Figure 1.1. Product-process design flowsheet (Seiden et al., 2009)

The workflow of chemical product-process design can be represented as the "process design funnel" presented in Figure 1.2. This illustrates the amount of data needed through different steps of the process design workflow. The largest number of ideas and concepts generated is at the earliest stage. The number of feasible ideas and concepts is then reduced though the subsequent steps of the workflow by the concept screening and refinement steps. The concept screening is the decision-making process to evaluate the feasibility and plausibility of the ideas and concepts with respect to the design specifications and targets. At the end of the funnel (on the right), the result is the final, feasible and optimal concept with respect to every design target and constraint.

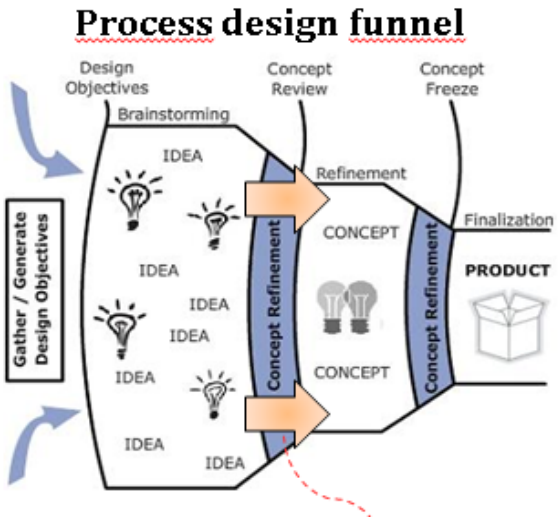

Figure 1.2. Process development funnel (moving from idea generation on the left to the final concept on the right through multi-level screening)

The traditional chemical product-process design follows the steps presented in Figure 1.1, and performs the concept screening by using the existing knowledge or experience from the experts. This is generally time-consuming and costly at the detailed stage (*development stage, stage 3*) where the available information is realistic and adequate for decision-making as illustrated in Figure 1.3 (red dashed line). However, the activities at this stage have less impact on the overall project and result in a higher cost of changing the design than the activities at the early-stage design. Therefore, most of the effort used in product-process design should be moved to the early-stage as presented in Figure 1.3 (the red dashed line is replaced by the blue dashed line). To this end the decision-making process at the early-stage needs to be improved to support large and complex problems which consist of multidisciplinary, limited and uncertain data. The improved quality of the decisions at the early stage will result in reduced time consumption and project cost during the later stage of the project life cycle (Klatt & Marquardt, 2009).

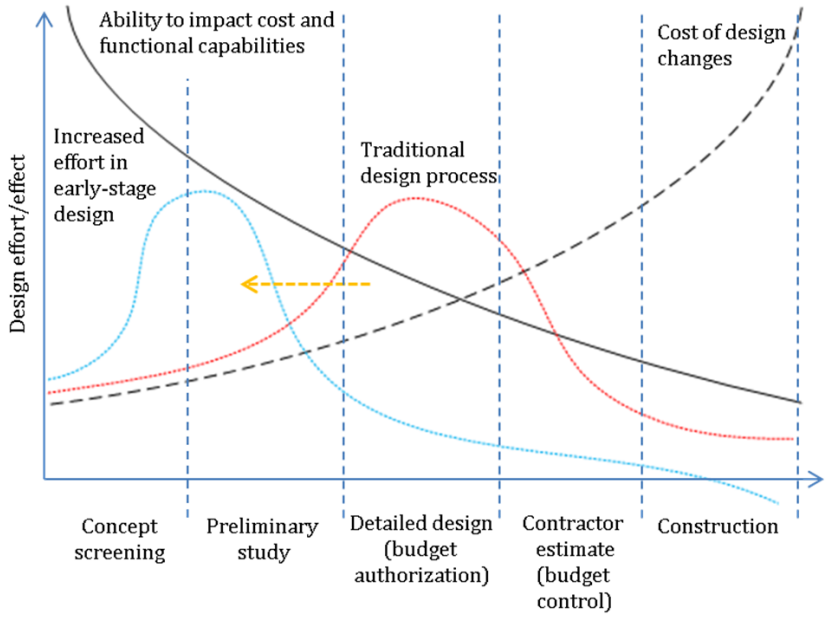

Figure 1.3. The design effort and impact on the project development (adopted from Towler and Sinnott, 2013)

Biorefinery design concept

In this PhD study, the chemical process-product design framework presented above is adopted for the biorefinery design problem. In a typical biorefinery, the system generally works by processing a bio-based feedstock to produce various products such as fuels, chemicals, or power/heat. As there are several feedstock sources, as well as many alternative conversion platforms and technologies to choose from to match a range of products, this creates a number of potential processing paths during the early stage of product-process design for biorefinery development.

The design of a biorefinery is, therefore, a challenging task. These challenges include but are not limited to:

(a.) challenges to achieve the maximum efficiency in terms of improved designs as well as through expansion by integration of different conversion platforms (e.g. biochemical and thermochemical) or upstream and downstream processes;

(b.) challenges to account for a wide range of feedstocks and formulate local/regional solutions;

(c.) challenges to take several dimensions of the design problem into account (i.e. feedstock characteristics, feedstock quality and availability; trade-offs between energy consumption for feedstock and product distribution, production and product market prices).

Furthermore, being based on biomass (natural feedstock), the economic and environmental viability of these processes is highly dependent on local factors such as land use and availability, weather conditions, national or regional subsidies and regulations. Thus, designing a biorefinery requires a detailed screening among a set of potential configurations to identify the most suited options that satisfy a wide set of constraints. A detailed evaluation among process alternatives accounting for local conditions and constraints is required for a robust decision-making. This demands a substantial amount of information (e.g. conversions, efficiencies, cost, and prices) which are both time and resource intensive.

(d.) challenges related to data collection, management and uncertainty analysis. The mentioned challenges at the early stage of biorefinery planning and design therefore require an enormous amount of data, which are often not available. Hence, proper assumptions and simplifications need to be made to manage the complexity of the problem. The problem is especially complicated when one broadens the scope of biorefinery network design, i.e. by simultaneously focusing on different conversion platforms, as it will be done in this thesis. The data for characterization and representation of each process alternative requires a substantial amount of information: parameters, variables, models of known reactions, thermodynamic properties, process efficiencies resulting in a detailed and complex model, and these require the adapted systematic optimization approach to solve the complex problem. Moreover, the challenges that generally come along with data and models used in biorefinery synthesis research are the uncertainties, both external (anticipated raw material and product prices, etc.) and technical (e.g. related to process performance metrics). This challenge

needs to be formally addressed, and is often tackled by ad hoc based scenario analysis rather than being addressed systematically.

1.2 Objective of PhD project

With the background information presented earlier, the aim of this PhD project is to develop a decision support tool for identifying optimal biorefinery concepts at the early stage of the project life cycle, while considering uncertainties inherent to this stage of project development. To achieve this objective, a systematic methodology for process synthesis and design together with formal uncertainty analysis was developed for the purpose of biorefinery concept design. To support the developed framework, the database (data, models, processing technologies) needed is developed as well as the mathematical formulation with respect to design metrics (techno-economics or sustainability). Finally, several case studies of biorefinery design are used to highlight and verify the applicability of the design toolbox.

1.3 Structure of the Thesis

This PhD thesis consists of 10 chapters as follows:

- *Chapter 1* is an introduction to this PhD thesis which briefly explains the challenges related to designing a biorefinery and the decision-making at the early stage. The motivation of this study is also presented including the structure of this PhD thesis and the dissemination activities.
- *Chapter 2* is a review on early-stage design of biorefineries. This review consists of three main sections. The first section briefly explains the development of the biorefinery. The second section discusses the role of PSE related to biorefinery design and its development (i.e. methodologies, models). The third section expands on the challenges which need further development. The objective of this chapter is to identify the gaps, which also form the motivation of this study.
- *Chapter 3* presents a systematic framework for synthesis and design of a biorefinery. The framework consists of a step-by-step procedure which uses the superstructure based optimization approach to: (i) generate the design space and alternatives (feedstock, conversion technologies, and products); (ii) formulate

the optimization problem with respect to the problem definition; and, (iii) identify the optimal processing paths using a suitable set of optimization tools (GAMS).

- *Chapter 4* presents the data collection and management step. This chapter aims at presenting in detail how to manage the complexity of the collection of a large amount of multidisciplinary and uncertain data. This step consists of: (i) the collection and management of the data; and, (ii) the verification of the collected data.
- *Chapter 5* presents the first application of the systematic framework of biorefinery design on a lignocellulosic biorefinery through a combined thermochemical and biochemical conversion platform. The framework is presented step-by-step together with the analysis of the results obtained. In particular, the effect of market price uncertainties on the design of the biorefinery is discussed in more detail.
- *Chapter 6* presents the second application which concerns upgrading a lignocellulosic biorefinery to convert bioethanol to value-added chemical products. A comprehensive economic risk assessment is performed as well on the feasibility of the concept.
- *Chapter 7* presents an uncertainty analysis in early-stage cost estimation of the lignocellulosic biorefinery. This chapter focuses on early-stage cost estimation, and in particular, on the characterization of cost estimation data and the impact and propagation of uncertainty on the decision-making solutions.
- *Chapter 8* presents the third application on an algal biorefinery. The framework is followed and presented step-by-step. The results are also verified and discussed with respect to the most optimal algal biorefinery concept.
- *Chapter 9* presents the critical analyses and comparison in terms of techno-economic performance and associated risk of a number of biorefinery concepts. The optimal biorefinery concepts which provide robustness and resilience against unknown disturbances from the market fluctuation are recommended.
- *Chapter 10* summarizes the main conclusions and achievements of the PhD study. The future perspectives of the work are also discussed.

1.4 Dissemination activities

The concepts applied and results obtained have been presented and discussed in the following international conferences and scientific journals.

Peer-reviewed scientific journal articles

- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2014) Toward a Computer-Aided Synthesis and Design of Biorefinery Networks: Data Collection and Management Using a Generic Modeling Approach. ACS Sustainable Chemistry & Engineering, Vol. 2, p. 19-29. (*chapter 4*)
- Peam Cheali; Alberto Quaglia; Krist V. Gernaey; Gürkan Sin. (2014) Effect of Market Price Uncertainties on the Design of Optimal Biorefinery Systems—A Systematic Approach. Industrial and Engineering Chemistry Research, Vol. 53, No. 14, p. 6021-6032. (*chapter 5*)
- Peam Cheali; John A. Posada; Krist V. Gernaey; Gürkan Sin. (2015) Upgrading of lignocellulosic biorefinery to value-added chemicals: sustainability and economics of bioethanol-derivatives. Biomass and Bioenergy, Vol. 75, p. 282-300. (*chapter 6*)
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2015) Uncertainties in early-stage capital cost estimation of process design – a case study on biorefinery design. Frontiers in Energy Research, Vol. 3 (3), Doi:10.3389/fenrg.2015.00003 (*chapter 7*)

Peer-reviewed conference proceedings (Web of Science/SCOPUS listed)

- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2013) Synthesis and design of optimal biorefinery using an expanded network with thermochemical and biochemical biomass conversion platforms. Computer Aided Chemical Engineering, Vol. 32, p. 985–990.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2013) A computer-aided support tool for synthesis and design of biorefinery networks under uncertainty. SCPPE2013, Dalian, China.

- Peam Cheali; Alberto Quaglia; Krist V. Gernaey; Gürkan Sin. (2014) Uncertainty analysis in raw material and utility cost of biorefinery synthesis and design. Computer Aided Chemical Engineering, Vol. 33, p. 49–54.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2015) Optimal Design of Algae Biorefinery Processing Networks for the production of Protein, Ethanol and Biodiesel. Computer Aided Chemical Engineering. Accepted.

Book chapter

- Peam Cheali; Alberto Quaglia; Carina L. Gargalo; Krist V. Gernaey; Gürkan Sin; Rafiqul Gani. (2015) Early stage design and analysis of biorefinery networks. Process Design Strategies for Biomass Conversion Systems, John Wiley & Sons, Inc. In press.
- Peam Cheali; Carina L. Gargalo; Krist V. Gernaey; Gürkan Sin. (2015) A framework for sustainable design of Biorefineries: life cycle analysis and economic aspects. Algal Biorefineries Vol. 2, Springer. In press.

Dissemination in international conferences

- Peam Cheali; Alberto Quaglia; Krist V. Gernaey; Gürkan Sin. (2013) Synthesis and Design of Thermochemical and Biochemical Biomass Processing Networks under Uncertainty. 9th European Congress of Chemical Engineering, The Hague, Netherlands. Oral presentation.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2013) A computer-aided support tool for synthesis and design of biorefinery networks under uncertainty. SCPPE2013, Dalian, China. Oral presentation.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2013) Synthesis and design of optimal biorefinery using an expanded network with thermochemical and biochemical biomass conversion platforms. 23rd European Symposium on Computer Aided Process Engineering, Lappeenranta, Finland. Poster presentation.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2013) Synthesis and design of optimal biorefinery. Biorefinery Öresund Conference 'Biorefining from raw material to high value products'. Ørestad, Denmark. Poster presentation.

- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2013) Synthesis and Design of Biorefinery Processing Networks with Uncertainty and Sustainability analysis. 2013 AIChE Annual Meeting, San Francisco, CA, United States. Oral presentation.
- Peam Cheali; Alberto Quaglia; Krist V. Gernaey; Gürkan Sin. (2014) Uncertainty analysis in raw material and utility cost of biorefinery synthesis and design. 24th European Symposium on Computer Aided Process Engineering, Budapest, Hungary. Oral presentation.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2014) Synthesis and design of hybrid biorefinery systems a structural optimization approach and uncertainty analysis. 21st International Congress of Chemical and Process Engineering, CHISA, Prague, Czech Republic. Oral presentation.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2014) Cost estimation for early-stage synthesis and design of biorefinery networks. 2014 AIChe Annual Meeting, Atlanta, GA, United States. Oral presentation.
- Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2015) Optimal Design of Algae Biorefinery Processing Networks for the production of Protein, Ethanol and Biodiesel. 25th European Symposium on Computer Aided Process Engineering, Copenhagen, Denmark. Poster presentation.

2.
LITERATURE REVIEW

Chapter 2 briefly reviews research work on early-stage design of biorefineries. This chapter consists of three main sections. The first section briefly presents an introduction to biorefinery challenges and concepts. The second section discusses the role of PSE in supporting the development of a biorefinery (i.e. published methodologies, models). The third section discusses the remaining challenges and identifies the gaps which set the motivation of this PhD study.

2.1 Introduction

2.1.1 Drivers and challenges of biorefinery development

In 1980 and 2006-2013, traditional and mature processes based on fossil fuels have been significantly affected by the fluctuation of oil prices. This motivated among others diversification efforts such as the development of blended fuels that make use of gasoline and diesel blended with high octane bioethanol to reduce the dependency on and consumption of fossil fuels. Moreover, in the past decade, the chemical industries which mainly use fossil-based chemicals as raw material and as fuel have been claimed as the main sources of anthropogenic CO_2 emission released to the environment which contributes to climate change and global warming (M. Bruscino, 2009). These challenges act as important drivers for the development of the technologies to efficiently utilize bio-based feedstock as alternative and more sustainable solution to reduce the dependency of the chemical industries on fossil-based feedstock and help alleviate the climage change impact of the chemical industry.

2.1.2 Biorefinery concept

A biorefinery is the system processing a bio-based feedstock to produce bio-based products such as biofuels (bioethanol, biogasoline and biodiesel), biochemicals (e.g. succinic acid and polylactic aicd), or bioenergy (power/heat). As there are several bio-based feedstock sources, and many conversion concepts and technologies to choose from to match a range of products (presented in Figure 2.1), this results in a large and complex system. This large and complex system can be grouped into two main conversion concepts: biochemical and thermochemical conversion platforms. These two concepts are briefly explained below.

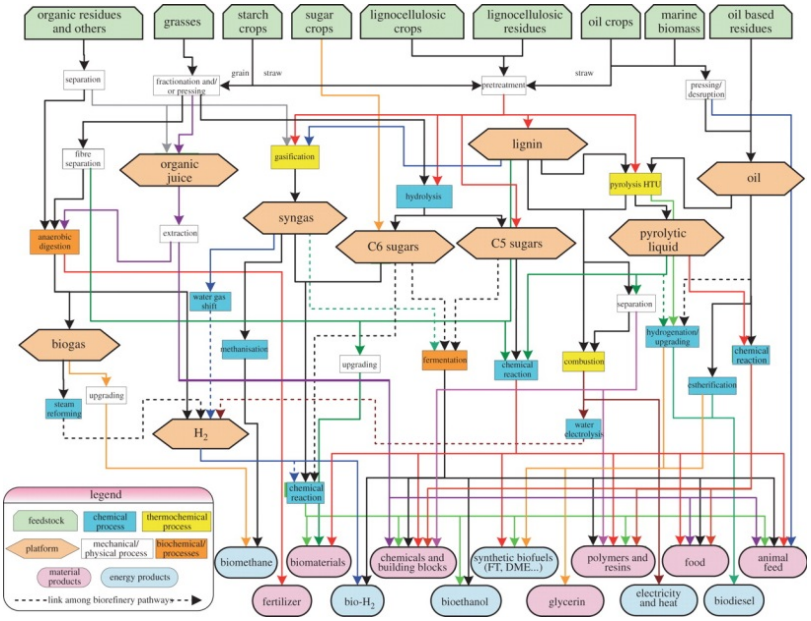

Figure 2.1. Technological routes and biorefinery system network (IEA Bioenergy, 2009)

Biochemical conversion concept - pretreatment, hydrolysis and fermentation technologies

The main goal in these processing steps is the transformation of the complex polymers in the feedstock such as cellulose and hemicellulose into simple sugars that can be utilized by microorganisms during fermentation. First, the size of the biomass is reduced by milling, grinding, or chipping. Subsequently, the separation of the lignocellulosic components (lignin, hemicellulose, and cellulose) is achieved and finally conversion to sugar and ethanol are performed. *Steam explosion, liquid hot water treatment,* a*cid hydrolysis, dilute acid hydrolysis, alkaline hydrolysis, and enzymatic hydrolysis in addition to fermentation technologies using engineered strains* are the main technologies developed in this processing step. Moreover, the S*imultaneous Saccharification and Fermentation* (SSF) process has recently been developed to combine hydrolysis (or saccharification) and fermentation in one reactor to efficiently

produce ethanol (Karp et al., 2013). Subsequently, the resulting sugar compounds are converted to ethanol using relatively well-known fermentation technology which is the main conversion technology producing bioethanol in the biochemical conversion concept. For bioethanol production, both (fed-) batch and continuous reactor systems have been developed with two main micro-organisms, *Saccharomyces cerevisiae and Zymomonas mobilis*. The latter micro-organism has recently been developed to achieve an ethanol yield as high as 97% (Bai et al., 2008). The biochemical conversion concept has been developed and is currently operated in large-scale production plants producing first and second generation bioethanol from sugar/starch-based biomass and lignocellulosic biomass, respectively. A French company called Tereos produces bioethanol from sugar beet, sugarcane and cereals in Europe and Brazil, with a production volume of 1.1 million m^3 in 2011-2012 (Tereos, 2015). In USA, ADM, Poet, Valero Energy Corporation, Green Plain Renewable Energy, and Flint Hill Resources LP are the five largest bioethanol producers which produced first and second generation bioethanol, with a total production of 5.7 billion gallon in 2013. In 2013, ABENGOA also produced first and second generation bioethanol – around 1500 ML in Europe and 400 MGal in USA (ABENGOA, 2013).

Thermochemical conversion concept – gasification, pyrolysis, Fischer-Tropsch, alcohol synthesis

This concept aims to efficiently utilize the whole biomass to produce value-added intermediates, fuels, chemicals or heat/power (Zhang, 2010). *Gasification* is the main thermochemical conversion concept converting solid feedstock into useful gaseous fuel (syngas) that can be burned to produce heat (*combustion*) or used for production of value-added chemicals (Arkansasenergy, 2003; Ridjan et al., 2013). The heat supply approach and the gasifying agent are key factors influencing the syngas yield. *Pyrolysis* is also one of the main technologies of thermochemical concept which aims at decomposing biomass into a range of useful products, either in the total absence of oxidizing agents or with a limited supply. Pyrolysis of biomass is typically carried out at a relatively lower temperature (300 to 650 °C) compared to *Gasification* (700 to 1300

°C). *Torrefaction or carbonization* has also been recently developed to produce a solid fuel with a better quality.

Contaminants produced along with syngas which have an impact on the catalyst or materials in the downstream processes, then need to be removed (Koch, 2008). Raw syngas which is generally at a temperature of 300-500 ^{o}C after heat integration is subsequently cooled and simultaneously cleaned by removing moisture, particulates and alkali. A filter or scrubber (i.e. water scrubber, venture scrubber) is used to remove particulates. The remaining hydrocarbons and tar are converted to H_2 and CO using a reformer (i.e. catalytic, steam reformer). A water-gas-shift reactor (WGS) is used to adjust the molar ratio of H_2/CO with respect to the requirement of downstream processes. Finally, H_2S and COS are removed using liquid-liquid absorption with a basic solvent (i.e. MEA, DEPG).

After primary conversion and cleaning/conditioning processing steps, the clean intermediates (i.e. syngas, pyro-oil) are converted to final products in the product synthesis step. *Alcohol synthesis* can be chosen to produce methanol, ethanol or higher alcohols, while *Fisher-Tropsch (FT) synthesis* can produce a wide range of transportation fuels (Dry, 2008). *Alcohol synthesis* is operated at 250-400 ^{o}C with higher pressure (5-30 MPa) to produce alcohol, mainly ethanol, using catalysts (i.e. modified high/low pressure, modified FT, and modified sulfide catalysts) with a high overall conversion of 75-90% (He & Zhang, 2011). In *Fisher-Tropsch (FT) synthesis,* hydrocarbons are produced from a gas mixture of H_2 and CO. Typical operating conditions of FT are 200-250 ^{o}C and 25-60 bar. The reaction is exothermic where CO reacts catalytically (cobalt or iron catalyst) with H_2 forming a growing polymer chain and producing a wide range of hydrocarbon products (C_1-C_{30+}). Syngas conversion in an *FT* synthesis reactor is typically reported to be 80% with a selectivity of 95% for liquid products. The heavier product can also be further cracked into fuels, and unconverted syngas can be recycled or used to generate heat and power. *FT* processes have currently been operated in large scale to produce synthesis fuels for countries that have no oil available (Subiranas, 2008). Shell and Sasol use natural gas and coal as feedstock to produce syngas, respectively. Shell operates the Shell Middle Distillate Synthesis

process in Malaysia using a Co-catalyst in multi-tubular fixed bed reactors which produce heavy waxes, while Sasol operates several types of reactors.

Many concepts and technologies for processing lignocellulosic feedstock explained above are under development, or in operation at pilot or demonstration scale as presented in Figure 2.2. Thus, the concepts still require an intensive effort from the product-process development point of view to develop a competitive and mature technology. This also requires the support from Process Systems Engineering (PSE) which is one of the main research areas in chemical process development.

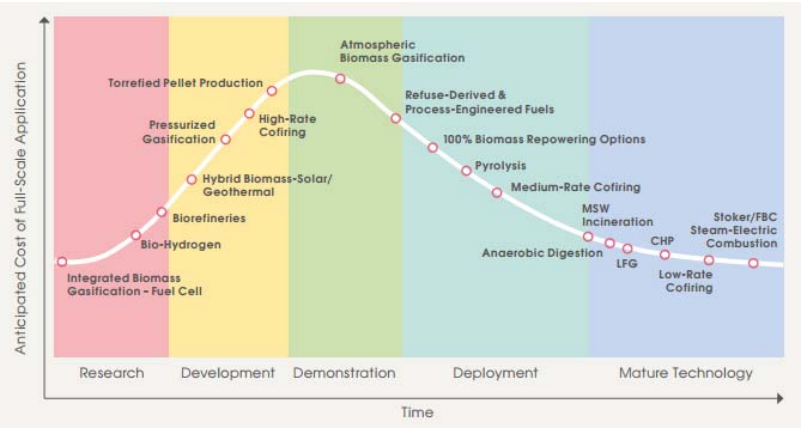

Figure 2.2. Maturity status of biomass processing technologies (IRENA, 2012)

2.2 Role of process systems engineering (PSE)

This section presents the definition of a systems approach (namely as Process System Engineering, PSE) and explains its role for supporting further optimization and development of biorefinery concepts. PSE relies on systematic methods and tools, including process modeling, simulation and optimization (MSO) to support decision-making of chemical product-process development. The benefits of PSE are typically a reduction in time and resources needed for specific development and R&D tasks (e.g. experimentation at laboratory and pilot-scale preceding further optimization efforts), or a cost reduction of changes required during the operational stage (Klatt & Marquardt, 2009). All PSE domains (i.e. product and process design, control and operations) have

been applied using model-based application methodologies which are further automated by developing computer-aided process engineering (CAPE) tools. There are two major paradigms in PSE – analysis and synthesis problems (Klatt & Marquardt, 2009). The *analysis problem* assumes that the process flowsheet, the equipment and operating data or the molecular structure are given. The model is then used to predict the performance indicators of the process and the structural and functional properties of the product. If the specifications are given as process performance indicators (or as physical properties of the products), the *synthesis problem* – as the process flowsheet is not known *a priori* – is concerned with identifying an appropriate process flowsheet for the task at hand. This problem has to be solved, either by searching in the design space, or by deploying numerical optimization algorithms which automate the search for the best alternative.

In the *synthesis problem (*or *synthesis and design problem)*, there are two main approaches. The *heuristic approach* is based on the experience of the engineer or a researcher. The *mathematical programming based approach* (or optimization based approach) uses algorithmic methods (i.e. mixed integer non-linear programming (MINLP) or stochastic programming) to identify the optimal solution regarding the specified objectives together with the mathematical representation of the nature of the technologies or properties of the components. Both approaches have been widely applied in process synthesis and design. However, there are some drawbacks related to each method: (i) for the heuristic or strategic method, there is no guarantee of an optimal solution because of the lack of interaction between the design levels; (ii) for the mathematical or algorithmic method, the process flowsheet and superstructure cannot be automatically generated, and a considerable computational effort is required. Therefore, integrating these two methods has recently been developed and has resulted in the so-called *hybrid method*. This integration approach aims at developing a systematic way to achieve truly optimal solutions, and combines the advantages of both the heuristic and the mathematical based approach.

PSE contributions on process synthesis and design of a biorefinery

As mentioned earlier, PSE is obviously a multi-disciplinary field at the interface of chemical engineering, mathematics, computer science, management science and economics. The research in this study applies PSE methods and tools focusing on synthesis and design of a biorefinery at the early-stage of product-process development. In this section, the use of PSE for synthesis and design of a biorefinery is therefore briefly reviewed.

Berhane et al. (2013) have developed models and algorithms for life cycle analysis, supply-chain, design and operation of algal and hydrocarbon biorefineries. A two-stage heuristic solution algorithm was proposed to solve a non-convex MINLP problem, and trade-off solutions between economic and environmental criteria were presented. Kokossis & Yang (2010) reviewed the studies that used PSE at different scales and levels of product-process design, and concluded that systems engineering has a huge impact on the development of each scale of the process design (i.e. supply chain, unit operation, molecular design). Furthermore, the impact of PSE will improve significantly if the scales are integrated and combined as a multi-scale formulation including multi-stage problem-solving to cope with the complexity of biorefinery processes, and to generate novelty and innovation. Shabbir et al. (2012) studied the economic viability of the biorefinery by optimizing the production of biofuels and biochemicals. The superstructure-based optimization approach and insight-based automated targeting were combined to handle the allocation of biomass feedstock. Then, fuzzy optimisation was used for the synthesis of a sustainable integrated biorefinery which takes economic and environmental performance into consideration. Voll and Marquardt (2011) introduced a reaction flux network analysis (RFNA) as a novel and rapid screening method for synthesis and design of biorefinery processing paths for the biochemical platform, and considering both techno-economic and environmental impacts. Potential reaction pathways converting biomass to biofuels were generated using this approach. Consequently, the optimal pathways were identified through the formulated MINLP problem. Baliban et al. (2012) identified the optimal biorefinery design flowsheet producing liquid transportation fuels together with integration of energy (heat and power) and water consumption for the thermochemical platform. Čuček et al. (2014)

identified the optimal supply-chain network using a multi-period synthesis framework. The multi-period optimization of a heat-integrated biorefinery's supply network was formulated as a MILP problem which extended in four layers (seasonality, and availability of resources, enabling recycles of products and total site heat integration) in order to address a real-world decision-making problem. It was concluded that (i) switchgrass and algae are promising raw materials for producing biofuels; (ii) using 20% of of existing agricultural land satisfies the demand for food and transportation fuels. Martin and Grossmann (2012) reviewed results of a biorefinery design using mathematical programming to systematically evaluate a large number of alternatives and to identify the optimal solution for economic feasibility and sustainability (dealing with energy and water consumption, and with process integration). Pham and El-Halwagi (2012) proposed a systematic two-stage methodology to reduce the number of processing steps. The superstructure-based optimization approach was used with a proposed two-stage methodology which generates 5 processing steps to reduce the complexity. Abdelaziz et al. (2015) proposed a hierarchical approach to improve the efficiency of the existing biorefinery plant using a mass and heat integration method. The results show a significant reduction of energy consumption and a slightly lower total annualized cost. Posada et al. (2013) applied a quick screening method called early-stage sustainability assessment to identify the most promising bioethanol derivatives resulting from catalytic conversion. The early-stage sustainability assessment consists of 5 main design criteria (economic, environmental impact from raw material and process, safety and hazard) which are the important factors for designing a sustainable biorefinery. Zondervan et al. (2011) studied the use of a superstructure-based optimization approach with a generic process model block to identify the optimal processing paths among the processing alternatives used in a biochemical conversion platform producing bioethanol, gasoline blends and chemicals. The aforementioned studies have not only provided interesting methodological approaches, but have also generated many promising biorefinery configurations that might be considered for commercial scale exploitation in the future.

2.3 Remaining challenges and perspectives for PSE to support optimal biorefinery synthesis and design

The aforementioned developments in PSE are great contributions in their own right. However, the design and identification of optimal biorefinery concepts for the complete processing paths still remains a challenging task. The main challenges are:

(i) The challenge to achieve the true optimal solutions by expanding the biorefinery concepts with more promising conversion concepts, to produce multiple value-added products. Biorefinery research typically focuses either on the biochemical route or the thermochemical route or the algal route. Hence, the expansion would avoid that promising alternatives are potentially ignored, and will improve the viability of the biorefinery. However there is no truly integrated approach that forms a design space that encompasses all these alternatives in a single decision space. Therefore, a developed systematic approach which generates a large, versatile and promising design space of processing networks is required.

(ii) The challenge to obtain good data to generate a good representation of biorefinery design candidates. Data obtained from different experiments, studies, or resources are generally not consistent as a consequence of different assumptions, conditions or methods. Therefore, the data should be obtained from dependable sources and a systematic verification approach is required in order to generate the dependable database that can be used as a knowledge base during the design.

(iii) The challenge to manage the uncertainties in data. At the early-stage design stage, many data (i.e. yield, operating conditions, separation efficiencies, etc.) are obtained from technologies that are still under development, and as a consequence a considerable part of the information is generally uncertain. One clear example is the fluctuation of market prices. This uncertainty in data should therefore be addressed because the optimal solutions are strongly dependent on the input data.

(iv) The challenge to manage a large and complex problem which includes all the possible combinations of biomass feedstock and their processing technologies.

This combination is composed of a wide range of specific and multi-disciplinary characteristics, (un)certain data and (non)linear models of the processing technologies. Hence, this large and complex design network needs to be managed. The management in a more compact and generic structure would reduce the complexity of the problem, thus providing flexibility for further analyses with respect to multi-objective design criteria (i.e. economic, sustainability).

(v) The challenge to compare the solutions with conventional fossil-based approaches and the relevant processes in order to attract more interest for developing future biorefineries.

Therefore, these challenges motivate the development of systematic product-process development methods as a decision support tool for identifying optimal biorefinery concepts at the early design stage. What is needed is a systematic biorefinery process synthesisframework which: (i) supports a large design space, including multi-criteria decision problems and uncertainties in data; and, (ii) provides a ranking of promising optimal processing paths including risk quantification prior to the next stage of product-process development to enhance the development of robust and sustainable concepts of future biorefineries.

3.
A systematic framework for synthesis and design of biorefinery

In this chapter, the superstructure optimization based framework for synthesis and design is presented. The framework consists of 5 steps, which are explained in detail. The framework is divided into two parts. *Part-I* is the generation of the database (superstructure, models and data). *Part-II* is the mathematical formulation of the optimization problem under deterministic and stochastic conditions, and includes the generation of the solution in terms of optimal design concepts.

Note that this chapter is a modified version of a manuscript which has been published in *(i)* ACS Sustainable Chemistry and Engineering as Peam Cheali, Krist V. Gernaey and Gürkan Sin (2014), *Towards a computer-aided synthesis and design of biorefinery networks – data collection and management using a generic modeling approach.* 2, 19-29 and *(ii)* Industrial and Engineering Chemistry Research as Peam Cheali, Alberto Quaglia, Krist V. Gernaey and Gürkan Sin (2014), *Effect of market price uncertainties on the design of optimal biorefinery systems - a systematic approach.* 53(14), 6021-6032.

The overall systematic framework (Figure 3.1) which uses a superstructure-based optimization formulation can be separated into two parts: *(i)* data handling and representation (*step 1* and *step 2*); and *(ii)* mathematical formulation and solution. The individual steps of a systematic framework (Figure 3.1) are explained in the following.

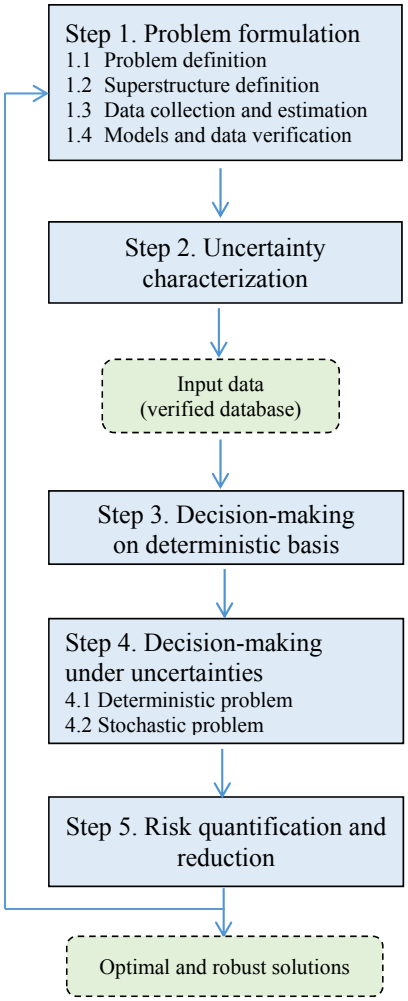

Figure 3.1. A systematic framework for synthesis and design of biorefinery networks

A systematic framework for synthesis and design of processing networks (Quaglia, 2013) is adapted and developed further in this study for biorefinery systems. The systematic framework uses a superstructure-based optimization approach to generate the design space, and it enables effective formulation and solution of a mixed integer (non-) linear problem under deterministic conditions and uncertainty. The framework (presented in Figure 3.1) consists of 5 main steps as explained below.

3.1 Step 1: Problem formulation: (i) problem definition; (ii) superstructure definition and data collection; (iii) model selection and validation

The first step includes the definition of the problem scope as well as the selection of suitable objective functions and optimization scenarios with respect to certain design specification metrics. Superstructure definition together with data collection, model selection and verification are then performed, respectively.

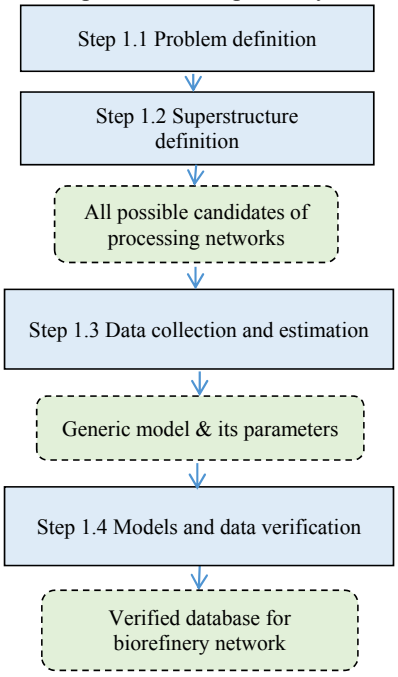

Figure 3.2. A systematic framework for the problem formulation step

Step 1.1: Problem definition

The first step includes the definition of the problem scope, the selection of suitable objective functions and optimization scenarios with respect to either economic or business metrics, engineering performance, environmental impact or sustainability or a combination of such objectives.

Step 1.2: Superstructure definition

A superstructure is defined in this study as a group of processing paths simultaneously *(i)* connecting sources (feedstock) to sinks (products) through a number of processing steps and *(ii)* comparing alternatives within each processing task as presented in Figure 3.3. In particular, a superstructure representing different biorefinery concepts and networks is formulated by performing a literature review. A typical biorefinery network consists of a number of processing steps converting or connecting biomass feedstock to bio-products such as pretreatment, primary conversion (gasification, pyrolysis), gas cleaning and conditioning, fuel synthesis and product separation and purification. Each processing step is defined by one or several blocks depending on the number of unit operations considered in the step (several unit operations can be modeled using one process block). Each block incorporates the generic model to represent various tasks carried out in the block such as mixing, reaction and separation as presented in Figure 3.4. Detailed presentation of the generic model itself is given below.

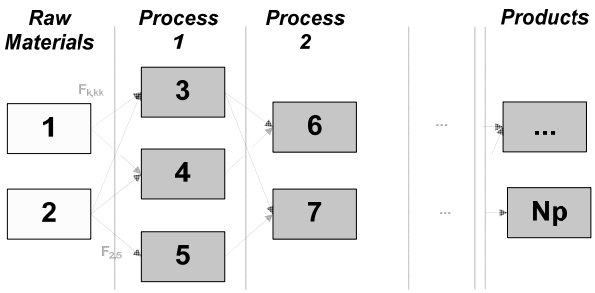

Figure 3.3. A superstructure definition (Quaglia, 2013)

Step 1.3: Data collection and modeling

Once the superstructure is defined, the data are collected and modeling is performed. Generally, the models for each processing technology are rigorous, non-linear and complex models (e.g. kinetics, thermodynamics). In this step, however, a simple input-output type generic model is used and put in a model block, and is identified from the data generated from the above mentioned complex model. This generic block thus consists of four parts of the typical simple mass balance equations: *(i)* mixing; *(ii)* reaction; *(iii)* waste separation; and, *(iv)* product separation.

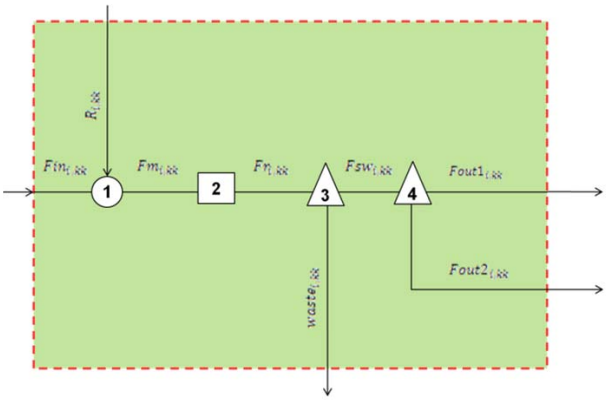

Figure 3.4. The generic process model block

Equations 3.1-3.7 are the equations used for the generic block to estimate the outlet mass flow ($Fout1_{i,kk}$, $Fout2_{i,kk}$) using simple mass balances. In Equations 3.1-3.2, the chemicals and utilities used ($R_{i,kk}$) for each processing technology are calculated by using the ratio ($\mu_{i,j,kk}$) to the inlet mass flow rate ($Fin_{i,kk}$). The parameter $\alpha_{i,kk}$ represents the consumption of the utilities or chemicals: 0 corresponds to 100% consumption; 1 represents no consumption. In Equation 3.3, the reaction outlet mass stream ($Fr_{i,kk}$) is calculated based on stoichiometry, $\gamma_{i,rr}$ and conversion fraction, $\theta_{react,rr}$. In Equations 3.4-3.5, the waste stream ($waste_{i,kk}$) and the remaining stream ($Fsw_{i,kk}$) are calculated on the basis of the removal fraction, $SW_{i,kk}$.The product outlet streams are calculated in Equations 3.6-3.7 on the basis of a product separation fraction,

$Split_{i,kk}$. Moreover, in order to connect each generic model block and thereby formulate the superstructure, the equations 3.8-3.10 are used.

$$Fm_{i,kk} = Fin_{i,kk} + R_{i,kk} \quad (3.1)$$

$$R_{i,kk} = (\mu_{i,j,kk} * Fin_{i,kk} * \alpha_{i,kk}) \quad (3.2)$$

$$Fr_{i,kk} = Fm_{i,kk} + MW_i * \sum_{rr}(\gamma_{i,rr} * \theta_{react,rr} * Fm_{i,kk}/MW_{react}) \quad (3.3)$$

$$Fsw_{i,kk} = (1 - SW_{i,kk}) * Fr_{i,kk} \quad (3.4)$$

$$waste_{i,kk} = SW_{i,kk} * Fr_{i,kk} \quad (3.5)$$

$$Fout1_{i,kk} = Split_{i,kk} * Fsw_{i,kk} \quad (3.6)$$

$$Fout2_{i,kk} = (1 - Split_{i,kk}) * Fsw_{i,kk} \quad (3.7)$$

$$F1_{i,k,kk} \leq S_p^{\mathrm{k,kk}} * Fout1_{i,kk} \quad (3.8)$$

$$F2_{i,k,kk} \leq (S_p^{\mathrm{k,kk}} - S^{k,kk}) * Fout1_{i,kk} \quad (3.9)$$

$$\mathrm{Fin}_{i,kk} = \sum_k (F1_{i,k,kk} + F2_{i,k,kk}) \quad (3.10)$$

The mass outlet flows mentioned earlier ($Fout1_{i,kk}$, $Fout2_{i,kk}$) are called primary and secondary outlet flow, respectively. The primary and secondary outlet flows are connected to the next generic blocks by specifying binary parameters (S_p, S), respectively. The outlet flows between the generic blocks ($F1_{i,k,kk}$, $F2_{i,k,kk}$) of each stream (primary and secondary) are summed up as the input of the next generic block. Note as well that recycle flows can be considered using Equations 3.8-3.10 with specification of S_p, S. There are two potential cases of recycle flows addressed: *(i)* recycle flows within the same processing step, i.e. internal recirculation - the simulation of the recycle flows and their impact on process performance needs to be done prior to estimating the parameter values for the corresponding generic model block; and *(ii)* recycle flows to one of the previous processing steps, which is handled by using Eq. 3.8-3.9.

The appropriate values for the above-mentioned parameters can be collected in several ways including: *(i)* literature sources or technical reports; *(ii)* experimental data; *(iii)* simulation results; or, *(iv)* stream table or operating data of a designed flowsheet. The

collected data are in the end organized in a multi-dimensional matrix form which represents processing steps, alternatives, components, among others etc.

Step 1.4: Models and data verification

After the superstructure is defined and the parameters are collected, a validation of the selected models and parameters needs to be performed for quality and consistency check. The validation can be performed in this step by fixing the decision variables in the problem formulation of mixed integer (non)-linear programming (MINLP) – i.e. the vector *y* (see *section 3.3*) – and thereby to perform a simulation for each processing technology or path followed by comparison of the simulation results against the available data. Such data can originate either from experiments or from the literature. All the necessary equations and constraints relevant to each processing technology are also formulated in this step prior to being solved as MILP or MINLP problems in the optimization tool (GAMS – General Algebraic Modeling System). The output of this step is a verified database representing the biorefinery superstructure formulated earlier and stored in an excel worksheet.

3.2 Step 2: Uncertainty characterization

In this step, the domain of uncertainty is defined. Statistical analysis tools, Monte Carlo simulation and Latin Hypercube Sampling with correlation control (Iman et al., 1982) are therefore integrated with the deterministic problem. Firstly, specific data or parameters need to be selected as uncertain inputs to the optimization problem. Secondly, the selected data need to be characterized in terms of a probability distribution (e.g. normal or uniform distribution). Thirdly, the correlations between the selected data are analyzed in terms of covariance, such that this information can be incorporated in the sampling if such information is available. Finally, the sampling of uncertain data is performed to generate the possible scenarios. It is important to note that this step has been expanded to support the two distinct situations of the availability of the cost estimation data at early-stage design which is explained in detail in *Chapter 7*.

3.3 Step 3: Deterministic formulation and solution

The deterministic optimization problem is solved in this step by varying the decision variable (y) and using the nominal values for parameters – in case a parameter is characterized by a certain statistical distribution (hence uncertain input) then its mean value is used in this step. For example, a general form of optimization problem (MINLP) is briefly presented below to indicate how the generic models and parameters are embedded in the optimization problem formulation. The general structural optimization formulation is presented in Eq. 3.11-3.18 which consists of the objective function (e.g. maximize product sales, Eq. 3.11) subjected to process constraints, the process models and constraints (Eq. 3.1-3.10) of the generic model block mentioned earlier (x is a process variable, the mass flow rate), structural constraints (Eq. 3.14-3.15) representing the superstructure which allows selection of only one process alternative in each step and cost functions (Eq. 3.16-3.18) to calculate the operating and capital costs using cost parameters ($P1_{i,kk}^{waste}$, waste treatment cost, $P2_{i,kk}^{utilities/chemicals}$, utility or chemicals cost, $P3_{a}^{kk}$, reactor investment cost, $P3_{b}^{kk}$, separation investment cost, $capex_{kk}$, capital expentidure).

As an example, the objective function is formulated such as to maximize product sales,

$$max.\ OBJ = \sum_{i,kk \in product} Fout1_{i,kk} * prices_i \tag{3.11}$$

Subject to:

Process models of the generic block as mentioned earlier (see Eqs. 3.1-3.7 and 3.10):

$$h\left(\mu_{i,j,kk}, \alpha_{i,kk}, \gamma_{i,rr}, \theta_{react,rr}, MW_i, SW_{i,kk}, Split_{i,kk}\right) = 0 \tag{3.12}$$

Process constraints as mentioned earlier (see Eqs. 3.8-3.9):

$$g\left({S_p}^{k,kk}, S^{k,kk}\right) \leq 0 \tag{3.13}$$

Structural constraints:

$$\sum_k y_k \leq 1 \tag{3.14}$$

$$y \in \{0;1\}^n \tag{3.15}$$

Cost constraints:

$$OPEX_{kk} = (P2_{i,kk}^{utilities/chemicals} \cdot R_{i,kk}) + (P1_{i,kk}^{waste} \cdot F_{i,kk}^{waste}) \tag{3.16}$$

$$CAPEX_{thermochem} = \sum_{kk} capex_{kk} \tag{3.17}$$

$$CAPEX_{biochem} = \sum_{kk}\left[P3_a^{kk} * {Fm_{i,kk}}^{n1} + P3_b^{kk} * {Fr_{i,kk}}^{n2}\right] \tag{3.18}$$

The problem can be formulated and solved using appropriate software (e.g. GAMS) and the generic model parameters and other data appearing in the constraints (e.g. $\alpha_{i,kk}$, $\gamma_{i,rr}$, $\theta_{react,rr}$, $P1_{i,kk}^{waste}$, $P2_{i,kk}^{utilities/chemicals}$, etc) can be accessed from the database. Moreover, different scenarios can be analyzed in this step by using different objective functions selected in *Step 1* (i.e. maximizing profit, minimizing waste and utilities, etc.). The result of this step is the deterministic solution of the optimal processing path, i.e. yielding one optimized biorefinery flowsheet scenario on the basis of mean values of the input data. The ranking of optimal solutions is also presented.

3.4 Step 4: Decision-making under uncertainty

Step 4.1: deterministic problem

In this step, the deterministic optimization problem formulated in *step 3* is solved repeatedly for each scenario generated by the sampling from the uncertainty domain from *step 2* (e.g. 200 samples). The results are the probability distribution of the objective value and the frequency of occurrence of the resulting optimal processing path candidates that are selected for given combinations of uncertain inputs. This analysis presents the changes in optimal solutions due to the changes of input uncertainty.

Step 4.2: stochastic problem

In this step, the optimization problem is modified and formulated as a two-stage stochastic programming problem (first stage, *I* and second stage *II*) by including the uncertainty domain into the parameter domain (presented in Eqs. 3.19-3.26). The first stage is where the exact values of the uncertain data are unknown. The second stage is where exact value of the uncertain data is known and corrective actions are taken accordingly in order to find a network which is feasible over the whole uncertain domain. In the equations below, Θ represents the uncertain data and $E_{\Theta}\left(f_{II}(x_I, x_{II}, y, \Theta)\right)$ represents the expected value of the objective function within the uncertain domain.

The expected value of the objective function is solved using the sample average approximation (SAA) technique (Birge and Louveaux, 1997). While formulating SAA, the constraints are converted into a number of constraints which is determined by the number of uncertain scenarios defined previously (i.e. *NS*- number of samples), which consequently increases the size of the optimization problem, and thus its complexity. Consequently, the objective function value is calculated by averaging the sum of all the values obtained for different uncertain scenarios. Therefore, the objective function is formulated in terms of minimizing or maximizing the expected value of the objective function over the uncertain domain.

$$max_{x,y}\ f_I(x_I, y) + E_\Theta\big(f_{II}(x_I, x_{II}, y, \Theta)\big) \tag{3.19}$$

Subject to:

$$g(x_{II}, y, \Theta) \geq 0 \tag{3.20}$$

$$h(x_{II}, y, \Theta) = 0 \tag{3.21}$$

$$p(x_I, x_{II}, y, \Theta) \geq 0 \tag{3.22}$$

$$q(x_I, x_{II}, y, \Theta) = 0 \tag{3.23}$$

$$x_{LO} \leq x \leq x_{UP} \tag{3.24}$$

$$y \in \{0; 1\}^n \tag{3.25}$$

$$\Theta \in [\Theta_{LO}, \Theta_{UP}] \tag{3.26}$$

Report generation

In order to analyze the results of the optimal solutions under uncertainty, a number of indicators are suggested (Birge and Louveaux, 1997; Quaglia, 2013) for summarizing and analyzing the solution under uncertainties: *i*) Expected Value of Perfect Information (EVPI), which estimates the cost of lacking the exact information on the uncertain data (Eq. 3.27). This indicator shows the possible gain from reducing the uncertainty in data; *ii*) Value of Stochastic Solution (VSS), which estimates the differences in performance between stochastic and deterministic solutions (Eq. 3.28). This indicator shows the possible gain from solving the stochastic optimization problem; and *iii*) Uncertainty Penalty (UP), which estimates the reduction in performance when the system is affected by uncertainties (Eq. 3.29).

$$EVPI = E\_\theta\ (max(f(x, y, \theta))\ ) - max(E\_\theta\ (f(x, y, \theta))) \tag{3.27}$$

The first term on the right hand side of Equation 3.25 is the expected value of the results of the decision-making under uncertainty with deterministic basis (*step 4.1*). The second term is the solution of the stochastic problem (*step 4.2*).

$$VSS = max(E\_\theta(f(x,y,\theta))) - (E\_\theta\ (f(x\_det\hat{}*, y\_det\hat{}*, \theta))) \quad (3.28)$$

The first term in Equation 3.26 is the solution of the stochastic problem (*step 4.2*). The second term is calculated by evaluating the performance of the optimal network selected against the uncertainty domain (*step 4.1* but fixing the solution from *step 3*).

$$UP = max(f(x,y)) - max(E\_\theta\ (f(x,y,\theta))) \quad (3.29)$$

In Equation 3.27, the first term is the solution of the deterministic problem (*step 3*). The second term corresponds to the solution of the stochastic problem (*step 4.2*).

3.5 Step 5: Risk quantification and reduction

In this step, the optimal solutions from *Step 4.1* (see Figure 3.1) are analyzed as risk. Risk can be represented as economic loss or environmental impact. Risk is quantified by the probability of the actual point which is lower than the referenced/specified point times its consequence, which is defined as the difference between the actual point and the referenced/specified point. The information on risk results in more robust solutions. Moreover, risk can also be reduced as presented in the following step.

3.5.1 Optimal flexible network

This step aims at enlarging the search space including redundancy in the resulting topology which allows the trade-off between investment and operational flexibility in order to mitigate the negative consequences of the uncertainty. Therefore, the decision variables (y) are in both the first stage and second stage allowed to follow a wider range of optimal processing paths or topologies which are different from previous steps. The mathematical formulation is presented in equations 3.30-3.37 (Birge and Louveaux, 1997).

$$max_{x,y}\ f_I(x_I, y_I) + E_\Theta\big(f_{II}(x_I, x_{II}, y_I, y_{II}, \Theta)\big) \tag{3.30}$$

Subject to:

$$g(x_{II}, y_{II}, \Theta) \geq 0 \tag{3.31}$$

$$h(x_{II}, y_{II}, \Theta) = 0 \tag{3.32}$$

$$p(x_I, x_{II}, y_I, y_{II}, \Theta) \geq 0 \tag{3.33}$$

$$q(x_I, x_{II}, y_I, y_{II}, \Theta) = 0 \tag{3.34}$$

$$x_{LO} \leq x \leq x_{UP} \tag{3.35}$$

$$y \in \{0; 1\}^n \tag{3.36}$$

$$\Theta \in [\Theta_{LO}, \Theta_{UP}] \tag{3.37}$$

4.
Data collection and management

The topic of this chapter is the collection and management of the complex biorefinery data which are needed among others to support the superstructure based optimization studies. To this end, we first formulate an integrated thermo-chemical and biochemical biorefinery superstructure and then use a generic modeling approach to represent each processing technology in the superstructure. The generic model parameters includes reaction yield, utility consumption, and separation efficiency among others, which are identified on the basis of input-output data (generated from rigorous models) collected from detailed biorefinery case studies reported in the open literature. The outcome is a verified database for the extended biorefinery networks combining thermo-chemical and biochemical platforms which represents 2882 potential biorefinery routes. The validated biorefinery database is made public and can be used to cross-validate and benchmark new biorefinery technologies and concepts as well as in superstructure-based optimization studies

The chapter is structured as follows: first the challenges and the motivation for this chapter is introduced and second, the application of the framework for data collection and management is presented and discussed.

This chapter is a modified version of a manuscript which has been published in ACS Sustainable Chemistry and Engineering as Peam Cheali, Krist V. Gernaey and Gürkan Sin (2014), *Towards a computer-aided synthesis and design of biorefinery networks – data collection and management using a generic modeling approach.* 2, 19-29.

4.1 Introduction

The biorefinery design space includes a large number of potential processing paths and technologies as mentioned in *Chapter 2*. The characterization of each process alternative requires a substantial amount of information: parameters, variables, models of known reactions, thermodynamic properties, process efficiencies or experimental data (Baliban et al., 2012). In order to manage the complexity of designing a biorefinery, several publications have focused on simplification i.e. *(i)* to find an optimal processing route considering only the reactions (Voll et al., 2012); *(ii)* to limit the number of processing steps to five steps (Pham et al., 2012); or, *(iii)* a systematic study of the superstructure of integrated biorefineries by using a combined process and economic modeling (Sammons et al., 2008). Clearly, in the early stage of biorefinery planning and design − a phase that is often characterized by lack of detailed data − it is important to simplify and manage the complexity related to the huge amount of data that is to be processed prior to identifying the optimal biorefinery processing path with respect to economics, consumption of resources, and sustainability.

The methodology presented in *chapter 3* (*Section 3.1,* Figure 3.1) is based on superstructure optimization and consists of tools and methods including databases, models, a superstructure, and solution strategies to represent, describe and evaluate various processing network alternatives. The data collection and management form a significant part of this methodology (presented in Figure 3.2 as the extended methodology), which is the highlight of this chapter. In particular, we expand the scope and the size of the biorefinery network problem by extending the database, the models and the superstructure of the methodology with thermochemical biomass conversion routes, and integrate them with the superstructure of the biochemical conversion network (Zondervan et al., 2011). We highlight the use of a generic process modeling approach to collect and manage multi-disciplinary and multi-dimensional data related to process alternatives in a biorefinery process network. We then perform a verification of the generic models and its parameters against the actual data source for quality control purposes. We also briefly introduce the MI(N)LP-based problem formulation to indicate how the generic model and data developed in this contribution are embedded in the

optimization problem setting. The solution and the analysis of the optimization problem itself, including the effect of data uncertainties, is however presented in the following chapters.

4.2 Data management, collection, verification and discussion

4.2.1 Step 1.1: Problem definition

The problem to be addressed is the design of an optimal biorefinery network consisting of a thermochemical platform integrated with a biochemical platform, which is indeed rather data intensive. The availability of data is however critically important for the quality of decisions to be generated using the decision support tool. Details about data collection and validation are therefore presented below.

4.2.2 Step 1.2: Superstructure definition

The thermochemical biomass conversion routes were reviewed to formulate the superstructure (Figure 4.1, top). The data and models of thermochemical conversion were collected from several U.S. National Renewable Energy Laboratorty (NREL) technical reports (Dutta et al., 2009; 2011; Phillips et al., 2007; Swanson et al., 2010; Wright et al., 2010) and one U.S. Pacific North National Laboratory (PNNL) report (Jones et al., 2009). Based on these NREL reports, the superstructure was defined. The proposed processing network for thermochemical conversion consists of 27 process intervals: 2 raw materials; 19 processing technologies; 3 main products and 3 by-products resulting in 156 parameters, 619,364 variables and 26 discrete variables.

The proposed superstructure of thermochemical conversion was then combined with the superstructure of biochemical conversion (Zondervan et al., 2011) resulting in a superstructure with a total of 96 processing intervals: 3 raw materials, 79 processing technologies and 14 products (Figure 4.1) with 576 parameters, 4,705,181 variables and 668 discrete variables.

The above-mentioned studies contain the complex, non-linear, rigorous models resulting in the simulated mass flow rate for each designed process stream. This

information provides an adequate basis for estimating the parameters of each generic block using input-output information. Further explanation and examples are presented in the next section.

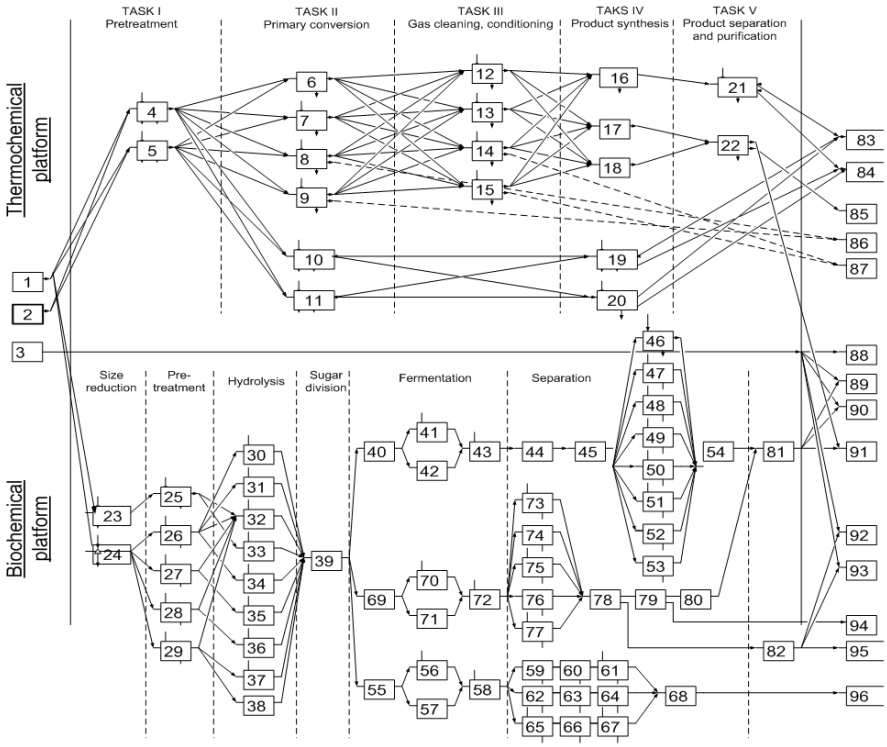

Figure 4.1. Combined superstructure of two biorefinery conversion platforms: thermochemical (top) and biochemical platform (bottom).

4.2.3 Step 3: Data collection and estimation

The data and parameters required for the generic blocks that are used to define the superstructure (*section 3.1*), are presented here and in Table 4.1-4.5. When the reported data are available from experimental or pilot plant studies, the data were collected directly. If not, the data need to be obtained from simulations, or should be estimated to

obtain the parameters used in the general block using commercial process simulators such as Pro II, Aspen, etc.

Here two examples are presented. Table 4.1, Table 4.2 and Figure 4.2 illustrate how the data were collected for the entrained flow gasifier, which is one of the processing steps in the combined superstructure. The entrained flow gasifier is used to convert solid fuels (coal, biomass) into raw syngas. It requires a special size reduction equipment, steam and O_2. Char, ash, soot and slag are collected at the bottom as wastes. It is normally operated at high temperature (1300 ^oC), and the reactions during the gasification are complex. We have used the design data reported by an NREL study (Swanson et al., 2010) for estimating generic process block parameter values for steam and O_2 ratio, conversion fraction, char and ash removal efficiencies. On the other hand, the complete stoichiometry of the reaction is not available. Thus, the stoichiometry of the reaction needs to be estimated, in this case by using Eq. 4.1 combined with the reported mass inlet and outlet streams of the processing unit shown in Table 4.2. The resulting estimated stoichiometry is given in Table 4.2 as well, and the reaction stoichiometry is shown in Figure 4.2. We note that there is no recycle stream for the entrained flow gasifier as a consequence of the very high conversion efficiency of biomass in such an entrained flow gasifier.

Table 4.1. The data collection example for the entrained flow gasifier

Descriptions	**Raw data from NREL study (Swanson et al., 2010)**		**Generic block model parameters**	
Utilities	Steam to biomass ratio	0.48	Mixing: steam ratio	0.48
	O_2 to biomass ratio	0.35	Mixing: O_2 ratio	0.35
Reaction	Stoichiometry	N/A	Reaction: Stoichiometry was estimated from stream table (Table 2a)	(eq. 4.1)
	Conversion fraction of C	1	Reaction: Conversion fraction	1

Waste separation	Char, ash, soot, slag removal	99%	$SW_{i,kk}$	0.99
	Ash removal	95%	$SW_{ash,kk}$	0.95
Product separation	Stream separation	1 outlet stream	$Split_{i,kk}$	1

$$\gamma_{i,rr} = \frac{-(mass_{(i,rr)-out} - mass_{(i,rr)-in})/MW_i}{(mass_{(reactant,rr)-out} - mass_{(reactant,rr)-in})/MW_{reactant}} \quad (4.1)$$

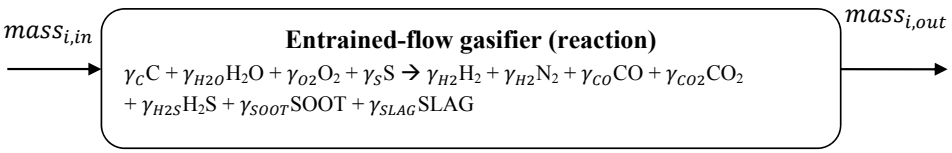

Figure 4.2. Process diagram showing mass inlet/outlet, the reaction and its stoichiometry for the entrained flow gasifier

Table 4.2. The example of the stream table of the entrained flow gasifier (Swanson et al., 2010)

Component	Gasifier inlet flow (tpd)	Gasifier outlet flow (tpd)	$\gamma_{i,rr}$ (stoichimetry)	$\theta_{i,rr}$ (conversion fraction)
H_2O	1182	988	-0.13	-
H_2	101	123	0.13	-
C	945	-	-1	1
S	4.4	-	-0.0017	-
N_2	16	17.7	0.0007	-
O_2	1512.6	-	0.6	-
ASH	120	-	-	-
CO	-	1457	0.66	-
CO_2	-	1184	0.34	-
H_2S	-	4.5	0.002	-
SOOT	-	6	0.07	-
SLAG	-	100	1.3	-

Another example of the data collection is the gas cleaning and conditioning step (task 3 in Figure 4.1). This step has an important function and is used to *(i)* remove solid particles, *(ii)* convert the remaining hydrocarbons including tar into syngas, *(iii)* adjust the H_2/CO ratio, *(iv)* remove CO_2 and H_2S which will otherwise have a negative effect on the catalysts in the next processing step. There are several unit operations that can be used in this step such as a tar reformer, a steam reformer, a water gas shift reactor, pressure-swing adsorption, venturi and water scrubber and acid removal. Here, one of the gas cleaning and conditioning steps of the NREL studies (Phillips et al., 2007) is selected as the second illustrative example. It consists of three main processing sections: tar reformer, venturi scrubber and acid removal. The function of the tar reformer is to convert tar and hydrocarbons into syngas, and the process consists of two reactors: the reformer and combustor which requires air as utility. The function of the venturi scrubber is mainly to remove solid particles and water. And the acid removal process is necessary to remove CO_2 and H_2S using aqueous solutions of amines, 35 wt% monoethanol amine (MEA). Table 4.3, Table 4.4 and Figure 4.3 illustrate the data collection for these processes. With regards to recycle streams, this was modeled using Eqs. 3.8-3.9.

Table 4.3. Data collection example for the processing units for gas cleaning and conditioning: tar reformer, venturi scrubber and acid removal.

Descriptions	**Raw data from NREL study**		**Generic block model parameters**	
Utilities	Air required for combustion (tpd)	3123	Air to inlet flow ratio	1.2
Reaction	Stoichiometry	N/A	Stoichiometry was estimated from stream table	(see Table 4.4 and Figure 4.3)
	Conversion fraction of tar	1	Conversion fraction	1
Waste separation	Water removal	50%	$SW_{i,kk}$	0.5
	CO_2 removal	36%	$SW_{ash,kk}$	0.36
	H_2S removal	85%	$SW_{H_2S,kk}$	0.85
Product separation	Stream separation	2 outlet streams	$Split_{i,kk}$	(see Table 4.4)

Table 4.4. The stream table of the tar reformer (Phillips et al., 2007)

Component	Inlet stream (tpd)	Recycle stream (tpd)	Air inlet (tpd)	Outlet stream (tpd)	$\gamma_{i,rr}$	$\theta_{i,rr}$	Primary outlet (tpd)	$Split_{i,rr}$
H_2O	901	0.35	60.9	1128	0.4	-	523.9	0.46
H_2	37.7	68.8	-	168.75	1.48	-	168.75	1
N_2	-	43.1	2312	2360.3	-	-	45.4	0.019
O_2	-	-	708.6	86.4	-0.98	-	0	0
CO	874	903.5	-	2345.7	0.94	-	2345.7	1
CO_2	408	1153.8	1.53	1873.6	0.29	-	978	0.52
H_2S	1.75	0.29		2.04	-	-	2.04	1
NH_3	3.8	0.27		0.3	-	-	0.3	1
AR	-	-	39.4	39.4	-	-	0	0
TAR	19.8	-		-	-1	1	-	-
CH_4	180	84.9		43	-0.7	-	43	1
C_2H_6	5.2	3.52		0.08	-0.015	-	0.08	1
C_2H_4	86.7	6.6		6.9	-0.15	-	6.9	1
C_2H_2	8.2	0.6		0.65	-0.0159	-	0.65	1
C_6H_6	6.6	-		0.04	-0.0042	-	0.04	1
C_3	-	17.4		17.4	-	-	17.4	1
C_4	-	3.2		3.2	-	-	3.2	1
C_5	-	0.6		0.6	-	-	0.6	1
C_1-ol	-	4.3		4.3	-	-	4.3	1
C_2-ol	-	11.6		11.6	-	-	11.6	1
C_3-ol	-	0.67		0.67	-	-	0.67	1

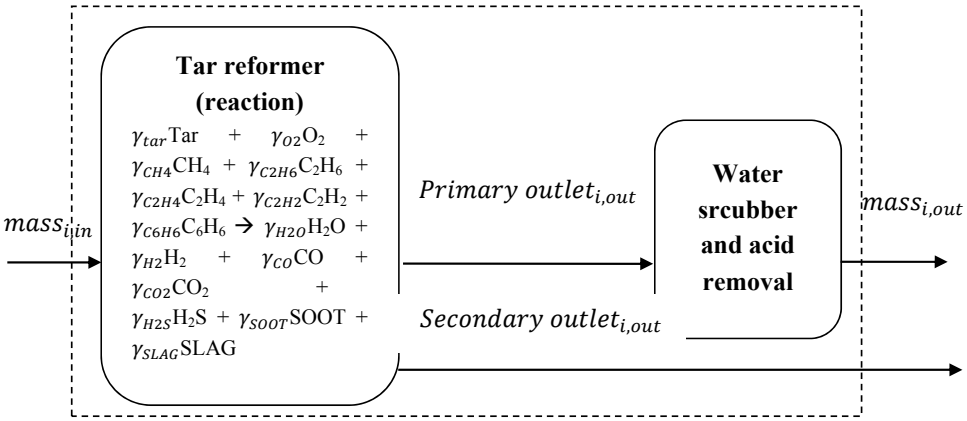

Figure 4.3. Process diagram showing mass inlet/outlet, the reaction and its stoichiometry for the gas cleaning and conditioning step (modified according to NREL report (Phillips et al., 2007).

The two examples above show how the complex data (simulation results, kinetics, separation efficiency, etc.) are converted into a generic form as a set of constant parameters. The collected data are then stored as a database in a multi-dimensional matrix (database uses Excel spreadsheet environment but any other software environment would work, e.g. Matlab, MS Access, etc). In this way, storage of the data is flexible as it only requires simple column and row operations to add, modify or update data from the database. At the same time, storing the data in the matrix form provides a certain structure to organize the data and manage the complexity in a compact and efficient way.

The description and the data collection (plus parameter estimation where necessary) for the other process intervals included in the superstructure of the thermochemical platform (Figure 4.1, top) is summarized in Table 4.5. For each process interval, mixing parameters ($\mu_{i,j,kk}, \alpha_{i,kk}$), reaction parameters ($\gamma_{i,rr}, \theta_{i,rr}$), waste separation parameters ($SW_{i,kk}$) and product separation parameter ($Split_{i,kk}$) are provided. These values are then validated by comparing the simulation results with the reported results of the NREL/PNNL reports (Dutta et al., 2009; 2011; Phillips et al., 2007; Swanson et al., 2010; Wright et al., 2010). The validation is presented in the next section and the full simulation results are presented as supporting information in Cheali et al. (2014). Note that the process intervals which are feedstock and products are presented here as follows, *(i)* feedstock (block no. 1-3, respectively): corn stover, wood, gasoline (for blending); *(ii)* products (blocks no. 83-96, respectively): FT gasoline, FT diesel, mixed alcohols, waste heat from gasifier, waste heat from reformer, gasoline (100%), bioethanol (5%), bioethanol (10%), bioethanol (100%), biobutanol (5%), biobutanol (10%), acetone, biobutanol (100%) and succinic acid. The detailed description for the biochemical platform (Figure 4.1, bottom) can be found in the previous study (Zondervan et al., 2011).

Table 4.5. Summary table for the data collection (mixing, $\alpha_{i,kk}$, $\mu_{i,kk}$, reaction, , $\gamma_{i,rr\cdot}$, $\theta_{react,rr}$, waste, $SW_{i,kk}$, and product, $Split_{i,kk}$, separation) for thermochemical processing networks

No.	Description	Mixing ($\alpha_{i,kk}$ = 1)	$\mu_{i,kk}$	Reaction (stoichiometry, $\gamma_{i,rr\cdot}$)	$\theta_{react,rr}$	Waste separation	$SW_{i,kk}$	Product separation	$Split_{i,kk}$
4	Hammer mill, rotary dryer (indirectly-contact with steam)	- Electricity to biomass ratio - steam to %moist ratio	4 5.9	-	-	Moisture removal	0.6	Steam	0
5	Hammermill and rotary dryer (directly-contact with hot flue gas)	- Electricity to biomass ratio - waste heat from process	4	-	-	Moisture removal	0.96	Waste heat	0
6	Entrained-flow (free-fall) gasifier	- O2 to biomass ratio - steam to %moist ratio	0.35 0.48	C + 0.13H2O + 0.6O2 + 0.0017S -> 0.13H2 + 0.0007N2 + 0.66CO + 0.34CO2 + 0.002H2S + 0.07SOOT + 1.3SLAG	1	Ash, soot removal	0.999	One outlet stream	1
7	Bubbling fluidized bed gasifier	- O2 to biomass ratio - steam to %moist ratio	0.26 0.17	C + 0.11H2O + 0.34H2 + 0.5O2 + 0.002S + 0.007N2 -> 0.36CO + 0.41CO2 + 0.002H2S + 0.01NH3 + 0.08CH4 + 0.01C2H6 + 0.02C2H4 + 1.2CHAR	1	Ash, char removal	0.999	One outlet stream	1
8	Indirectly-heated with circulating FB gasifier	- Air to biomass ratio - steam to %moist ratio - Fresh olivine to biomass ratio - MgOto ash ratio	2.2 0.38 0.003 0.004	C + 0.4H2 + 0.6O2 + 0.006S + 0.001N2 -> 0.7CO + 0.39CO2 + 0.12H2O + 0.006H2S + 0.002NH3 + 0.13CH4 + 0.02C2H6 + 0.03C2H4 + 0.237AR	1	Ash removal	0.999	- H2O, in primary outlet - CO2, in primary outlet - O2, N2, Ar in primary outlet	0.75 0.25 0
9	Directly-heated with bubbling gasifier	- O2 to biomass ratio - steam to %moist ratio - Fresh olivine to biomass ratio - MgOto ash ratio	0.22 0.2 0.003 0.004	C + 0.47H2 + 0.04H2O + 0.4O2 + 0.006S + 0.001N2 -> 0.19CO + 0.39CO2 + 0.006H2S + 0.002NH3 + 0.18CH4 + 0.01C2H6 + 0.013C6H6 + 0.55TAR + CHAR	1	Ash, char removal	0.999	Two product stream (same component)	0.6
10	Pyrolysis (bubbling fluidized bed)			C + 0.3O2 + 0.6H2 + 0.007N2 + 1.5ASH + -0.001S -> 0.05H2O + 0.05CO + 0.07CO2 + 0.01CH4 + 4.5CHAR + 15PYRO-OIL	1	Ash, char removal	0.85	- H2, O2, N2, CO, CO2, CH4 - H2O	0 0.63
11	Fast Pyrolysis (fluidized bed)			C + 0.5O2 + 0.7H2 + 0.45ASH + -0.0001S -> 1.4H2O + 0.002CO + 0.25CO2 + 15PYRO-OIL	1	Ash, char removal	1	- H2, O2, N2, CO2 - H2O - CO	0 0.15 0.01
12	SWGS, acid removal-amine, PSA-H2	steam to inlet flow	0.14	CO + H2O -> CO2 + H2	0.3	- H2O, N2, CO2, NH3, H2S removal - COS removal	1 0.7	One outlet stream	1
13	Direct cooler, SMR, WGS, acid removal-amine	steam to inlet flow	0.36	- CH4 + 0.1C2H6 + 0.2C2H4 + 1.6H2O -> 4.4H2 + 1.6CO - CO + H2O -> CO2 + H2	0.35 0.25	- NH3, TAR, Ash, Char, H2O removal - H2S removal - CO2 removal	0.99 0.95 0.9	One outlet stream	1
14	Tar reformer, scrubber, acid removal-amine	Air to inlet flow	1.2	TAR + 0.7CH4 + 0.015C2H6 + 0.15C2H4 + O2 -> 1.5H2 + CO + 0.3CO2 + 0.4H2O	1	- H2O removal - H2S removal - CO2 removal	0.98 0.8 0.6	- Ar, N2 in primary outlet - H2O, CO2 in primary outlet	0 0.5
15	Tar reforming, scrubber, acid removal-DEPG	Air to inlet flow	1	TAR + 0.8CH4 + 0.02C2H6 + 0.14C2H4 + 0.8O2 + 0.2CH4O -> 2.5H2 + 1.3CO + 0.5CO2 + 0.1H2O	1	- NH3, H2O, TAR, Ash, Char removal - H2S removal - CO2 removal	1 0.65 0.6	- Ar, O2, N2 in primary outlet - H2O in primary outlet - CO2 in primary outlet	0 0.6 0.4
16	Fischer-Tropsch	-	-	CO + 2.1H2 -> 10.8C1 + 9.8C2 + 8.8C3 + 7.9C4 + 7.1C5 + 6.4C6 + 5.7C7 + 5.2C8 + 4.6C9 + 4.2C10 + 3.7C11 + 3.4C12 + 3C13 + 2.7C14 + 2.5C15 + 2.2C16 +2C17 + 1.8C18 + 1.6C19 + 1.5C20 + 13Wax + H2O	0.4	-	-	One outlet stream	1
17	Alcohol synthesis (modified FT catalyst, MoS2)	-	-	CO + H2 + 0.006H2O -> 0.36CO2 + 0.06CH4 + 0.04CH4O + 0.24C2H6O + 0.026C3H8O	0.4	-	-	One outlet stream	1
18	Alcohol synthesis (metal sulfide synthesis catalyst)	-	-	CO + 1.2H2 -> 0.07H2O + 0.07CO2 + 0.1CH4 + 0.1CH4O + 0.2C2H6O + 0.017C3H8O	0.26	-	-	- H2, N2, CO, CH4 in primary outlet - H2O, alcohols in primary outlet - CO2 in primary outlet	0.01 1 0.08
19	Hydroprocessing (H2-production)	- O2 to biomass ratio - steam to %moist ratio	1.87 0.37	Pyro-oil + 0.02H2O + 0.01O2 -> 0.02CO2 + 0.001Agasoline + 0.0007diesel	1	-	-	H2O, O2, CO2 in primary outlet	0
20	Hydroprocessing (H2-purchasing)	H2 to inlet flow ratio	0.05	Pyro-oil + 0.014H2O + 0.027H2 -> 0.003CO2 + 0.003CH4 +0.002gasoline +0.0012diesel	1	-	-	H2O, O2, CO2, CH4 in primary outlet	0
21	Hydroprocessing unit	H2 to wax ratio	0.0257	Wax + 5.4H2 + 0.5C5 + 0.48C6 + 0.44C7 + 0.35C9 + 0.32C10 + 0.28C11 + 0.25C12 + 0.23C13 + 0.2C14 + 0.18C15 + 0.15C17 + 0.14C18 + 0.12C19 + 0.11C20 -> 2Gasoline+ 2.76Diesel	1	-	-	H2O, H2, CO, CO2 in primary outlet, light hydrocarbon	0
22	Mol sieve and distillations	-	-	-	-	- H2, N2, CO, CH4 removal - H2O removal	1 0.8	- CH4O in primary outlet - C2H6O in primary outlet - Higher alcohols in primary outlet	0.07 0.99 0.05

4.2.4 Step 4: Models and data verification

Seven processing paths based on five NREL reports (Dutta et al., 2009; 2011; Phillips et al., 2007; Swanson et al., 2010; Wright et al., 2010) and a PNNL report (Jones et al., 2009) were used to validate the models and data used for each process interval and processing path. As explained in *section 3.1*, the verification can be performed by fixing the processing path and comparing the simulation results with the NREL and PNNL studies. Table 4.6 summarizes the short descriptions, processing paths and the amount of biofuel products generated for each of the seven base cases used in this study. The simulation results of each processing path were verified by comparing with the detailed results published in NREL-PNNL reports.

Table 4.6. The seven processing paths used as base cases.

Cases	Descriptions	Processing path (see Figure 4.1)	Biofuels production (tpd)
1	Corn stover-entrained flow gasifier-hot gas cleaning-Fischer Tropsch (Swanson et al., 2010)	1 4 6 12 16 21 83 84	111[a], 262[b]
2	Corn stover-fluidized bed gasifier-cold gas cleaning- Fischer Tropsch (Swanson et al., 2010)	1 4 7 13 16 21 83 84	87[a], 206[b]
3	Wood-fluidized bed gasifier-tar reformer-alcohol synthesis (Phillips et al., 2007)	2 5 8 14 17 22 85 91	429[c]
4	Wood-fluidized bed gasifier-tar reformer-alcohol synthesis (Dutta et al., 2009)	2 5 9 14 17 22 85 91	526[c]
5	Wood-fluidized bed gasifier-tar reformer-alcohol synthesis (Dutta et al., 2011)	2 5 8 15 18 22 85 91	549[c]
6	Corn stover-fast pyrolysis (Wright et al., 2010)	1 4 10 19 83 84	160[a], 160[b]
7	Wood-fast pyrolysis (Jones et al., 2009)	2 5 11 20 83 84	245[a], 311[b]

[a]FT-gasoline, [b]FT-diesel, [c]bio-ethanol

The verification between the reported results from NREL-PNNL reports and the simulation results of this study (implemented in GAMS) is necessary in order to validate the quality of the collected data and the models used in this study. In the previous section, the data collection was presented as examples for (i) the entrained-flow gasifier and (ii) gas cleaning and conditioning processes. Here, the collected data for both examples are validated and presented in Table 4.7 and 4.8, respectively. The

validation results confirm that the quality of the collected data is good and the data are consistent. The full simulation results (implemented in GAMS) can be found as supporting information in Cheali et al. (2014).

Table 4.7. Summary of the validation results for the entrained flow gasifier.

		The reported results from NREL report[18]				The simulation results of this study			
	Inlet flow	R(i)	waste(i)	Fout1	Fout2	R(i)	waste(i)	Fout1	Fout2
Total (tpd)	**2222.22**	**1704**	**106**	**3819**	**0**	**1704**	**106**	**3818**	**0**
H_2O	222.22	960		988.4		960		988	
H_2	101.2			122.8				123	
O_2	812.6	700		0		700		0.1	
N_2	16			17.7				17.7	
S	4.4			0				0.1	
C	945.6			0				0.1	
ASH	120			0				0.1	
CO				1457				1457	
CO_2				1184				1184	
H_2S				4.5				4.5	
NH_3				0.1				-	
COS				0.3				-	
AR		43.7		43.7		43.7		43.7	
CH_4									
SLAG			100				100		
SOOT			6				6		
CHAR									

Table 4.8. Summary of the validation results for the gas cleaning and conditioning step of case 3: tar reformer, water scrubber and acid removal (Phillips et al., 2007).

		The reported results from NREL report					**The simulation results of this study**				
	Inlet flow	**Recycle**	**R(i)**	**waste (i)**	**Fout1**	**Fout2**	**Recycle**	**R(i)**	**waste (i)**	**Fout1**	**Fout 2**
Total (tpd)	**2534**	**2302**	**3123**	**1089**	**3063**	**3940**	**2302**	**3123**	**1089**	**3063**	**3940**
H_2O	901.3	68.8	60.9	514.7	9.2	604	68.8	60.9	515	9.2	604
H_2	37.7				168.7					168.7	
O_2		43.1	708.6			86.4	43.1	708.6			86
N_2			2313		45.4	2315		2313		45.4	2315
CO	874.3	903.6			2346		903.6			2346	
CO_2	408	1153.8	1.5	572.7	405.3	895.6	1153.8	1.5	573	405.3	896
H_2S	1.8			1.3					1.3		
NH_3	3.9										
TAR	19.8									0.1	
COS											
AR			39.4			39.4		39.4			39.4
CH_4	180.5	84.9			43.0		84.9			43	
C_2H_6	5.2	3.5			0.1		3.5			0.1	
C_2H_4	86.8	6.6			6.9		6.6			6.9	
C_2H_2	8.2	0.6			0.7		0.6			0.7	
C_6H_6	6.6	-					-			0.1	
C_3		17.4			17.4		17.4			17.4	
C_4		3.2			3.2		3.2			3.2	
C_5		0.6			0.6		0.6			0.6	
C_{1}-ol		4.3			4.3		4.3			4.3	
C_2-ol		4.3			11.6		4.3			11.6	
C_3-ol		11.6			17.4		11.6			17.4	

4.3 Uncertainties in data

Another important aspect to consider when collecting data is that there are uncertainties which could be related to technical, economic and environmental parameters. It is important therefore to address uncertainties in data, which is needed for making decisions under uncertainty when applying the computer-aided synthesis and design approach (Quaglia et al., 2013). In order to exploit this feature, sources of uncertainties in the data need to be identified and characterized. In this study, the feedstock cost and the product price are considered to have significant uncertainty associated with their reported range. After identifying the uncertain parameters, data were then collected for statistical analysis. For estimating the uncertainty on product prices namely gasoline, diesel and ethanol prices, historical data (year-2012) have been used (USDA and US EIA). The historical data were statistically analyzed using the Matlab statistics toolbox which returned the correlation matrix (given in Table 4.9, bottom) as well as empirical distribution functions (shown in Figure 4.4). Based on the empirical distribution function, a uniform distribution was selected to be appropriate to describe the uncertainty range for these data together with upper and lower range as reported in Table 4.9 (top). For the characterization of uncertainty on the feedstock, as no historical data was available for these, instead, the open literature was reviewed to find out lower and upper bound, and reported in Table 4.9 (top). Further, an uniform distribution was assumed for these parameters, which is common practice in the uncertainty and sensitivity analysis field to use non-informative priors in case of no data availability (Helton et al., 2003; Sin et al., 2011).

Table 4.9. Input uncertainty for feedstock and products

Input uncertainty	Min.	Max.	References
Corn stover cost ($/dry ton)	60	100	NREL (Swanson et al., 2010)
Wood cost ($/dry ton)	60	100	NREL (Dutta et al., 2011)
	Mean	Std.	References
Gasoline price ($/gal)	3.53	0.21	U.S. EIA
Diesel price ($/gal)	3.97	0.14	U.S. EIA
Ethanol price ($/gal)	2.24	0.18	U.S. Department of Agriculture
Correlation matrix between uncertain data (USDA, US EIA)			

Correlation matrix	Stover cost	Wood cost	Gasoline price	Diesel price	Ethanol price
Stover cost	1	0	0	0	0
Wood cost	0	1	0	0	0
Gasoline price	0	0	1	0.71	0.12
Diesel price	0	0	0.71	1	0.36
Ethanol price	0	0	0.12	0.36	1

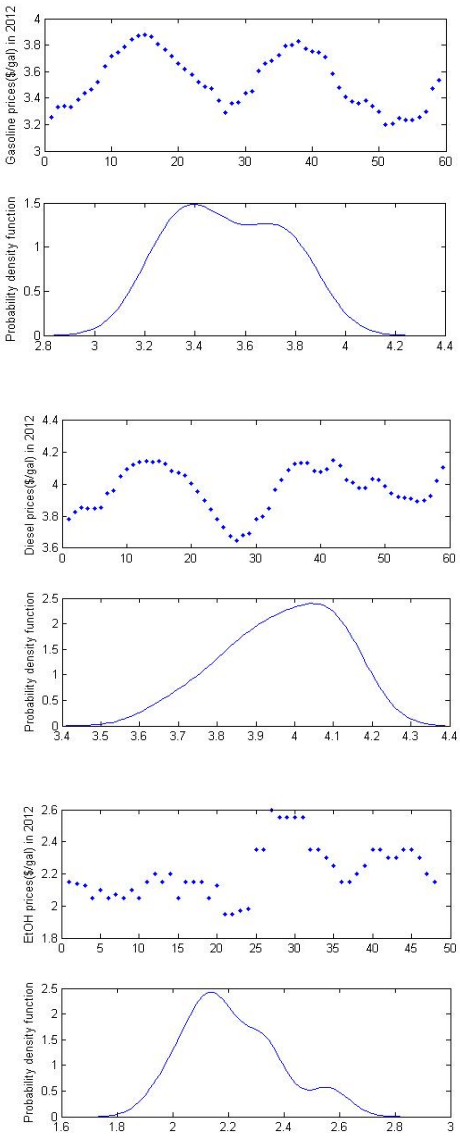

Figure 4.4. Fuel price ($/gal) in 2012 and the corresponding probability density function for gasoline (top), diesel (middle) and ethanol (bottom).

4.4 Discussion

The expanded network provides an expanded space for optimization studies meaning that it can generate more scenarios to compare a large number of processing alternatives before generating an optimal decision for biorefinery designs, but it can also generate a large amount of data.

The problem of optimal biorefinery design is data intensive with several categories of data (thermodynamic properties, kinetics, operating conditions or processing technologies), and it is therefore important to organize the data in a compact and generic way. This is achieved by defining and using a generic process model block. In this way, it becomes relatively easy to collect and summarize different types of data (kinetics, experimental data, thermodynamics properties, simulation results, operating conditions, etc.) from many resources (literatures, reports, etc.) following the generic data structure. Indeed, the generic model reduces the data needs to six parameters representing mixing ($\mu_{i,j,kk}, \alpha_{i,kk}$), reaction ($\gamma_{i,rr}, \theta_{i,rr}$), waste ($SW_{i,kk}$) and product separation ($Split_{i,kk}$), which are obtained from experimental and rigorous simulation studies reported. Moreover, the resulting database and its structure can be used for cross-checking and validating data.

The availability of informative data resources is important, also with the use of the generic model blocks, since the quality of the results strongly depends on the quality of the input data. In this study, therefore, peer-reviewed sources and reports from national and renowned institutes such as NREL-PNNL studies were used for several reasons: *(i)* the data are in general considered to be objective and of high quality as the data source (i.e. NREL-PNNL) confirms to quality check and assurance and remains impartial to technology developers; *(ii)* the studies are easily accessible through public resources (open literature, books, reports); and, *(iii)* the commercial technologies together with their improved process designs (heat integration, techno-economic analysis, etc.) are represented in the alternatives. For these reasons, the superstructure defined and data collected represents a technically realistic and validated database of biorefinery relevant processing technologies. The database can be accessed from the following link:

(http://www.capec.kt.dtu.dk/documents/biorefinery/InputData_biorefinery_for_public.xls).

The database also features an option to include uncertainties for data by defining an appropriate statistical distribution function together with their parameters (e.g. lower and upper bounds for uniform distribution). This provides a means to assess quality of the data source – the larger the uncertainty, the lower the reliability of the data which affects the performance of the included alternatives. In this study, we considered raw material costs and product prices to be major sources of uncertainty and provided a corresponding uncertainty characterization. Such uncertainty information is valuable for making robust decisions as discussed elsewhere (Quaglia et al., 2013).

The database will be maintained and expanded with more biorefinery relevant technology development efforts to keep it up-to-date and use it in our research for identifying optimal biorefinery concepts with respect to technical, economic and environmental objectives using the developed computer-aided synthesis and design toolbox.

4.5 Conclusion

The development of a superstructure and a database for thermochemical conversion and its integration with a biochemical conversion route were presented. The intensive data requirement of the biorefinery network design problem was addressed by using a structured and generic model to represent process alternatives. The structured and generic approach is important to manage and check the quality and consistency of multidimensional data. In the future, the database will be maintained and expanded with more biorefinery pathways and process alternatives, and will be used to perform multi-criteria evaluation to identify optimal biorefinery concepts under various applications and optimization scenarios including sustainability metrics. The biorefinery database features also characterization of important sources of uncertainties in data, which is valuable for assessing risk associated with biorefinery design as well as supporting risk-based decision making during early project planning/development stages.

5.
CASE STUDIES I: INTEGRATED BIOREFINERY - THERMOCHEMICAL, BIOCHEMICAL CONCEPTS

This chapter presents the development of a computer-aided decision support tool for identifying optimal biorefinery concepts for production of biofuels at an early design stage. To this end, the superstructure-based process synthesis approach integrated with uncertainty analysis is used. The developed superstructure, verified database and models from *chapter 4* are used as the input in this chapter. The application of the tool for generating optimal biorefinery concepts for a lignocellulosic biorefinery is demonstrated. In particular, the mathematical formulation and solution of an optimization problem under deterministic and stochastic conditions is highlighted to identify the optimal processing route for multiple raw materials and products. Furthermore, the impact of market price uncertainties on the optimal solutions is evaluated, and the associated risk to enable informed and risk-aware decisions is calculated.

This chapter is a modified version of an article which has been published in Industrial and Engineering Chemistry Research as Peam Cheali, Alberto Quaglia, Krist V. Gernaey and Gürkan Sin (2014), *Effect of market price uncertainties on the design of optimal biorefinery systems - a systematic approach.* 53(14), 6021-6032.

5.1 Introduction

In a typical biorefinery, the system generally works by processing a bio-based feedstock to produce various products such as fuels, chemicals, or power/heat. As there are several feedstock sources, as well as many alternative conversion technologies to choose from to match a range of products, this creates a number of potential processing paths during the early stage of product-process design of biorefinery development. Therefore, during the early stage of planning and design, it is important to identify the optimal biorefinery processing path with respect to economics, consumption of resources, and sustainability, as well as considering the impact of uncertainties on decision making.

As presented in *chapter 2*, a number of studies have been published on the synthesis and design of biorefinery networks focusing on different aspects of the challenges and opportunities of such a synthesis and design task. While each of these studies provided a valuable contribution, however the scope of the study was always limited to one processing/conversion platform (i.e. biochemical, thermochemical, chemical or biological platforms). In this chapter, this challenge is tackled by broadening the scope of biorefinery synthesis to consider thermo-chemical and biochemical platforms, simultaneously.

Another challenge during the early stage of biorefinery planning and design is the enormous need for data and models as presented in *Chapter 4*. This challenge generally comes with uncertainty, both external (anticipated raw material and product prices, etc.) and technical (e.g. related to process performance metrics). This challenge needs to be formally addressed, and is often tackled by ad hoc based scenario analysis. With this background information in mind, the aim of this chapter is to develop a decision support tool for identifying optimal biorefinery concepts at the early stage of the project life cycle, while considering uncertainties inherently present at this stage of project development.

To this end, a systematic methodology for process synthesis and design together with formal uncertainty analysis (presented in *Chapter 3*, *Section 3.1*) was applied. As mentioned earlier, the developed superstructure with the verified database and models

from *chapter 4* was used as an input for optimization, in combination with the definition of a suitable feedstock. Following the definition of the superstructure, different optimization problems were solved: the deterministic problem, the deterministic problem under uncertainties and a stochastic problem were all solved with the final goal to identify the optimal solutions under uncertainties and to calculate the associated risk.

5.2 Synthesis and design of biorefinery network under uncertainties: results and discussion

In this section, the application of the framework to the formulation and solution of the biorefinery design problem is demonstrated, and the results obtained for different scenarios are discussed.

5.2.1 Step 1: Problem formulation: *(i)* problem definition; *(ii)* superstructure definition and data collection; *(iii)* model selection and validation

The goal of the problem was the identification of the optimal biorefinery concept, with respect to a given techno-economical objective. Four objectives have been considered, resulting in the definition of 4 scenarios for the analysis, which have the following objectives: *(1)* maximize production of FT-products (FT-gasoline and FT-diesel); *(2)* maximize Earnings Before Interest, Taxes, Depreciation and Amortization (EBITDA) for FT-products; *(3)* maximize production of bioethanol; *(4)* maximize Earnings Before Interest, Taxes, Depreciation and Amortization (EBITDA) for bioethanol production.

The developed superstructure (combining thermochemical and biochemical processing routes, which was to convert corn stover or wood to biofuels and bioethanol, Figure 4.1), and the collected data from the previous chapter are used as a basis for this chapter, and these tasks are therefore not described in the present chapter.

5.2.2 Step 2: Uncertainty characterization

In this step, the most relevant sources of uncertainties based on the data analysis were identified and characterized using statistical distribution functions. The uncertainties of

market prices (raw material cost and product prices) identified in *chapter 4* as the important sources affecting the decision concerning the biorefinery design are also used as the input for this chapter. We are of course aware of the fact that other sources of uncertainties are present in the system such as uncertainties in technical performance data (yield, conversion, utility consumption, etc.). These uncertainties are kept outside of the scope of this study for the sake of simplicity, but also because many pilot and demonstration scale studies as well as NREL and PNNL studies have demonstrated the feasibility of the technological alternatives.

Selection and characterization of uncertainties

It is obvious that the feedstock costs (corn stover and wood costs) and biofuels prices have fluctuated considerably in the past, e.g. in the year 2012 (USDA; US EIA). These inputs were therefore selected as major sources of uncertainties. The probability density functions were estimated empirically from the historical observations for these market prices and were used to infer a proper statistical distribution function. The analysis was presented and explained in *chapter 4*, indicating that feedstock costs and product prices can be characterized as uniform and normal distributions, respectively.

Sampling with correlation control

The parameters of the distribution (Table 4.9, top) together with the correlation matrix (Table 4.9, bottom) were used to generate 200 samples (Figure 5.1) from this defined uncertainty domain by using Latin Hypercube Sampling with the correlation control method. As regards the correlation matrix, it is noted that the correlation coefficients for fuel products were identified from historical data, whilst no correlation was assumed between feedstock costs and product market prices as no information or data were available to this end.

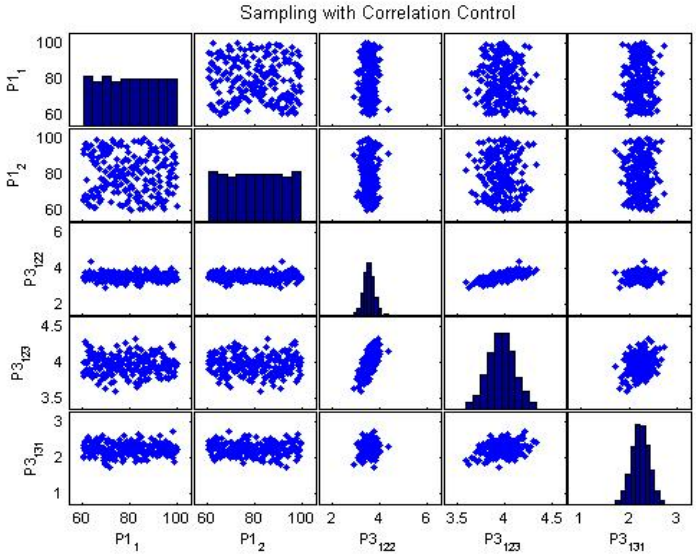

Figure 5.1. The sampling results with correlation control of corn stover cost ($P1_1$), wood cost ($P1_2$), gasoline price ($P3_{122}$), diesel price ($P3_{123}$), ethanol price ($P3_{131}$).

As a result (Figure 5.1) of the sampling procedure, 200 samples representing future scenarios defined by different sets of feedstock costs and product prices were defined. In the uncertainty domain defined for the analysis, these samples have equal probability of realization.

5.2.3 Step 3: Deterministic formulation and solution

Mathematical formulation

The optimization problems for different scenarios of objective functions were solved in this step. The full optimization formulation used for this study is presented below.

The objective functions,

Scenario-1: $$max.FT-products = \sum_{i,kk}\left(F_{i,kk}^{out}\right); \quad (5.1)$$

Scenario-2: $$max.EBITDA = \sum_{i,kk}\left(P3_{i,kk}\cdot F_{i,kk}^{out}\right) - \sum_{kk} OPEX - \frac{CAPEX_1+CAPEX_2}{t};\ i \equiv FT-products \quad (5.2)$$

Scenario-3: $$max.Ethanol = \sum_{i,kk}\left(F_{i,kk}^{out}\right); \quad (5.3)$$

Scenario-4: $$max.EBITDA = \sum_{i,kk}\left(P3_{i,kk}\cdot F_{i,kk}^{out}\right) - \sum_{kk} OPEX - \frac{CAPEX_1+CAPEX_2}{t};\ i \equiv bioethanol \quad (5.4)$$

Subject to the following constraints:

(i) process models: material balances of the generic block

Raw materials,

$$F_{i,kk}^{out} = \phi_{i,kk} \quad (5.5)$$

Mixing-1: main equation,

$$F_{i,kk}^{M} = \sum_{k}\left(F_{i,k,kk}\right) + \alpha_{i,kk}\cdot R_{i,kk} \quad (5.6)$$

Mixing-2: chemicals or utilities used,

$$R_{i,kk} = \mu_{i,kk}\cdot\sum_{i,k}\left(F_{i,k,kk}\right) \quad (5.7)$$

Reaction,

$$F_{i,kk}^{R} = F_{i,kk}^{M} + MW_i * \sum_{rr}(\gamma_{i,rr} * \theta_{react,rr} * F_{i,kk}^{M}/MW_{react}) \quad (5.8)$$

Waste separation,

$$F_{i,kk}^{out} = F_{i,kk}^{R}\cdot\left(1 - SW_{i,kk}\right) \quad (5.9)$$

$$F_{i,kk}^{WASTE} = F_{i,kk}^{R} - F_{i,kk}^{out} \quad (5.10)$$

Product separation,

$$F_{i,kk}^{out1} = F_{i,kk}^{out} \cdot Split_{i,kk} \quad (5.11)$$

$$F_{i,kk}^{out2} = F_{i,kk}^{out} \cdot (1 - Split_{i,kk}) \quad (5.12)$$

(ii) process constraints: rules defining the superstructure together with the flow constraints,

$$F_{i,k,kk}^{2} \leq F_{i,kk}^{out2} \cdot (S - S_p) \quad (5.13)$$

$$F_{i,k,kk}^{2} \leq F_{i,kk}^{out2} \cdot (S - S_p) \quad (5.14)$$

$$F_{i,kk}^{in} = \sum_k (F_{i,k,kk}^{1} + F_{i,k,kk}^{2}) \quad (5.15)$$

$$\sum_k F_{i,k,kk}^{1} = F_{i,kk}^{out1} \quad (5.16)$$

$$\sum_k F_{i,k,kk}^{2} = F_{i,kk}^{out2} \quad (5.17)$$

$$\sum_i F_{i,kk}^{out} \leq F_{kk}^{MAX} \quad (5.18)$$

(iii) structural constraints: to define the extended superstructure (the referenced number presented with decision variable (y) refers to the process intervals presented in Figure 4.1)

Raw materials,

$$y_1 + y_2 + y_3 \leq 1 \quad (5.19)$$

Processing step 1: pretreatment (thermochemical) together with a size reduction step (biochemical),

$$y_4 + y_5 + y_{23} + y_{24} \leq 1 \quad (5.20)$$

Processing step 2: primary conversion (thermochemical) together with pretreatment (biochemical),

$$y_6 + y_7 + y_8 + y_9 + y_{10} + y_{11} + y_{25} + y_{26} + y_{27} + y_{28} + y_{29} \leq 1 \quad (5.21)$$

Processing step 3: gas cleaning and conditioning (thermochemical) together with hydrolysis (biochemical),

$$y_{12} + y_{13} + y_{14} + y_{15} + y_{30} + y_{31} + y_{32} + y_{33} + y_{34} + y_{35} + y_{36} + y_{37} + y_{38} \leq 1 \quad (5.22)$$

Processing step 4: product synthesis (thermochemical) together with fermentation (biochemical),

$$y_{16} + y_{17} + y_{18} + y_{19} + y_{20} + y_{40} + y_{69} + y_{55} \leq 1 \quad (5.23)$$

Processing step 5: product separation and purification,

Thermochemical:

$$y_{21} + y_{22} \leq 1 \quad (5.24)$$

Biochemical:

$$y_{46} + y_{47} + y_{48} + y_{49} + y_{50} + y_{51} + y_{52} + y_{53} \leq 1 \quad (5.25)$$

$$y_{73} + y_{74} + y_{75} + y_{76} + y_{77} \leq 1 \quad (5.26)$$

$$y_{59} + y_{62} + y_{65} \leq 1 \quad (5.27)$$

(iv) cost models

Operating cost,

$$OPEX_{kk} = P1_{kk}^{RM\ costs} + (P2_{i,kk}^{utilities/chemicals/catalysts} \cdot R_{i,kk}) + (P4_{i,kk}^{waste} \cdot F_{i,kk}^{waste}) \quad (5.28)$$

Capital cost: *(i)* data collected and *(ii)* piecewise linearization,

$$CAPEX_1 = \sum_{kk} capex_{kk} \quad (5.29)$$

$$CAPEX_2 = \sum_{kk}\left[\sum_j \left(\alpha_{j,kk} \cdot w_{j,kk} + \beta_{j,kk} \cdot Q_{j,kk}\right)\right] \quad (5.30)$$

$$F_{kk}^{M} = \sum_j Q_{j,kk} \quad (5.31)$$

$$Q_{j,kk}^{o} \cdot w_{j,kk} \leq Q_{j,kk} \leq Q_{(j+1),kk}^{o} \cdot w_{j,kk} \quad (5.32)$$

$$\sum_j w_{j,kk} = 1 \quad (5.33)$$

(v) optimization constraints: big-M formulation,

$$F_{i,kk}^{out} \leq M \cdot y_{kk} \tag{5.34}$$

$$R_{i,kk} \leq M \cdot y_{kk} \tag{5.35}$$

$$y_{kk} \leq M \cdot \sum_i F_{i,kk}^{out} \tag{5.36}$$

$$\sum_i F_{i,kk}^{in} \leq M \cdot y_{kk} \tag{5.37}$$

Results

In this step, the optimal solutions were also identified under the aforementioned specific scenarios of the nominal data (or mean values) and the results are presented in Table 1 illustrating the comparison results between different specific optimization scenarios. Production rate, EBITDA and total annualized cost (TAC) as well as the optimal processing paths were presented. This solution corresponded to the deterministic solution of the optimization problem where no uncertainties were considered. The formulation of the optimization problem for the specific scenarios (scenario 2) consists of 3,887,985 equations, 3,858,131 variables and 612 discrete variables. This problem was solved using the DICOPT solver using Windows 7, Intel® Core™ i7 CPU@ 3.4GHz, 4GB RAM, and required 10 seconds of execution.

Table 5.1. The optimization results and comparison to the reference studies (Processing paths referred to Figure 4.1)

Sce-nari-os	Objective function	Process intervals selection (Figure 4.1)	FT produc-tion (tpd)	EBITDA (MM$/year)	TAC (MM$/year)	References
1	Max. FT-products	2 4 6 15 16 21 83 84	171[a], 403[b]	205	92	This study
2	Max. FT-products sales, min. utility, waste, investment	2 5 6 14 16 21 83 84	170[a], 402[b]	210	88	
NREL (thermo-chemical)		1 4 6 12 16 21 83 84	111[a], 262[b]	105	91	Swanson et al. (2010)
PNNL (thermo-chemical)		2 5 11 20 83 84	245[a], 311[b]	149	133	Jones et al. (2009)

Sce-nari-os	Objective function	Process intervals selection	Ethanol production (tpd)	EBITDA (MM USD/year)	TAC (MM USD/year)	References
3	Max. Etha-nol	2 4 6 15 18 22 85 91	600	86.2	102	This study
4	Max. Etha-nol sales, min. utility, waste, investment	2 5 6 14 17 22 85 91	590	86.6	79	
Max. Ethanol (biochemical)		1 24 26 32 39 40 41 42 43 44 45 50 54 81 91	556	58	98	Zondervan et al. (2011)
Max. Ethanol - min.utility, waste, equipment cost (biochemical)		1 23 25 33 39 40 41 42 43 44 45 49 54 81 91	520	51	95	Zondervan et al. (2011)
NREL (biochemi-cal)		2 5 9 15 18 22 85 91	544	75	79	Dutta et al. (2011)
NREL (biochemi-cal)		-	527	55.5	92.5	Foust et al. (2009)
NREL (thermo-chemical)		-	589	75	90	Foust et al. (2009)

[a]FT-gasoline, [b]FT-diesel

As presented in Table 5.1, the entrained-flow gasifier (block no. 6) was the favourite alternative due to its higher raw syngas yield and high biomass conversion. Woody biomass (block no. 2) was also the favourite feedstock due to its high carbon content. The scenarios 1 and 2, which were to produce transportation fuels (FT-gasoline and FT-diesel) had a higher EBITDA compared to scenarios 3 and 4 (in Table 5.1) because of higher market prices, even though higher costs were presented. The total annualized costs (capital and operating costs) had a direct effect on the optimal solution. The feedstock costs, on the contrary, have no effect on the optimal solutions in this case study because similar market prices were defined. Moreover, in comparison, the new optimal processing paths show a better production rate with reduced TAC.

In addition to the optimal solution, the top-five optimal solutions are presented in Tables 5.2a-5.2d for the four scenarios mentioned earlier. Each table presents the objective value, production rates, EBITDA and total annualized cost (TAC).

Table 5.2. Top-five rank of the optimal solutions

5.2(a): Top-five rank of the optimal solutions: scenario 1: max. production of FT-products					
Rank no.	**Process intervals selection**	**Objective value**	**Production (tpd)**	**EBITDA (MM USD/year)**	**TAC (MM USD/year)**
1	2 **4 6 15** 16 21 83 84	171[a], 403[b]	171[a], 403[b]	205	92
2	2 **5 6 14** 16 21 83 84	170[a], 400[b]	170[a], 400[b]	210	88
3[24]	2 **5 11 20** 83 84	245[a], 311[b]	245[a], 311[b]	149	133
4	2 **5 8 15** 16 21 83 84	141[a], 334[b]	141[a], 334[b]	170	77.5
5	2 **4 8 14** 16 21 83 84	138[a], 327[b]	138[a], 327[b]	166	76
5.2(b): scenario 2: max. FT-products sales, min. operating cost and investment cost (max. EBITDA)					
Rank no.	**Process intervals selection**	**Objective value**	**Production (tpd)**	**EBITDA (MM USD/year)**	**TAC (MM USD/year)**
1	2 **5 6 14** 16 21 83 84	210	170[a], 400[b]	210	88
2	2 **4 6 15** 16 21 83 84	205	171[a], 403[b]	205	92
3	2 **5 8 15** 16 21 83 84	170	141[a], 334[b]	170	77.5
4	2 **4 8 14** 16 21 83 84	166	138[a], 327[b]	166	76
5[26]	2 **5 11 20** 83 84	75	160[a], 160[b]	75	89
5.2(c): scenario 3: max. production of bioethanol					
Rank no.	**Process intervals selection**	**Objective value**	**Production (tpd)**	**EBITDA (MM USD/year)**	**TAC (MM USD/year)**
1	2 **4 6 15** 17 22 85 91	600	600	86.2	82
2	2 **5 6 15** 17 22 85 91	600	600	85.2	83
3	2 **5 6 14** 17 22 85 91	590	590	86.6	79
4	2 **4 8 15** 17 22 85 91	565	565	86.2	73
5[10]	1 24 26 32 39 40 41 42 43 44 45 50 54 81 91	556	556	58	98
5.2(d): scenario 4: max. ethanol product sales, min. operating cost and investment cost (max. EBITDA)					
Rank no.	**Process intervals selection**	**Objective value**	**Production (tpd)**	**EBITDA (MM USD/year)**	**TAC (MM USD/year)**
1	2 **5 6 14 17** 22 85 91	86.6	590	86.6	79
2	2 **4 6 15 17** 22 85 91	86.2	600	86.2	82
3	2 **4 8 15 17** 22 85 91	86.2	565	86.2	73
4	2 **5 6 15 17** 22 85 91	85.2	600	85.2	83
5[23]	2 **5 8 15 18** 22 85 91	77	544	77	76

[a]FT-Gasoline, [b]FT-Diesel

The optimal solutions for producing FT-gasoline, -diesel and bioethanol are presented in Table 5.2 (5.2a-5.2b and 5.2c-5.2d, respectively). The results illustrate that the thermochemical conversion platform (pyrolysis, gasification) was most of the time selected. In contrast, there was only a single processing path of the biochemical platform selected, ranking fourth (as shown in Table 5.2c). Wood, entrained flow gasifier and catalytic reformer together with DEPG acid removal were the most frequently selected processing intervals. Moreover, the differences between the top-three ranking solutions are small meaning that the input data are very important. This issue will be addressed in more detail in future work by performing uncertainty analysis on uncertain parameters of the selected biorefinery alternatives.

5.2.4 Step 4a: Solution under uncertainty - deterministic condition

For each of the 200 samples generated in *step 2*, the optimization problem was formulated and solved to identify the optimal processing path, resulting in 200 optimal solutions, which are then statistically analysed for example using a cumulative distribution function (CDF) to fully characterise the effect of uncertainties on the decision making. The full results were then mapped and analysed, in order to identify the optimal solution under uncertainties. The processing paths, frequency of selection and their objective value are presented in Table 5.3 and Figure 5.2.

Table 5.3. The frequency of selection of the optimal processing paths for 200 scenarios

Network no.	Processing path	Frequency of selection	EBITDA (MM$/a)
1	2 **4** 6 **15** 16 21 83 84	83/200	138-230
2	2 **5** 6 **14** 16 21 83 84	74/200	140-197
3	1 4 11 20 83 84	18/200	133-195
4	1 5 11 20 83 84	16/200	146-177
5	1 5 10 20 83 84	7/200	154-175
6	1 5 6 14 16 22 83 84	2/200	138-173

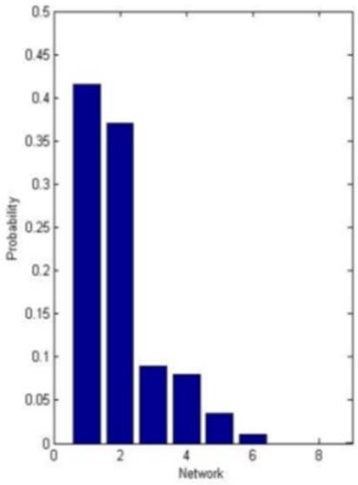

Figure 5.2. Uncertainty mapping and analysis: the frequency of selection of the optimal processing paths.

As can be seen in Table 5.3 and Figure 5.2, with 200 potential scenarios resulting from considering uncertainties, there were 6 processing paths selected and network 1 (first bar on the left) and network 2 (second bar on the left) were good candidates under uncertainties. Then, the internal rate of return (IRR) was used in order to analyze and evaluate the different potential engineering projects resulting from the optimizations. IRR is an indicator of the efficiency, quality, or yield of an investment. IRR is commonly used to evaluate the desirability of investments or projects (Schmidt, 2004). IRR is mathematically equal to the internal rate of return where net present value (NPV) is zero, $NPV = \sum_{n=0}^{N} \frac{C_n}{(1+r)^n} = 0$. The higher a project's IRR, the more desirable it is to undertake the project.

In Figure 5.3 (left and right), the impact of market price uncertainties on the IRR for network 1 and 2 is presented in terms of IRR cumulative distribution functions (CDF), from which the probability of obtaining a return equal to or higher than a given threshold value can be obtained.

In order to highlight the application of this tool, a company that has a target IRR for engineering projects of 10% within 20 years of project life time is assumed. For the

network 1, the CDF indicates that there is a 10% probability of failure to reach this target IRR of the company (hence Pr (IRR<10%) is 0.1). For the network 2, the probability of failure to reach the target IRR (10%) is 15%, hence Pr(IRR<=10%) . This provides the probability of occurrence of an undesirable situation.

For a more complete picture of uncertainties, risk analysis is usually needed. Risk is defined as the product of probability of occurrence and its consequences (Crowl et al., 2002). The consequence in this case is defined as lower rate of economic return of an engineering project making it a bad investment option. Hence, the risk is calculated as the product of the probability of occurrence (P_j) of a lower rate of return (IRR) (within 20 years of project investment life time) times the magnitude of the economic impact of the risk (M_j in \$) as follows: $Risk = \sum_j P_j \cdot M_j$, where j is the occurrence of the undesirable event, P_j is the probability of that occurrence and M_j is the consequence (in \$) of the undesirable event. The calculation of risk is in fact equal to the integral of the area highlighted in the cumulative distribution function for IRR shown in Figure 5. In this calculation, EBITDA corresponding to IRR at 10% is assumed as break-even point, hence the risk in economic terms is calculated as the summation of probability of occurrence times the deviation of EBITDA from the break-even point: $[EBITDA_{i,(@IRR<10\%)} - EBITDA_{(@IRR=10\%)}]$. The risk calculation is summarized for network 1 and network 2 in Table 5.4 (above). The results indicate that there is a risk of 0.84 MM\$/a versus 1.35 MM\$/a for network 1 and network 2, respectively. Relative to the expected return the risk can be considered small at hindsight. However, the absolute risk number calculated in this study reflects the market uncertainties definition (see *step 5.2.2*) and is intended for illustration purposes on how the market uncertainty can be included in economic evaluation of the project. For a more comprehensive analysis, it is noted that the scenario definition for the market price uncertainties and investment costs (capital, interest rates, depreciation etc.) should be provided following typical corporate guidelines. All in all the risk calculation indicates that network 1 is a safer investment option compared to network 2.

Table 5.4. The comparison of risk occurring under uncertainties and the distribution characterization of %IRR between network 1 and network 2

	Units	Network 1	Network 2
A quantified economic risk			
Total investment	(MM$)	575	600
Expected return	(MM$/a)	210.25	205
Risk	(MM$/a)	0.84	1.35
Data characterization			
Frequency of selection	-	83/200	74/200
Average IRR (%)	(%)	11.06	10.99
Standard deviation of IRR	-	0.94	1.19

*Risk is calculated for a break-even at IRR of 10%.
$Risk = \sum_i (EBITDA_{i,@IRR<10\%} - EBITDA_{@IRR=10\%})$, which is the area under CDF (Figure 5.3).

Moreover, with respect to the data characterization presented in Table 5.4 (below), the standard deviation of network 1 is lower confirming that the network 1 is more robust under uncertainties, which is in agreement with the risk analysis performed for the economic return of biorefinery investment options above. This information provides a deeper analysis and insights on the risks due to a defined source(s) of uncertainties on the technology/biorefinery concept selection at the early stage.

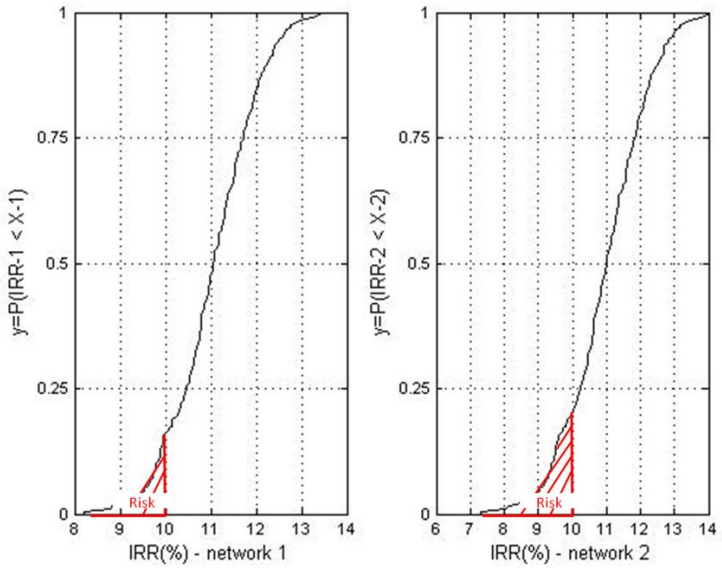

Figure 5.3. Uncertainty mapping and analysis: the probability distribution of %IRR for network 1 (left) and network 2 (right).

5.2.5 Step 4b: Solution under uncertainty – stochastic conditions

In this step, the domain of uncertainty defined in step 2, and used in step 4, was used again. Instead of performing the optimization individually for each uncertain combination of input data, a stochastic programming was formulated and incorporated into the optimization problem. In this problem, the uncertain data are raw material costs ($P1_{kk,\theta}$) and product prices ($P3_{i,kk,\theta}$). Therefore, the equations 5.4 and 5.28 were re-formulated by adding the uncertainty domain to the domain of the parameter as follows.

$$max.\,EBITDA = \sum_{i,kk}\left(P3_{i,kk,\theta} \cdot F_{i,kk}^{out}\right) - \sum_{kk} OPEX - \frac{CAPEX_1 + CAPEX_2}{t}; \tag{5.38}$$

$$OPEX_{kk} = P1_{kk,\theta}^{RM\ costs} + \left(P2_{i,kk}^{utilities/chemicals/catalysts} \cdot R_{i,kk}\right) + \left(P4_{i,kk}^{waste} \cdot F_{i,kk}^{waste}\right) \tag{5.39}$$

The result of this step is 210.215 (MM$/a) which is lower than the result of step 3 because of the effect of uncertainties. The result of the optimal solution under uncertainties was presented in Table 5.5.

Report generation

As explained earlier in the previous section, this section presents the results of the indicators presenting the effect of uncertainties in Table 5.5. All the results obtained from each step (*step 5.2.3*-*5.2.5*), were used to determine each indicator.

Table 5.5. Report generation (Processing paths refer to Figure 4.1)

Solutions	**Processing paths**		**EBITDA (MM$/a)**
Optimal network (*step 5.2.3*, scenario 2)	Wood, entrained-flow gasifier, steam reforming, Fischer-Tropsch, Hydroprocessing		210.24
Network under uncertainties (*step 5.2.5*)			210.215
Indicators	**EVPI (MM$/a)**	**VSS (MM$/a)**	**UP (MM$/a)**
Network under the effect of uncertainties (*step 5.2.3*-*5.2.5*)	0.09	0	0.025

As shown in Table 5.5, the same process topology was selected and this confirms therefore the robustness of the deterministic solution. The analysis of the uncertainty indicators (EVPI, VSS and UP) confirms this observation. A small value is obtained as Expected Value of Uncertainty Information (EVPI), indicating that the exact knowledge of the uncertain data (market price) would not allow identifying a better solution than the one already identified in the deterministic case. Moreover, the Value of Stochastic Solution (VSS) is zero, since the solution obtained under uncertainty is equal to the one obtained for the deterministic case. Similarly, a small value is obtained as Uncertainty Price. This is due to the fact that the same solution remains optimal over the uncertainty domain, whose symmetric structure results in a balance between positive and negative effects of data uncertainty on the objective function value. It is important to note that there is no requirement to include a risk reduction step due to the small impact of uncertainties.

5.3 Discussion

The results of each step of the framework presented earlier confirms that a wide range of biorefinery designs can be compared, ranked and new optimal processing paths were found by following the framework. However, a number of issues need to be discussed.

The superstructure of the thermochemical platform considered raw materials and processing technologies to produce two major products mainly used for industries: (i) transportation fuels (in this study, FT-gasoline, FT-diesel); (ii) bioethanol. Furthermore, the superstructure considered two major, commercial raw materials (corn stover and wood). A number of appropriate alternatives were considered based on the NREL and PNNL studies including the general, commercial and well-studied technologies. In parallel many studies performed systematic selection of technology, heat integration, pinch analysis, life cycle assessment, sensitivity and sustainability analysis which resulted in the superstructure that is able to cover all of the potential alternatives. The extended biorefinery networks (combined thermochemical and biochemical platforms) were developed to expand the design space, meaning that it can compare more platforms, processing paths, and alternatives. The extended networks can also generate more scenarios, solutions and satisfy more requirements and specifications of end-users (engineers, researchers, managers, etc.). As can be seen, the new optimal processing path can be successfully identified using the approach and methodology, resulting in a significant improvement and reduction of product yield and costs, respectively. This implementation and improvement provides a more robust optimal solution. Moreover, a relatively high number of initial ideas can be reduced into a smaller number prior to evaluating the final decisions. Alternatively, the bottleneck can be identified for the existing processes, and this can also help end-users (e.g. engineers) improving their processes.

The plausibility and feasibility of the optimal solutions were also checked and discussed as follows. For the primary conversion task (processing task 2, Figure 4.1), the comparison among the gasification technologies has been studied by Zhang (2010) and it was concluded that entrained-flow gasification is the most promising gasification technology which is an agreement with the study of Boerrigter et al. (2004). Moreover,

van der Drift et al. (2004) have also reported a high conversion efficiency of entrained flow gasification and also concludeded that the similar pretreatment and gas cleaning processes as obtained here provided the highest overall efficiency to convert biomass to clean syngas (H_2/CO=2). An entrained flow gasifier has been commercially used for coal gasification processes that are part of the manufacturing operations of Shell, Teaco, Krupp-Uhde, Dow, MHI, etc. Recently, it has been adapted and widely used for biomass conversion by CHOREN, Range Fuel, KIT with Siemens, MHI and Pearson technology (E4tech, 2009). These aforementioned studies confirm and verify the selection of the entrained flow gasifier in this study. For the gas cleaning and conditioning (processing task 3, Figure 4.1), raw syngas containing tar/heavy hydrocarbons and raw syngas containing a little fly-ash/slag are produced from the fluidized-bed gasifier and the entrained flow gasifier, respectively. The produced tar needs to be removed or converted by catalytic conversion (Gassner et al., 2009) or scrubbing liquid (Boerrigter et al., 2004). On the other hand, raw syngas from the entrained flow gasifier contains lower impurities and is easier to clean, however the H_2/CO ratio needs to be adjusted resulting in a high amount of CO_2 which needs to be removed. In this task, the process configuration, which depends on a downstream application, has a major effect on the process selection resulting in an optimized arrangement of unit operations and recycles (Swanson et al., 2010; Zhang, 2010; Clausen, 2011; Kumar et al., 2009). This confirms the selection results that the recycle flow rate and the sequence of unit operations are the critical points and should be optimized. For the fuel synthesis task (processing task 4, Figure 4.1), there are two major processes producing fuels which are Fischer-Tropsch and Methanol to Gasoline (MTG) presented by Spath & Dayton (2003). However, only Fischer-Tropsch is considered in this study because MTG can only produce gasoline (Baliban et al., 2012; Zhoa et al., 2008). Fischer-Tropsch is a promising process producing clean synthetic fuels (straight-chain paraffin) directly from syngas (Baliban et al., 2012; Boerringer et al., 2004). The hydroprocessing unit is required to treat FT-liquids and convert wax into the suitable fuels. Moreover, ethanol can also be produced directly from syngas via alcohol synthesis (Spath & Dayton, 2003). The aforementioned studies indicate that FT and alcohol synthesis are the promising alternatives. In addition, pyrolysis is also considered as one of the promising technologies for biomass conversion and utilization,

however, having an efficient technology available for upgrading a pyrolysis-oil is crucial (Mohan et al., 2006) because of the presence of a substantial amount of water and mixed oxygenated compounds. Moreover, the different types and operation modes of pyrolysis produce different compositions of pyrolysis-oil which leads to different process configurations of the upgrading processes (Bridgwater, 2012). This confirms that there was no selection of the pyrolysis pathway from the superstructure because of the high total annualized cost of the upgrading processes. In addition to the biochemical platform, the type of feedstock presents a significant impact on the conversion platforms: herbaceous biomass (agricultural residue and energy crops) is suitable for biochemical conversion; in contrast, wood is suitable for the thermochemical platform (Foust et al., 2009). The thermochemical platform produces a higher amount of product, although it has a higher total annualized cost resulting in a very comparable operating profit when comparing both platforms. Each platform has its individual strengths and weaknesses. However, the objective functions defined in this study (maximizing products and maximizing operating profit) lead to no selection of the biochemical platform because lignin utilization is not considered. The results are in agreement with the comparison study in the thesis of Falano (2012). In addition to product portfolio, this study focuses on converting biomass into transportation fuels which are FT-gasoline, FT-diesel and bioethanol. Building on these results, further work is directed at exploring more biorefinery concepts including the lignin utilization in a hybrid manner as well as the multi-product biorefinery considering more diversified chemical products and by-products such as DME, methanol, H_2, fertilizer, etc.

The input data and its quality are of major significance as they directly influence the optimal solution. Therefore, uncertainty analysis was used in order to estimate and predict the probabilities and economic risks of the optimal solution under market uncertainties. As uncertainty analysis clearly demonstrated that there is a considerable risk in decision metrics concerning the optimal biorefinery concept, hence this shows the importance of both formally treating the uncertainties as well as – if possible – making an investment to reduce the sources or magnitude of uncertainties. Three indicators (EVPI, VSS, UP) also highlight the effect of the uncertainties on the solutions and they indicated that the uncertainty of market prices had an impact on the expected

performance of the optimal design, although the process topology did not change under the defined uncertainty domain regarding the linearity and symmetry of the problem. This is proven by the Basic Sensitivity Theorem (Fiacco & Bank, 1984) in which there is a linear relationship between the value of an uncertain parameter (θ) and the value of the objective function of the linear problem (Eq. 5.40).

$$f(\theta) = f(\theta_o) + c(\theta - \theta_o) \tag{5.40}$$

Therefore, it is proven that for the linear problem, at the optimal network (y^*) - at the point in the uncertainty domain (θ_o), the same feasible and optimal solutions exist when comparing deterministic ($f(x, y^*, \theta_o)$) and stochastic solutions ($max_{x,y}\, E_\theta(\, f(x, y, \theta))$).

Alternatively, the optimal flexible network concept (*step 5, 3.5.1*) can be applied to manage the uncertainties by selecting more than one processing technology, and then choosing the best one to be operated after the uncertainties are known better. This alternative method was successfully shown to be the most favorable choice in an earlier study (Quaglia et al., 2013). Sensitivity and uncertainty on process performance and investment cost related parameters can complement further the economic risk evaluation of the optimal biorefinery concept during early project planning/development stages.

5.4 Conclusion

The extended biorefinery network coupled with a superstructure optimization based approach and uncertainty analysis framework was presented and discussed. The optimal solutions show that wood, entrained-flow gasifier, steam reforming, acid removal (amine) and the optimized recycles were favorable. Two optimal solutions analyzed under market price uncertainties revealed significant economic risks in the range of 0.84 and 1.35 MM$/a. This analysis helps identify and quantify the economic risk of investment in biorefinery concepts and technology at the early stage and is expected to contribute to more robust decision making.

6.
CASE STUDIES II: UPGRADING BIOETHANOL TO VALUE ADDED CHEMICALS

The upgrading strategies to improve the overall economy of the lignocellulosic biorefinery are presented in this chapter. First, the superstructure representing the lignocellulosic biorefinery design network (presented in *Chapter 4* and analyzed in *Chapter 5*) is extended to include the options for catalytic conversion of bioethanol to value-added derivatives. Second, the optimization problem for biorefinery upgrading is formulated and solved for two different objective functions: (i) maximization of operating profit (i.e. the techno-economic criteria); and (ii) minimization of the sustainability single index ratio (i.e., the sustainability criteria). This chapter aims to (i) improve overall economy of the lignocellulosic biorefinery presented in *Chapter 5,* (ii) compare the solutions with petro-based processes using sustainability index; and (iii) analyze the impact of market prices uncertainties. The results are presented and discussed in detail.

This chapter is a modified version of a paper which has been published in Journal of Biomass and Bioenergy as Peam Cheali, John A. Posada, Krist V. Gernaey and Gürkan Sin (2015), *Upgrading of lignocellulosic biorefinery to value added chemicals: sustainability and economics of bioethanol-derivatives.* Biomass and Bioenergy, Vol. 75, p. 282-300.

6.1 Introduction

An important concept related to the efficient processing of renewable feedstock into bio-based products is the "integrated biorefinery", which aims to convert all biomass fractions into a range of marketable products. This concept can be identified as "the integrated production of bio-based chemicals, biofuels, bio-based polymers, pharmaceuticals, food and/or feed" (adapted from Cherubini and Strømman, 2011). However, for this integrated production there are usually multiple bio-based feedstocks and conversion technologies that match a range of pre-defined products, resulting in a large number of potential processing combinations and production paths for the conceptual design of biorefineries (Aden et al., 2004). Therefore, during the early stage of planning and design, a methodology capable of rapidly reducing the number of alternatives, and thus reducing the complexity of the design problem, would strongly support decision-making in the early stage of the conceptual design (Klatt and Marquardt, 2009).

There are, however, a number of challenges related to the synthesis and design of biorefinery systems (as presented in *chapter 2*), for example: (a) challenges to achieve the maximum efficiency with improved designs as well as expansion by integration of conversion platforms (e.g. biochemical and thermochemical) or upstream and downstream processes; (b) challenges to account for a wide range of feedstocks and formulate local/regional solutions instead of solutions on a global basis as is the case for fossil-fuel based processes; (c) challenges to take several dimensions of the design problem into account (i.e. feedstock characteristics, feedstock quality and availability; trade-offs between energy consumption for feedstock and product distribution, production and product market prices).

To overcome these challenges, a number of studies on lignocellulosic biorefineries have been performed in the past covering different areas, e.g. supply-chain, process synthesis and design, and product design. These studies looked at different aspects of the biorefinery concept such as type of feedstock, processing technologies, and products as reviewed by Yuan et al. (2013). Moreover, most of these aforementioned studies deal with bioenergy and biofuels production, in particular with bioethanol as end product.

However bioethanol can be used as intermediate feedstock to further synthesize and produce a large number of higher value-added chemicals, which can improve the overall economy of the biorefinery (Zwart, 2006; Posada et al., 2013). This study therefore expands the scope of the biorefinery concept in two ways: *(a)* by simultaneously considering both thermochemical and biochemical conversion technologies in the design space; and, *(b)* by considering upgrading bioethanol to produce value-added chemicals.

Therefore, this chapter aims to address the problem of finding an optimal upgrading strategy for lignocellulosic biorefineries towards production of bioethanol derived value-added chemicals. A systematic evaluation methodology is used which was developed on the basis of earlier studies (*chapter 4* and *chapter 5*). In particular, the following is presented: *(i)* an extension of the lignocellulosic biorefinery superstructure by including the processes needed for bioethanol upgrading into value-added chemicals to improve the overall biorefinery economy; and, *(ii)* a comparison of two objective functions (i.e. techno-economic and sustainability) under market uncertainties. The techno-economic objective function considers the operating profit, while the sustainability objective function is a multi-criteria index that compares the bio-based reference system to its equivalent petrochemical counterpart, and which considers: techno-economic aspects of feedstock and products, greenhouse gas emission (GHG) and cumulative energy demand (CED) of raw materials and processes, hazards indicators of all chemicals present in the system and economic aspects related to external agents.

6.2 Materials and methods

As mentioned earlier, two objective functions are used for two analyses in this chapter: the first one is a purely techno-economic evaluation (*i.e.* maximization of Earnings Before Interest, Taxes, Depreciation and Amortization (EBITDA) for producing bioethanol-derivatives, while the second one is a simplified version of the comparative early stage sustainability assessment method for bio-based materials. A description of both functions is provided below.

6.2.1 Techno-economic analysis of ethanol derivatives (maximization of operating profit)

This first objective function aims to identify the optimal processing paths which provide the highest annual profit or EBITDA (MM$/a) as presented in Eq. 6.1. Product sales are calculated based on the predicted amount of bioethanol-derivatives to be produced combined with product market prices. Moreover, the total annualized cost (TAC) consists of an annualized capital cost and operating cost as presented in Eq. 6.2.

$$\max. EBITDA\ (MM\$/a) = Product\ sales - Total\ annualized\ cost \quad (6.1)$$

$$Total\ annualized\ cost\ (MM\$/a) = annualized\ capital\ cost + operating\ cost \quad (6.2)$$

In this study, the capital investment for bioethanol conversion processes is estimated using the order of magnitude approach (Towler and Sinnott, 2013) ($C_{V_y} = C_{V_x}\left(\frac{V_y}{V_x}\right)^n$) based on the relevant information (capacity and investment) of the existing plant. C_{V_y} represents the required capital at a volume y, C_{V_x} represents the required capital at a volume x, V_y and V_x represent the volume y and volume x, respectively; n is an exponent varied between 0.5-0.9 based on the type of process considered (*i.e.* n = 0.6 is an average value of this exponent across the whole chemical industry (Towler and Sinnott, 2013)). Moreover, when the operating cost (MM$/a, excluding the raw material costs) is unable to be estimated, the rule of thumb of 2% of the total capital investment can roughly be used. This method has for example been applied by Dow Chemical (Anderson, 2009) in the early stage design where the lack of complete information is most prominent.

Furthermore, during the project evaluation, EBITDA is then transformed to the internal rate of return (IRR) using Eq. 6.3 for an improved analysis and evaluation of the economic potential of the engineering projects resulting from the optimizations – the higher a project's IRR, the better.

$$NPV = 0 = -capital\ investment + \frac{EBITDA}{(1+IRR)^1} + \frac{EBITDA}{(1+IRR)^2} + \cdots + \frac{EBITDA}{(1+IRR)^{19}} + \frac{EBITDA}{(1+IRR)^{20}} \quad (6.3)$$

Subsequently, the probability of failure to reach the target IRR is calculated, and the risk analysis is performed. Risk is defined as the product between probability of occurrence and its consequences (Crowl and Louvar, 2002) where these are lower than the defined favorable target.

6.2.2 Sustainability analysis (min. sustainability single index ratio)

The early-stage sustainability assessment method was developed to allow a quick preliminary analysis of chemical conversion routes for bio-based products within a broader sustainability context (it contains elements of green chemistry, techno-economic analysis and environmental life-cycle assessment (LCA)). The method evaluates a (novel) proposed chemical route against a comparable existing process using a multi-criteria approach that combines five dimensionless quantitative and qualitative proxy indicators (describing economic, environmental, health and safety and operational aspects) in a single score index (Posada et al., 2013; Patel et al., 2012). These five proxy indicators are briefly described below. A full description is available in an earlier study (Posada et al., 2013), while the general aspects of the methodology are briefly recalled below.

The *economic constraint* (EC) is defined as the ratio of raw material costs ($\sum_i^{RM} m_i^{RM} C_i^{RM}$) to product sales ($\sum_j^p m_j^p C_j^p$) as represented by Eq. 6.4. Therefore, a lower ratio reflects a higher economic potential. This index aims to evaluate the economic viability for a new project or an early-stage process design.

$$EC = \sum_i^{RM} m_i^{RM} C_i^{RM} \,/\, \sum_j^p m_j^p C_j^p \quad (6.4)$$

Environmental impact of raw material (EIRM) is determined by the cumulative energy demand (CED) and the greenhouse gas (GHG) emissions of the raw material as represented by Eq. 6.5. The two impact categories (CED and GHG) are considered equally important with equal contributions to EIRM, *i.e.* 50% each. CED is the total energy consumption of a cradle-to-factory gate system for feedstock production. GHG

emissions reflect the use of fossil resources for feedstock production. The used values include fossil carbon embedded in the product, following a cradle-to-grave approach. This approach was applied based on the assumption that the embedded carbon would be released at a later point in time by either waste incineration or by the action of micro-organisms in the case of organic chemicals.

In the case of multi-product systems, an economic allocation factor (AF) is additionally applied to ensure a suitable assessment as presented by Eq. 6.6 which is the ratio between sales of main products ($m_n^p C_n^p$) and total product sales ($\sum_j^p m_j^p C_j^p$).

$$EIRM = (0.5AF_n/m_n^p)\sum_i^{RM} m_i^{RM} CED_i^{RM} + (0.5AF_n/m_n^p)\sum_i^{RM} m_i^{RM} GHG_i^{RM} \quad (6.5)$$

$$AF_n = m_n^p C_n^p / \sum_j^p m_j^p C_j^p \quad (6.6)$$

Process cost and environmental impact (PCEI) indicates the process complexity and therefore indirectly represents the process cost, energy use and emissions associated to the reaction and separation stages. PCEI is estimated based on 7 subcategories (represented by Eqs. 6.7 – 6.15) namely: *1*) presence of water in the outlet; *2*) product (molar) concentration in the outlet; *3*) minimum boiling point difference between main product and other products in the outlet stream; *4*) mass loss index (MLI); *5*) reaction enthalpy; *6*) number of co-products; and *7*) requirement of feedstock pre-treatment. The last category is especially useful when the pre-treatment technology has not been defined at the early-stage design, and the aim of the analysis is only the intermediate or final conversion step. These categories are scored between 0 and 1 for low and high impacts, respectively.

$$PCEI = \left(\frac{1}{no.of\ sub-PCEI}\right)\sum_i^{PCEI} PCEI_i \quad (6.7)$$

$$PCEI_1 = 0, if\ no\ water; 0.5, if\ water\ is\ presented; 1, if\ water\ must\ be\ separated. \quad (6.8)$$

$$PCEI_2 = 1 - (0.5log_5(100C_n)) \quad (6.9)$$

$$PCEI_3 = 1 - (0.5log_2(\Delta T_{bp}/5)) \quad (6.10)$$

$$PCEI_4 = 0.5(log_{10}MLI + 1) \quad (6.11)$$

$$PCEI_5 = \frac{|\Delta H^0_{rxn}|-100}{200}, if\ \Delta H^0_{rxn} \geq 0\ or\ , if\ \Delta H^0_{rxn} < 0\ and\ T_R < 200℃ \quad (6.12)$$

$$PCEI_5 = \frac{100-|\Delta H^0_{rxn}|}{200}, if\ \Delta H^0_{rxn} < 0\ or\ , if\ \Delta H^0_{rxn} < 0\ and\ T_R > 200℃ \quad (6.13)$$

$$PCEI_6 = -0.015N^2_{cp} + 0.28N_{cp} - 0.25 \quad (6.14)$$

$$PCEI_7 = \quad (6.15)$$
$$0, feedstock\ pretreatment\ is\ not\ required; 1, feedstock\ pretreatment\ is\ required$$

Environmental-Health-Safety index (EHSI) represents a proxy measure of the EHS characteristics of a chemical process. EHSI is estimated based on 3 categories and 10 subcategories as shown by Eq. 6.16: *i*) the environmental category consists of persistency (half-life in water), air hazard (index value of chronic toxicity), water hazard (L(E)C_{50} aquatic, R-codes) and solid waste; *ii*) the health category consists of irritation (EU-class, R-codes, $LD50_{dermal}$) and chronic toxicity (EU-class, GK, R-codes); *iii*) the safety category consists of mobility (partial pressure, boiling point), fire/explosion (flash point, R-codes), reaction/decomposition (NFPA reactivity, R-codes) and acute toxicity (IDLH, EU-class, GK, R-codes).

$$EHSI = AF_n(0.4EH + 0.2HH + 0.4SH) \quad (6.16)$$

The indicator *Risk aspects* (RA) indicates the risk associated with economic and technical aspects estimated based on 5 categories: global feedstock availability (GFA), local feedstock potential (LFP), market size (MS), compatibility with current infrastructure (CCI) and inherent benefits (IB) as shown by Eq. 6.17.

$$RA = 0.25GFA + 0.15LFP + 0.25MS + 0.2CCI + 0.15IB \quad (6.17)$$

Each one of the 5 indicators is first calculated for both processes that are to be compared, *i.e.* bio-based route and petrochemical counterpart. The 5 indicators are then normalized by considering the maximum score out of the two analyzed processes. The normalized values for each indicator are integrated in a single score index by using the specific weighting factors as shown in Eq. 6.18 for the total score (TS).

$$TS = 0.30EC + 0.20EIRM + 0.20PCEI + 0.20EHSI + 0.10RA \quad (6.18)$$

The selection of these weighting factors was based on expert opinions as reported by Patel et al. (2012) and Posada et al. (2013). They performed an uncertainty analysis using Monte Carlo simulation in order to study the effect of variations of the weighting factors for the five indicators. This uncertainty analysis demonstrated that absolute differences between the originally obtained index ratio and the mean value resulting from the uncertainty analysis did not exceed 5%, and hence this factor was deemed not to be significant.

The TS indicators are then compared via the index ratio (IR) (Eq. 6.19), which is the ratio between the bio-based TS and the petrochemical TS. The IR provides a direct comparison of the new conversion route with respect to existing petrochemical technologies; *i.e.*: IR < 1 indicates that the bio-based conversion route is favorable, and IR >1 indicates that the bio-based conversion route is unfavorable compared to the petrochemical process.

$$Total\ index\ ratio = \frac{TS_{biobased}}{TS_{petrochemical}} = \frac{0.30EC_{bio}+0.20EIRM_{bio}+0.20PCEI_{bio}+0.20EHSI_{bio}+0.10RA_{bio}}{0.30EC_{petro}+0.20EIRM_{petro}+0.20PCEI_{petro}+0.20EHSI_{petro}+0.10RA_{petro}} \quad (6.19)$$

It is important to note that, in this study, EHSI and RA are beyond the scope of the analysis and only the first three indicators are taken into account. Note that this is because the EHSI and RA are qualitative indicators which are unable to model mathematically and not standardized.

The sustainability assessment method is integrated into the developed framework in the second part of the analysis by reformulating the objective function (minimization of the index ratio) and by including the additional constraints (Eq. 6.4-6.19) for calculating the sustainability indicators. This integration results in the optimal sustainable solutions with respect to techno-economics, environmental impacts (greenhouse gas emission and energy usage) and the reference petrochemical processes.

6.3 Results and discussion

In this section, the developed superstructure is presented. The results obtained from two different evaluation objectives, i.e. techno-economic and sustainability, are presented and discussed.

Design-space development

The superstructure developed earlier for producing biofuels (*Chapter 4, Figure 4.1*) was combined with the bioethanol-upgrading superstructure developed in this study (Figure 6.1). The scope of the combined superstructure was extended and defined to convert lignocellulosic biomass (corn stover (block no. 1) and poplar wood (block no. 2)) to both biofuels (bioethanol and FT-products) and bioethanol-derivatives. The extension of the design space of the biorefinery aims to significantly improve the overall economics of a biorefinery by upgrading bioethanol to higher value added products.

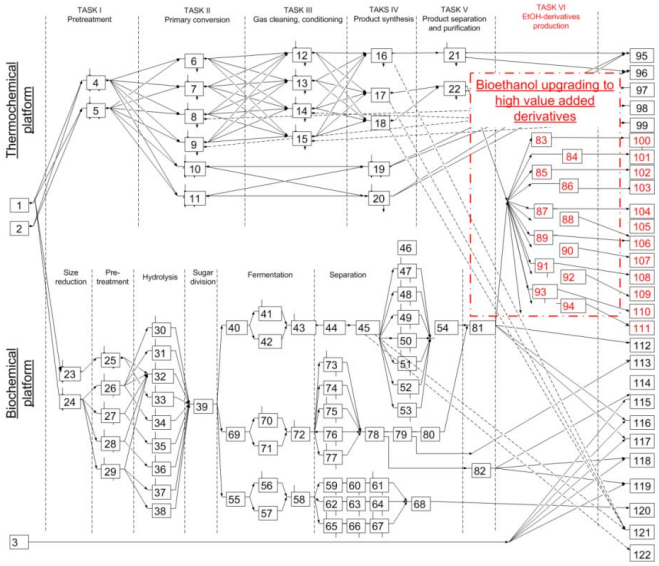

Figure 6.1. The superstructure of the biorefinery network extended with bioethanol based derivatives (highlighted in red: box 83-94, and box 100-111).

The full description is presented in Appendix B for biomass feedstock (block no. 1-2); thermochemical conversion (block no. 4-22); biochemical conversion platform (block

no. 23-82); ethanol-derivatives conversion (block no. 83-94); bioproducts (block no. 95-122; FT-products, bioethanol, ethanol-derivatives, electricity).

The identification and selection of bioethanol-upgrading products was performed in the previous study (Posada et al., 2013) in which 12 potential candidates were selected based on more than 200 studies. As presented in Figure 6.11, the bioethanol-upgrading processing step, containing 12 bioethanol conversion processes (box 83 to box 94), was built (highlighted area) and combined into the superstructure earlier developed resulting in a superstructure with a total of 122 processing intervals, composed of: 2 biomass feedstocks, 1 gasoline for blending, 91 processing technologies and 28 products.

The data collection and management for the thermochemical and biochemical processing network is based on a previous study (presented in *chapter 4*), while for the bioethanol-upgrading processes those steps were performed as presented in the following example for diethyl ether (DEE) production. DEE is produced from bioethanol through a dehydration process (block no. 85). Therefore, following the framework (*section 3.1*), the stoichiometry is required for the generic process model block (see Figure 3.4) to allow the estimation of the product outlet for the dehydration process. The design data (input-output flow rate) were collected in the previous study (Posada et al., 2013). The stoichiometric coefficients were calculated using Eq. 6.20, and are presented in Table 6.1 and Figure 6.2. The results of the data collection for the 12 bioethanol-upgrading processes are presented in Table 6.2. Note that the extended superstructure and the collected data were used for two analyses presented in the following sub-sections.

$$\gamma_{i,rr} = \frac{-(mass_{(i,rr)-out} - mass_{(i,rr)-in})/MW_i}{(mass_{(reactant,rr)-out} - mass_{(reactant,rr)-in})/MW_{reactant}} \quad (6.20)$$

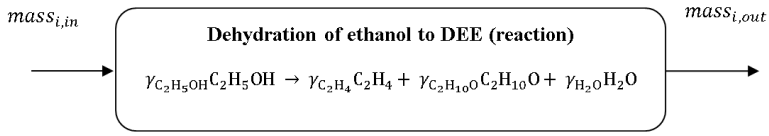

Figure 6.2. Simplified process diagram presenting mass inlet/outlet, and the stoichiometry for DEE production. The stoichiometric coefficients are presented in Table 6.1.

Table 6.1. The stream table for the DEE production from the dehydration process of bioethanol

Component	Inlet flow (tpd)	Outlet flow (tpd)	$\gamma_{i,rr}$ (stoichimetry)	$\theta_{i,rr}$ (conversion fraction)
Ethanol	556	57.6	-1	0.89
N_2	1690	1690	-	-
Ethylene	-	53.8	0.18	-
Diethyl ether	-	329.7	0.41	-
Water	-	114.7	0.6	-

Table 6.2. Summary table for the data collection for ethanol derivative processes

Processing technologies	Products	Mixing	Reaction ($\gamma_{i,rr}$)	$\theta_{i,rr}$	Waste separation	Product separation
(83) Dehydration	Ethylene	-	$C_2H_5OH \rightarrow 0.99\mathbf{C_2H_4} + 0.004C_2H_4O + 0.0015C_4H_{10}O + 0.002C_2H_6 + H_2O$	0.995	-	-
(84) Oxidation	Acetaldehyde		$C_2H_5OH + 0.63O_2 \rightarrow 0.95\mathbf{C_2H_4O} + 0.1CO_2 + 1.1H_2O$	0.82		
(85) Vapor-phase dehydration	Diethyl ether		$C_2H_5OH \rightarrow 0.18C_2H_4 + 0.41\mathbf{C_4H_{10}O} + 0.6H_2O$	0.89		
(86) Fermentation	n-Butanol		$C_2H_5OH \rightarrow 0.036C_2H_4 + 0.023C_2H_4O + 0.22\mathbf{C_4H_{10}O} + 0.06H_2 + 0.04C_4H_6 + 0.5H_2O + 0.14C_6$Alcohols $+0.243$Others	0.575		
(87) Fischer esterification	Ethylacetate		$C_2H_5OH \rightarrow .058C_2H_4O + 0.47\mathbf{C_4H_8O_2} + 0.994H_2$	0.7		
(88) Fermentation	Acetic acid		$C_2H_5OH + 1.06O_2 \rightarrow 0.97\mathbf{C_2H_4O_2} + 0.06CO_2 + 1.06H_2O$	0.99		
(89) High temperature ethanol reforming	Hydrogen		$C_2H_5OH + 2.4H_2O \rightarrow 4.8\mathbf{H_2} + 0.3CH_4 + 1.7CO_2$	0.998		
(90) Metathesis	Propylene		$C_2H_5OH \rightarrow 0.5C_2H_4 + 0.3478\mathbf{C_3H_6} + 0.15C_4H_8 + 0.4H_2O + 0.087$Others	1		
(91) Fermentation	Iso-Butylene		$C_2H_5OH + 0.37H_2O \rightarrow 2H_2 + 0.64CO_2 + 0.28\mathbf{C_4H_8} + 0.08(CH_3)_2CO$	1		
(92) Fermentation	Acetone		$C_2H_5OH + 0.3876H_2O \rightarrow 1.78H_2 + 0.0894C_2H_4 + 0.447CO_2 + 0.447\mathbf{(CH_3)_2CO}$	1		
(93) Oxidation	Ethylene oxide		$C_2H_5OH \rightarrow 0.994H_2 + 0.0203C_2H_4 + 0.994\mathbf{C_2H_4O} + 0.0203H_2O$	0.98		
(94) Catalytic dehydrogenation	1,3-butadiene		$C_2H_5OH \rightarrow 0.46H_2 + 0.11C_2H_4 + 0.43\mathbf{C_4H_6} + 0.02C_2H_4O + 0.98H_2O$	1		

6.3.1 Techno-economic analysis of ethanol derivatives (maximization of operating profit)

The objective function for techno-economic analysis is to maximize the EBITDA of the extended superstructure. The optimization problems (MILP or MINLP) formulated and

implemented in GAMS for the defined objective functions were solved in this step. The full optimization formulation can be found in Appendix C.

a. Deterministic solution

In this section, the deterministic solutions, where no uncertainties were considered, were identified under the aforementioned specific scenarios of the nominal data (or mean values, Table 6.3). The formulation of the optimization problem (MILP) for this techno-economic analysis consists of 3,972,533 equations and 3,941,332 variables (595 discrete variables). This MILP problem was solved in about 10 seconds using the CPLEX solver using Windows 7, Intel® Core™ i7 CPU@ 3.4GHz, 4GB RAM.

Table 6.3. Input uncertainty for ethanol-derivatives prices (Tecnon OrbiChem, 2013)

No.	Bioethanol derivatives	Average prices (2011-2013, $/ ton)	std.
1	C_2H_5OH	1010	520
2	C_2H_4	1050	100
3	C_2H_4O	980	220
4	$C_4H_{10}O$	2270	410
5	$C_4H_{10}O$	2190	190
6	$C_4H_8O_2$	1290	40
7	$C_2H_4O_2$	490	20
8	H_2	2290	420
9	C_3H_6	1400	210
10	C_4H_8	750	170
11	$(CH_3)_2CO$	1230	230
12	C_2H_4O	1330	80
13	C_4H_6	2010	710

The results are presented in Table 6.4 as the top-five ranking solutions. Production rate, EBITDA and total annualized costs (TAC) as well as the optimal processing paths are presented. The results illustrate that the thermochemical platform using poplar wood as feedstock, and with the unit operation steps size reduction, indirectly contacted dryer, entrained-flow gasifier, steam reforming, scrubber, acid gas removal with amine, alcohol synthesis, molecular sieve, distillation and diethyl ether production (by dehydration of bioethanol) were preferably chosen with respect to the specified techno-economic criteria.

Table 6.4. Top-five ranking optimal solutions (max. EBITDA of producing ethanol-derivatives)

Rank no.	Process intervals selection	Objective value (EBITDA (MM$/year))	Products	Production (tpd)	TAC (MM USD/year)
1	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	247	Diethyl ether	345	82.9
2	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylene oxide production**	241	1,3-butadiene	292	86.9
3	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	202	Butanol	118	81.3
4	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **acetic acid production**	163	Ethylacetate	371	91.9
5	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylacetate production**	138	Ethylene oxide	544	126.3

Moreover, the differences among the solutions show that the input data are important for the decision-making process, and especially the market prices as shown in Table 6.3, which includes a very high standard deviation of the prices of ethanol derivatives. This issue will be addressed in more detail in the following section by performing an uncertainty analysis.

b. Stochastic solution

The historical data about the prices of the ethanol derivatives were analyzed. The prices have fluctuated considerably in the period 2011-2013 (Tecnon OrbiChem, 2013), and therefore these inputs were selected as major sources of uncertainties to be studied further. The fluctuation of ethanol-derivative prices was characterized using a normal distribution function for which a mean and standard deviation were calculated for each product using its corresponding historical set of data. In addition the linear (Pearson) correlation coefficient between each pair of product prices was also calculated from historical data to be used for Monte Carlo sampling. The other sources of uncertainties such as yield and conversion were analyzed in a previous study (Posada et al., 2013) and

found negligible. Thus, they were not repeated here. Subsequently, the Latin Hypercube Sampling (LHS) method with correlation control method was applied to generate 200 samples in total, which formed the dataset used for solving the optimization problem under uncertainty (Iman and Conover, 1982).

A stochastic programming was formulated (presented in Appendix C) using the sample average approximation (SAA) of the objective function over the uncertainty domain, and was solved in GAMS. The stochastic solution is 161 (MM$/a) which is lower than the deterministic solution (*i.e.*, 247 MM$/a) due to the effect of uncertainties. The result of the optimal solution under uncertainties is presented in Table 6.5, and further discussed below.

Table 6.5. Report generation for the identification of an optimal solution under market price uncertainties (max. EBITDA)

Solutions	**Processing paths**		**EBITDA (MM$/a)**
Optimal network (Step 3)	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**		247
Network under uncertainties (Step 4.2)			161
Optimal flexible network (Step 5)	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether and 1,3-butadiene production**		187
Indicators	**EVPI (MM$/a)**	**VSS (MM$/a)**	**UP (MM$/a)**
Network under the effect of uncertainties (Step 3-4.2)	139	84	86
Flexible network (Step 5)		100	60

As shown in Table 6.5, the same process topology was selected in the different solutions (deterministic and stochastic solutions), which confirms the robustness of the deterministic solution. However, the analysis of the uncertainty indicators, *i.e.* Expected Value of Uncertainty Information (EVPI), Value of Stochastic Solution (VSS) and Uncertainty Price (UP), shows a significant effect of market price uncertainties. A large value of EVPI indicates that the operating profit could be improved significantly if market price uncertainties are reduced. Moreover, the VSS is high confirming that the market price uncertainties are highly important. These observations are also confirmed by the high value of the UP indicator, which is due to the high impact of the uncertainty

in product market prices compared with the deterministic scenario where no uncertainties are considered.

The impact of uncertainty can be reduced by proposing a design with high/optimal flexibility, meaning that modifications are allowed during the operational stage where the data are available. This allows building two or more redundant technologies to generate/yield a larger variety of products, which enables to switch the operational mode or to derive/yield products with a higher economic value. Therefore, the stochastic formulation was modified to identify the redundant networks. It resulted in an improved result compared to the stochastic solution (from 161 MM$/a to 187 MM$/a).

6.3.2 Sustainability analysis (minimization of sustainability single index ratio)

In this part, the optimization problem was reformulated in order to identify the optimal processing path with respect to economic performance, greenhouse gas emissions and energy use, compared to the petrochemical-based equivalent as a reference, and using the single score sustainability index ratio (mentioned in Section 2). The framework applied in techno-economic analysis was here repeated using the reformulated objective function and the additional constraints presented in Appendix C.

a. deterministic solution

The modified objective function, as shown in Eq. 6.21, is applied to minimize the index ratio as presented below. In this study, only three indicators regarding sustainability (EC, EIRM, and PCEI) are considered (as described in Section 2) and the original weighting factors (30% for EC, 20% for EIRM, and 20% for PCEI) are used as normalized value (as shown in Eq. 6.21). The additional constraints mentioned earlier (Eqs. 6.4-6.19) for estimating the sustainability indicators were also included in the optimization problem.

$$\min.\ Total\ index\ ratio = \frac{TS_{biobased}}{TS_{petrochemical}} = \frac{\left(\left(\frac{0.3}{0.7}\right)EC_{bio}+\left(\frac{0.2}{0.7}\right)EIRM_{bio}+\left(\frac{0.2}{0.7}\right)PCEI_{bio}\right)}{\left(\left(\frac{0.3}{0.7}\right)EC_{petro}+\left(\frac{0.2}{0.7}\right)EIRM_{petro}+\left(\frac{0.2}{0.7}\right)PCEI_{petro}\right)} \quad (6.21)$$

The reformulated optimization problem was then solved allowing a direct comparison of bio-based processes to conventional fossil-based processes using the single index ratio (IR). The single index ratio (IR) is defined as TS_{bio}/TS_{petro}, where IR<1 indicates that the bio-based conversion route is favorable; and IR>1 indicates that the bio-based conversion route is unfavorable compared to the petrochemical process.

In Table 6.6, the top-five ranking solutions consisting of the optimal processing path, the sustainability indicators and the index ratio are presented. The deterministic solutions (Table 6.6) show that 1,3-butadiene and diethyl ether were the favorable derivatives with respect to the evaluation criteria specified in this study (economic performance, greenhouse gas emissions, and energy use, and comparison with the fossil-based processes as reference).

Table 6.6. Top-five rank of the optimal solutions (min. total index ratio)

Rank	Processing path	EC	EIRM	PCEI	Index (bio-based)	Index (petrochemical-based)	Index ratio
1	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	0.25	0.16	11.4	0.41	0.8	0.51
2	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	0.246	0.12	10.7	0.4	0.74	0.54
3	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylacetate production**	0.32	0.15	11.3	0.44	0.73	0.61
4	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **propylene production**	0.39	0.16	10.9	0.47	0.77	0.62
5	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **acetaldehyde production**	0.42	0.193	10.8	0.47	0.75	0.63

b. stochastic solution

In the sustainability analysis, the relatively high fluctuation of the market prices of ethanol-derivatives which was also addressed as economic constraints were also considered as one of the sustainability criteria. Table 6.6 illustrates that production of 1,3 butadiene is more favorable than diethyl ether production in this analysis compared to the result of a purely techno-economic analysis. The reason is that from the sustainability point of view (economic performance, greenhouse gas emissions, energy use and fossil-based equivalent), production of 1,3-butadiene is more attractive. Moreover, the uncertainty effects on the sustainability index ratio were low because market prices affected only one out of three sustainability indicators (*EC*). Therefore, a slight improvement from the optimal flexible network was found which provided a robust solution in decision-making under uncertainties.

6.4 Discussion

In the *chapter 5*, the optimal design network for converting biomass to biofuels was identified. In this study, the perspective of the lignocellulosic biorefinery concept was expanded to consider bioethanol as a raw material by including the conversion step to value-added derivatives. Moreover, the sustainability analysis was also performed. In this section, these perspectives are compared and discussed.

Upgrading strategy - 1: improving the economy of a lignocellulosic biorefinery by upgrading bioethanol to high value added derivatives

The different perspectives of biorefinery design with respect to techno-economic criteria are compared and presented in Table 6.7. The profitability (EBITDA and IRR) was significantly improved by bioethanol-upgrading compared to the more traditional standalone bioethanol production (no. 1-2 compared to no. 3-6, in Table 6.7), providing a strong case for establishment of a biorefinery concept including bioethanol upgrading. Moreover, the production of diethyl ether is more favorable compared to 1,3-butadiene production with respect to the purely techno-economic criteria.

Table 6.7. Comparison of different biorefinery design perspectives

No.	Processing path	Products	EBITDA (MM$/a)	TAC (MM$/a)	IRR (%)	Index ratio	Reference
1	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	diethyl ether	247	82.9	26	0.54	(this study)
2	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	1,3-butadiene	241	86.9	21	0.51	(this study)
3	Corn stover, AFEX pretreatment, hydrolysis by spezyme, fermentation, distillation, extraction with BMIMCI	bioethanol	92.8*	77.2	13	-	(Zondervan et al., 2013)
4	Corn stover, AFEX pretreatment, hydrolysis by spezyme, fermentation, distillation, extraction with BMIMCI incl. lignin utilization (electricity)	bioethanol	99.8*	79	11	-	(*chapter 5*)
5	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation incl. electricity production	bioethanol	114*	78	12	-	(*chapter 5*)
6	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, Fischer-Tropsch (FT), hydroprocessing unit	FT-products	210	88	17	-	(*chapter 5*)
7	Wood waste, energy crop, biofuels	Bioethanol	200	-	-	-	(Andippan et al., 2015)
8	Black liquor, Fischer-Tropsch (FT), Gas turbine	Biofuels	133-200	-	-	-	(Tay et al., 2011)
9	Wood, fermentation	Bioethanol	110	90	-	-	(Voll and Marquardt et al., 2012)
10	Lignocellulosic biomass, acid fermentation, esterification	Bioethanol	108	54	-	-	(Pham et al., 2012)

*The lignin utilization was included and the market prices were updated from the previous study.

These results are also in agreement with the outlook and perspectives presented by Kamm et al. (2012), where the financial success is dependent on co-product utilization and the ability to shift to high value-added products. Bruscino (2009) also reported that the benefit of integrating bioethanol and chemicals production (in particular ethylene) reduces the operating and capital cost compared to the cost of pure bioethanol production from biomass. The analysis presented here provides a quantitative evidence for these perspectives.

Upgrading strategy - 2: improving sustainability of lignocellulosic biorefinery by producing more sustainable bioethanol-derivatives

Another important aspect of the biorefinery concept is its potential contribution to sustainable development of chemical/biochemical industries (Zwart, 2006). Therefore, sustainability analysis was performed using a single index ratio indicator to identify the promising, competitive and sustainable solutions. As presented earlier, the production of 1,3-butadiene is more sustainable compared to diethyl ether production. This is in agreement with the study from Angelici et al. (2013) – the study of the chemocatalytic conversion of bioethanol to chemicals – which concluded that butadiene production from bioethanol provides an excellent opportunity for sustainable development of a biorefinery.

Upgrading strategy - 3: multi-product biorefinery offers a more robust and risk-aware upgrading strategy against the inherently stochastic market price uncertainties

Market uncertainties are found to have considerable impact on the economic targets of biorefinery design. In response, a risk-based decision making relying on quantitative analysis of economic risks is suggested. Figure 6.3 presents the IRR cumulative distribution with a quantified risk of Network 1 (production of diethyl ether) and Network 2 (production of 1,3-butadiene). As mentioned in Section 2, IRR was used to allow an improved project evaluation. The calculation of risk is equal to the integral of the highlighted area. In this calculation, the EBITDA value corresponding to IRR@15% is considered as break-even point, hence the risk in economic terms is calculated as the summation of the probability of occurrence times the deviation of EBITDA from the

break-even point: $[EBITDA_{i,(@IRR<15\%)} - EBITDA_{(@IRR=15\%)}]$. The results indicate that there is a risk of 12 MM$/a for network 1, meaning 12 MM$/a (240 MM$ over the project life time). The risk of network 2 is much higher with 92 MM$/a.

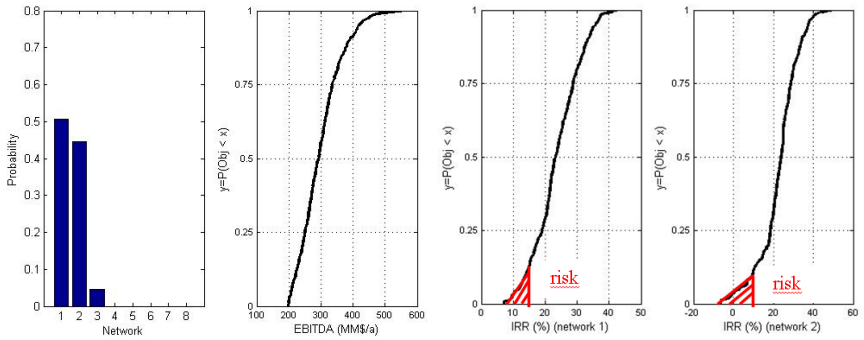

Figure 6.3. Uncertainty mapping and analysis (max. EBITDA): *i*) the frequency of selection of the optimal processing paths; *ii*) EBITDA cumulative distribution; *iii*) IRR cumulative distribution with a quantified risk of network 1; *iv*) IRR cumulative distribution with a quantified risk of network 2.

Moreover, the impact of market price uncertainties was reduced by 16% (compared to a stochastic solution) by implementing the flexible network analysis to produce multiple products (producing diethyl ether and 1,3-butadiene) as presented in Table 6.5. Therefore, this analysis of flexible network design indicates that the multi-product biorefinery design offers a promising alternative that allows covering future market price fluctuations.

Further verification and highlights

Table 6.7 also compares the results here obtained to those reported in other studies performing detailed process synthesis with fuzzy optimization (Andippan et al., 2015; Tay et al., 2011), path synthesis with reaction network flux analysis (RNFA) (Voll and Marquardt, 2012), and path synthesis with forward-backward (Pham and El-Halwagi et al., 2012) methodologies. The results in this study are in agreement with other studies (refer to No. 4-5 to No. 7-10 in Table 6.7). However, the superstructure-based optimization approach presented here provides more flexibility as illustrated with the following examples. First, a larger size of the design space can be obtained and more alternatives can be compared. Second, the database obtained is large and at the same

time compact and structured which is also easy to access and update. Third, a large set of models and information about constraints can be represented using a generic modeling approach to support uncertainty analysis and multi-criteria evaluation (techno-economic, environmental impact, LCA, sustainability). These advantages point out a high flexibility of the superstructure-based optimization approach to manage a large amount of information which is multi-disciplinary and inherently uncertain. This approach is thus well suited for obtaining robust solutions. The advantages are highlighted and verified in the following example.

The current drop of oil prices regarding shale oil/gas revolution (among others) causes the fluctuation of chemicals prices. In this study, market prices of chemicals used are also highly fluctuated as revealed by the high standard deviation of the mean price values (Table 6.3). After that an uncertainty analysis is performed, the results (Table 6.5) confirm that highly fluctuating market prices of the high value-added chemicals have a high, direct and negative impact on economic performance – as shown by the high standard deviation of the estimated economic profits (e.g. EBIDTA in Table 6.5). Among other parameters oil prices are one of the key factors affecting the prices of commodity chemicals considered in this study as bioethanol derivatives. This can also be confirmed by the recent drop of chemical price due to sharp reduction in oil prices (Wood and Marshall, 2015). However, the reduction of this economic impact can be counter-addressed by carefully diversifying the product portfolio and producing multiple products as presented in *upgrading strategies 3*. In the case of the sustainability index (section 6.2.2), the results (i.e., products ranking) are not significantly affected by the low prices of the fossil-based chemicals. This behaviour may be explained because the prices of the petrochemical counterparts are expected to decrease by equivalent ratios. Thus, the economic potential for all bio-products is reduced with similar percentages while the ranking, from the best to the worst, remains quite similar. Of course, many of the bio-based products would now be categorized as unfavourable derivatives because of their limited economic potential.

Although low oil prices can slow down the development and production of bio-based materials, the search of alternative routes for chemicals and fuels production will remain a need for a sustainable society, and in this context efficient integrated and multi-

product biorefineries will play an important role. Some examples of successful companies producing biofuels show the potential for bio-based products in the current economy. In 2010, Mascoma Corporation (Faber et al., 2010) reported the study of a wood biorefinery with an annual profit of 97 MM$ for 207 ML. In 2013, ABENGOA (2013), one of the leading biofuels producers, produced in total 3180 ML first and second generation biofuels (bioethanol and biodiesel) from biomass resulting in an annual EBITDA of 273 MM$. In 2014, Green Plains (Lane, 2015), an ethanol production company in Nebraska, produced 933 ML of ethanol annually from corn with an EBITDA of 350 MM$. Similarly, in the case of the Archer Daniels Midland company (ADM) (Lane, 2015), the company reported an annual operating profit of 395 MM$ with an annual production of 3000 ML. These reported data confirm that biorefineries producing bioethanol are profitable which is in agreement with this study.

6.5 Conclusion

A systematic framework consisting of a superstructure optimization based approach under uncertainty integrated with a sustainability assessment method was applied for designing lignocellulosic biorefineries that include the conversion of ethanol to value-added products. The results showed that bioethanol-upgrading improves in general the economics and sustainability of a lignocellulosic biorefinery. In particular, the thermochemical platform from poplar wood producing diethyl ether and 1,3-butadiene was favorable with respect to techno-economic and sustainability criteria (considering economics, greenhouse gas emissions and energy use). Moreover, the market price uncertainties identified from historical data were found to bring about a considerable economic risk on the biorefinery design – in the range of 12 MM$/a to 92 MM$/a for the studied domain of price uncertainties. The multi-product biorefinery design offers a promising strategy to minimize the risk against price fluctuations. The comparison between bio-based processes and fossil-based processes represented by the sustainability index ratios was improved by 19% resulting in a more sustainable integrated biorefinery system. These analyses provide useful information regarding economic and sustainability drivers for the future development of a biorefinery.

7.
CASE STUDIES III: UNCERTAINTY ANALYSIS IN EARLY STAGE CAPITAL COST ESTIMATION

In this chapter, an uncertainty analysis of the cost estimation at early-stage design of a biorefinery is presented. Capital investment, next to the product demand, sales and production costs, is one of the key metrics commonly used for project evaluation and feasibility assessment. Estimating the investment costs of a new product/process alternatives during early stage design is a challenging task, which is especially relevant in biorefinery research where information about new technologies and experience with new technologies is limited. Four well-known models of early-stage cost estimation are reviewed and used for this analysis. An impact of uncertainties in cost estimation on the identification of optimal processing paths is quantified and presented.

This chapter is a modified version of a paper published in Frontiers in Energy System Engineering as Peam Cheali, Krist V. Gernaey and Gürkan Sin (2015), *Uncertainties in early stage capital cost estimation of process design – a case study on biorefinery design.* doi: 10.3389/fenrg.2015.00003.

7.1 Introduction

Cost estimation is one of the major challenges of chemical and biochemical process design. The cost estimation (including fixed and variable cost) during each stage of the project design (concept screening, preliminary study, budget authorization, budget control, construction) is different since the quality and quantity of the information available in the successive stages of the project life cycle is different. (Towler and Sinnott, 2013). The Association of the Advancement of Cost Estimating International (AACE International) classifies the capital cost estimation into five classes, according to the level of accuracy and the purpose of the estimation in specific parts of the project life cycle (Table 7.1).

Table 7.1. Cost estimate classification matrix for the process industries (adapted from Christensen and Dysert, 2011)

Estimate Class	Project deliverables	Purpose of estimate	Methodology (Typical estimating method)	Accuracy range (expected)*
Class 5	0% - 2%	Concept screening	Order-of-magnitude	*L*: -20% to -50% *H*: +30% to +100%
Class 4	1% - 15%	Preliminary	Equipment factored or parameter models	*L*: -15% to -30% *H*: +20% to +50%
Class 3	10% - 40%	Budget authorization	Detailed unit cost	*L*: -10% to -20% *H*: +10% to +30%
Class 2	30% - 75%	Budget control	Costs from the contractor	*L*: -5% to -15% *H*: +5% to +20%
Class 1	65% - 100%	Construction	Cost from the completed design and bidding	*L*: -3% to -10% *H*: +3% to +15%

**L* corresponds to low range of estimation or underestimation; *H* corresponds to high range of estimation or overestimation.

Class 5, concept screening (order of magnitude). This class is based on the cost data and the capacity from similar plants, and it is usually used for initial feasibility studies and for screening purposes. *Class 4, preliminary (study of feasibility)*. This class mainly uses factors for the estimation, relying on so-called factored estimation methods. This method is based on material and energy balances as well as types and size of major

equipment. It is used to make a rough screening among the design alternatives. *Class 3, detailed design (budget authorization or definitive estimate)*. The project control estimate method is based on the approximate sizes of the major equipments; it is used for the authorization of project funds. *Class 2, contractor estimate (budget control or detailed estimate)*. The quotation or contract estimate is based on the front-end engineering design (FEED) including the complete quotation of the equipment. This cost estimation is very detailed and is generally used to make a fixed price contract and to control the project cost. *Class 1, construction (check estimates)*. The bid or tender estimate is based on the completed design and concluded negotiation on procurement.

The cost estimation has a significant impact on the project life cycle as presented in Figure 7.1. At the early stage, the possibility to change the design (black full line) is the highest and comes along with the lowest cost (black dashed line). Therefore, the main motivation for investing in such a detailed analysis and treatment of cost data uncertainties at the early stage of process design is simply that this stage has the highest impact on the overall project economics and feasibility considering the typical life cycle of a project (to move the red dashed line to the blue one). Hence, since increased investment of time and resources is required by these analyses, it will mean that the project cost will be high at the beginning of the project life cycle. However, the advantage is that the improved quality of decisions that is achieved thanks to these rather detailed early stage analysis efforts will translate to reduced project cost during the later stages of the project life cycle.

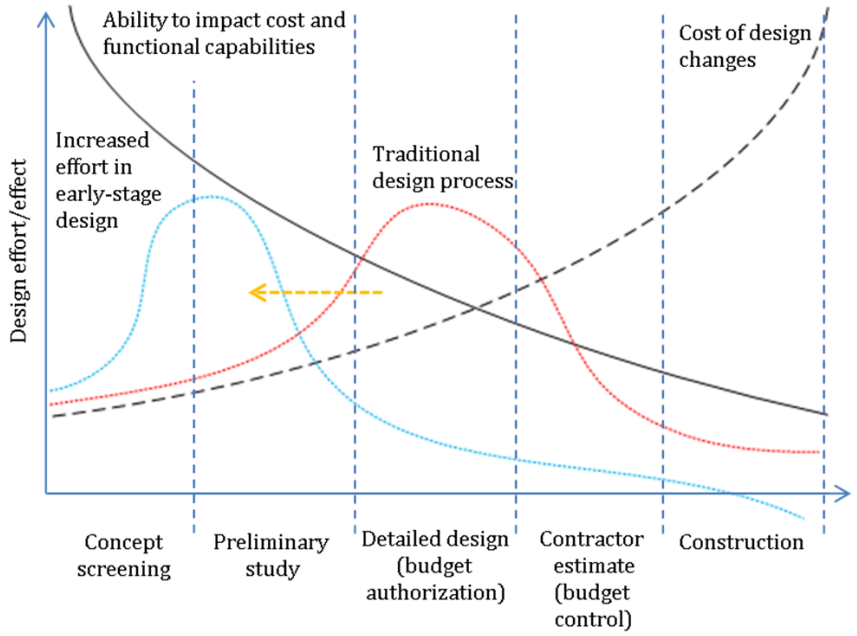

Figure 7.1. The design effort and impact on the project development (adopted from Towler and Sinnott, 2013)

In this chapter, we perform an in-depth analysis of the issues and challenges related to performing cost data estimation, and we develop methods and tools to properly address these issues in order to provide a robust decision-making platform for process synthesis and design. An assessment of the uncertainties of early stage cost estimation methods will be performed. In particular, the four standard models for cost estimation during the early stage were considered for the analysis, and will be explained in the next section. Moreover, the systematic framework is extended for two different situations considered for the uncertainty characterization and the cost estimation methods: *(i)* When historical cost data are available: the uncertainties of the cost estimation were obtained from regression analysis using the bootstrap regression technique (presented as motivating example in *section 7.3*); *(ii)* When cost data are not available: the Monte Carlo technique in combination with expert review of uncertainties is used (presented in *section 7.4*).

7.2 Materials and Methods

7.2.1 Cost estimation methods

Estimating the manufacturing costs of a new product/process during early stage design can provide a good indication of the project's economic viability (Christensen and Dysert, 2011). Early estimates generally used for conceptual screening have the purpose of allowing businesses to assign the most suitable resources and new/different alternatives (feedstock, technologies, or products) with respect to the defined specification. Anderson (2009) reported the methods to estimate three main cost components accordingly: i) *Variable cost.* A good and insightful resource of relevant information (prices and availability) about the raw materials, and has a significant impact. If relevant information cannot be found, the risk related to this lack of information should be quantified using uncertainty analysis. The utility costs can be estimated using a rule of thumb approach, (e.g., 2% of capital investment); ii) *Capital investment*. The capital investment can be estimated using the order-of-magnitude or the Viola method, which requires only information about capacity and capital investment for similar existing technologies. If both the type and number of unit operations are known, the relative factor regarding each unit operation is applied further to refine the results. The depreciation can be estimated rapidly as well using the ratio of capital investment and the product of project lifetime and production rate. iii) *Other fixed costs* (e.g., labour cost, maintenance). The factor-based rule of thumb is used for estimating the other fixed costs. In addition to the above, there are a variety of other estimation methods reported in the literature (Petley, 1997). Those, that use the recorded capacities and investment cost, are called *exponent estimates*. Those that use factors to multiply equipment costs to generate an overall investment cost are called *factorial estimates*. Those that use the plant parameters and functional units known in the early stage design are called *functional unit estimates*. Those that use the production profit to estimate the overall production cost are called *pay-back method*. In this study, the four mentioned methods of early stage cost estimation are used. These methods require different types of information, and therefore the results using different cost estimation methods will be compared and discussed.

a. Model 1: Order of magnitude estimates [production rate and investment of the existing plant]

Exponent estimates are used in the early stage design. The required capital cost is estimated by scaling the known investment cost corresponding to the capacity of an existing manufacturing plant (Eq. 7.1). This requires no complete design information. The value of the exponent (n) in Eq. 7.1 varies between 0.5 and 1 depending on the type of manufacturing process, as explained in Table 7.2.

Model 1,

$$\binom{Capital\ cost\ of}{the\ NEW\ plant, C_2} = \frac{\binom{Capital\ cost\ of}{the\ OLD\ plant, C_1}}{(Capacity\ of\ the\ OLD\ plant, S_1)^{exponent}} (Capacity\ of\ the\ NEW\ plant, S_2)^{(exponent, n)};$$

$$\frac{\binom{Capital\ cost\ of}{the\ old\ plant, C_1}}{(Capacity\ of\ the\ old\ plant, S_2)^{(exponent, n)}} = a \tag{7.1}$$

Table 7.2. The range of exponents typically used in the exponent based cost estimation methods (Towler and Sinnott, 2013)

Exponent, n	Type of manufacturing process
0.8 to 0.9	A lot of mechanical work or gas compression (i.e. methanol, paper pulping)
0.7	Typical petrochemical processes
0.4 – 0.5	Small-scale highly-instrumented processes (i.e. specialty chemical or pharmaceuticals)
0.6	Averaged across the whole chemical industry.

It is important to note that when there are insufficient data available, n = 0.6 can be used for a rough estimation. This case is commonly referred as the *six-tenths rule* method. This approach refers to the economy of scale, meaning that increasing capacity of the plant decreases unit marginal production cost. The disadvantage of this method is the requirement of having information available about the capacity and investment data of

similar plants. Therefore as well, this method can be particularly problematic for new processes. This method has been further developed by estimating the cost of the main equipment instead of the investment of the entire plant (Garrett, 1989). Using this method for estimating the cost during the R&D phase, the typical accuracy for chemical processes has been found by Uppal and Van Gool (1992) to be ± 40 %. Of course, it could be better or worse depending on the design criteria defined.

b. Model 2: Bridgewater's methods [production rate, number of functional units and conversion fraction]

Factorial estimates were first introduced by Lang (1947) to estimate the investment cost by multiplying the equipment costs with a factor (Eq. 7.2).

$$C = f * E \tag{7.2}$$

Where C is the capital cost, \$; f is the factor (3.10 for solid processing; 3.63 for combined solid and fluid processing; 4.74 for fluid processing); *E* is the equipment cost, \$). The equipment costs can be determined from the quotations of vendors, from published data or by estimation using design information. The overall factors can be divided into different categories, i.e. for foundations, supports, insulation, installation, piping and contractors and engineering expenses. Cran (1981) suggested using a universal factor of 3.45 instead of classifying the plants into three types as shown above. Miller (1965) reported that the factors depend on the size of the equipment, the material of construction and the operating pressure resulting in an effect on the average cost of each piece of equipment in the process. The factorial method has been developed by many authors. However, this is a complicated method considering that there are many types of components of several manufacturers related to each process (process type, equipment, functional units, capacity, piping and instrumentation). Moreover, the companies generally develop their own values taking into account their specific requirements resulting in a wide range of the factors.

Alternatively, when the cost data for a similar process are not available, then, the order of magnitude estimate can be used with some modifications by employing the different

plant sections or functional units. For example, experienced engineers provide a quick guideline for many petrochemical processes by considering that 20% of the investment is for the reactor and 80% is for the distillation and product separation. This alternate approach, called *Functional unit estimates* uses the process parameters and the functional units during the early stage design to predict the investment cost instead of using the equipment cost and factors as in the *Factorial estimates* method. The method has been derived by a statistical analysis of existing plants for determining the sequence of significant process steps (functional units). The method was introduced by Wessel (1953) who used the number of processing steps to calculate the labor costs. The functional units separate the process into these processing steps where the material compositions are significantly changed, for instance, a reaction or separation. The equipment cost (E) Eq. 7.2 of *Factorial estimates,* is replaced by the number of functional units (N) as presented in Eq. 7.3.

$$C = F * (IEC) = F * \left(N * \left[\frac{Q}{10} \right]^{0.6} * 30000 \right) \tag{7.3}$$

Where C is is the capital cost in 1954 ($); F is the Chilton factor to allow for piping, instrumentation, facilities, engineering, construction and capacity; IEC is installed equipment cost ($); Q is the capacity (tons per year).

Bridgwater's method (Bridgwater and Mumford, 1979) has been developed and applied for early capital cost estimation using ($\frac{capacity}{overall\ conversion}$) as the capacity together with the functional units as presented in Eq. 7.4 and the recently developed models in Eq 7.5, which are used as *Model 2* for the analysis in this study.

$$C = k * N * \left[\frac{Q}{s} \right]^{x} \tag{7.4}$$

Model 2,

$$Q \geq 60000:\ C = 4320 * N * \left[\frac{Q}{s} \right]^{0.675};\ Q < 60000:\ C = 380000 * N * \left[\frac{Q}{s} \right]^{0.3} \tag{7.5}$$

Where C is is the capital cost in 1992 (£); Q is the capacity (tons per year); k is a constant; x is an exponent. However, determining the value for the number of functional units U_N is a major challenge of this method due to the inconsistency of the definition of the functional units.

c. Model 3: Pay-back method [production rate, raw material and product price]

Apart from the general methods mentioned above, using the profit and production cost can also be applied for a rough cost estimation. The *pay-back* method (Eq. 7.6) estimates the plant cost by assuming that the company would be paid back within 3-5 years (average is 4 years, the first factor) of pay-back period, for a rough estimate of the plant cost. The net profit is then estimated by assuming that the raw materials costs represent 80-90% of the total annualized cost (TAC), resulting in the second factor of 1.2. It is important to note that this method is normally used under the assumption that the specific project will generate a reasonable return.

Model 3,

$$Plant\ cost = 4 * (product\ sales - 1.2 * raw\ material\ cost) \quad (7.6)$$

d. Model 4: Total cost of production (TCOP) method [production rate, raw material and product price]

Total cost of production (TCOP) is simpler than the *pay-back* method using the raw material cost for estimating the annualized production cost. This method (Eq. 7.7) is normally applied for a large-scale production (>500,000 pieces per year). This method is a rule of thumb method assuming that the annualized capital cost is one-fifth of the total annualized production cost (including raw material cost, utility cost, annualized capital cost).

Model 4,

$$Plant\ cost = project\ life\ cycle\ (year) * \frac{TCOP}{5}; TCOP = 2 * raw\ material\ cost \quad (7.7)$$

The methods reviewed above have been applied to many cases and provide a good guideline during the decision-making processes. However, when extrapolating to fundamentally different plants and processes, the accuracy of their estimation becomes challenged due to uncertainties in their assumptions/factors/parameter values.

7.2.2 Uncertainty characterization and estimation of cost data

In this step, the uncertainties involved in cost estimation are reviewed and analyzed. As mentioned, uncertainty characterization (presented in *Chapter 3*) is extended to support the two distinct situations of the availability of the cost estimation data at early-stage design as presented in Figure 7.2. To this end, two different methods are presented: a) **cost data available**: in this case, cost data are reported from prior experiences with plant construction and operations. In this case, the challenge is to estimate the parameters of the cost estimation model using the data and then to quantify the accuracy of the estimation using regression analysis; b) **cost data not available:** this case refers to situations where new technology is developed, and hence there are no prior experiences or the technology in question is not mature. For this situation, the uncertainties can be characterized by using an expert judgment and peer review procedure (Sin et al., 2009). Once uncertainties have been defined, then the Monte Carlo technique can be used to propagate these uncertainties in the analysis.

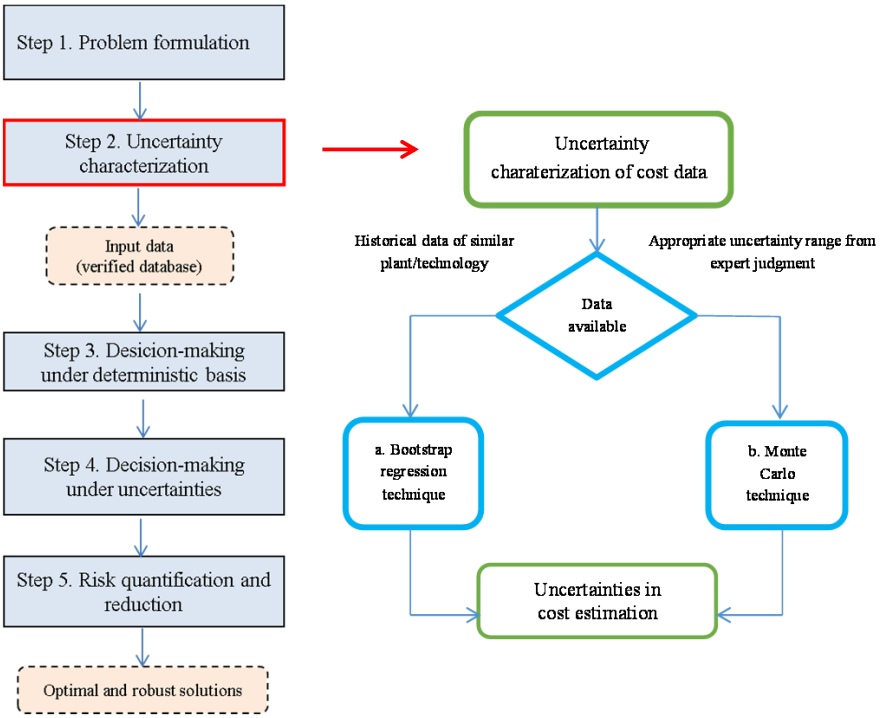

Figure 7.2. A systematic framework for synthesis and design of biorefinery (left), and an extended framework for uncertainty characterization (right).

a. Data available: bootstrap regression for parameter estimation

Bootstrap regression (Efron, 1979) is a method for assigning measures of accuracy (defined in terms of bias, variance, confidence intervals, etc.) to sample estimates. This technique allows estimation of the sampling distribution of almost any statistic using only very simple methods.

This method can be divided into three main steps: *(i)* Parameter estimation; *(ii)* Generation of synthetic data (bootstrap sampling); *(iii)* Evaluation of the distribution of theta. The bootstrap theory is briefly explained in the following using a simple non-linear model ($y_i = f_i(\theta) + \varepsilon_i$) as an example.

Parameter estimation: The actual data set $D_{(0)}$, "measures" a set of parameters θ_{true}. These true parameters are statistically realized as a measured data set $D_{(0)}$. The data set

$D_{(0)}$ is known as the experimenter. The experimenter fits a model to the data by a minimization (i.e. using least squares; $\hat{\theta}$: $min_\theta \|y - f(\theta)\|^2$) or other techniques and obtains measured, fitted values for the parameters, $\theta_{(0)}$.

Generate synthetic data (bootstrap sampling): In this step the actual data set $D_{(0)}$is then used with its N data points to generate a number of synthetic data sets ($D^s_{(1)}, D^s_{(2)}, \dots$), also with N_s data points. N_s data points are replaced at a time from the set $D_{(0)}$. Therefore, based on the given non-linear example, the bootstrap defines $\hat{F} = mass\frac{1}{n}$ as the sample probability distribution of $\hat{\varepsilon} = (y_i - f_i(\hat{\theta}))$. Then, for the given $\hat{F}$ and $\hat{\varepsilon}$, the bootstrap sample is $y_i^* = f_i(\hat{\theta}) + \varepsilon_i^*$.

Evaluate distribution of theta. For each data set, the same estimation procedure is performed giving a set of simulated measured parameters ($\theta^s_{(1)}, \theta^s_{(2)}, \dots$). The distribution of errors (θ) is estimated by minimizing the error of each data point using the least squares method. The distribution of errors (θ) which is estimated as sample is plotted for graphical analysis.

b. Data not available: Monte Carlo technique

Uncertainty analysis using the Monte Carlo technique can be divided into four steps: *(i)* Input uncertainty characterisation; *(ii)* Sampling; *(iii)* Model evaluations; and, *(iv)* Output uncertainty analysis.

Input uncertainty: Based on historical data, experiences and realizations, the parameters, which are inconsistent, are generally selected as uncertain data. The parameters are then characterized by choosing a distribution function such as a uniform or normal distribution.

Sampling: The domain of uncertainty defined previously is sampled to generate a list of possible future scenarios, with equal probability of realization. In order to facilitate this task, and assure the quality of the sampling procedure (in terms of coverage of the uncertain space) the approach integrates a Latin Hypercube Sampling (LHS) based sampling technique with the rank correlation control method proposed by Iman and

Conover (1982), in order to reflect the correlation between the uncertain parameters in the generated future scenarios.

Model evaluations: The generated Monte Carlo samples are then used as discretization points to approximate the probability integral, appearing in the objective function of optimization under uncertainty problems. The relationship between samples and outputs is established using a linear regression. In this regression, the parameter β_{jk} is the standardized regression coefficient (SRC) of the parameter j on output k; if β_{jk} has a negative sign, it means that a parameter j has a negative influence on the output *k*; if β_{jk} has a positive sign it indicates that a parameter has a positive influence on the output k; a high value of β_{jk} means a high impact on the output k. The sum of squares of the standardized regression coefficients is equal to one ($\sum_{j=1}^{M} \beta_{jk}^2 = 1$).

Output uncertainty. The results are then analysed by using a non-parametric distribution function such as a cumulative distribution function (CDF), and frequentist statistics such as mean, variance and percentile analysis etc.

7.3 Motivating example: estimation of uncertainty in cost data

Ethylene is an important and widely used intermediate in the chemical industries. The production of ethylene is used as a case study to highlight the uncertainties involved in cost estimation methods. The systematic methodology consists of two parts: *(i)* bootstrap parameter estimation; *(ii)* Monte Carlo technique with an expert judgment of uncertainties, are illustrated below.

3a. Bootstrap regression for parameter estimation

Table 7.3 presents the capacity and investment cost of the existing plant, which can be used for estimating the capital investment using the order-of-magnitude method (Eq. 7.1). This information is reported annually by SRI Consulting, Chem Systems, NREL or NETL. As presented in Table 7.3, there are five data points available, and the bootstrapping method is therefore applied.

Table 7.3. Historical data for order-of-magnitude cost estimation (Towler and Sinnott, 2013)

No.	Licensor	Technology	Capital cost (MM$/a)	a = C_1/S_1^n	S_2 (tpd)	S_2 (MMlb/a)	n	Conversion
1	Generic	ethane cracking	620	9.57	1300*	1045*	0.6	0.8
2	UOP/INEOS	UOP/Hydro MTO	559	8.63				0.8
3	Generic	LN cracker	1063	16.41				0.3
4	Generic	ethane/propane cracking	510	7.88				0.45
5	Generic	gas oil cracker	1109	17.12				0.25

Consequently, these data (Table 7.3) are regressed and characterized as the input parameters presented in Table 7.4. As shown in Table 7.4, the standard deviation is significant, and therefore, the parameter a is considered to be an uncertain parameter.

Table 7.4. The input parameter for cost estimation using *Model 1*

Model	Parameter	Mean	Std.
Model 1: $C_{new\ plant} = aS_{new\ plant}{}^{n}$	a	11.92	4.47
	n	0.60	0

3b. Early stage cost estimation – Monte Carlo technique

When data of similar plants are unavailable, the suggestion from an expert can be used. In this section, the Monte Carlo simulation with expert judgment is used for uncertainty analysis on the cost estimation. Table 7.5 presents the input uncertain data for cost estimation methods which are defined using the $uncertainty\ factor$ with respect to the cost estimation accuracy in *Class 5* (Table 7.1). To avoid any inaccuracy in the correlation between the parameters (the production rate, overall conversion and the number of functional units), the $uncertainty\ factor$ value, representing the uncertainties of the estimated capital cost, is used. The input data in Table 7.5 consist of two sections regarding two ranges of expert judgment: *(i)* lower range (underestimate), -20% to -50%; *(ii)* higher range (overestimate), +30% to +100%.

Table 7.5. The input parameters for three cost estimation models

Model	Parameter	Mean	Min	Max	Mean	Min	Max
		(-20% to -50%)			(+30% to +100%)		
Model 2: $C = \left(4320 * N * \left[\frac{Q}{s}\right]^{0.675}\right) * uncertainty\ factor$	$uncertainty\ factor$	1	0.5	0.8	1	1.3	2
Model 3: $C = \left(4 * (product\ sales - 1.2 * RM\ cost)\right) * uncertainty\ factor$							
Model 4: $C = \left(project\ life\ cycle\ (year) * \left(\frac{2 * raw\ material\ cost}{5}\right)\right) * uncertainty\ factor$							

Results

The results of the different cost estimation methods are presented and compared in Table 7.6. The estimation results obtained from different models yield significant differences. This motivating example confirms the significant impact on the selection of the methods for early stage cost estimation. This impact on process synthesis and design will be analyzed and discussed in the next section.

Table 7.6. The comparison of early stage cost estimation for an ethylene production plant of 1300 tpd

	Model 1		Ranges of expert judgement	Model 2		Model 3		Model 4	
	(MM$)	std.		(MM$)	std.	(MM$)	std.	(MM$)	std.
Capital cost estimation	772.5	289.4	-20% to -50%	143	19	2156	288	185	25
			+30% to +100%	363	45	5427	671	470	57

7.4 Process synthesis and design of biorefinery: impact of uncertainties in cost estimation on the decision making

7.4.1 Step 1: Problem formulation (Step 1.1: problem definition, superstructure definition, data collection, model selection and validation), Step 1.2: Superstructure definition, and Step 1.3: Data collection, modeling and verification).

The problem in this chapter has been defined earlier (*chapter 6*). The biorefinery design networks resulting from *chapter 6* are used again here, and therefore, the development of the superstructure and the data collection/management were not repeated. However, it is necessary to present the superstructure again (Figure 7.3). The objective function defined in this study was to maximize the operating profit (product sales – operating cost – annualized capital cost).

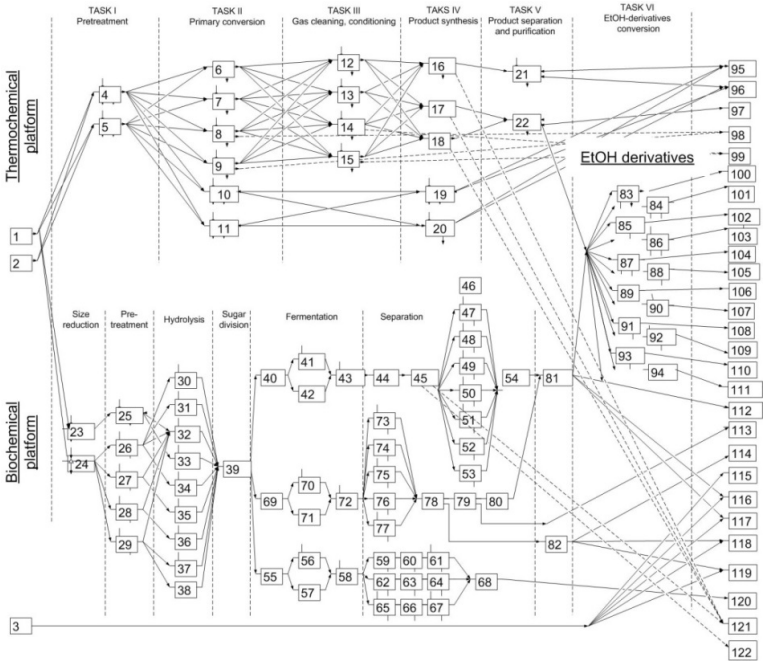

Figure 7.3. The superstructure of the biorefinery network extended with bioethanol based derivatives (presented again in this chapter).

7.4.2 Step 2: Uncertainty characterization.

In this step, the methodology presented earlier in (Figure 7.2) was applied to characterize the early stage cost estimation. Since there is very little information on the existing plant producing bioethanol derivatives, the *bootstrapping regression model* could not be applied. The *Monte Carlo approach* with Latin Hypercube Sampling was therefore applied instead.

Prior to any further analysis, it is important to note that there is only an overestimation scenario (+30% to +100%) that is presented in this context because it has a negative impact on the operating profit of the project. An underestimation scenario (-20% to -50%) is presented in the appendix D.

The input uncertainty for early stage cost estimation is presented in Table 7.7. The parameters of each cost estimation method were selected as uncertain data, and they were characterized as a uniform distribution (mean/min./max.) for two ranges of expert judgment with respect to the accuracy range presented in Table 7.1. The input uncertainties from Table 7.7 were then sampled for 200 scenarios.

Table 7.7. Input uncertainties for early stage cost estimation of ethanol derivatives for 4 cost estimation models

Model	Parameter	R1: ethylene			R2: acetaldehyde			R3: diethyl ether			R4: n-butanol			R5: ethylacetate			R6: acetic acid		
		a	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***
1	a	6.3	8.19	12.6	0.62	0.81	1.24	0.3	0.39	0.6	-			18.9	24	37.7	4.8	6.2	9.6
2,3,4	Uncertainty factor	1	1.3	2	1	1.3	2	1	1.3	2	1	1.3	2	1	1.3	2	1	1.3	2
Model	**parameter**	**R7: hydrogen**			**R8: propylene**			**R9: isobutylene**			**R10: acetone**			**R11: ethylene oxide**			**R12: 1,3-butadiene**		
		a	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***	***a***	***b***	***c***
1	a	0.87	1.13	1.74	7.1	9.23	14.2	0.05	0.07	0.10	-			5.6	7.28	11.2	1.85	2.4	3.8
2,3,4	Uncertainty factor	1	1.3	2	1	1.3	2	1	1.3	2	1	1.3	2	1	1.3	2	1	1.3	2

a is mean; *b* is min; *c* is max.

7.4.3 Step 3: Deterministic problem

The deterministic optimization problem is solved in this step. The result of this step is the deterministic solution of the optimal processing path, i.e. one optimal processing path on the basis of mean values representing the input data (Table 7.7). The top-five ranking of maximum operating profit is presented in Table 7.8.

Table 7.8 Top-five ranking of the optimal solutions using *Model 1-4* for capital cost estimation of +30% to +100% over-estimates for max. EBITDA of producing ethanol derivatives

Model 1						
Rank no.	**Process intervals selection**	**EBITDA (MM$/a)**	**Products**	**Production (tpd)**	**TAC (MM $/a)**	**Capex (MM $/a)**
1	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	246	Diethyl ether	345	83.42	23.62
2	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	238	1,3-butadiene	292	90.2	29.35
3	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
4	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethanol production**	133	Ethanol	590	81.3	22
5	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylene oxide production**	121	Ethylene oxide	544	143	25.7
Model 2						

Rank no.	Process intervals selection	EBITDA (MM$/a)	Products	Production (tpd)	TAC (MM $/a)	Capex (MM $/a)
1	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	241	Diethyl ether	345	88	29.6
2	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	240	1,3-butadiene	292	87.4	27.44
3	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
4	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylacetate production**	164	Ethylacetate	371	90	30.6
5	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **Ethylene oxide production**	139	Ethylene oxide	544	123	30.7
Model 3						
Rank no.	**Process intervals selection**	**EBITDA (MM$/a)**	**Products**	**Production (tpd)**	**TAC (MM $/a)**	**Capex (MM $/a)**
1	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	183	1,3-butadiene	292	133	84
2	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
3	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol.	179	Diethyl ether	345	150	93

	sieve, distillation, **diethyl ether production**					
4	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethanol production**	133	Ethanol	590	81.3	22
5	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylacetate production**	127	Ethylacetate	371	129	67.6
Model 4						
Rank no.	**Process intervals selection**	**EBITDA (MM$/a)**	**Products**	**Production (tpd)**	**TAC (MM $/a)**	**Capex (MM $/a)**
1	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	239	1,3-butadiene	292	94.6	28
2	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	238	Diethyl ether	345	93.5	31.3
3	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
4	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylacetate production**	161	Ethylacetate	371	95	33
5	Wood, entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **Ethylene oxide production**	136	Ethylene oxide	544	129	33

The results presented in Table 7.8 show that there are slight differences in the results with respect to the identification of the optimal processing paths. Diethyl ether is

predicted to be the most profitable using *Model 1, Model 2*, and *Model 4* for estimating capital cost. On the other hand, 1,3-butadiene is predicted as being the most favorable product when using *Model 3*. Overall, the production of diethyl ether, 1,3-butadiene and butanol are in the top-three ranking for every scenario.

7.4.4 Step 4: Decision-making under uncertainty

Step 4.1 Deterministic problem

Instead of using a certain (mean) value as input data, the sampling results (200 samples generated in *Step 2*) from the uncertainty domain were used as the input data for the deterministic problem resulting in 200 optimal solutions.

The results (Table 7.9) are *(i)* the probability distribution of the objective value; and *(ii)* the frequency of selection of the optimal processing path candidates under the generated uncertain samples. These identify the promising processing paths given the considered uncertainties.

Table 7.9. Uncertainty mapping and analysis: frequency of selection with respect to 200 input uncertainty scenarios

Model	Range of expert judgement	Operating profit (MM$/a)		Annualized capital cost (MM$/a)		Frequency of selection	
		(MM$)	std.	(MM$)	std.	Diethyl ether production	1,3 butadiene production
1	+30% to +100%	246.6	0.24	22.92	0.24	200/200	-
2		242	0.8	29.6	1	145/200	55/200
3		196.6	9.4	86	7.9	36/200	164/200
4		236.6	1.37	31	1.2	176/200	24/200

The results show that using *Model 1*, there were no changes of the optimal processing path compared to the deterministic solution. On the contrary, using *Model 3*, the production of 1,3 butadiene was more favorable confirming the results in *Step 3 (section 7.4.3)*. Overall, the production of diethyl ether and 1,3-butadiene were reported to be the most favorable and profitable. The results in this step confirm the robustness of the deterministic solutions in *Step 3 (section 7.4.3)*.

7.4.5 Step 5: Risk quantification

The results from *Step 3* and *Step 4.1* presented previously show that the production of diethyl ether and 1,3-butadiene are the most profitable/promising. Therefore, these two productions were further analyzed. In this step, EBITDA is converted into IRR (Eq. 7.8) which is an appropriate economic indicator for project evaluation. Figure 7.4 and Figure 7.5 present the cumulative distribution of the %IRR related to diethyl ether and 1,3-butadiene production, respectively.

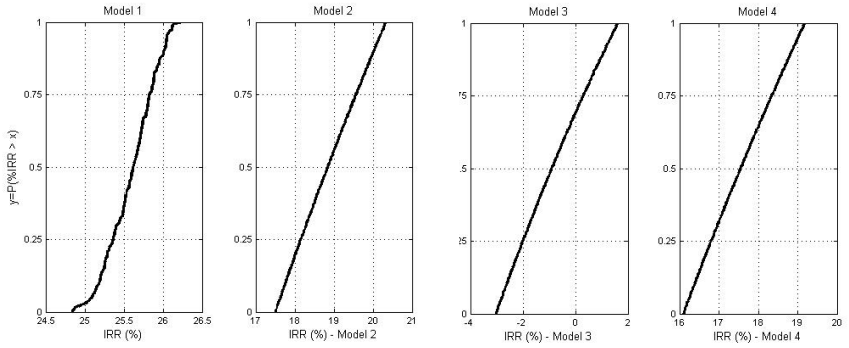

Figure 7.4. Diethyl ether production: the empirical cumulative distribution function (ECDF) of the IRR estimated from four estimation models

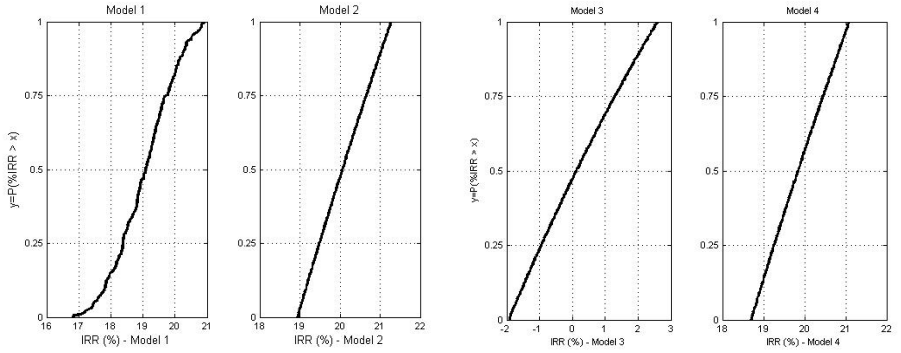

Figure 7.5. 1,3-butadiene production: the empirical cumulative distribution function (ECDF) of the IRR estimated from four estimation models

Risk analysis was also performed and analyzed based on the production of diethyl ether and 1,3-butadiene. Risk is defined as the probability (failed to achieve the target) times

the consequence (the deviation from the target). In this study, the target is the internal rate of return (IRR) which is estimated based on the certain value (mean) of the input parameter used for capital cost estimation. Table 7.10 presents the risks quantified based on the two production processes (diethyl ether and 1,3-butadiene), four cost estimation models and the reference estimation (no uncertainty considered).

Table 7.10. Risk analysis of the production of diethyl ether and 1,3-butadiene

Model	Diethyl ether production			1,3 butadiene production		
	Referenced estimation (%)	Estimated IRR (%), Fig.6	Quantified risk (MM$/a)	Referenced estimation (%)	Estimated IRR (%), Fig.7	Quantified risk (MM$/a)
1	26.2	25.6 ± 0.31	0.24	22.7	19.1 ± 0.91	4.9
2	24.2	20.6 ± 0.89	0.02	25.2	21.7 ± 0.7	6.4
3	8.9	-0.2 ± 1.98	20.3	8	2.6 ± 2.1	13.9
4	20.1	16.5 ± 0.95	3.63	23.6	15.9 ± 0.9	8.7

As presented in Table 7.10, the risks quantified for diethyl ether production are lower compared to 1,3-butadiene production except for the case where *Model 3* was used. The reason for this is that the price of diethyl ether is lower resulting in a lower operating profit and IRR. Moreover, *Model 3* resulted in a significantly lower IRR compared to the results from the other models. Therefore, *Model 3* should be considered as invalid.

7.5 Discussion

The comparison results show that different cost estimation methods lead to different results. This is because of the differences in the assumptions and the types of data used for the estimation. Therefore, the selection of the proper cost estimation method is critical.

Moreover, the results show that the uncertainty impact of cost estimation on the optimal processing paths is significant in the case study considered for the analysis. Hence, we conclude here that cost analysis cannot be based on a deterministic approach, but should be done using a probabilistic approach in which uncertainties are accounted for. Moreover, the *Model 3* is found not to be preferable because the results are inconsistent

compared to the other models. The underlying reason is attributed to the fact that the *Model 3* is an indirect method that requires too much input information including the assumption of pay-back period, product sales and raw material cost. Hence, *Model 3* is more vulnerable to input uncertainties. On the contrary, the *Model 4* – another indirect method, uses only one assumption (raw material cost) and provides more consistent results with the cost estimation obtained from direct methods, i.e. the *Model 1* and *Model 2*.

In this study, IRR and EBITDA were used as economic indicators according to industrial practice (Towler and Sinnott, 2013). The results are expected to be the same as using net present value (NPV) due to the direct relation between IRR and NPV as presented in Eq. 8 (Towler and Sinnott, 2013).

$$NPV = 0 = -capital\ investment + \frac{EBITDA}{(1+IRR)^1} + \frac{EBITDA}{(1+IRR)^2} + \cdots + \frac{EBITDA}{(1+IRR)^{19}} + \frac{EBITDA}{(1+IRR)^{20}} \qquad (7.8)$$

In engineering companies, the cost estimation is usually refined in each successive phase of the project. For example in the detailed engineering phase, the cost estimation will be made based on the vendor information about pipes, tanks etc. resulting in more accurate estimates compared to the rough estimation obtained at the early project stage using simple methods (the *Model 1*, *2*, *3* and *4* as presented here). Hence as a future scope for further improving the accuracy of early stage cost models, it is suggested to calibrate the model parameters against more accurate cost estimation models.

Overall the results in this study support the argument that while the early stage assessment of the main cost components (capital investment and operating costs) is an approximation, these estimation results can still be useful for comparing and screening among alternatives (Anderson, 2009). Therefore, if the assumptions are reasonable, the process alternatives that are clearly economically infeasible can be identified early and removed from further analysis in subsequent project design stages.

7.6 Conclusions

An assessment of uncertainties in early stage cost estimation of process synthesis and design of a biorefinery was studied and discussed. A systematic framework was applied consisting of a superstructure optimization based approach under uncertainty integrated with the proposed uncertainty characterization framework supporting the different types of data available (i.e. historical data from existing plants, an expert judgment). The comparison results from the case study on the process synthesis and design of the biorefinery problem showed that the results are different when using different cost estimation models. The *Model 3* is found not to be favourable in this study because the results are inconsistent with the other models. Moreover, using the same methods including the uncertainties resulted in a significant impact on changing the selection of the processing paths. Therefore, the selection of early stage cost estimation method is critical. Furthermore, the cost analysis cannot be based on a deterministic approach but should be evaluated by means of a probabilistic approach in which uncertainties are accounted for. It was found that the production of diethyl ether and 1,3-butadiene are the most economically profitable. These analyses provide useful information supporting the future development of biorefineries.

8.
CASE STUDIES IV: ALGAL BIOREFINERY

In this chapter, optimal design of an algal biorefinery using microalgae is presented with respect to techno-economic criteria. A superstructure representing a wide range of technologies developed for processing microalgae to produce end products is formulated. The corresponding technical and economic data is collected and structured using generic input-output mass balance models. An optimization problem is formulated and solved to identify the optimal designs. The effect of uncertainties inherent in economic analysis such as microalgae production cost, composition of microalgae (e.g. oil content) in microalgae and biodiesel/bioethanol market prices is investigated and presented as well.

Parts of this chapter have been published in the following publications: (i) Peam Cheali; Krist V. Gernaey; Gürkan Sin. (2015) *Optimal Design of Algae Biorefinery Processing Networks for the production of Protein, Ethanol and Biodiesel*. Computer Aided Chemical Engineering, in press; (ii) Peam Cheali; Carina L. Gargalo; Krist V. Gernaey; Gürkan Sin. (2015) *A framework for sustainable design of Biorefineries: life cycle analysis and economic aspects*. Algal Biorefineries Vol. 2, Springer, in press.

8.1 Introduction

Among other renewable feedstocks (i.e. corn stover, wood, palm or soybean), algae contain the highest oil yield per hectare per year (Demirbas & Demirbas, 2011). Moreover, high growth rate, CO_2 consumption, clean technologies, and a variety of potential products (i.e. biofuels, bioenergy, animal feed, cosmetics, fertilizer, fibers, and intermediate protiens) enhance the development of algae cultivation and conversion technologies (FAO 2010).

In development of the algal biorefinery, there are a number of alternatives potentially available to choose from depending on the specific type of microalgae and the processing technologies used to produce biodiesel, glycerol, ethanol and protein-based compounds. The typical algal biorefinery consists of algae cultivation, harvesting, pretreatment, extraction, and conversion (i.e. transesterification). Thermochemical processes (i.e. hydrothermal liquefaction or pyrolysis) can also be used to convert algae to biofuels. Moreover, algae, which contain a number of nutrients, can also be converted into non-energy products (i.e. intermediate protein, animal feed or fertilizer). In this chapter, only the typical algal biorefinery is addressed.

One of the challenges in identifying optimal algal biorefinery concept is the underlying uncertainties in data used for comparison and evaluation. These include the volatility of market prices, process conversion factors and yields inherent to new technologies. Therefore, it is important to use a systematic methodological approach at the early stage design phase to identify the optimal designs under uncertainties.

To this end, a systematic framework that uses superstructure-based optimization is applied to identify the optimal algal biorefinery concept in this chapter. The study considers the effect of uncertainties in raw material composition and product prices on the decision making as well. First, a superstructure representing the design space of the algal biorefinery is developed containing various types of microalgae and subsequent pretreatment, reaction and separation technologies to produce biodiesel, ethanol and protein-based compounds. Subsequently, the database (generic model and parameters and data) is collected The superstructure which is formed by the combination of the

alternatives (types of feedstock, technologies, and products) together with the collected data, is then mathematically formulated as an optimization problem and solved to identify the optimal designs with respect to techno-economic constraints. Further product market prices and algae oil content uncertainties are analyzed for robust decision making purposes.

8.2 Identification of algae biorefinery optimal designs

In this section, synthesis and design of algal biorefinery networks under uncertainty was performed using the systematic framework presented in earlier sections.

8.2.1: Step 1-Problem formulation: *(1.1)* problem definition; *(1.2)* superstructure definition and data collection; *(1.3)* model selection and validation

The problem statement was formulated as the identification of optimal biorefinery concepts with respect to techno-economic specifications under a specific objective function aiming at maximizing company earnings. The superstructure (Figure 8.1) of the algae biorefinery processing network was generated producing biodiesel and co-products by processing microalgae cultivated in a raceway pond with a 1300 tpd capacity (the same basis as Pacific Northwest National Laboratory (PNNL), Jones, et al., 2014). The superstructure has four main processing steps consisting of 12 harvesting technologies; 4 pretreatment technologies; 4 extraction technologies; 6 transesterification alternatives; and 4 conversion technologies of co-products, resulting in a total of 1920 processing paths. The data collection including model verification was performed against the experimental data published prior to the identification of optimal processing paths in the next steps.

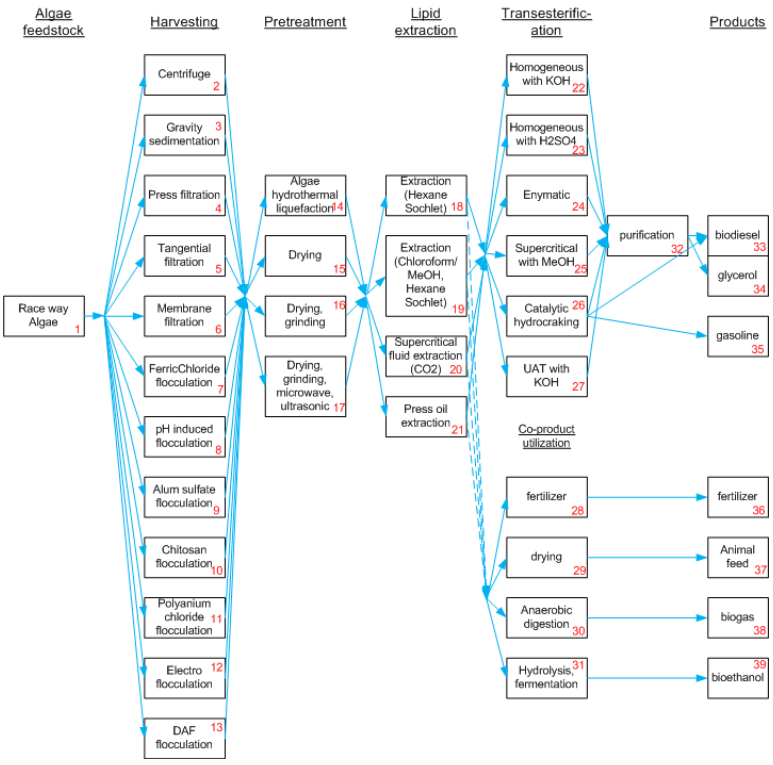

Figure 8.1. The superstructure of algae biorefinery processing networks

Data collection and estimation

The data and parameters required for the generic process model blocks (*section 3.1*) that are used to define the superstructure, are presented in this section and in Table 8.1-8.3. The alternatives technologies presented and defined in this study are based on the available data from publications (i.e. literature, technical reports). Cost estimation was performed on the basis of the amount of utilities consumed (operating cost) and the available information of the existing plant/technologies by applying the six-tenth rule (capital cost).

Table 8.1 presents the parameters for the generic process model block in the harvesting processing step. The harvesting step is used to collect the algae. The algae form a dilute suspension in water and the main purpose of the harvesting step is to increase the

concentration of algae in the feed stream to the biorefinery. Therefore, there are three parameters presented: *(i)* the ratio of utilities or chemicals added ($\mu_{i,j,kk}$); *(ii)* the consumption of added utilities or chemicals ($\alpha_{i,kk}$); *(iii)* product separation ($Split_{i,kk}$).

Table 8.1. The parameters for the generic process model block in the harvesting processing step ($Split_{algae,kk}$ = 1)

Process blocks		$\mu_{i,j,kk}$	$\alpha_{i,kk}$	References
(2) Centrifuge				Price et al. (1974)
(3) Gravity sedimentation				Sim et al. (1988)
(4) Press filtration				Sim et al. (1988)
(5) Tangential filtration				Petrusevski et al. (1995)
(6) Membrane filtration				Zhang et al. (2010)
(7) Ferric Chloride floccula-tion	Ferric Chloride	1.25	1	Granados et al. (2012)
(8) pH induced flocculation	NaOH	0.2	1	Wu et al. (2012)
(9) Alum sulfide flocculation	Alum	0.27	1	Sirin et al. (2012)
(10) Chitosan flocculation	Chitosan	0.18	1	Divakaran et al. (2002)
(11) Polyanium chloride flocculation	Polyanium chloride	0.27	1	Divakaran et al. (2002)
(12) Electro flocculation				Granados et al. (2012)
(13) Dissolved air floccula-tion				Sim et al. (1988)

The pretreatment step is used to increase the concentration of the algae to 20 wt% or higher. Therefore, the parameters here are (i) the heat and electricity required; and (ii) the concentration of algae at the outlet (20 wt %). In this step, there are four alternatives: (i) algae hydrothermal liquefaction (AHTL) with a conversion fraction of 0.52 of raw algae to algae oil (Jones et al., 2014); (ii) drying and grinding; (iii) drying, grinding and microwave; (iv) drying, grinding, microwave, and ultrasonic treatment.

Table 8.2 presents the parameters in the lipid extraction step. This step is used to extract algae oil (lipid) from the algae feed (20 wt %) after the drying processes. Therefore, solvents are required and product separation of algae oil (lipid) is done in practice. The primary product of this step is algae oil (lipid) and the secondary products which are separated are then processed in the co-product utilization step.

Table 8.2. The parameters for the generic process block in the lipid extraction processing step

Process blocks		$\mu_{i,j,kk}$	$\alpha_{i,kk}$	$Split_{lipid,kk}$	References
(18) Extraction	Hexane Sochlet	0.18	0	0.26	Prommuak et al. (2012)
(19) Extraction	Chloroform and Hexane Sochlet	0.18	0	0.2	Long et al. (2011)
(20) Supercritical fluid extraction	CO_2			0.1	Herrero et al. (2006)
(21) Press oil extraction	(Expeller)			0.75	Topare et al. (2011)

Table 8.3 presents the parameters for the generic process model block in the transesterification processing step. Transesterification is used to convert algae oil (lipid) to biodiesel and glycerol. Acid or base catalysts are required as well as methanol which is then recycled. The stoichiometric coefficient ($\gamma_{i,rr}$) following the typical transesterification reaction (Algae oil (lipid) + 3MeOH ↔ 3Fatty acid methyl ester (FAME) + glycerol) and conversion fraction ($\theta_{react,rr}$) are furthermore required in this processing step.

Table 8.3. The parameters for the generic process block in transesterification, co-product utilization, purification processing step

Transesterification		$\mu_{i,j,kk}$	$\alpha_{i,kk}$	$\theta_{react,rr}$	References
(22) Homogeneous	KOH, MeOH	0.05, 16	0, 1	0.92	Vicente et al. (2004)
(23) Homogeneous	H_2SO_4, MeOH	0.03, 9	0, 1	0.95	Miao et al. (2006)
(24) Enzymatic	Enzyme, MeOH	0.0012, 6	0, 1	0.83	Levine (2013)
(25) Supercritical	MeOH	9	1	0.89	Levine (2013)
(26) Catalytic hydrocracking	Cobalt-modified MoS2 catalyst			0.82	Jones (2014)
(27) Ultrasonic assisted transesterification (UAT)	KOH	9	0	0.925	Levine (2013)

Fertilizer (block no. 28) in this study is used to produce potassium nitrate. The constant (0.9) is used to simply convert a protein and starch mixture to fertilizer. The amount of dry cake of protein and starch mixture produced by the dryer (block no. 29) corresponds

to the animal feed product. Bio-methane is produced using anaerobic digestion (block no. 30). The constant (0.03) is also used to produce bio-methane and carbon dioxide as the by-product. Hydrolysis and fermentation (block no. 31) are used to produce bioethanol. The constant (0.3) is also used for this process. These constants are estimated based on the available information from the literature (Alabi et al., 2009).

Models and data verification

In this step, models and data are verified by checking the conservation of mass for each process model block. The output of this step is the verified database for the algae biorefinery which is then used as the input data for the optimization problem in the next step to identify the optimal processing paths. This step is highlighted for two processes below.

The first example is for hydrothermal liquefaction process to produce algae oil (lipid) from raw algae. Heat is used as the main utility in this process. The mass balance (inlet stream(s) – outlet streams) for this process is closed by 100% as shown in Figure 8.2.

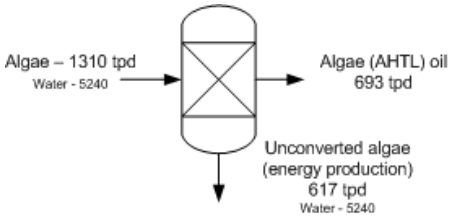

Figure 8.2. The simplified process diagram showing mass inlet/outlet for hydrothermal liquefaction

The second example is for homogeneous transesterification with H_2SO_4 to produce FAME (biodiesel) and glycerol from algae oil (lipid). Similarly the mass balance around this processing block is 100% closed by as shown in Figure 8.3.

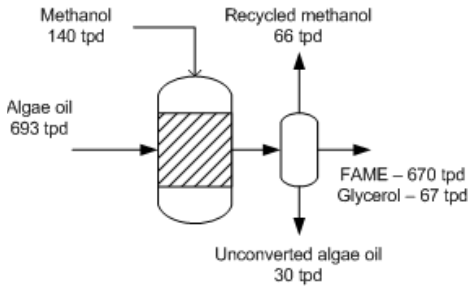

Figure 8.3. The simplified process diagram showing mass inlet/outlet for homogeneous transesterification with H_2SO_4

8.2.2 Step 2: Uncertainty characterization.

In this chapter, the uncertainties of market prices (biodiesel and bioethanol prices) and oil content in microalgae were identified as the important sources of uncertainty affecting the decision making process. Other potential sources of uncertainties (i.e. yields, reaction conversions, efficiencies) were not considered because of the low values of reported uncertainties. A summary of the input uncertainties and the correlation coefficient if available used in this study is presented in Table 8.4. These data form the input uncertainty domain, which was then sampled to generate 200 samples of the uncertain inputs. The Latin Hypercube Sampling (LHS) technique was used to this end.

Table 8.4. Input uncertainty and correlation control coefficient

	mean	**Std**	**Reference**	
Biodiesel price ($/kg)	1,43	0,07	EIA	
Bioethanol price ($/kg)	0,72	0,08	USDA	
	min	**Max**		
Oil content (Raceway pond)	7,5	50	Alabi et al. (2009) and Jones et al. (2014)	
Raw algae cost ($/ton)	300	560	Jones et al. (2014)	
Correlation matrix				
	DO	EtOH	RC	Algae
Biodiesel price (DO)	1	0,194	0	0
Bioethanol price (EtOH)	0,194	1	0	0
Oil content (RC)	0	0	1	0
Algae cost	0	0	0	1

8.2.3 Step 3: decision making on the deterministic basis

In this study, the objective function was defined as maximizing the operating profit (MM$/a) for the biodiesel scenario. The formulated MI(N)LP was solved in this step for the deterministic basis (mean input values), in particular, by maximizing Earnings Before Interest, Taxes, Depreciation and Amortization (EBITDA). The optimization solutions are presented in Table 8.5. The results show that a new optimal processing path (no. 1 in Table 8.5) was found slightly better compared to the case study from the PNNL report (Jones et al., 2014).

Objective function,

$$max.\,EBITDA = Revenue - Expenses\ (excluding\ interest,\ \ taxes, depreciation\ and\ amortization \tag{8.1}$$

In this step, the formulated MILP/MINLP problem was solved; the optimal solutions were identified (max. EBITDA); and the results are presented in Table 8.5 illustrating the top-three ranking of the solutions. The production rate of diesel and glycerol, EBITDA, production rate, total capital cost and operating cost as well as the optimal processing paths were presented. This solution corresponded to the deterministic solution of the optimization problem where no uncertainties are considered. The formulation of the optimization problem consists of 99,437 equations and 97,319 variables and 40 decision variables. This problem was solved using DICOPT solver using Windows 7, Intel® Core™ i7 CPU@ 3.4GHz, 4GB RAM, resulting in 10 seconds of the execution.

Table 8.5. Top-three ranking processing paths of algal biorefinery with respect to economic criteria

Rank	Processing path	EBITDA (MM$/a)	Production (biodiesel/glycerol) (tpd)	Capital cost (MM$)	Operating cost (MM$/a)
1	Algae, hydrothermal liquefaction, transesterification with H_2SO_4	87	670/67	252	198
2	Algae, hydrothermal liquefaction, transesterification with KOH	60	648/65	252	201
3	Algae, hydrothermal liquefaction, super/subcritical transesterification with methanol	47	627/63	252	196

As presented in Table 8.5, hydrothermal liquefaction was selected because it results in the highest yield of algae oil produced compared to lipid extraction alternatives. The homogeneous transesterification using H_2SO_4 as catalyst was selected because it reaches the highest conversion. The results are in agreement with the PNNL report (Jones et al., 2014) which used hydrothermal liquefaction and catalytic hydrotreating resulting in 280 MM$/a. The differences are due to the use of transesterification with H_2SO_4 instead of catalytic hydrotreating which has a lower yield and higher cost. It also shows that the cost of algae feedstock (190 MM$/a, 1300 tpd) is accounted for 90% of total annualized cost which is much higher than the feedstock cost for lignocellulosic biomass (60 MM$/a, 2000 tpd).

8.2.4 Step 4: decision-making under uncertainties

Step 4.1 Deterministic problem

In this step the 200 samples generated from the LHS sampling were used as the input data for the MIP/MINLP problem, resulting in 200 optimal solutions. The full results were then analysed to identify the optimal solution under uncertainty. As presented in Table 8.6, two processing paths were selected under uncertainty.

From the 200 considered scenarios under uncertainty, network 1 and network 2 are identified as the best candidates. Moreover, network 1 resulted in higher EBITDA, however, the standard deviation is slightly higher compared to network 2 meaning that

further analysis should be performed to mitigate the impact of uncertainties such as flexible network solution.

Table 8.6. The frequency of selection of the optimal processing paths for 200 input scenarios under uncertainties

Network no.	Processing path	Frequency of selection	EBITDA (MM$/a)	Std.
1	Algae, hydrothermal liquefaction, transesterification with H_2SO_4	130/200	122	26
2	Algae, hydrothermal liquefaction, transesterification with KOH	70/200	87	25

Step 4.2 Stochastic problem

The mathematical formulations used in *Step 3* and *Step 4.1* were reformulated as stochastic programming and solved in this step. Table 8.7 presents the optimal solutions (processing paths and operating profits) under uncertainty. As regards the optimal network solutions under uncertainty, the process topologies selected were slightly different from the deterministic case, which was the result of the trade-off between conversion and utility cost, and therefore confirming the robustness of the deterministic solution and the strong impact of uncertainties.

Table 8.7. Optimal solutions under uncertainty

Solution	Network	EBITDA (MM$/a)	Capital cost (MM$)	Operating cost (MM$/a)		
				Microalgae cost	Natural gas	Catalyst/Chemicals
Optimal network (Step 3)	Algae, hydrothermal liquefaction, transesterification with H_2SO_4	87	252	190	6.6	4.5
Network under uncertainty (Step 4b)	Algae, hydrothermal liquefaction, transesterification with KOH	85	252	190	6.6	3.8

Summarizing, based on the techno-economic analysis of the optimal biorefinery network presented in the previous steps of the methodology, the network presented in Figure 8.4 is found as the optimal solution both for the deterministic case and under uncertainty – in particular market uncertainties. Hence the result from the optimal

flexible network (Algae, hydrothermal liquefaction, transesterification with H_2SO_4 and KOH) is then recommended as the best candidate for further research and development efforts among the design space candidates.

Moreover, it is important to note that 90% of the biodiesel production cost is represented by the microalgae cost (1300 tpd of microalgae, 190 MM$/a) which is much higher compared to lignocellulosic biomass (60 MM$/a, *chapter 5* and *chapter 6*). Furthermore, for the same capital investment, the algal biorefinery has a lower capacity compared to a lignocellulosic biorefinery meaning that it is more expensive (Jones et al., 2014). However, the biodiesel yield is higher, 51% maximum for the algal biorefinery and 28% for the lignocellulosic biorefinery (*chapter 5* and *chapter 6*).

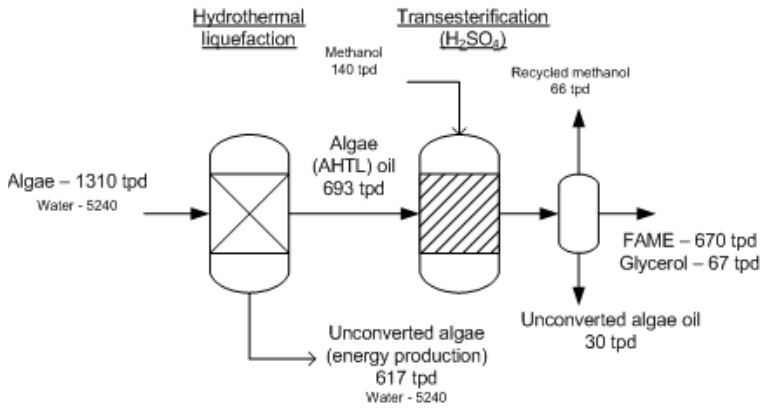

Figure 8.4. The optimal processing network (simplified flowsheet)

8.3 Discussion

The systematic framework for synthesis and design of processing networks followed in this chapter generated a large verified database resulting in a large design space with a number of scenario that were produced prior to the identification of optimal designs.

The input data were collected from the literature and the PNNL report. The resulting optimal design concept consisted of whole algae cultivation from a raceway pond, hydrothermal liquefaction, and transesterification with H_2SO_4. The algae feedstock cost was estimated earlier by U.S. Department of Energy (DOE 2013) as a fixed price of 430

$/ton (340 $/ton for cultivation, 90 $/ton for dewatering) or 204 MM$/a for biodiesel production from lipid extraction. This cost was reduced to 300 $/ton (or 190 MM$/a) due to the use of whole algae reported by PNNL (Jones et al. 2014). Therefore, an algae cost of 300 $/ton was used in this study. Moreover, a new optimal design concept was found in this study resulting in slightly higher EBITDA compared with the result in PNNL; 319 and 280 MM$/a, respectively. It is important to note that 90% of the biodiesel production is related to the cost of algae feedstock (190 MM$/a, 1300 tpd) which is much higher than for lignocellulosic biomass (60 MM$/a, 2000 tpd). However, the maximum biodiesel yield for an algal biorefinery (51%) is much higher than for a lignocellulosic biorefinery (28%) reported in the previous study (*chapter 5* and *chapter 6*).

The results in this study are in agreement with the PNNL report. However, the study from British Columbia (Alabi et al. 2009) which performed economic analysis on the algal biorefinery based on three different algae feedstock concluded that algae cultivated from raceway pond and photobioreactor cannot produce oil at competitive prices except for algae cultivated from a fermenter due to the productivity of algae and the oil content in algae feedstock. Therefore, the identification of optimal designs of the algal biorefinery is still a challenging problem due to the quality of the data available. The database should be kept up to date and will be expanded with more promising data and technologies. Moreover, uncertainty analysis should also be performed in the future work as the data are highly uncertain at the early development stage of algal biorefinery design.

8.4 Conclusion

In this study, the systematic framework for synthesis and design of processing networks under uncertainty was applied for designing an optimal algal biorefinery processing network. A new optimal processing path was identified which includes the following processing scheme: hydrothermal liquefaction and transesterification with acid (H_2SO_4) or KOH. Moreover, the solutions – both deterministic and under uncertainties in product market prices, algae cost and oil content are slightly different. These confirm the strong impact of the oil content in algae and the biodiesel market prices for algae biorefinery

processing networks. It is also important to note that the microalgae cost is around 90% of the biodiesel production which indicates that research and development efforts need to focus to bring down the production costs of microalgae by and large.

Using the framework, many processing network alternatives are generated and evaluated at their optimality resulting in the identification of the optimal processing paths. The generated database and superstructure provide a versatile process synthesis toolbox used in designing future and sustainable algal biorefineries.

9. ECONOMIC RISK ANALYSIS AND CRITICAL COMPARISON OF OPTIMAL BIOREFINERY CONCEPTS

In this chapter a number of optimal biorefinery concepts presented earlier are critically analyzed and compared in terms of techno-economic performance and associated economic risks against historical market fluctuations. Moreover, the economic analysis of each biorefinery concept is tested against a sudden drop in oil prices to compare fitness/survival of the biorefinery concept under extreme market disturbances.

9.1 Introduction

Chemical industries and other manufacturing and industrial sectors strongly depend on fossil-based feedstock for raw materials and energy production. This dependence results in issues related to supply security and long-term availability, price volatility, and negative environmental impacts like climate change effects (Tuck et al., 2006). This context has motivated the development of sustainable technologies for processing renewable feedstock into fuels, chemicals and materials. The biorefinery concept has thus become a promising solution for efficiently using and processing different types of renewable biomass feedstock.

The wide range of biomass characteristics has resulted in a significant development in the area of biorefinery processing technologies (i.e. hydrolysis, fermentation, gasification, product synthesis) in lab-, pilot-, demonstration- to full-scale production (Rødsrud et al., 2012). However, the development and design of optimal biorefinery concepts in a competitive market and considering uncertainties still remains an open challenge.

Therefore, a quick, robust and systematic approach for designing optimal biorefineries under market price uncertainties was developed to support decision-making processes (*Chapter 3*). The approach has been used to design optimal biorefineries for: (*i*) lignocellulosic ethanol production via thermochemical and biochemical conversion from corn stover and poplar wood (*Chapter 5*); (*ii*) ethanol-based production of high value-added derivatives (*Chapter 6)*; and (*iii*) biodiesel, ethanol and protein production from microalgae (*Chapter 8*).

In this chapter a number of optimal biorefinery concepts capable of producing biofuels and biochemicals employing different feedstock (lignocellulosic versus microalgal biomass) and with biochemical versus thermochemical conversion platforms are critically studied for in-depth comparison and economic risk analysis against market price uncertainties. To perform economic risk analysis, two market uncertainty scenarios were evaluated: (a) long-term historical trend of fluctuation for product prices; and, (b) the recent sudden drop in oil prices and the corresponding effect on product

prices. For the economic performance analysis, the following metrics were used: (i) EBITDA: Earnings before interests, taxes, depreciation and amortization – for deterministic analysis and comparison, (ii) MESP: minimum selling price – to compare cost breakdown for production cost (feedstock versus utility costs), and (iii) IRR: internal rate of return – a typical investment parameter which is also used to quantify the economic risk of failure for investment in a given biorefinery concept. This comprehensive quantitative comparison of technically and conceptually different systems allows identifying the cases with the most attractive strategy, i.e. choice of feedstock, choice of processing/conversion technology and product portfolio that performs best against past and present market price uncertainties.

9.2 Synthesis and design of biorefinery network under uncertainties: results and discussion

As mentioned in earlier chapters, the superstructure based optimization methodology developed earlier (*Chapter 3*) has been used to perform techno-economic performance and economic risk analysis on the major biorefinery concepts (*Chapter 5-8*) to identify their optimal processing paths. These biorefinery concepts and their optimal solutions are summarized again in Table 1.

Table 9.1. The optimal biorefinery concepts investigated for economic risk analysis and critical comparison

Concept	Feedstock	Optimal conversion technology	Products	Data sources
Biorefinery 1A	2000 tpd of corn stover	Biochemical conversion concept (APR pretreatment, spezyme hydrolysis, fermentation) (Zondervan et al., 2011)	556 tpd of Bioethanol	NREL(Aden et al., 2002) and literatures
Biorefinery 1B	2000 tpd of corn stover	Thermochemical conversion concept (*Chapter 5*)	544 tpd of Bioethanol	NREL (e.g. Swanson et al., 2010)
Biorefinery 1C	2000 tpd of poplar wood	Biochemical conversion concept (APR pretreatment, spezyme hydrolysis, fermentation) (*Chapter 5*)	468 tpd of Bioethanol	NREL and Zondervan et al. (2011)
Biorefinery 1D	2000 tpd of poplar wood	Thermochemical conversion concept (*Chapter 5*)	590 tpd of Bioethanol	NREL (e.g. Dutta et al., 2009; 2011)
Biorefinery 2A	2000 tpd of poplar wood	Thermochemical conversion concept (*Chapter 5*)	170 tpd of FT-gasoline, 400 tpd of FT-diesel	NREL(e.g. Swanson et al., 2010
Biorefinery 2B	1300 tpd of microalgae	Thermochemical conversion concept (liquefaction and transesterification) (*Chapter 8*)	670 tpd of Biodiesel	PNNL (Jones et al., 2014)
Biorefinery 3A	2000 tpd of poplar wood	Thermochemical conversion concept and bioethanol upgrading processes (*Chapter 6*)	356 tpd of Diethyl ether	NREL and Posada et al. (2013)
Biorefinery 3B	2000 tpd of poplar wood	Thermochemical conversion concept and bioethanol upgrading processes (*Chapter 6*)	306 tpd of 1,3-butadiene	

[1]The lignin utilization was included and the market prices were updated from the previous study. [2]Biodiesel price was updated to be comparable with the previous study (*Chapter 5*).

In the earlier studies (Table 9.1), the processing networks (or the so called superstructure) are defined together with data collection and management regarding feedstock composition, technological factors (*e.g.* reaction stoichiometry, yields, separation units, utilities/chemicals usage, capital and operating costs), and market prices of raw materials and products. The data of market price uncertainties are characterized as probability distributions and used to generate possible future scenarios using the Monte Carlo technique. The Monte Carlo technique consists of the following

four steps: *(i)* Input uncertainty characterisation; *(ii)* Sampling; *(iii)* Model evaluations; and, *(iv)* Output uncertainty analysis.

Input uncertainty: This is based on historical data, experiences and realization, the parameters, which are inconsistent, are generally selected as uncertain data. The parameters are then characterized by choosing a distribution function such as a uniform or normal distribution.

Sampling: The domain of uncertainty defined previously is sampled to generate a list of possible future scenarios with equal probability of realization. Latin Hypercube Sampling (LHS) with the rank correlation control method proposed by Iman and Conover (1982) are applied.

Model evaluation(s): The economic objective function(s) (see detailed discussion below) is evaluated for each Monte Carlo sample and the results are recorded for statistical analysis below.

Output uncertainty: The results from the model evaluation step are analysed by using a non-parametric distribution function such as a cumulative distribution function (CDF), and frequentist statistics such as mean, variance and percentile analysis of the data.

In *model evaluation* step, optimization problems for each biorefinery concept are formulated and solved by maximizing EBITDA for *techno-economic analysis*. EBITDA is then converted into IRR for *economic risk analysis*. Risk is by definition equal to likelihood of occurrence of an undesired event (probability) multiplied with its consequence (e.g. economic loss). In this study, the economic risk resulting from market price uncertainties is calculated as follows: the summation of the probability of occurrence times the economic loss which is defined as deviation from EBITDA when the %IRR is lower than the targeted economic return. The target return is defined as 10% IRR and this case the deviation from the target is equal to: $EBITDA_{i,(@IRR<10\%)} - EBITDA_{(@IRR=10\%)}$. It is noted that an IRR of 10% is selected as this is considered to be the common target in industry which is also used in the economic performance of renewable energy technologies studied by the National Renewable Energy Laboratory (NREL, Short et al., 1995).

The IRR in this chapter is calculated for *economic risk analysis* of two market uncertainty scenarios namely the effect of long-term/historical fluctuations in product prices versus and the effect of sudden drop in oil prices to the prices of bioethanol and its chemical derivatives. IRR or discounted cash-flow rate of return (DCFROR) forms a measure of the maximum interest rate the project could pay and still break even by the end of project life, where net present value (NPV) is equal to zero (Towler & Sinnott, 2013). IRR is calculated using Equation 9.1-9.2 and fixed product prices (in Eq. 9.2).

$$NPV = 0 = -initial\ investment + \frac{CF_1}{(1+IRR)^1} + \frac{CF_2}{(1+IRR)^2} + \cdots + \frac{CF_{19}}{(1+IRR)^{19}} + \frac{CF_n}{(1+IRR)^n} \tag{9.1}$$

$$Cash\ Flow_{@year\ n}(CF_n) = Market\ price_{product,i}\left(\frac{\$}{ton}\right) * Production\ rate_{product,i}\left(\frac{ton}{year}\right) \tag{9.2}$$

The minimum selling price (MSP) metric is used here for *techno-economic analysis* in particular for detailed cost break-down and comparison among different biorefinery concepts. MSP is an economic indicator used for a critical comparison (Aden et al., 2002). The estimated capital cost and operating cost are used to estimate MSP at fixed IRR (e.g. 10%). MSP is the product price which is generally included in calculation of the discounted cash flow (CF_n) of year (n) (see Eq. 9.3). MSP is calculated by fixing IRR (e.g. 10%) and iterating MSP until NPV is equal to zero (Eq. 9.4). It is important to note that NREL excel worksheet can also be used for MSP estimation (http://www.nrel.gov/extranet/biorefinery/aspen_models).

$$Cash\ Flow_{@year\ n}(CF_n) = MSP_{product,i}\left(\frac{\$}{ton}\right) * Production\ rate_{product,i}\left(\frac{ton}{year}\right) \tag{9.3}$$

$$NPV = 0 = -initial\ investment + \frac{CF_1}{(1+IRR@10\%)^1} + \frac{CF_2}{(1+IRR@10\%)^2} + \cdots + \frac{CF_n}{(1+IRR@10\%)^n} \tag{9.4}$$

The economic assumptions and parameters (i.e. equity loan, depreciation period, cost year, indirect cost estimation) follows the NREL studies presented in their reports (i.e. Aden et al., 2002) which is also summarized here in Table 9.2.

Table 9.2. The economic parameter used for MSP and IRR calculation (NREL)

Equity	40%
Loan Interest	8,0%
Loan Term, years	10
Working Capital (% of FCI)	5,00%
Depreciation Period (Years)	
- General Plant	7
- Steam/Electricity System	20
Construction Period (Years)	3
% Spent in Year -2	8%
% Spent in Year -1	60%
% Spent in Year 0	32%
Start-up Time (Years)	0,25
EtOH production/Feedstock use (% of Normal)	50%
Variable Costs (% of Normal)	75%
Fixed Cost (% of Normal)	100%
Income Tax Rate	35,00%
FTproducts Production Rate (MMgal/yr)	92
Cost Year for Analysis	2007

9.3 Critical comparison of optimal biorefinery concepts

The optimal processing paths for the three main biorefinery concepts resulting from the previous studies (presented in Table 9.1) are compared and discussed in this section.

3.1. Concept 1: Lignocellulosic bioethanol production from corn stover versus wood feedstock.

This section presents the comparison of the MESP of the optimal bioethanol production from corn stover and wood using two conversion concepts (biochemical and thermo-chemical). *Concept 1A* and *1B* use corn stover as feedstock while *Concept 1C* and *1D* use poplar wood. *Concept 1A* and *1C* use hydrolysis and fermentation as biochemical

conversion concept while *Concept 1B* and *1D* use gasification as thermochemical conversion concept.

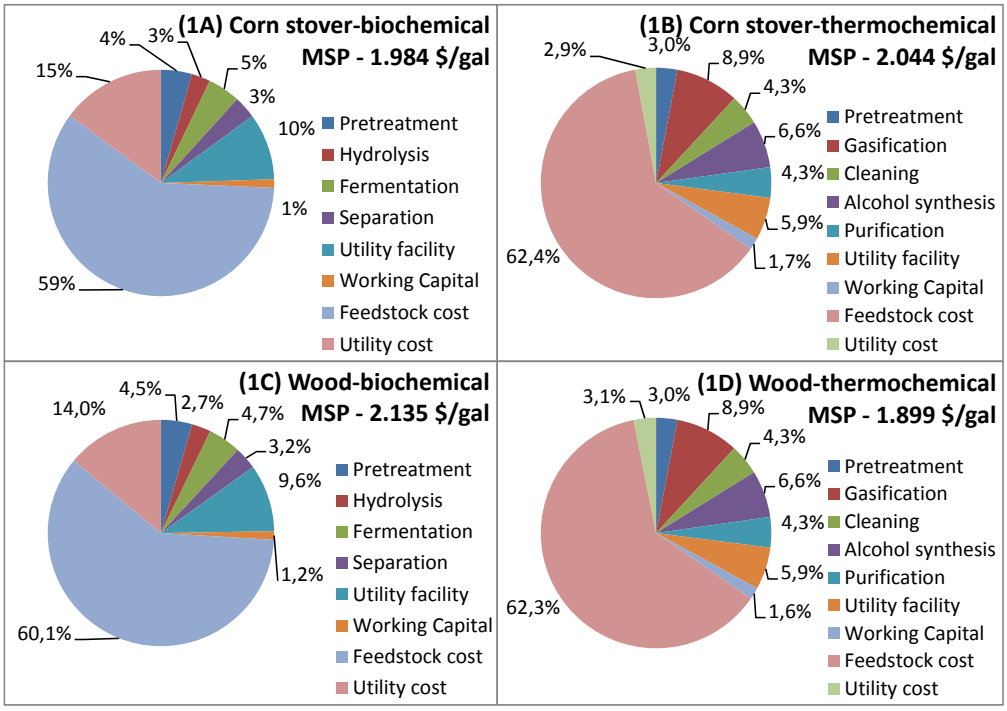

Figure 9.1. Minimum selling prices (MSP) and cost distribution of the four biorefinery concepts producing bioethanol

This comparison shows that the Concept 1D is the most promising one due to its relatively high EBITDA (99.8 MM$/a) and IRR (14%) resulting in the lowest MSP. This favorable result for the combination of woody biomass with thermochemical conversion is due to the higher carbon content of poplar which leads to a higher yield (43 wt%) of syngas (H_2/CO). It is important to note that corn stover, which has lower carbon content, is preferable with the biochemical conversion concept due to its lower lignin content compared to woody biomass, 19 and 27 wt%, respectively.

Moreover, the optimal solutions of biochemical and thermochemical concepts (Concept 1A and 1D) presented in Figure 9.1 show that the thermochemical conversion concept

provides a better techno-economic result compared to the biochemical conversion concept at the capacity of 2000 tpd of dry biomass input. This is due to *(i)* higher bioethanol yield; and *(ii)* a lower operating cost. On the contrary, at a smaller capacity of the biorefinery using the biochemical conversion concept is preferable due to the lower investment that is required. This is confirmed by Figure 9.2 which presents EBITDA and IRR compared among three biomass input capacities (1000, 2000, and 3000 dry ton biomass per day).

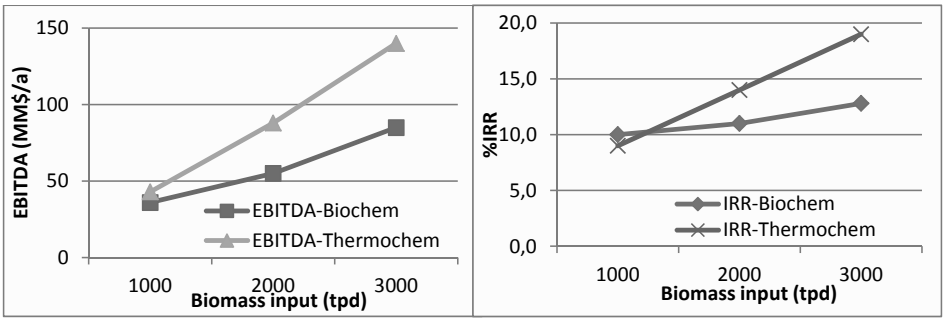

Figure 9.2. The comparison of EBITDA and IRR of biochemical and thermochemical conversion concepts with three biomass input capacities.

At 1000 tpd of biomass input, biochemical conversion concept is more preferable due to a significantly lower investment than the thermochemical concept at a similar bioethanol production. At higher biomass processing capacity, the thermochemical concept produces higher bioethanol resulting in higher EBITDA and IRR due to higher bioethanol production, lower operating cost, and the benefit from economy of scale of investment on scaling up the plant capacity. It is also important to note that the transportation cost of biomass (considered the same in this study) would be higher for plants with higher processing capacity (since a larger area of land availability would be needed to supply the needed biomass). This transportation cost would affect the economics of thermochemical conversion technologies (Akgul et al., 2010).

3.2. Concept-2: Transportation fuels production from wood versus microalgae feedstock

This section presents the comparison of the MSP of optimal transportation fuels production: *(i)* Concept 2A is gasoline and diesel production from poplar wood using gasification and Fischer-Tropsch; and *(ii)* Concept 2B is biodiesel production from microalgae using liquefaction and transesterification. Using liquefaction to produce algal oil from wet algae in a cultivation pond is the state of technology where lipid extraction is not required leading to lower cost of using traditional cultivation, harvesting, drying, and lipid extraction processes. This process pressurizes and condenses water and microalgae and subsequently converts them into a higher yield of biodiesel (Jones et al., 2014).

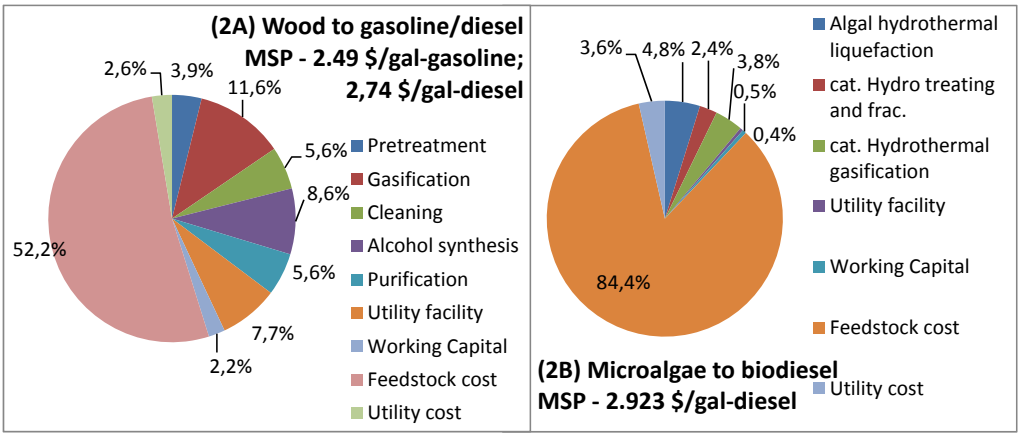

Figure 9.3. Minimum selling prices and cost distribution of two biorefinery concepts producing transportation fuels.

Concept 2A is the more promising concept due to its significantly lower feedstock costs as compared to the microalgae-based biorefinery. However, the *Concept 2B* has a higher EBITDA due to its significantly higher biodiesel yield (51 wt%) in comparison to the thermochemical conversion of wood (28 wt%). This high yield is due to the oil content of 50 wt%. reported by the PNNL study (Jones et al., 2014). It is important to note that oil content reported by PNNL is optimistic compared to other studies (Alabi et al., 2009). The uncertainty of the oil content, a variable which is highly uncertainty (10-50 wt%), has been addressed in earlier studies resulting in a significant impact on biodiesel

production and EBITDA *(Chpater 8)*. Moreover, the impacts of market price uncertainties on the thermochemical conversion concept are lower than for the algal biorefinery due to its higher operational flexibility to adapt to the market changes in gasoline and diesel demand (*Chpater 5*).

3.3. Concept-3: Lignocellulosic bioethanol versus ethanol-based high value-added chemicals production.

This section presents the comparison of the MSP of optimal bioethanol-upgrading processes (Figure 9.4): *(i) concept 3A* is diethyl ether (DEE) production from poplar wood using gasification, alcohol synthesis and catalytic dehydration of ethanol; and *(ii) concept 3B* is 1,3 butadiene (13BD) production from poplar wood using gasification, alcohol synthesis and catalytic conversion of ethanol.

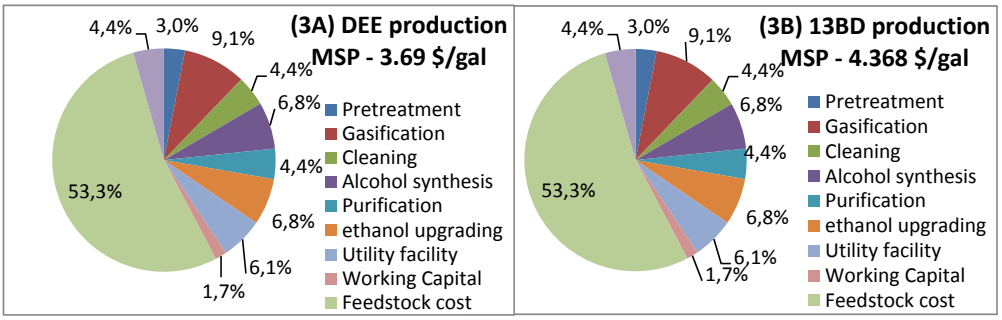

Figure 9.4. Minimum selling prices (MSP) and cost distribution of two biorefinery concepts producing high value-added chemicals.

The overall economic performance of the lignocellulosic bioethanol biorefinery using wood and thermochemical conversion platform (*Concept 1D*) is significantly improved from 99.8 to 247 MM$/a of EBITDA and 14 to 23% of IRR. These improved biorefinery concepts, built based on the lignocellulosic ethanol concepts, aim to *(i)* increase the overall economic performance of the biorefinery; *(ii)* identify more sustainable concepts with environmental and social benefits; and *(iii)* reduce the economic impacts from market price uncertainties which affect the viability of a biorefinery project. Moreover, multi-production of chemicals was found to offer a promising strategy to minimize risks against price fluctuations (*Chapter 6*). In this

context, economic-risk analysis provides a robust support for decision-making as it is discussed in the next section.

9.4 Economic-risks analysis - Impact of market price uncertainties on the optimal biorefinery concepts

A particular challenge when designing biorefinery concepts at the early-stage is uncertainties related to market prices of products as mentioned earlier. Uncertainty analysis is therefore required to provide economic-risk aware decision making. The optimal solutions under two market uncertainty scenarios are analysed: (i) long-term historical trend of fluctuation for product prices in 2011-2013 (EIA, Technon OrbiChem) and (ii) the fluctuation that includes a recent drop in oil prices (EIA, Technon OrbiChem). These analyses result in the comparison of corresponding effects between two market scenarios.

Here, EBITDA and the targeted IRR (10% commonly used in industry for this analysis) are used as economic indicators to support a risk-aware decision making. As mentioned in section 9.2, risks are here calculated as the summation of the probability of occurrence times economic losses (the deviation of EBITDA from the break-even point), $EBITDA_{i,(@IRR<10\%)} - EBITDA_{(@IRR=10\%)}$, as presented in the highlighted area in Figure 9.5.

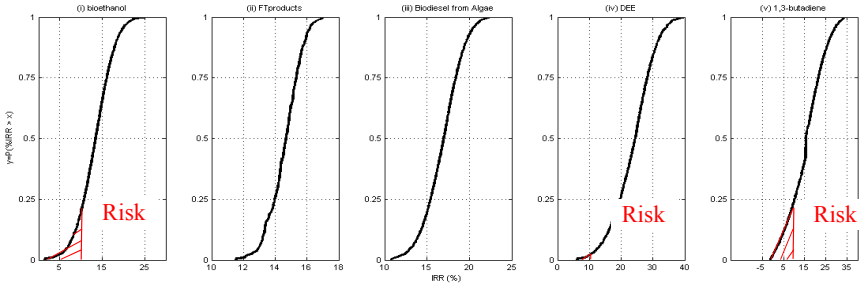

Figure 9.5. Probability distribution of IRR with respect to market prices uncertainty for the production of: (i) bioethanol (*Concept 1D*), (ii) FTgasoline/diesel (*Concept 2A*), (iii) biodiesel from microalgae (*Concept 2B*); (iv) diethyl ether (*Concept 3A*), and (v) 1,3-butadiene (*Concept 3B*).

The results indicate that there is a risk of 22.3, 0, 0, 2.12, and 72.8 MM$/a as highlighted in Figure 9.5, respectively. This shows that the economic impact from market price uncertainty for bioethanol and specialty chemicals is significant while the impact on transportation fuels production is low. To further highlight the effects of uncertainty of the market prices, the sudden oil-prices drop scenario is addressed. Table 9.3 compares the solutions from two market price scenarios: (i) the recent drop of market prices in December-2014 and January-2015; and (ii) long-term historical trend of product prices in 2011-2013.

Table 9.3. Impacts of market price uncertainty for low oil prices scenario in January-2015 with respect to the normal scenarios for 2011-2013 (EIA, Technon OrbiChem)

	Impact from oil prices drop			**Impact from market prices in 2011-2013**		
Bioethanol derivatives	**Spot price Jan-2015 ($/ton)**	**EBITDA (MM$/a)**	**%IRR**	**Average prices ($/ton)**	**EBITDA (MM$/a)**	**%IRR**
Single product						
Diesel (Algae)	1020 ↓	36 ↓	5 ↓	1300	87	17
Ethanol	490 ↓	29 ↓	2 ↓	700	76	11
Diethyl ether	1900 ↓	147 ↓	18 ↓	2270	161	21
1,3-butadiene	870 ↓	18 ↓	-1↓	2010	158	17
Ethyl acetate	920↓	50 ↓	4.5 ↓	1290	98	13
Multiple products						
Gasoline/Diesel	950/1020↓	120↓	12	1100/1300	169	17
DEE/1,3-butadiene	1900/870↓	147↓	18	2270/2010	187	24

Table 9.3 presents a significant economic impact from an oil price drop scenario resulting in much lower EBITDA and IRR. This leads to a significant economic loss at the operational stage. In particular, (i) bioethanol prices which dropped 30% causes the lignocellulosic bioethanol biorefinery unfavorable (IRR 11% to 2%); (ii) biodiesel prices dropped 21% and as a consequence the algal biorefinery idea became unfavorable (IRR 17% to 5%); (iii) chemical prices dropped 16-60% causing the high value-added biochemical biorefinery unfavorable (IRR 17% to -1% for 13BD).

Therefore, good design strategies with respect to pricing, data selection, market analysis against this type of impact should be an integral part of biorefinery concept development since ignoring these uncertainties may lead to outcompeting of the design/concept from the market.

One of the alternatives to reduce potential negative economic impacts, is to systematically diversify the product portfolio and produce multiple products as presented in Table 9.3 where *(i)* the multiple products biorefinery (gasoline/diesel and DEE/13BD) received a minimum impact from the oil prices drop; and *(ii)* EBITDA was improved by 16% by simultaneously producing multiple products (DEE and 1,3-butadiene) for a normal market prices scenario. This concept aims to increase the operational flexibility of a biorefinery in the supply chain (*e.g.* planning and scheduling) to optimize daily demand-supply and to maximize the product sales. This concept also helps to protect against the impacts of prices uncertainties by optimizing the production plan to produce a number of products to maintain higher profitability.

9.5 Conclusions and future perspectives

Biochemical or thermochemical conversion concepts should be selected based on the specific constraints (*e.g.* type of biomass feedstock available, production capacity, conversion technologies, and type of desired products). The biochemical conversion concept is preferable for biomass containing a small amount of lignin and with as relatively low production capacity (<2000 tpd), while, the thermochemical conversion concept is preferable for biomass with a high amount of carbon and a large production capacity. Biogasoline and biodiesel produced by the thermochemical conversion

concept with wood feedstock is economically competitive with low risks. The economic feasibility of algal biorefinery (e.g. using liquefaction and transesterification for biodiesel production) depends on high oil content assumption of algal biomass composition (e.g. 50%wt oil). Therefore, it is important to note that the economic viability of the algal biorefinery is critically dependent on the oil content in the algae feedstock as well as requires a huge cost of algal feedstock and capital investment compared to the other concepts analysed. Moreover, the production of high value-added chemicals via lignocellulosic ethanol, in particular diethyl ether, is the most promising concept for the biorefinery (EBITDA of 247 MM$/a, 23.5 %IRR and 3.7 $/gal of minimum selling price).

The sudden drop in oil prices lead to significant drops biofules and bioproduct prices which in turn severely and negatively affected economic profitability of biorefinery concept for biofuels and biochemicals production. One can be protected from this type of economic impact due to market uncertainities by either *(a)* upgrading the lignocellulosic bioethanol to high value-added chemicals; and/or *(b)* diversifying product portfolio to manufacture multiple products. In particular, the production of bioethanol-upgraded and multiple products (DEE and 13BD) is a concept is found promising to weather the negative impacts of significant reduction in oil prices. In this way, EBITDA and IRR are improved from 169 to 187 MM$/a and 17 to 24%, respectively.

With this economic risk analysis and comparison, the bioethanol-upgrading and multi-products concepts are recommended as a strategy that can provide robustness and resilience against unknown market disturbances in particular sustained low levels of oil price. For proper guidance on designing future competitive biorefineries, it is recommended that comprehensive economic risk analysis is performed.

10.
CONCLUSIONS AND FUTURE PERSPECTIVES

The overall conclusion and achievements of the research project are presented in this chapter, and some future perspectives are highlighted as well.

10.1 Summary of the outcomes and achievements

In this PhD project, the problem of computer-aided synthesis and design of biorefinery concepts is presented. To this end, the systematic framework developed earlier which uses a superstructure-based optimization approach has been adapted and further extended. A systematic approach is used to manage the complexity and solving simultaneously both the business and the engineering dimension of the problem. This allows generation and comparison of a large number of alternatives at their optimal point. The result is the identification of the optimal raw material, multi-product portfolio and process technology selection for a given market scenario, combined with the relevant sustainability metrics of the most promising alternative and the risk of investment under market uncertainties enabling risk-aware decision making. Several case studies of biorefinery networks focusing on production of bioethanol, biofuels, and high value-added chemicals have been used to highlight the application of the framework developed above, and including the case study of the algal biorefinery.

In particular, the studies and results presented in this thesis fulfill the objectives as defined and presented as follows.

(i) The development of an extended superstructure and database for thermochemical conversion and bioethanol-upgrading concepts was accomplished. This extended superstructure was combined with a biochemical conversion route developed earlier, generating an even larger design space. The intensive data requirement of the extended biorefinery network design problem was addressed by using a structured and generic model to represent process alternatives. The structured and generic approach is important to manage and check the quality and consistency of multi-dimensional data. The biorefinery database also features the characterization of important sources of uncertainties in data.

(ii) A systematic framework consisting of a superstructure optimization based approach under uncertainty was further developed and extended. The uncertainty characterization step in the systematic framework was extended to support the different types of data available (i.e. historical data from existing plants, an

expert judgment). The comparison results showed that the selection of the early stage cost estimation method is critical. Moreover, the cost analysis cannot be based on a deterministic approach but should be evaluated by means of a probabilistic approach in which uncertainties are accounted for. These analyses provide useful information supporting the future development of biorefineries.

(iii) A sustainability assessment method was also integrated with the systematic framework to broaden the analysis and the features of the framework from only techno-economic to multi-criteria (sustainability) evaluation, as well as including the direct comparison between bio-based processes and fossil-based processes. These analyses provide useful information regarding economic and sustainability drivers for the future development of a biorefinery.

(iv) Biorefinery concepts should be selected based on the specific constraints (*e.g.* type of biomass feedstock available, production capacity, conversion technologies, and type of desired products). The biochemical conversion concept is preferable for biomass with a small amount of lignin and for a small production capacity (<2000 tpd), while, the thermochemical conversion concept is preferable for biomass with high lignin content and for a large production capacity. Biogasoline and biodiesel produced by the thermochemical conversion concept using wood as feedstock is found to be economically competitive as well as having a lower economic risk. An algal biorefinery using liquefaction and transesterification is also found favourable at a high oil content (50% wt) assumption. It is important to note that the viability of the algal biorefinery is critically dependent on the oil content in the algae feedstock. It is noted that the algal biorefinery is very costly due to the algal feedstock cost, and therefore is capital intensive. Moreover, the production of high value-added chemicals via lignocellulosic ethanol, in particular diethyl ether is the most promising biorefinery concept (EBITDA of 247 MM$/a, 23.5 % IRR and 3.7 $/gal of minimum selling price).

(v) Economic risk analysis due to market price uncertainties shows that *(i)* upgrading lignocellulosic bioethanol to high value-added chemicals; and *(ii)* multiple-products production, in particular, the production of bioethanol-upgraded and multiple products (DEE and 13BD) are the most promising

concepts which can survive better against the negative impacts of a significant drop in oil prices. They are therefore recommended, which provides robustness and resilience against unknown disturbance from the market. All in all it is recommended that a comprehensive economic risk analysis becomes an integral part of future biorefinery concept development for proper guidance on designing future competitive biorefineries. This is valuable for assessing the risk associated with biorefinery design as well as for supporting risk-based decision making during early project planning/development stages.

Overall, the PhD project results in a framework implemented as a decision-making toolbox for synthesis and design of biorefineries at the early-stage of product-process development to serve as enabling technology for facilitating the innovation cycle in biorefineries and support development of renewable carbon-based technologies and industries.

10.2 Future perspectives

This PhD project has presented many contributions to support the development of biorefinery concepts. However, a number of issues presented below could still benefit substantially from further development.

(i) The optimal solutions are limited by the limited number of alternatives. Therefore, the design space should be further extended to identify or benchmark new solutions.

(ii) A large problem (more than 1 million variables and equations) creates difficulties to be solved using GAMS: (i) one challenge is related to initializing the large amount of data and models; and (ii) a second challenge is the slow execution. Moreover, the additional domain (uncertainty analysis), or the additional alternatives result in a significant higher number of variables and equations. Proper solution strategies are required to overcome this challenge by systematically reducing the size of the problem i.e. the number of alternatives, number of samples or number of constraints.

The resulting ranking of optimal solutions can also be used to systematically generate a smaller superstructure used for further designs and development.

(iii) The use of the generic process model block with the collected and estimated parameters allows managing a large complex problem. However, this limits the flexibility of the technology to only specific data and conditions (e.g. capacity, operating conditions, and efficiency). This limitation can be overcome by performing uncertainty analysis on the technical process parameters, but rigorous simulations are still required in the next design stages to further verify and optimize the design concept.

(iv) The data collection and verification is a very time-consuming step regarding the limited availability of existing technologies and data. Moreover, the estimation or the unavailability of data leads to significant uncertainties. Therefore, the data collection, estimation and verification should be further developed in more systematic way. An integration with the other methods and tools (i.e. computer-aided molecular/flowsheet design, CAMD, CAFD) is required to systematically generate or estimate the possible design networks consisting of a flowsheet with processing technologies and the relevant process parameters. In this way, one could overcome this issue and broaden the development in process synthesis and design of processing networks.

(v) In this study the biorefinery concepts were compared at their optimality. However, the optimization formulation can be extended to include heat/mass integration and supply-chain network analysis. Integration with the other methods and tools to generate additional model libraries would further broaden the design analysis of the process synthesis and design problem resulting in more robust solutions.

(vi) The database and model libraries, which are created manually, are not fully user-friendly and human errors can occur easily. A software implementation using a friendly graphical user interface (GUI) would facilitate the dissemination of this tool and the methods. The software implementation can be done by considering the following workflow: (i) drawing the processing network to define a superstructure, (ii) input the collected data (or estimated

data by integration tools) for each alternative, and (iii) verify the data. Consequently, the objective functions, design criteria and model libraries are selected to generate the optimization formulations which will be used and solved further in GAMS.

APPENDICES

Abbreviations, process description, model libraries and the remaining results are presented in the appendices.

Appendix A. – Nomenclature

Indexes

i,j	Components
n	Main products
k	Process Interval (origin)
kk	Process Interval (destination)
react	Key reactant
rr	Reaction
ss	Samplings
P	Product
RM	Raw material
bio	Bio-based processes
petro	Petro-based processes

Parameters

MW_i	Molecular weight
$P1_{kk}^{RM\ costs}$	Raw material costs
$P2_{i,kk}$	Utility Prices
$P3_{i,kk}$	Product prices
$SW_{i,kk}$	Waste fractions
$S_{k,kk}$	Superstructure: consisting of primary and secondary outlets (binary)
$S_{k,kk}^{p}$	Superstructure: primary outlet (binary)
a_{kk}	Investment and capacity ratio for capital cost estimation
n_{kk}	Exponent coefficient for capital cost estimation
$\alpha_{i,kk}$	Specific utility consumption
$\gamma_{i,kk,rr}$	Reaction stoichiometry

$Split_{i,kk}$	Split factors
$\theta_{react,kk,rr}$	Conversion of key reactant
$\mu_{i,kk}$	Fraction of utility mixed with process stream
t	Time (year)
N_s	Number of samples
N	Total years of the investment
C_i^{RM}	Raw material cost
C_i^p	Product price
CED_i^{RM}	Cumulative energy demand (MJ/kg) from processing raw material
GHG_i^{RM}	Greenhouse gas production (kg $CO_{2\ eq}$/kg) from processing raw material
ΔH_{Rxn}^0	Heat of reaction
$I_{i,j}^{ECat,HCat,SCat}$	Index value of the specific component emitted in the category of environmental, health, and safety hazards
$\phi_{i,kk}$	Feed composition of feedstock kk

Variables

$F_{i,k,kk}$	Component i flow from process intervals k to process intervals kk
$F_{i,kk}^M$	Component flow after mixing
$R_{i,kk}$	Utility flow
$F_{i,kk}^R$	Component flow after reaction
$F_{i,kk}^{out}$	Component flow after waste separation
$waste_{i,kk}$	Component flow of waste stream after waste separation
$F_{i,kk}^{out1}$	Component flow leaving process interval kk through primary outlet
$F_{i,kk}^{out2}$	Component flow leaving process interval *kk* through secondary outlet
y_{kk}	Selection of process intervals (binary variable)

$w_{j,kk}$	Selection of a piece of the piecewise linearization (linear)
m_i^{RM}	Raw material mass flow rate
m_i^p	Product mass flow rate
CF_n	Cash flow in year n
c_n	Molar concentration of main product
N_{cp}	Number of co-products
MLI	Mass loss index (ratio of total mass of undesired products to total mass of main and co-products)
ΔT_{bp}	The smallest absolute difference between the boiling point of the main product and the others
TS	Total score for sustainability assessment
IR	Index ratio for sustainability assessment

Abbreviations

GAMS	Generic algebraic modeling system
EVPI	Expected value of perfect information
VSS	Value of stochastic solution
UP	Uncertainty price
NPV	Net present value
CAPEX	Capital Investment
OPEX	Operating cost
$EBITDA$	Earnings Before Interest, Taxes, Depreciation and Amortization
IRR	Internal rate of return
MSP	Minimum selling price
EC	Economic constraint
EIRM	Environmental impact of raw material
CED	Cumulative energy demand

GHG	Greenhouse gas emission
AF	Allocation factor
PCEI	Process cost and environmental impact
EHSI	Environmental-Health-Safety index
EH	Environmental hazard
HH	Health hazard
SH	Safety hazard
RA	Risk aspect
GFA	Global feedstock availability
LFP	Local feedstock potential
MS	Market size
CCI	Current infrastructure
IB	Inherent benefits
TS	Total score
SAA	Sample average approximation
IR	Index ratio
UB	Upper bound of the objective function
LB	Lower bound of the objective function
GUI	Graphical user interface

Appendix B. – the description of processing alternatives

Table B.1 The description of process intervals presented in Figure 6.1

FEEDSTOCK			
1	Corn stover, 2000 tpd	3	Gasoline, 400 tpd
2	Poplar wood, 2000 tpd		
THERMOCHEMICAL CONVERSION PLATFORM			
	Processing Techniques	13	Scrubber, acid removal, SMR and WGS
4	Size reduction, dryer (steam, indirect contact)	14	Tar reformer, scrubber, acid removal
5	Size reduction , dryer (flue gas, direct contact)	15	Tar reformer, scrubber, DEPG
6	Entrained flow gasifier with size reduction	16	Fisher-Tropsch with special H2S removal
7	Bubbling fluidized bed gasifier	17	Alcohol synthesis (metal-sulfide catalyst)
8	Indirectly-heated with circulating gasifier	18	Alcohol synthesis (MoS_2 catalyst)
9	Directly-heated with bubbling gasifier	19	Hydroprocessing (H2-production)
10	Pyrolysis (bubbling fluidized bed)	20	Hydroprocessing (H2-purchasing)
11	Fast Pyrolysis (fluidized bed)	21	Decanter with hydroprocessing unit
12	Scrubber, sour WGS reactor, acid removal	22	Molecular sieve , two distillation columns
BIOCHEMICAL CONVERSION PLATFORM			
	Processing Techniques	53	Molecular sieve
23	Size reduction by 60% water	54	Anhydrous ethanol
24	Size reduction by 54% water	55	Fermentation feed handling
25	Ammonia fiber explosion	56	Seed production
26	Pretreatment dilute acid	57	Seed production bypass
27	Controlled pH pretreatment	58	Succinic acid fermentation by E-coli
28	Aqueous ammonia recycle pretreatment	59	Filtration
29	Lime pretreatment	60	Evaporation
30	Dilute acid hydrolysis	61	Crystallization

31	Concentrate acid hydrolysis	62	Water splitting electro dialysis
32	NREL enzyme hydrolysis	63	Electro dialysis
33	Spyzyme hydrolysis from AFEX	64	Crystallization
34	Spyzyme hydrolysis from dilute acid	65	Reactive distillation
35	Spyzyme hydrolysis from controlled pH	66	Vacuum distillation
36	Spyzyme hydrolysis from APR	67	Crystallization
37	Spyzyme hydrolysis from lime	68	Succinic acid storage
38	Hydrolysis bypass	69	Fermentation feed handling
39	Sugar division	70	Seed production
40	Fermentation feed handling	71	Seed production bypass
41	Seed production	72	Butanol fermentation
42	Seed production bypass	73	Gas stripping
43	Ethanol fermentation	74	Adsorption
44	Flash	75	Solvent extraction by oleyl alcohol
45	Distillation column	76	Pervaporation
46	Solvent-based extraction by ethylene glycol	77	Membrane separation
47	Solvent-based extraction by ethylene glycerol	78	Distillation for butanol
48	Extraction with ionic liquid - EMIMBF4	79	Distillation for acetone
49	Extraction with ionic liquid - EMIMCl	80	Distillation for ethanol
50	Extraction with ionic liquid - EMIM+EtSO4	81	Total ethanol production
51	Extraction with ionic liquid - EMIM+DMP	82	Butanol storage
52	Membrane separation		
ETHANOL DERIVATIVES CONVERSION			
83	Dehydration	89	Hihgh temperature reforming
84	Oxidation	90	Metathesis

85	Vapor-phase dehydration	91	Fermentation
86	Fermentation	92	Fermentation
87	Fischer esterification	93	Oxidation
88	Fermentation	94	Catalytic dehydrogenation
PRODUCTS and BY-PRODUCTS			
95	FT-gasoline	109	Acetone
96	FT-diesel	110	Ethylene oxide
97	Higher alcohols (C_3-ol, C_4-ol, C_5-ol)	111	1,3-butadiene
98	Hot flue gas from gasifier combustor	112	Ethanol (100%)
99	Hot flue gas from tar reformer combustor	113	Acetone
100	Ethylene	114	Butanol (100%)
101	Acetaldehyde	115	Gasoline (100%)
102	Diethyl ether	116	E5 (Ethanol-gasoline blend)
103	n-Butanol	117	E10 (Ethanol-gasoline blend)
104	Ethylacetate	118	B5 (butanol-gasoline blend)
105	Acetic acid	119	B10 (butanol-gasoline blend)
106	Hydrogen	120	Succinic acid
107	Propylene	121	Electricity
108	Iso-Butylene	122	Lignin pellet

Appendix C. – The optimization formulation for the deterministic and stochastic problems

Deterministic problem

The objective functions,

Economic analysis:

$$\max. EBITDA = \sum_{i,kk}\left(P3_{i,kk} \cdot F_{i,kk}^{out}\right) - \sum_{kk} OPEX - \frac{CAPEX_1 + CAPEX_2}{t}; i \equiv ethanol\ derivatives; \quad (C.1)$$

Sustainability analysis:

$$\min. \quad = \frac{TS_{biobased}}{TS_{petrochemical}} = \frac{0.44EC_{bio} + 0.28EIRM_{bio} + 0.28PCEI_{bio}}{0.44EC_{petro} + 0.28EIRM_{petro} + 0.28PCEI_{petro}} \quad (C.2)$$

Subject to the following constraints:

i) process models: material balances of the generic block

Raw materials,

$$F_{i,kk}^{out} = \phi_{i,kk} \quad (C.3)$$

Mixing-1: main equation,

$$F_{i,kk}^{M} = \sum_k\left(F_{i,k,kk}\right) + \alpha_{i,kk} \cdot R_{i,kk} \quad (C.4)$$

Mixing-2: chemicals or utilities used,

$$R_{i,kk} = \mu_{i,kk} \cdot \sum_{i,k}\left(F_{i,k,kk}\right) \quad (C.5)$$

Reaction,

$$F_{i,kk}^{R} = F_{i,kk}^{M} + MW_i * \sum_{rr}(\gamma_{i,rr} * \theta_{react,rr} * F_{i,kk}^{M}/MW_{react}) \quad (C.6)$$

Waste separation,

$$F_{i,kk}^{out} = F_{i,kk}^{R} \cdot \left(1 - SW_{i,kk}\right) \quad (C.7)$$

$$F_{i,kk}^{WASTE} = F_{i,kk}^{R} - F_{i,kk}^{out} \quad (C.8)$$

Product separation,

$$F_{i,kk}^{out1} = F_{i,kk}^{out} \cdot Split_{i,kk} \quad (C.9)$$

$$F_{i,kk}^{out2} = F_{i,kk}^{out} \cdot (1 - Split_{i,kk}) \quad (C.10)$$

ii) process constraints: rules defining superstructure together with the flow constraints,

$$F_{i,k,kk}^{1} \leq F_{i,kk}^{out1} \cdot S_p \quad (C.11)$$

$$F_{i,k,kk}^{2} \leq F_{i,kk}^{out2} \cdot \left(S - S_p\right) \quad (C.12)$$

$$F_{i,kk}^{in} = \sum_k \left(F_{i,k,kk}^{1} + F_{i,k,kk}^{2}\right) \quad \text{(C.13)}$$

$$\sum_k F_{i,k,kk}^{1} = F_{i,kk}^{out1} \quad \text{(C.14)}$$

$$\sum_k F_{i,k,kk}^{2} = F_{i,kk}^{out2} \quad \text{(C.15)}$$

$$\sum_i F_{i,kk}^{out} \leq F_{kk}^{MAX} \quad \text{(C.16)}$$

iii) structural constraints: to define the extended superstructure

Raw materials,

$$y_1 + y_2 + y_3 \leq 1 \quad \text{(C.17)}$$

Processing step 1: pretreatment (thermochemical) together with a size reduction step (biochemical),

$$y_4 + y_5 + y_{23} + y_{24} \leq 1 \quad \text{(C.18)}$$

Processing step 2: primary conversion (thermochemical) together with pretreatment (biochemical),

$$y_6 + y_7 + y_8 + y_9 + y_{10} + y_{11} + y_{25} + y_{26} + y_{27} + y_{28} + y_{29} \leq 1 \quad \text{(C.19)}$$

Processing step 3: gas cleaning and conditioning (thermochemical) together with hydrolysis (biochemical),

$$y_{12} + y_{13} + y_{14} + y_{15} + y_{30} + y_{31} + y_{32} + y_{33} + y_{34} + y_{35} + y_{36} + y_{37} + y_{38} \leq 1 \quad \text{(C.20)}$$

Processing step 4: product synthesis (thermochemical) together with fermentation (biochemical),

$$y_{16} + y_{17} + y_{18} + y_{19} + y_{20} + y_{40} + y_{69} + y_{55} \leq 1 \quad \text{(C.21)}$$

Processing step-5: product separation and purification,

$$y_{21} + y_{22} \leq 1 \quad \text{(C.22)}$$

Processing step: separation (biochemical),

$$y_{46} + y_{47} + y_{48} + y_{49} + y_{50} + y_{51} + y_{52} + y_{53} \leq 1 \quad \text{(C.23)}$$

$$y_{73} + y_{74} + y_{75} + y_{76} + y_{77} \leq 1 \quad \text{(C.24)}$$

$$y_{59} + y_{62} + y_{65} \leq 1 \quad \text{(C.25)}$$

Processing step: bioethanol-upgrading process,

$$y_{83} + y_{84} + y_{85} + y_{86} + y_{87} + y_{88} + y_{89} + y_{90} + y_{91} + y_{92} + y_{93} + y_{94} \leq 1 \quad \text{(C.26)}$$

iv) cost models

Operating cost,

$$OPEX_{kk} = P1_{kk}^{RM\ costs} + (P2_{i,kk}^{utilities/chemicals/catalysts} \cdot R_{i,kk}) + (P4_{i,kk}^{waste} \cdot F_{i,kk}^{waste}) \quad \text{(C.27)}$$

Capital cost: *i*) data collected and *ii*) piecewise linearization,

$$CAPEX_1 = \sum_{kk} capex_{kk} \quad \text{(C.28)}$$
$$CAPEX_2 = \sum_{kk}\left[\sum_j\left(\alpha_{j,kk} \cdot w_{j,kk} + \beta_{j,kk} \cdot Q_{j,kk}\right)\right] \quad \text{(C.29)}$$
$$F_{kk}^{M} = \sum_j Q_{j,kk} \quad \text{(C.30)}$$
$$Q_{j,kk}^{o} \cdot w_{j,kk} \le Q_{j,kk} \le Q_{(j+1),kk}^{o} \cdot w_{j,kk} \quad \text{(C.31)}$$
$$\sum_j w_{j,kk} = 1 \quad \text{(C.32)}$$

v) optimization constraints: big-M formulation,

$$F_{i,kk}^{out} \le M \cdot y_{kk} \quad \text{(C.33)}$$
$$R_{i,kk} \le M \cdot y_{kk} \quad \text{(C.34)}$$
$$y_{kk} \le M \cdot \sum_i F_{i,kk}^{out} \quad \text{(C.35)}$$
$$\sum_i F_{i,kk}^{in} \le M \cdot y_{kk} \quad \text{(C.36)}$$

vi) sustainability assessment index constraints,

Economic constraint (EC),

$$EC = \sum_{i,kk}^{RM} \phi_{i,kk} P1_{kk}^{RM\ costs} / \sum_{j,kk}^{p} F_{i,kk}^{out} P3_{kk}^{Product\ prices} \quad \text{(C.37)}$$

Environmental impact of raw material (EIRM),

$$EIRM = (0.5AF_{kk}/F_{i,kk}^{product}) \sum_{i,kk}^{RM} \phi_{i,kk} CED_{i,kk}^{RM} + (0.5AF_{kk}/F_{i,kk}^{product}) \sum_{i,kk}^{RM} \phi_{i,kk} GHG_{i,kk}^{RM} \quad \text{(C.38)}$$
$$AF_{kk} = F_{i,kk}^{main-product} P3_{kk}^{main-product\ prices} / \sum_j^p F_{i,kk}^{by-product} P3_{kk}^{by-product\ prices} \quad \text{(C.39)}$$

Process cost and environmental impact (PCEI),

$$PCEI = \left(\frac{1}{no.of\ sub-PCEI}\right) \sum_i^{PCEI} PCEI_i \quad \text{(C.40)}$$
$$PCEI_1 = 0, if\ no\ water; 0.5, if\ water\ is\ presented; 1, if\ water\ must\ be\ separated. \quad \text{(C.41)}$$
$$PCEI_2 = 1 - (0.5log_5(100C_n)) \quad \text{(C.42)}$$
$$PCEI_3 = 1 - (0.5log_2(\Delta T_{bp}/5)) \quad \text{(C.43)}$$
$$PCEI_4 = 0.5(log_{10} MLI + 1) \quad \text{(C.44)}$$
$$PCEI_5 = \frac{|\Delta H_{rxn}^0| - 100}{200}, if\ \Delta H_{rxn}^0 \ge 0\ or\ , if\ \Delta H_{rxn}^0 < 0\ and\ T_R < 200℃ \quad \text{(C.45)}$$
$$PCEI_5 = \frac{100 - |\Delta H_{rxn}^0|}{200}, if\ \Delta H_{rxn}^0 < 0\ or\ , if\ \Delta H_{rxn}^0 < 0\ and\ T_R > 200℃ \quad \text{(C.46)}$$
$$PCEI_6 = -0.015N_{cp}^2 + 0.28N_{cp} - 0.25 \quad \text{(C.47)}$$
$$PCEI_7 = 0, feedstock\ is\ not\ required; 1\ feedstock\ is\ required \quad \text{(C.48)}$$

Total score (TS)

$$TS = 0.44EC + 0.28EIRM + 0.28PCEI \quad \text{(C.49)}$$

Total index ratio

$$Total\ index\ ratio = \frac{TS_{biobased}}{TS_{petrochemical}} = \frac{0.44EC_{bio} + 0.28EIRM_{bio} + 0.28PCEI_{bio}}{0.44EC_{petro} + 0.28EIRM_{petro} + 0.28PCEI_{petro}} \quad \text{(C.50)}$$

***Stochastic problem**:* price parameters were reformulated consisting of uncertainty domain (θ)

Economic analysis:

$$\text{max. } EBITDA = \sum_{i,kk}\left(P3_{i,kk,\theta} \cdot F_{i,kk}^{out}\right) - \sum_{kk} OPEX - \frac{CAPEX_1 + CAPEX_2}{t}; i \equiv ethanol\ derivatives; \quad \text{(C.51)}$$

Sustainability analysis:

$$\text{min. } = \frac{TS_{biobased}}{TS_{petrochemical}} = \frac{0.44EC_{bio} + 0.28EIRM_{bio} + 0.28PCEI_{bio}}{0.44EC_{petro} + 0.28EIRM_{petro} + 0.28PCEI_{petro}} \quad \text{(C.52)}$$

$$EC = \sum_{i,kk}^{RM} \phi_{i,kk} P1_{kk}^{RM\ costs} / \sum_{j,kk}^{p} F_{i,kk}^{out} P3_{kk,\theta}^{Product\ prices} \quad \text{(C.53)}$$

$$TS_{bio} = 0.44EC_{bio} + 0.28EIRM_{bio} + 0.28PCEI_{bio} \quad \text{(C.54)}$$

***Optimal flexible network problem**:* all the process variables ($F_{i,kk}$) and decision variables (y_{kk}) were reformulated integrating the uncertainty domain (θ). The following equations are some examples of the reformulation.

$$F_{i,kk,\theta}^{out} \leq M \cdot y_{kk,\theta} \quad \text{(C.55)}$$

$$\sum_i F_{i,kk,\theta}^{in} \leq M \cdot y_{kk,\theta} \quad \text{(C.56)}$$

Raw materials,

$$y_{1,\theta} + y_{2,\theta} + y_{3,\theta} \leq 1 \quad \text{(C.57)}$$

Objective function - Part 1:

$$\text{max. } EBITDA = \sum_{i,kk}\left(P3_{i,kk,\theta} \cdot F_{i,kk,\theta}^{out}\right) - \sum_{kk} OPEX - \frac{CAPEX_1 + CAPEX_2}{t}; i \equiv ethanol\ derivatives; \quad \text{(C.58)}$$

Objective function - Part 2:

$$\text{min. } = \frac{TS_{biobased}}{TS_{petrochemical}} = \frac{0.44EC_{bio} + 0.28EIRM_{bio} + 0.28PCEI_{bio}}{0.44EC_{petro} + 0.28EIRM_{petro} + 0.28PCEI_{petro}} \quad \text{(C.59)}$$

$$EC = \sum_{i,kk}^{RM} \phi_{i,kk,\theta} P1_{kk}^{RM\ costs} / \sum_{j,kk}^{p} F_{i,kk,\theta}^{out} P3_{kk,\theta}^{Product\ prices} \quad \text{(C.60)}$$

Optimization constraints,

$$F_{i,kk,\theta}^{out} \leq M \cdot y_{kk,\theta} \quad \text{(C.61)}$$

$$\sum_i F_{i,kk,\theta}^{in} \leq M \cdot y_{kk,\theta} \quad \text{(C.62)}$$

Process constraints: raw materials,

$$y_{1,\theta} + y_{2,\theta} + y_{3,\theta} \leq 1 \quad \text{(C.63)}$$

Appendix D. – The additional input uncertainties and results regarding under-estimate of cost estimation (as presented in *Chapter 7*)

Table D.1 Input uncertainties for early stage cost estimation of ethanol-derivatives (expert judgement for under-estimates: -20% to -50%)

Model	Parameter	R1: ethylene			R2: acetaldehyde			R3: diethyl ether			R4: n-butanol			R5: ethylacetate			R6: acetic acid		
		mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
1	a	6.3	3.15	5.04	0.62	0.31	0.5	0.3	0.15	0.24	-			18.85	9.43	15.08	4.8	2.4	3.84
2,3,4	Uncertainty factor	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8
Model	**parameter**	**R7: hydrogen**			**R8: propylene**			**R9: isobutylene**			**R10: acetone**			**R11: ethylene oxide**			**R12: 1,3-butadiene**		
		mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
1	a	0.87	0.44	0.7	7.1	3.55	5.68	0.05	0.03	0.04	-			5.6	2.8	4.48	1.85	0.93	1.48
2,3,4	Uncertainty factor	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8	1	0.5	0.8

Table D.2. The comparison of early stage cost estimation for ethanol-derivatives production (expert judgement for under-estimates: -20% to -50%)

	Products	Model 1		Model 2		Model 3		Model 4	
		(MM$)	std.	(MM$)	std.	(MM$)	std.	(MM$)	std.
Capital cost estimation	Ethylene	237	35	54	7	165	22	60	8
	Acetaldehyde	27	4	73	10	224	30	93	12
	Diethyl ether	13	2	66	9	567	79	79	11
	Butanol	(butanol is converted directly from biomass)							
	Ethylacetate	858	134	73	10	365	49	93	12
	Acetic acid	200	34	90	12	-6	1	126	17
	Hydrogen	32	5	33	5	168	22	29	4
	Propylene	261	40	56	7	340	45	62	8
	Butylene	2	0	48	7	8	1	50	7
	Acetone	(acetone is converted directly from biomass)							
	Ethylene oxide	203	33	74	10	345	46	95	13
	1,3-butadiene	58	9	48	7	498	67	50	7

Table D.3. Top-five ranking of the optimal solutions using *Model 1-4* for capital cost estimation and expert scenario for under-estimates (-20% to -50%)

Model 1						
Rank no.	**Process intervals selection**	**EBITDA (MM$/a)**	**Products**	**Produc-tion (tpd)**	**TAC (MM $/a)**	**Capex (MM $/a)**
1	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	247	Diethyl ether	345	82.9	22.64
2	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	242	1,3-butadiene	292	85.8	24.89
3	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
4	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylene oxide production**	138	Ethylene oxide	544	127	30.16
5	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethanol production**	133	Ethanol	590	81.3	22
Model 2						
Rank no.	**Process intervals selection**	**(EBITDA (MM$/a)**	**Products**	**Produc-tion (tpd)**	**TAC (MM $/a)**	**Capex (MM $/a)**
1	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	246	Diethyl ether	345	82.9	24.6
2	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	241	1,3-butadiene	292	85.8	23.7

3	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
4	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylene oxide production**	136	Ethylene oxide	544	127	25
5	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethanol production**	133	Ethanol	590	81.3	22
Model 3						
Rank no.	**Process intervals selection**	**(EBITDA (MM$/a)**	**Products**	**Production (tpd)**	**TAC (MM $/a)**	**Capex (MM $/a)**
1	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	220	Diethyl ether	345	108	49.6
2	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	219	1,3-butadiene	292	102	46
3	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
4	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylacetate production**	154	Ethylacetate	371	101	40
5	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethanol production**	133	Ethanol	590	81.3	22
Model 4						

Rank no.	Process intervals selection	(EBITDA (MM$/a)	Products	Production (tpd)	TAC (MM $/a)	Capex (MM $/a)
1	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **diethyl ether production**	245	Diethyl ether	345	86.4	25.3
2	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **1,3-butadiene production**	244	1,3-butadiene	292	87.5	23.8
3	Wood, ammonia explosion, Spyzyme enzyme hydrolysis from AFEX, Butanol production by *Clostridium beijirickii* Gas stripping by CO_2 and H_2, distillation, **butanol production**	180	Butanol	118	75	15
4	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **ethylacetate production**	167	Ethylacetate	371	87.8	26
5	Wood, Entrained-flow gasifier, steam reforming, scrubber, acid gas removal using amine, alcohol synthesis, mol. sieve, distillation, **Ethylene oxide production**	142	Ethylene oxide	544	122	26

Table D.4. Uncertainty mapping and analysis: frequency of selection with respect to 200 input uncertainty scenarios

Model	Range of expert judgement	Operating profit (MM$/a)		Annualized capital cost (MM$/a)		Frequency of selection	
		(MM$)	std.	(MM$)	std.	Diethyl ether production	1,3 butadiene production
1	-20% to -50%	247.6	0.1	21.9	0.1	200/200	-
2		246.9	0.2	24.6	0.44	200/200	-
3		226.9	3.9	47.2	3.5	56/200	144/200
4		243.6	0.62	25.3	0.53	200/200	-

Table D.5. Risk analysis of the production of diethyl ether and 1,3-butadiene

Model	Diethyl ether production			1,3 butadiene production		
	Referenced estimation (%)	Estimated IRR (%)	Quantified risk (MM$/a)	Referenced estimation (%)	Estimated IRR (%)	Quantified risk (MM$/a)
1	26.2	31 ± 4.9	0.31	22.7	23 ± 0.5	2.78
2	24.2	23.6 ± 0.89	0.7	25.2	23.9 ± 0.4	4
3	8.9	8.7 ± 1.3	1.14	8	9.5 ± 1.26	1.6
4	20.1	17.6 ± 0.89	2.84	23.6	23.8 ± 0.4	4.3

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