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Process design, supply chain, economic and environmental analysis for chemical production in a glycerol biorefinery: Towards the sustainable design of biorefineries

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Process design, supply chain, economic and environmental analysis for chemical production in a glycerol biorefinery

Towards the sustainable design of biorefineries

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To the memory of my grandmother Lena

Preface

This project was prepared at the department of Chemical and Biochemical Engineering at the Technical University of Denmark in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Ph.D) in Chemical Engineering. It has primarily been carried out at the Process and Systems Engineering Center (PROSYS), at the department of Chemical and Biochemical Engineering of the Technical University of Denmark. This project has received funding from the Reneseng Project, Marie Curie Initial Networks (ITN), under grant agreement 607415. The project has included two external research stays, carried out at the École polytechnique fédérale de Lausanne (EPFL), with the group of Farnçois Maréchal, IPESE; and at the company Quantis. I would like to thank my supervisors Gürkan, Krist and Ana, for their support along three years of challenging and rewarding work. In addition to my academic supervisors, I want to thank Dr. Peam Cheali, former PhD student at DTU and Dr. John A. Posada from Delft University, for the close collaboration, valuable training and constructive discussions. I am grateful to my family for their support and love. Here at PROSYS I was very lucky to meet wonderful people to which I owe greatly for their friendship. I would especially like to thank Søren, for his never ending support and encouragement over the past years.

Kongens Lyngby, July 10, 2017

Carina L. Gargalo

Carina Loureiro da Costa Lira Gargalo

“If we knew what it was we were doing, it would not be called research, would it?” -
Albert Einstein

Abstract

Drivers such as our deep dependence on fossil fuels availability and price volatility, global concern about climate change and social distress, are steering the economy to be more sustainable and based on a greater use of renewable resources. Therefore, the concept of integrated biorefineries has attracted much attention by aspiring at replacing fossil sources. However, as has been recently witnessed through multiple failures and the shutdown of biorefinery plants all over the world, a biobased economy that heavily depends on the production of biofuels, leads to unsatisfactory results. Thus, it seems that an economy based on the innovative and cost–efficient use of bio-resources for the production of both chemicals and biofuels/bioenergy, is in fact very promising regarding the three pillars of sustainability (economic, environmental and social). Notwithstanding, to be competitive in the long run and to present an advantage in the global markets, robust systems for the acquisition, production and distribution of these bioproducts must be in place.

Although considerable studies have been carried out on the analysis and optimization of biomass conversion to biofuels and bioenergy, up to date limited research has been done on the valorization of biorefinery by-products. This is especially noticeable concerning the valorization of glycerol, which is, as main by-product of the biodiesel industry, responsible for approximately 2/3 of the world supply of glycerol. Despite the many uses for pure glycerol, the exponential growth of biodiesel production in a recent past due to fossil-based energy insecurity and environmental concerns, has led to a significant surplus of glycerol, resulting in a significant drop of its market value. Then, how to deal with the large quantities of low price crude glycerol surplus may become an environmental problem. As a result, exploratory research being carried out along the years has been pointing to glycerol as a powerful starting material for the production of a plethora of value-added chemicals and biofuels. A significant challenge is that emerging technologies are accompanied by uncertain performance characteristics, as well as exogenous sources of uncertainty such as product price and demand. This leads to a significant number of possible options regarding the design, operation and product portfolio offered by biorefineries, from which the most suitable process configurations must be selected, with regards to economics, environmental constraints and overall sustainability. Therefore, uncertainties should not be overlooked. Furthermore, given the multiplicity of large (bio)chemical operations and the often-conflicting objectives among the several business divisions, such as planning, manufacturing, distribution and corresponding environmental consequences and concerns, it is therefore vital to model these activities and to develop comprehensive and systematic methods to capture the synergies and the trade-offs within this complex system. Therefore, the foremost aim of this thesis is to provide a roadmap for early-stage managerial decisions targeting at identifying feasible alternatives for the design and planning of sustainable glycerol biorefineries and corresponding value chains. In this way the thesis is contributing to the transition towards the sustainable development and implementation of these concepts. To achieve this, significant effort is firstly invested into process understanding and into the development of data-driven process models ('gate-to-gate'). Secondly, detailed methodologies for the economic and environmental assessment are developed, where uncertainty and sensitivity analysis play a significant role. Nevertheless, in order to further advance the development and implementation of glycerol based biorefinery concepts, it is critical to analyze the glycerol conversion into high value-added products in a holistic manner, considering both production as well as the logistics aspects related to the supply chain structure. Therefore, the boundaries of analysis were extended to include all activities and operations involved in the glycerol-based biorefinery to bioproducts supply chain. To this end, the GlyThink model is proposed so as to identify operational decisions - including locations, capacity levels, technologies and product portfolio, as well as strategic decisions such as inventory levels, production amounts and transportation to the final markets. GlyThink is a multi-period, multi-stage and multi-product Mixed Integer Linear Programming optimization model based on the maximization of the associated Net Present Value (NPV). Furthermore, strongly based upon the GlyThink model, alongside with detailed economic and environmental assessment, a multi-layered framework for the optimal design and planning of glycerol based biorefinery supply chains under uncertainties is developed in this thesis. The proposed integrated framework ultimately leads to the identification of the optimal design and planning decisions for the development of environmentally conscious biorefinery supply chains, where the consequences of external economic uncertainties on the environmental objective function are analyzed and the trade-offs identified. In summary, this thesis covers the development of methods and tools for the modeling and optimization at the strategic and tactical level, along with detailed economic and environmental assessment techniques, including the incorporation of multi-level uncertainties. All in all, despite the fact that all methods and tools derived in this thesis have been developed to address the optimal design and planning of the glycerol-based biorefinery, they are flexible and applicable to other biorefineries similar in nature.

Resumé

Konceptet af en integreret bioraffinaderi tiltrækker stor opmærksomhed, idet dette koncept har potentialet til at konkurrere med og ideelt erstatte fossile brændsler til produktion af kemikalier, brændstoffer og energi. Ydermere, er det interessant at kigge på integrerede bioraffinaderier, idet økonomien i større og større grad, globalt set, fokuserer på bæredygtige og vedvarende ressourcer. Dette kommer bl.a. som konsekvens af store pris variationer på fossile brændsler, samt usikkerhed omkring tilgængeligheden af disse inden for en relativ kort fremtid. Derudover har der i den senere tid været flere eksempler på nedlukning af bioraffinaderier, samt fejlslagne forsøg på at etablere bioraffinaderier, grundet dårlige økonomiske resultater. Dette har resulteret i at integrerede bioraffinaderier har fået øget fokus, idet det virker mere lovende at basere økonomien på innovativ og omkostningseffektiv anvendelse af bioressourcer til produktion af kemikalier, biobrændstoffer og bioenergi på denne måde.

Der er dog flere udfordringer i at etablere en økonomi der i større grad er baseret på bæredygtige løsninger, som samtidig er konkurrencedygtig på det globale marked. Blandet andet er der behov for at etablere robuste systemer til, at anskaffe genanvendelige råvarer og sikre bæredygtig produktion, samt distribution af de producerede produkter.

Til dato er der mange eksempler på videnskabelige studier der udelukkende har fokuseret på at analysere og identificere optimeringsmuligheder af biomasseomdannelsen til biobrændstoffer og bioenergi. Hvorimod der kun har været relativt få studier med fokus på den potentielle værdi der kan findes i biprodukterne fra bioraffinaderier, som er et vigtigt element i integrerede bioraffinaderier. I forhold til dette er det specielt interessant at kigge nærmere på glycerol, som er det vigtigste biprodukt fra biodieselindustrien og udgør ca. 2/3 af verdensforsyningen.

Specielt for glycerol har den eksponentielle vækst i produktionen af biodiesel resulteret i et væsentligt overskud af tilgængelig glycerol. På trods af de mange anvendelsesmuligheder for glycerol, giver det nye miljømæssige udfordringer. Der er derfor en stigende interesse i at forske i brugen af glycerol som råvare til at producere et bredt vifte af værdifulde kemikalier og biobrændstoffer i integrerede bioraffinaderier. Der er dog væsentlige udfordringer forbundet med dette, idet der er usikkerhed omkring effektiviteten og robustheden af nye teknologier der er nødvendige for at etablere en glycerol baseret produktionsplatform. Derudover er produktpriser og efterspørgsel varierende og usikre. Det er derfor nødvendigt at tage højde for sådanne usikkerheder når man evaluerer forskellige alternativer i forhold til procesdesign, drift og produktionsportefølje for integrerede bioraffinaderier. Derudover er det vigtigt at inddrage forskellige forretningsområder, som: planlægning, fremstilling, distribution og miljømæssige konsekvenser for at kunne udvikle omfattende og systematiske metoder til at modellere og analysere sådanne

systemer. Ved at inkludere alle disse faktorer i evalueringen sikres et mere robust beslutningsgrundlag for at udvælge de mest egnede proceskonfigurationer, med udgangspunkt i økonomi, miljøbegrænsninger og overordnet bæredygtighed. Evaluering af integrerede bioraffinaderier baseret på sådanne omfattende og systematiske modeller gør det også muligt at fange synergi i forhold til forretningsmodeller, samt fordele og ulemper.

Formålet med denne afhandling var at etablere en platform der kan bidrage, i den tidlige beslutningsproces, i at identificere mulige alternativer til design og planlægningen i etableringen af bæredygtige glycerol baserede bioraffinaderier. Samt bidrage til at identificere og analysere værdikæden for disse bioraffinaderier, hvilket vil være med til at understøtte overgangen til bæredygtig procesudvikling og implementering. Dette er opnået ved først og fremmest at fokusere på procesforståelse, samt udviklingen af datastyrede procesmodeller ('gate-to-gate'). Derudover blev der fokuseret på udvikling af detaljerede metoder, der inddrager usikkerheder og robusthedsanalyser, til evaluering af økonomi og impakt på miljøet.

Yderligere, for at fremme udviklingen og gennemførelsen af glycerolbaserede bioraffinaderikoncepter er det vigtigt at analysere glycerolomdannelsen til højt værditilvækstprodukter på en holistisk måde. Her bør der tages hensyn til såvel produktion som logistikaspekter i forbindelse med forsyningskædens struktur. Derfor blev grænserne for de udførte analyser udvidet til at omfatte alle aktiviteter og operationer involveret fra det glycerolbaserede bioraffinaderi til bioprodukternes forsyningskæder. For at evaluere dette blev GlyThink modellen udviklet. Brugen af GlyThink gjorde det muligt at identificere vigtige operationelle beslutninger, - herunder placeringer, kapacitetsniveauer, teknologier og produktportefølje - såvel som strategiske beslutninger såsom lagerniveauer, produktionsbeløb og transport til de endelige markeder. GlyThink er en multi-periode, multi-stage og multi-produkt blandet integer lineær programmeringsoptimeringsmodel baseret på maksimering af den tilhørende Net Present Value (NPV). Derudover, baseret på GlyThink-modellen, er der i denne afhandling udviklet en flerlagsrammemodel, der inkluderer usikkerheder, for den optimale udformning og planlægning af glycerol baserede bioraffinaderi forsyningskæder. I denne flerlagsrammemodel er der også er taget højde for økonomiske og miljømæssige forhold. Denne flerlagsrammemodel vil i sidste ende føre til at optimale design og planlægnings beslutninger bliver identificeret og dermed sikrer udviklingen af miljøbevidste bioraffinaderier, hvor der også er taget højde for eksterne økonomiske usikkerheder.

Overordnet dækker denne afhandling udvikling af metoder og værktøjer til modellering og optimering på strategisk og taktisk niveau sammen med detaljerede økonomiske og miljømæssige teknikker, herunder inkorporering af usikkerheder på flere niveauer. På trods af det faktum, at alle metoder og værktøjer, der er afledt i denne afhandling, er blevet udviklet for at imødegå det optimale design og planlægning af det glycerolbaserede bioraffinaderi, er de fleksible og anvendelige til andre bioraffinaderikoncepter af samme art.

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CHAPTER 1

Introduction

The aim of this chapter is to give a general introduction to the topics studied in the thesis. The research area is introduced and a review of the state of art is presented. With that state of the art in mind, the project motivation is framed, deriving the specific goals of the project and accordingly also outlining the thesis structure. This thesis is built upon a collection of published and submitted papers as detailed in the following chapters. The review of the state of the art is to a large extent based on the introductory paragraphs of the papers that form the basis for this thesis.

1.1 Background & State of the art

Global concerns about climate change, energy security, exhaustion of fossil resources and its societal impacts, have been driving the development towards sustainable manufacturing and the use of renewables. Even though the chemical industry is still improving its energy and mass efficiency, it remains highly dependent on oil and gas. Furthermore, fossil fuels are the dominant products obtained in the chemical industry but add significantly to the polluting emissions, as greenhouse gas emissions (GHG). Worldwide, transport is responsible for 22% of all energy-related GHG polluting emissions, and it's still increasing at a faster pace than any other sector [1].Therefore, driven by the urgency to find sustainable alternatives, there has been a solid interest in the use of biomass and its biorefining for the production of biofuels [2],[3],[4]. Compelling parallels should/can be drawn between the fossil-based refining and biorefining, where biorefining is defined as a way to fractionate biomass into a multitude of products which differ greatly depending on the nature of the feedtstock. The range of products may vary from transportation fuels, such as bioethanol and biodiesel, to platform chemicals, building blocks, polymers and speciality chemicals [5]. As has been witnessed along the years, if biomass biorefining focuses solely on the production of biofuels, fossil-based conventional refining remains more economically attractive [3],[6]. Therefore, an analogy to the fossil-based industry should/can be made, targeting the production of high volume/low value alongside with low volume/ high value products [7]. Hence, in recent years, the bio-based economy has been seen as a key approach that may meaningfully lead/contributte to long term sustainable development, where bio-based chemicals and fuels may play a relevant role towards the replacement (partly or completely) of fossil-based resources [8], [9]. This coproduction of bio-based derivatives could take place in integrated biorefineries [10] [11], which converts biomass feedstocks into a spectrum of valuable molecules, materials and energy carriers including biofuels, heat and power. Therefore, due to an increasing interest in the topic of biorefineries, the need for a robust bio-industry is paramount/significant/preeminent. To this end, it is essential to assess and develop the economic and structural understanding about biorefineries, which implies careful selection of supply chain design, minimizing the threats, all the way from feedstock suppliers to downstream building block technologies and sustainable materials that are converted into higher value chemicals [3].

Furthermore, these processes and corresponding value chains are expected to be efficient and sustainable in the long term so that this industry can compete efficiently with the fossil/petro-based industry. This implies a fair balance among economic benefits, environmental impacts and social consequences. Thus, companies are, now more than ever, not only focusing on economic performance, but they are also attempting to integrate green practices, in order to comply with environmental legislation. In particular, managerial decisions integrating proactive sustainable thinking, bring competitive advantage to enterprises [12]. Hence, there is an immediate need for developing strategies aiming at screening and gathering the most appropriate/feasible/viable designs/technologies and associated value chains, regarding tangible economics, environmental constraints and overall sustainability. Therefore updated models are required in the frame of the optimal design and planning of integrated biorefineries, that would support engineers to identify and validate not only the economic viability of the potential future commercialization of a given product and value chain, but also its overall sustainability.

However, from a systems perspective, due to the multidimensional nature of sustainability, the design and analysis of sustainable biorefineries is an entanglement of multi-criteria and multi-objective decision-making, leading to complex procedures. The complexities seldom arise not only from the multi-evaluation techniques to be chosen, but also from the significant amount of input data required to perform the sustainability analysis, data which may originate from different sources, with different degrees of uncertainty [13],[14]. This is due to the fact that, emerging technologies suffer not only from uncertain reliability but also are surrounded by uncertain performance characteristics, which lead to a great number of possible alternatives regarding the design, operation and product portfolio offered by biorefineries, from which the most suitable process configurations with regards to economics, environmental constraints and overall sustainability must be selected [3],[15],[16].

Furthermore, the comparison and screening of potential processes at the conceptual design phase of biorefineries is marked by assumptions, hypotheses and simplifications that need to be made in order to represent the complexity of the problem. Therefore, it implies that during the first stages of biorefinery design and development, since real data is often incomplete or not available, there are several alternative technologies, feedstocks and products, generating a great number of potential processing pathways and related supply/value chains (see Figure 1.1). Also, as presented in Figure 1.2, since preliminary process engineering assessments can address "what if" questions, early-stage analysis can reduce economic investment and risks once the cost of design changes are at their lowest. Given the multiplicity of large (bio)chemical operations and the often-conflicting objectives among the different business divisions, such as planning, manufacturing, distribution and environmental concerns, it is therefore vital to develop a robust framework to capture the synergies and the tradeoffs within bio-based manufacturing.

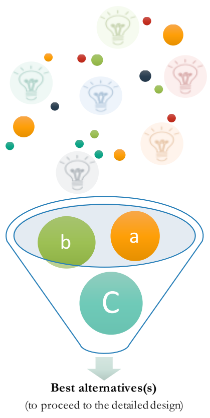

Figure 1.1: Early-stage and screening of alternatives.

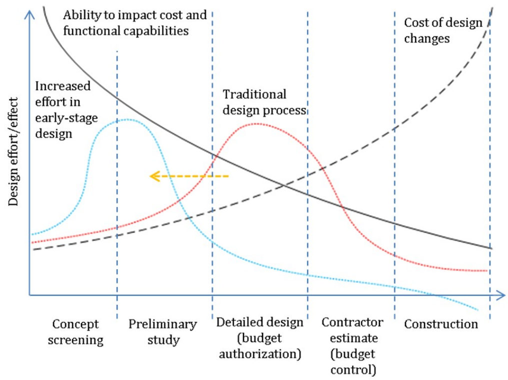

Figure 1.2: Process design stages [17].

Therefore, to guide the user towards informed decision-making, and aiming at managing the complexity associated with the design of biorefinery systems, research has been conducted along the years, focusing in particular on mathematical programming. Several multi-scale and multi-period models have been developed/employed for biorefinery design and planning, where notably supply chain management through optimization has become a widespread method to address and analyse the multiplicity of potential alternatives. The supply chain is defined as a network of facilities that perform a set of operations ranging from the acquisition of raw materials, the transformation of these raw materials, and the transportation of finished goods to the clients [18]. Thus, supply chain optimization seeks to identify the optimal strategic, tactical and operational decisions in order to maximize the performance of the supply chain regarding a certain performance indicator(s).

Several authors have directed/conducted research in this area, with special emphasis on biomass to biofuel (mostly based on bioethanol) value/supply chain optimization problems, and greatly based on Mixed Integer (Linear) Programming - MI(L)P. This is due to the fact that nonlinear problems are very demanding in terms of mathematical modelling, appropriate tuning of the algorithms, etc; while MI(L)P is handled most successfully. Furthermore, MI(L)P is one of the most useful and suitable methods to drive the decision-making process, since it generates a quantitative basis for decisions [19] and it can be efficiently coupled with other significant attributes such as the principles behind sustainable design [20]. Being the goal not to provide an extensive literature review, but to illustrate the direction of research in a recent past, a survey of works/approaches/studies is presented in Table 1.1. The review has been narrowed to include examples of design of biorefinery networks (gate-to-gate, references a to i) and supply chain optimization problems (references j to cc) which share common trades as: (i) being MILP problems; and, (ii) having common strategic decisions such as product portfolio design, supply allocation, multi-period, technology and capacity selection.

Notwithstanding, the above-mentioned approaches consider all model parameters to be known prior to the decision. However, as above-mentioned, uncertainties are intrisic to the systems and are introduced into the design of biorefinery processes and supply chains in many ways. Thereby, since they introduce significant variability and noteworthy risk into the decision-making processes/systems, if uncertainties are disregarded it may lead to the identification of inefficient, sub-optimal or even unfeasible solutions.[21],[22],[23]

Uncertainties directly related to technology-evolution and technology readiness level are, for example, the parameters for the estimation of the fixed capital investment, and production yields. In addition, the presence of exogenous uncertain parameters composes a great challenge to control and account for during the planning horizon of the biorefinery plant. Examples of potential exogenous sources of techno-economic uncertainty include, among others [21]: (i) product market prices fluctuation/variability/volatility; (ii) feedstock market price fluctuation; (iii) feedstock supply; and, (iv) product demand.

Likewise, with regards to the environmental analysis, even though the LCA methodology is widely accepted in the field, the presence of uncertainties is fundamentally important because it threatens to give qualitatively different or even contrasting results when applying LCA on the same products or systems [24]. Summarizing, as presented in Figure 1.3 uncertainty in LCAs can be seen as an input/output box, with three subproblems regarding the assessment and quantification of: (1) errors in the input data, (2) the propagation of errors in the calculations, and, (3) errors in the output data.

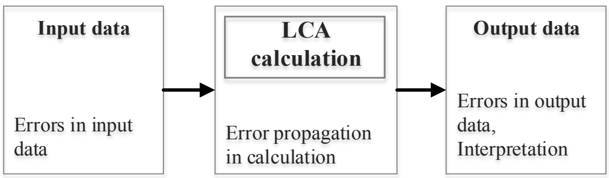

Figure 1.3: Three sub-problems in the LCA calculation related to quantitative errors. Adapted from [25]

The distinguished types of uncertainty presented by [26] and referred in [27], are model uncertainty, parameter uncertainty, uncertainty due to methodological choices, spatial and temporal variability, and variability between objects/sources. For example, parameter uncertainty arises due to empirical inaccuracy (imprecise knowledge) in the inventory and impact assessment parameters, such as imprecise, incomplete, outdated or no measurements of, for example, characterization factors, *CFs*, mass flows and/or substance properties. Interval calculation (Chevalier Téno 1996), fuzzy logic [28], Gaussian formulas [29] and Monte Carlo Simulation, are some of the proposed approaches to deal with error propagation. The latter is the most commonly used method for the propagation of parameter uncertainty onto the model outputs [30], [31], [32]. However, despite inherent uncertainties portrayed in the LCI and LCIA stages, and the considerable work being done on the development of initiatives to address and include propagation of uncertainty in environmental assessments, existing LCA guidelines give little instructions on how to perform such analyses [24], [33]. Consequently, uncertainty still plays a minor role in LCA studies, and the results are tipically reported based on deterministic models [25],[33],[34].

A major hinderance when performing optimization under uncertainty is handling the uncertainty space/domain, usually very large, which leads to very computationally demanding optimization models. Furthermore, this issue is even more prominent when considering decision-making processes, which frequently carry more complexity due to the use of integer decision variables to model logical and other discrete variables in a multi-scale and/or multi-period context [35]. So as to deal with the complexity of optimization problems under uncertainty, extensively used methodologies for the incorporation of uncertainty include the recourse-based stochastic programming, robust programming, chance-constraint programming and fuzzy programming. The most generally used approach is two-stage stochastic programming, where the first- and second-stage variables correspond to supply chain strategic (design) and planning decisions, respectively. In order to account for the growing number of scenarios, Monte Carlo sampling and the Sample Average Approximation technique have been usually used. Although stochastic programming mirrors a risk-neutral approach, chance-constrained programming can be used to improve the accuracy of supply chains by imposing a minimum fulfillment on the probability of satisfying constraints. Furthermore, to reflect the decision-maker's risk-adverse attitude (conservative), robust optimization can be used to avoid the worst case realization of uncertainty in the supply chain design and operations. At last, the third most used approach to deal with uncertainty in the supply management and design, is fuzzy programming, which considers the random parameters as fuzzy numbers and constraints as fuzzy sets [36],[21]. Aiming at providing an up-to-date review of relevant works that deal with uncertainty in the biorefinery optimization field, a survey of approaches is presented in the next sub-section.

Biorefinery optimization under uncertainties: a review

A review of works with particular interest to the topic is presented in Table 1.3, which is built upon the following attributes: (i) mixed integer linear programming (MILP) models developed specifically for the (ii) optimal design of biomass/biofuel/bioproducts biorefinery networks (gate-to-gate, references a to g) and supply chains (references h to jj); and, (iii) considering uncertainty conditions. The survey on the design of gate-to-gate biorefinery networks was limited to product portfolio design problems under uncertainties. Among these, only 29% were found to be multi-period optimization problems (models that accommodate multiple time periods). Furthermore, as the main goals of this thesis involve the design and planing of biorefinery supply chains under uncertainties, focusing on product portfolio design, a more detailed analysis covering the studies that propose multi-product approaches for the optimization of biorefinery supply chains under uncertainties is performed and described based on relevance, and in chronological order.

Kim et al. (2011a,b)[37],[38] proposed a two-stage stochastic optimization problem for the identification of optimal decisions on the supply and facility location, along with production capacity, by maximizing the single-period total profit, under uncertainties on biomass supply, biofuel demand and prices. Further, Gebralssie (2012) [39] proposed a bi-objective stochastic optimization model that enables technology and capacity selection, and production and logistics planning, by minimizing the multi-period total cost and financial risk, under supply and demand uncertainties. Similarly, Kostin et al. (2012) [40] aiming at maximizing the expected performance of the SC under financial risk mitigation, presented a multi-period and multi-objective scenario based optimization problem under demand uncertainty, to decide on the capacity of production plants and storage, along with production rates and product flows. McLean and Li (2013) [41] also suggested a scenario based optimization model however limited to the identification of supply location and production technology through the maximization of the total profit considering both uncertainties on the biomass supply and product demand. To determine only the optimal planning decisions regarding the biomass supply and amounts of product manufactured, Awudu and Zhang (2013) [42] introduced a single-period stochastic programming model maximizing the expected total profit, under uncertainties on product demand and prices. Tong et al. (2013) [43] suggested a multi-period scenario-based stochastic optimization problem to identify the optimal decisions regarding design and operations of the biorefinery to be incorporated into crude refineries, by minimizing the total cost when subjected to price and quantity uncertainties. Also addressing the minimization of the total annualized costs of incorporating a biorefinery into the crude refineries, Tong et al. (2014a) [44] (ref s) proposed a multi-period stochastic model to optimize the expectation of the objective function under a number of scenarios associated with biomass availability, fuel demand, crude oil prices, and technology evolution. However, in a further work, Tong et al. (2014b) [45] presented a single-period fractional programming model where the aim was to optimize the unit cost of the downstream design and planning of the same case study, tackling uncertainties on the biomass supply and biofuel demand. However addressing the effect of the same uncertainties also on the downstream supply chain, Kasivisvanathan et al. (2014) [46] presented a single-period robust programming model that, by minimizing the total cost, led to the optimal decisions regarding technology and capacity selection. In a more recent work by Geraili and Romagnoli (2015) [22], a multi-objective stochastic optimization approach is proposed to, under price uncertainty, incorporate the tradeoffs between the cost and the financial risk, leading to the optimal decision regarding technology and capacity selection. In a subsequent study also based on a stochastic optimization model, Geraili et al. (2016) [47] presents a decision support tool for the maximization of the NPV in order to optimize the production capacity, and the operating conditions of the plant. This tool includes a simulation based global sensitivity analysis to identify the most critical uncertainties concerning market and operational uncertainties. Overall, it is observed that, with regards to the supply chain design: (i) 100% of the studies here listed were developed for the biomass to biofuel supply chain, mostly focused on the bioethanol production; (ii) multi-product SC design problems are rare (48%); (iii) only 15% of the studies are multi-period, including technology selection, portfolio design and incorporation of parameters uncertainties; (iv) where from these 15% only one study ([40]) used Net Present Value as economic objective function; and, (v) no studies were found with more than 3 products in the design space. One can infer that there is a trade-off between computational effort and SC complexity, since the higher the number of decisions, products, technologies in the design space, along with higher intricacy of the objective function, the higher the modeling and computational effort.

Moreover, as observed in Table 1.3, studies considering uncertainties for the design and planning of biorefineries that cover both economic and environmental concerns are rather limited. For example, Giarola et al. (2012) [48] presented a MILP model for the optimal upstream strategic and planning decisions of the ethanol supply chain, where both the economic (NPV) and the environmental impact (global warming potential, GWP) of the supply chain are optimized considering carbon trading cost uncertainty. In a similar fashion, Giarola et al. (2013) [49] also proposed a model for the optimal strategic and planning decisions under carbon trading uncertainty of the ethanol supply chain based on the previous work. However, both the economic (NPV) and the environmental impact (global warming potential, GWP) are optimized considering the user's risk mitigation preferences. More recently, Santibanez-Aguilar et al. (2016) [50] proposed a scenario–based optimization problem to identify the optimal supply allocation under biomass price uncertainty, where the environmental impact is measured through the Eco-indicator99 method, and the economic performance is determined by the net annual profit.

Also, noteworthy is that, regarding all works collected (presented in Tables 1.1 and 1.3), only 11 out of 61 (18%) include environmental concerns besides the economic objective function. Among these studies, only 9% consider environmental concerns when performing optimization under uncertainties. Therefore, a comprehensive overview and discussion on optimization studies that included the environmental assessment as an objective function is given below.

Optimization and environmental assessment: a review

As previously mentioned, the increasing awareness of environmental concerns has been witnessed in a recent past especially motivated by governmental regulations. Therefore, crescent effort has been made on the incorporation of environmental impact assessment, alongside with typical economic criteria. In order to do so, Life-Cycle Assessment (LCA) has been described as the most scientifically reliable method currently available for studying and evaluating the environmental impacts of a certain product or process [51]. Further this is enforced by the fact that the European Commission stated in the Sustainable Development Strategy that a significant goal is to develop and standardize LCA methodologies [52],[53]. Thus, LCA has become the main tool to analyze environmental consequences related to a product, process or activity. A standard LCA method begins by establishing the boundaries of analysis of a given good or service, followed by the collection of the life-cycle inventory within those boundaries. Afterwards follows the characterization stage where the emitted substances or resources consumed are converted into environmental categories of impact by using component and category specific characterization factors, followed by normalization and weighting, leading to a single indicator. To this end, a specific life cycle impact assessment method (LCIA method) is selected. Several different LCA methods are available and continuously being developed. These use different models in the characterization step, different normalization assumptions and/or different weighting factors [54]. Despite the great benefits of coupling optimization and LCA, there are still only few published works on the topic. Even less studies are found that include the environmental modeling through LCA in the supply chain optimization field. Frota Neto et al. (2008) [55] proposed a framework for the design and analysis of sustainable logistic networks, assessing the ecological impact through the environment index, taking the pulp and paper industry as example. Guillen-Gosalbez and Grossmann (2009) [56] addressed the design of sustainable chemical supply chains with uncertainty in the life cycle inventor, by using the Eco-indicator 99 LCIA method. Duque et al. (2010) [57] proposed a supply chain model to optimize the decisions regarding production and transportation routes, where the environmental impact is also quantified by using Eco-indicator 99. Likewise, Pinto-Varela et al. (2011) [58] also used Eco-indicator 99 to account for environmental concerns when optimizing the design and planning of supply chains. Of particular interest for the work described in this thesis, some examples are given that include environmental metrics on the field of biorefineries. Zamboni et al. (2009) [59] developed a spatially-explicit MILP model for the design of respectively first and hybrid generation ethanol SCs under economic and environmental performance (GHG emissions) optimization. Mele et al. (2011) [60] and Santibanez-Aguilar et al. (2011) [61] developed a mixed-integer linear program optimizing the economic and environmental performances of bioethanol supply chains using Eco-indicator 99, as well as Global Warming Potential. Similarly, Giarola et al. (2012a) [48]and Giarola et al. (2012b) [49] proposed a spatially-explicit MILP model for the design of respectively first and hybrid generation ethanol SCs under economic and environmental performance (GHG emissions) optimization, under deterministic and uncertainty conditions, respectively. Bernardi et al. (2012) [62] proposed a multi-objective MILP addressing hybrid corn grain and stover supply chains to ethanol production, where the environmental burdens were included through the estimation of the carbon and water footprints. Similarly, You et al. (2012) [63] suggested an approach towards the sustainable design of biorefinery supply chains by including the GHG emission as the environmental objective. More recently, as mentioned in the previous section, Santibanez-Aguilar et al. (2016) [50] proposed a scenario–based optimization problem optimizing the supply allocation under biomass price uncertainty, where the environmental impact is measured through the Eco-indicator 99 method. Lastly, d'Amore and Bezzo (2016) [64] proposed a multi-objective MILP model where the environmental objective is represented in terms of GHG emissions, as well as the analysis of the impact on emissions caused by indirect Land Use Change effects.

Acknowledging all the above-mentioned points, the motivation and goals of this thesis are outlined in the following section.

Table 1.1: List of publications: MILP deterministic problems for the design and planning of biorefinery networks and supply chains.

	references	supply allocation	facility location	technology selection	technology capacity	multi-product	final products	multi-period	objective functions			types of uncertainty	Region case study
									economic (Fobj)	environmental (Fobj)	social (Fobj)		
a	**Sammons et al. (2007) [65]**	-	-	x	-	x	chicken litter to syngas, hydrogen, and electricity	-	max profit	-	-	-	-
b	**Karuppiah et al. (2008) [66]**	-	-		-	-	corn-based bioethanol	x	min annualized costs	-	-	-	USA
c	**Chen et al. (2010) [67]**	-	-	x	-	x	coal and biomass to coproduce power, liquid fuels and chemicals	-	max NPV	-	-	-	-
d	**Kang et al. (2010) [68]**	-	-	-	-	x	corn, corn stover, and perenial grasses to DDGS and ethanol	x	min total costs	-	-	-	Illinois
e	**Zondervan et al. (2011) [69]**	-	-	x	-	x	lignocellulosic biomass and crude-oil to ethanol, butanol, succinic acid	-	min costs	-	-	-	-
f	**Martin et al. (2011) [70]**	-	-	x	-	-	switchgrass to H_2	-	min production cost	-	-	-	-
g	**Martin and Grossman (2011) [71]**	-	-	x	-	-	bioethanol	-	minimize the total annualized cost	-	-	-	-
h	**Pham and El-Halwagi (2012) [72]**	-	-	x	-	-	lignocellulosic biomas to ethanol	-	minimizations of production costs	-	-	-	-
i	**Giuliano et al. (2016) [73]**	-	-	x	-	x	lignocellulosic biomass to levulinic acid, succinic acid and ethanol	x	max NPV	-	-	-	-
j	**Sammons et al. (2008) [74]**	-	-	x	-	x	chicken litter to syngas, hydrogen, and electricity	-	max profit	-	-	-	-
k	**Ekşioğlu et al. (2009) [75]**	-	x	x	-	-	biomass to biodiesel, biogas, methane 1^{st} and 2^{nd} generation bioethanol	x	minimizes the annual costs	-	-	-	Mississipi, USA
l	**Zamboni et al. (2009a)**	x	x	-	x	-	corn to bioethanol		min operational cost	-	-	-	Italy
m	**Zamboni et al. (2009b)**	x	x	-	x	-	corn to bioethanol		min operational cost	min GHG	-	-	Italy
n	**Mele et al. (2009) [76]**		x	x	x	x	bioethanol and sugar	x	min annualized cost	min BOD20	-	-	Argentina
o	**Mansoornejad et al. (2010) [77]**	-		x	-	x	numerical example, 4 products from pulp and paper industry	-	max profit	-	-	-	Canada
p	**Akgul et al. (2011) [78]**	x	x	-	x	-	bioethanol	x	minimization of the total daily cost	-	-	-	Northern Italy
q	**Elia et al. (2011) [79]**	x	x	-	x	x	CBGTL		min production cost	-	-	-	USA
r	**You and Wang (2011) [80]**		x	x	x	-	-	-	-	-	-	-	Iowa
s	**Giarola et al. (2011) [20]**	x		x	x	x	lignocellulosic biomass to DDGS, ethanol and CHP	x	max NPV	min total GHG	-	-	-
t	**Bernardi et al. (2012) [62]**	x		x**	x		ethanol	x	max NPV	min (carbon + water footprint)	-	-	Italy
u	**Avami (2013) [81]**	-	-	x	-	-	wastes and residues to ethanol and ETBE	x	min annualized costs	-	-	-	Iran
v	**Ortiz-Gutiérrez et al. (2013) [82]**	x	x	x	-	x	corn to ethanol, DDGS, heat, power, biogas	x	max NPV	min total GHG	-	-	Northern Italy
x	**Mazzeto et al. (2013) [83]**	x		x	-	x	corn to ethanol, DDGS, heat, power, biogas	x	max NPV	-	-	-	Italy
z	**Yue et al. (2013) [84]**	x	x	x	-	-	from agricultural residues to diesel and gasoline	x	min cost	min GHG	max job cre-ation	-	-
aa	**Zhang and Writght (2014) [85]**	-	x	x	x	x	forest residue to H_2, liquid fuels, commodity chemicals, and lignin		min cost	-	-	-	-
bb	**Cambero et al. (2015) [86]**	x	x	x	x		forest residues and sawmill wastes to heat, electricity, pellets and pyrolysis bio-oil	x	max NPV	-	-	-	British Columbia, Canada
cc	**d'Amore and Bezzo (2016) [64]**	x	x	x	x	x	corn grain and stover to bioethanol, DDGS, power	x	max NPV	min total GHG	-	-	Italy

Table 1.2: *cont.* of Table 1.1.

	references	supply allocation	facility location	technology selection	technology capacity	multi-product	final products	multi-period	objective functions			types of uncertainty	Region case study
									economic (Fobj)	environmental (Fobj)	social (Fobj)		
s	**Giarola et al. (2011) [20]**	x		x	x	x	lignocellulosic biomass to DDGS, ethanol and CHP	x	max NPV	min total GHG	-	-	-
t	**Bernardi et al. (2012) [62]**	x		x**	x		ethanol	x	max NPV	min (carbon + water footprint)	-	-	Italy
u	**Avami (2013) [81]**	-	-	x	-	-	wastes and residues to ethanol and ETBE	x	min annualized costs	-	-	-	Iran
v	**Ortiz-Gutiérrez et al. (2013) [82]**	x	x	x	-	x	corn to ethanol, DDGS, heat, power, biogas	x	max NPV	min total GHG	-	-	Northern Italy
x	**Mazzeto et al. (2013) [83]**	x		x	-	x	corn to ethanol, DDGS, heat, power, biogas	x	max NPV	-	-	-	Italy
z	**Yue et al. (2013) [84]**	x	x	x	-	-	from agricultural residues to diesel and gasoline	x	min cost	min GHG	max job cre-ation	-	-
aa	**Zhang and Writght (2014) [85]**	-	x	x	x	x	forest residue to H_2, liquid fuels, commodity chemicals, and lignin		min cost	-	-	-	-
bb	**Cambero et al. (2015) [86]**	x	x	x	x		forest residues and sawmill wastes to heat, electricity, pellets and pyrolysis bio-oil	x	max NPV	-	-	-	British Columbia, Canada
cc	**d'Amore and Bezzo (2016) [64]**	x	x	x	x	x	corn grain and stover to bioethanol, DDGS, power	x	max NPV	min total GHG	-	-	Italy

Table 1.3: List of publications: MILP problems for the design and planning of biorefinery networks and supply chains *under uncertainties*.

	references	supply allocation	facility location	technology selection	technology capacity	multi-product	final products	multi-period	objective functions: economic (Fobj)	objective functions: environmental (Fobj)	types of uncertainty	Region case study
a	**Cheai et al. (2014a) [17]**	-	-	x	-	x	convert corn stover or wood to biofuels (FTgasoline, FT-diesel, and bioethanol)	-	max EBIDTA	-	market product price	-
b	**Cheali et al. (2014b) [87]**	-	-	-	-	x	corn stover and wood to gasoline diesel and ethanol	-	min total cost	-	biomass and products market price	-
c	**Kasivisvanathan et al. (2014) [46]**	-	-	x	x	x	palm oil to biochar, gasoline, bio-oil, acetone, butanol, ethanol, and animal feed	-	min total cost	-	production	-
d	**Cheali et al. (2015a) [88]**	-	-	x	-	x	corn stover and wood to gasoline diesel and ethanol	-	max EBIDTA	-	capital cost estimation	-
e	**Geraili and Romagnoli (2015) [22]**	-	-	x	x	x	conversion of lignocellulosic feedtsock to platform with three products: cellulosic ethanol, biosuccinic acid, and bioelectricity	x	max NPV + min risk	-	biannual crude oil prices	-
f	**Cheali et al. (2015b) [89]**	-	-	x	-	x	bioethanol derivaties		max EBIDTA	min total sustainability index	market price uncertainties	-
g	**Geraili et al. (2016) [47]**	-	-	x	x	x	ethanol, succinic acid, treated water, stem and electricity	x	max NPV	-	Market uncertainties ; processing technologies related parameters	-
h	**Mas et al. (2010) [90]**	-	x	-	x *	-	-	x	max total profit + minimize risk on investment	-	biofuel price	Italy
i	**Dal Mas et al. (2011) [91]**	x	x	-	x *	-	-	x	max NPV	-	biomass price	Italy
j	**Kim et al. (2011a) [38]**	x	x	-	x *	x	gasoline, biodiesel	-	max total profit	-	supply, market demands, market prices, processing technologies	USA
k	**Kim et al. (2011b) [37]**	x	x	-	x *	x	gasoline, biodiesel	-	max total profit	-	biomass availability, biofuel demand, price	USA
l	**Gebreslassie et al. (2012) [39]**		x	x	x	x	gasoline, diesel, jet fuel	x	minimize total costs + minimize conditional value at risk	-	supply, demand	Usa
m	**Chen and Fan (2012) [92]**	-	x	-	x *	-	-	-	minimize total costs	-	feedstock supply, biofuel demand	USA
n	**Walther et al. (2012) [93]**	x	x	x	x	-	-	x	max NPV	-	biomass production, investment cost, bioduel demand	germany
o	**Kostin et al. (2012) [40]**	x	-	x	x	x	sugr, bioethanol	x	max NPV	-	biofuel demand	Argentina
p	**Giarola et al. (2012) [48]**	x	x	x	x	x	bioethanol, DDGS, power	x	max NPV	min env impact (GWP)	feedstock cost, carbon cost	Italy
q	**Giarola et al. (2013) [49]**	x	x	x	x	x	bioethanol, DDGS, power	x	max NPV	min env impact (GWP)	raw materials, carbon allowances trading cost volatility	Italy
r	**Li and Hu (2014) [94]**	x	x	-	x *	-	-		max total profit	-	biomass availability, technology advancement, biofuel prices	USA
s	**Tong et al. (2013) [43]**	x	x	x	x	x	gasoline, diesel	x	minimize total costs	-	biomass availability, fuel demand, crude oil prices, technology evolution	USA
t	**Osmani and Zhang (2013) [95]**	x	x	-	-	-	-	-	minimize total costs	-	biomass yield, biomass price, bioethanol price, rainfall level	USA
u	**Foo et al. (2013) [96]**		x	-	-	-	-	-	-	minimized GHG emissions	biomass supply	Malaysia
v	**McLean and Li (2013) [41]**	x	-	x	-	x	bioethanol, heat, power	x	max total profit	-	amount of required crops, yield of crops, lower and upper demand limits for electricity	Central Europe
x	**Awudu and Zhang (2013) [42]**	x	x	x	-	x	from biomass to ethanol, corn oil and DDGS	-	max profit	-	product prices and demand	-
z	**Tong et al. (2014b) [44]**	x	-	x		x	gasoline, diesel, jet fuel		minimize total costs + minimize unit cost	-	supply, demand	USA

Table 1.4: *cont.* of Table 1.3.

	references	supply allocation	facility location	technology selection	technology capacity	multi-product	final products	multi-period	objective functions		types of uncertainty	Region case study
									economic (Fobj)	environmental (Fobj)		
aa	**Tong et al. (2014a) [45]**	x	x	x	x	x	gasoline, diesel, jet fuel	x	-	-	biomass availability, product demand	USA
bb	**Azadeh et al. (2014) [97]**	x	x	x	x		-	x	max total profit	-	supply, demand	numerical example - no location
cc	**Gonela et al.(2015a) [98]**	x	x	-	x *	x	bioethanol	x	max total profit	-	selling price and demand of bioethanol, yield rate of 1^{st} and 2^{nd} genaration biomass	USA
dd	**Sharifazedah et al. (2015) [99]**	x	-	-	-	-	-	x	max NPV	-	raw material availability, biofuel demand	UK
ee	**Gonela et al.(2015b) [100]**	x	x	-	x*	-	-		max total profit	-	bioethanol price, bioethanol demand, biomass yield	USA
ff	**Azadeh and Arani (2016) [101]**	x	x	x		-	-	x	max total profit	-	available biomass, demand	numerical example - no location
gg	**Mohseni et al. (2016) [102]**	x	x	-	x*	-	-	x	minimize total costs	-	Ressource supply, cost parameters, critical technical factors, biodiesel demand	Iran
hh	**Santibanez-Aguilar et al. (2016) [50]**	x	-	-	-	x	bioethanol, biodiesel	x	max total profit	min env impact	raw material price	Mexico
ii	**Balaman and Selim (2016) [103]**	x	x	x	x	-	-	x	minimize total costs and minimize total service level	-	unit cost of thermal energy storage, upper capacity limit of thermal energy storage, thermal energy demand per household	Turkey
jj	**Yue and You (2016)** [36]	x	x	-	x	-	ethanol from corn stover	x	min total cost	-	technology evolution (conversion efficiency), climate/weather (yield of biomass feedstock), biomass supply and biofuel demand	Illinois

1.2 Motivation & project goals

As previously pointed out, although a considerable number of studies have been done on the analysis and optimization of biomass conversion to biofuel and bioenergy (gate-to-gate and SC), up to date limited research has been done on the valorization of biorefinery by-products. This is especially true concerning the valorization of glycerol, (by-product of the biodiesel industry) which is responsible for 2/3 of today's worldwide glycerol supply.

Despite the fact that pure glycerol is an important industrial feedstock used in food, drugs, cosmetics, pharmaceuticals, pulp and paper, leather, textile and tobacco industries, the growth of the biodiesel industry has led to a glycerol surplus resulting into a ten-fold decrease in crude glycerol prices [8],[104]. The world biodiesel production has significantly increased with an average growth of 11% annually (growth rate end-2009 through 2014) and it reached a maximum of 125 billion liters in 2014 [105].

Henceforth, glycerol valorization by chemical and biochemical conversion to biofuels, high value-added chemicals and building blocks has been pointed out as a powerful alternative to add value to this side stream [8],[3],[106]. By transforming the conventional biodiesel industry into an integrated biorefinery, it would not only increase its economic viability, but also provide a potential replacement platform for fossil-based products, instigating a probable overall improvement of environmental performance.

Therefore, this project aims at filling this gap by developing multi-criteria computer aided decision-making techniques as a roadmap for early-stage managerial decisions, targeting at guiding the user towards the design and planning of sustainable glycerol biorefineries and corresponding value chains. To this end, this thesis covers the development of methods and tools for the modeling and optimization at the strategic and tactical level, along with detailed economic and environmental assessment techniques, including the incorporation of multi-level uncertainties. Hence, the realistic case study of glycerol valorization in Europe is used not only because it composes a currently realistic challenge, but also to highlight the features of the proposed design and assessment strategies.

In the next section, the structure of the thesis is defined, and the specific research objectives per chapter are delineated.

Thesis Keywords

glycerol; early-stage; concepts screening; economic assessment; Net Present Value; environmental assessment; LCA; optimization; uncertainties; supply chain

1.3 Structure of the thesis

The results section of the thesis consists of two parts, as presented in Figure 1.4. Part I consists of chapters 2, 3 and 4; and, Part II consists of chapters 5 and 6. Lastly, in chapter 7 overall conclusions and directions for future research are discussed. In the following sub-sections a summary of the main achievements in each chapter is presented.

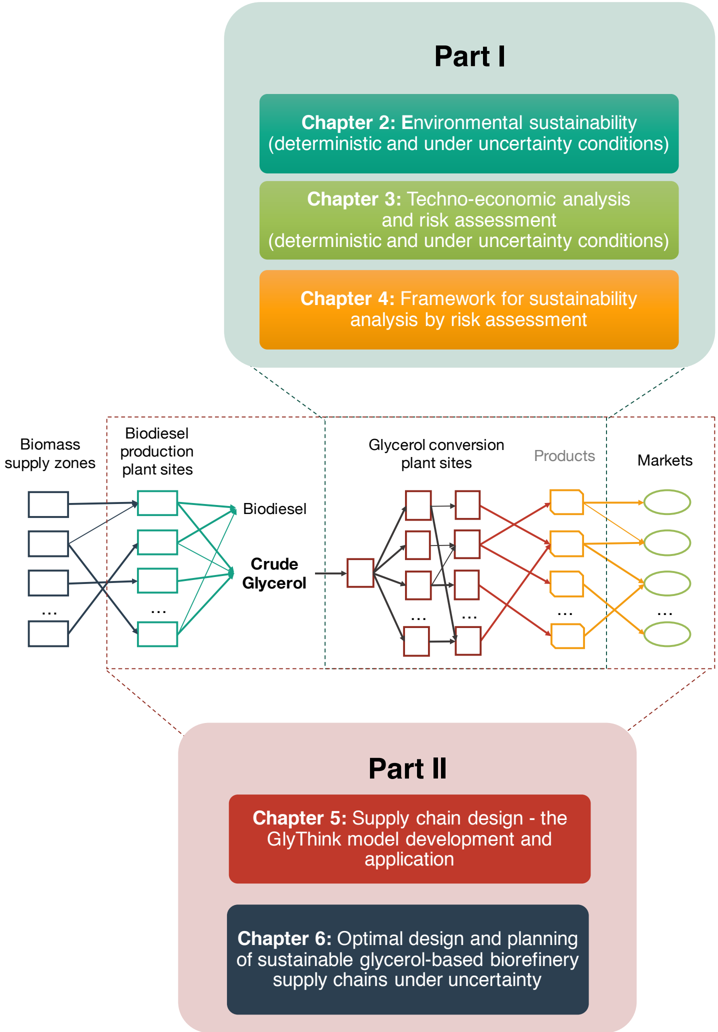

Figure 1.4: Thesis structure: Part I and Part II boundaries

Part I: process design, optimization & analysis

Part I of the results section of this thesis deals with the design, optimization and analysis of gate-to-gate glycerol-based biorefinery concepts.

The prime aim of chapter 2, is to recommend an early-stage methodology for the environmental evaluation and robust ranking of bioprocesses under uncertainty (called E3BU). This is achieved by focusing on (i) the reduction of uncertainty at the inventory stage of LCA; and, (ii) how to appropriately deal with parameter uncertainty at the characterization factors level. Furthermore, a model library (database) for glycerol-based biorefinery concepts for the production of biofuels and value-added products is developed in Chapter 2. In chapter 3, the main goals/achievements are: (i) to extend the database of glycerol-based biorefinery concepts for the production of value-added products; and,

(ii) to propose and apply a systematic methodology for the early-stage screening and assessment of alternatives through detailed techno-economic analysis and risk assessment by incorporating technical and economic uncertainties. At last, in chapter 4 a framework for techno-economic and environmental sustainability analysis by risk assessment is introduced. It aims at providing a way for a quick and visual screening and identification of alternatives. This is done through the interpretation of a sustainability risk matrix, targeting to ease the communication of results between different management levels.

Part II: towards the sustainable design of biorefinery supply chains

In Part II, in order to expand and consolidate the knowledge on the glycerol-based biorefinery, the boundaries of design and analysis are broadened so as to include the supply/value chain. In Chapter 5, both production and logistics aspects related to the glycerol biorefinery supply chain structure are analysed. To this end a multi-product, multi-stage/scale and multi-product MILP model (called *GlyThink*) based on the maximization of the Net present Value is proposed. Finally, in Chapter 6 the goal is to assess the supply chain (SC) in a holistic manner. To achieve this, a framework is developed for the design and planning of (glycerol-based) biorefineries. The framework presents a multi-layered strategy composed of different steps, and it is strongly based on optimization techniques, detailed economic and environmental assessment, and multi-objective optimization under stochastic environment.

1.4 Dissemination of the PhD results

Peer reviewed manuscripts

- Gargalo, C.L., Carvalho, A., Gernaey, K. V. Sin, G. 2017, *Supply chain design: the GlyThink model development and application*. Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.7b00908

- Gargalo, C.L., Carvalho, A., Gernaey, K. V. Sin, G. 2017, *Optimal design and planning of sustainable glycerol-based biorefinery supply chains under uncertainty*. Submitted. (2017)

- Gargalo, C.L., Cheali, P., Posada, J.A., Carvalho, A., Gernaey, K. V. Sin, G. 2016, *Assessing the environmental sustainability of early stage design for bioprocesses under uncertainties: An analysis of glycerol bioconversion*. Journal of Cleaner Production, vol 139, pp. 1245-1260. DOI: 10.1016/j.jclepro.2016.08.156

- Gargalo, C.L., Cheali, P., Posada, J.A., Gernaey, K. V. Sin, G. 2016, *Economic Risk Assessment of Early Stage Designs for Glycerol to Valorization in Biorefinery Concepts*. Industrial & Engineering Chemistry Research, vol 55, no. 24, pp. 6801-6814. DOI: 10.1021/acs.iecr.5b04593

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- L. Gargalo, C., Carvalho, A., Gernaey, K. V. Sin, G. 2017, *The impact of price correlations on economic assessment: Uncertainty & Global Sensitivity Analysis.* in Z Kravanja M Bogataj (eds), Proceedings of the 27^{th} European Symposium on Computer Aided Process Engineering. Accepted for publication.

- L. Gargalo, C., Gernaey, K. V. Sin, G. 2016, *Economic risk-based analysis: Effect of technical and market price uncertainties on the production of glycerol-based isobutanol.* in Z Kravanja M Bogataj (eds), Proceedings of the 26th European Symposium on Computer Aided Process Engineering. vol. 38, Elsevier Science. Computer-Aided Chemical Engineering. DOI: 10.1016/B978-0-444-63428-3.50058-8.

Conference contributions

- L. Gargalo, C., Carvalho, A., Gernaey, K. V. & Sin, G. 2017, *The impact of price correlations on economic assessment: Uncertainty & Global Sensitivity Analysis.* 27th European Symposium on Computer Aided Process Engineering (ESCAPE27). October 2017, Barcelona, Spain. Accepted for oral presentation.

- L. Gargalo, C., Carvalho, A., Gernaey, K. V. & Sin (2016). Global Sensitivity Analysis of Economic Assessment of Early Stage Process Design: The Case of the Glycerol Biorefinery. Abstract from 2016 AIChE Annual Meeting: American Institute of Chemical Engineers, San Francisco, United States. Accepted for oral presentation.

- L. Gargalo, C., Gernaey, K. V. Sin, G. 2016, *Economic risk-based analysis: Effect of technical and market price uncertainties on the production of glycerol-based isobutanol.* 26th European Symposium on Computer Aided Process Engineering (ESCAPE26). June 12-15 2016, Portorozˆ, Slovenia. Accepted for oral presentation.

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- L. Gargalo, C., Sin, G. (2014). Uncertainty and Sensitivity Analysis in Sustainable Process Design - Environmental Indicators. Abstract from 2014 AIChE Annual Meeting: American Institute of Chemical Engineers, Atlanta, United States. Accepted for oral presentation.

Other contributions

- L. Gargalo, C, Chairakwongsa, S., Quaglia, A., Sin, G. & Gani, R. 2015, Methods and tools for sustainable chemical process design. in JJ Kleme (ed.), Assessing and Measuring Environmental Impact and Sustainability. Elsevier Science, pp. 277-321. DOI: 10.1016/b978-0-12-799968-5.00009-9

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Part I

Process design, optimization & analysis

CHAPTER 2

Assessing the environmental sustainability of early stage design of glycerol bioconversion

Substantial uncertainty is involved in the early-stage design and analyses of bioprocesses, and thus the ranking and identification of potential sustainable solutions is a challenging task. Therefore, in this chapter a methodology is proposed that targets at facilitating the environmental sustainability assessment under uncertainty during the conceptual design of bioprocesses. This step-wise methodology aims at assisting decision-makers to: (i) collect and generate the input data for bioprocesses; (ii) systematically reduce uncertainty concerning the material fluxes at the early stage design of bioprocesses, decreasing overall uncertainty in the life cycle inventory; (iii) handle parameter uncertainty, by applying the Monte Carlo technique for the propagation of uncertainty in characterization factors to the environmental impact categories; (iv) establish sound quantitative thresholds for the comparison of alternatives by incorporating a probabilistic interpretation; and lastly, (v) rank the alternatives within the design space. ln summary, the proposed methodology, through its statistical approach, aims at providing a consistent and robust ranking of alternatives.

This chapter of the thesis is based upon the following article:

Assessing the environmental sustainability of early stage design for bioprocesses under uncertainties: An analysis of glycerol bioconversion. L. Gargalo, C., Cheali, P., Posada, J.A., Carvalho, A., Gernaey, K. V. Sin, G. *Journal of Cleaner Production*, vol 139, pp. 1245-1260. (2016)

Nomenclature

LCA	Life Cycle Assessment
CC	Climate change
CFs	Characterization factors to convert inventory into environmental categories of impact
CDF	Cumulative distribution function
$CF_{i,l}$	Characterization factors for component i, category of impact l
DCE	Dichloroethane
FU	Functional unit

FE	Freshwater eutrophication potential
FET	Freshwater ecotoxicity potential
HT	Human Toxicity potential
HFom	Formic acid
HSuc	Succinic acid
K_i	Degree of reduction of component i
LHS	Latin Hypercube Sampling
ME	Marine eutrophication potential
MET	Marine ecotoxicity potential
PMF	Particulate matter formation potential
POF	Photochemical oxidation formation potential
S_c	Environmental category of impact
S_{norm}	Normalized environmental category of impact
$S@5_{class1}$	Category of impact at 5^{th} percentile, class 1 uncertainty
$S@95_{class3}$	Category of impact at 95^{th} percentile, class 3 uncertainty
SI	Single Indicator
S^{eg}_{out}	Potential Environmental Impact that goes out of the energy generation system
S^{eg}_{in}	Potential Environmental Impact that goes into the energy generation system
S^{mp}_{in}	Potential Environmental Impact that goes into the manufacturing process
S^{mp}_{out}	Potential Environmental Impact that goes out of the manufacturing process
TA	Terrestrial acidification potential
TET	Terrestrial cotoxicity potential
TOA	Trioctylamine
X	Biomass
Y_{SN}	Yield of ammonia per C-mol of substrate consumed
Y_{SX}	Yield of biomass per C-mol of substrate consumed
Y_{SO}	Yield of oxygen per C-mol of substrate consumed
Y_{SC}	Yield of carbon dioxide per C-mol of substrate consumed
Y_{SP_1}	Yield of product or by-product produced per C-mol of substrate consumed
Y_{SW}	Yield of water produced per C-mol of substrate consumed
$\alpha_{i,k}$	Ratio of chemicals or utilities added per unit of inlet mass flowrate
$\mu_{i,j,k}$	Ratio of consumption of utilities or chemicals per unit of inlet mass flowrate
$\gamma_{i,r}$	Stoichiometry per unit of inlet mass flowrate
$split_{i,k}$	Product separation fraction per unit of inlet mass flowrate
V	Uncertainty type v, uncertainty due to choices

2.1 Introduction

As discussed in the Introduction section, despite inherent uncertainties portrayed in the LCI and LCIA stages, and the considerable work being done on the development of initiatives to address and include propagation of uncertainty in environmental assessments, existing LCA guidelines give little instructions on how to perform such analyses [24], [33]. Consequently, uncertainty still plays a minor part in LCA studies, and the results are normally reported based on deterministic models [25],[33], [34]. In short, the motivation of this work arises fundamentally from: (i) the inherent uncertainty concerning early-stage design of bioprocesses; (ii) little guidance/methods in existing literature and studies to perform and interpret LCA under uncertainty; and, (iii) missing thresholds for comparison of alternatives and decision-making. Therefore, this chapter aims at presenting and demonstrating a methodology for assisting the decision-maker towards identifying the more environmentally sustainable bioprocess design alternative under uncertainty, as well as aiding the user with reporting and interpreting uncertainty in environmental evaluation. It focuses on dealing with parameter uncertainty, firstly by focusing on reducing uncertainty on the life cycle inventory stage concerning the inter-process flows at the early stage design; and secondly, by handling the propagation of uncertainty regarding the characterization factors (which carry a high degree of uncertainty) to the environmental impacts. The proposed methodology is presented as a systematic support tool for decision-making at the conceptual (early-stage) phase, which aims at enabling the decision-maker to screen design alternatives, to establish a ranking and to identify the environmentally most sustainable pathway(s). To this end the following steps are formulated within the methodology: (i) collect and generate the input data for bioprocesses; (ii) systematically reduce uncertainty concerning the material fluxes at the early stage design of bioprocesses, reducing overall uncertainty in the inventory stage of LCI; (iii) handle parameter uncertainty introduced by the characterization factors used for flux classification by applying the Monte Carlo technique; (iv) establish sound quantitative thresholds for alternatives comparison by incorporating a probabilistic interpretation; and lastly, (v) rank the alternatives within the design space.

This chapter is organized as follows: (i) the proposed methodology is described in section 2.2, followed by (iii) the Results & Discussion section; and, (iv) Conclusions.

2.2 Early-stage Environmental Evaluation of Bioprocesses under Uncertainty (E3BU)

The proposed methodology is called Early-stage Environmental Evaluation of Bioprocesses under Uncertainty (*E3BU*). E3BU is based on the combination of methods which includes: the Life Cycle Assessment [107] steps, the Monte Carlo technique coupled with Latin Hypercube Sampling, and the establishment of quantitative thresholds for direct comparison and screening of alternatives acting as a support tool for decision-making at the conceptual design phase of bioprocesses. The methodology objective is to rank the alternatives in the design space and identify the potentially best and thus most environmentally friendly solution at the early stage design of bioprocesses. The methodology, as presented in Figure 2.1, is composed of five steps: (1) goal and scope; (2) adapted Life Cycle Inventory; (3) life cycle impact assessment; (4) dealing with parameter uncertainty: Monte Carlo technique; and, (5) ranking and selection of the best processing network.

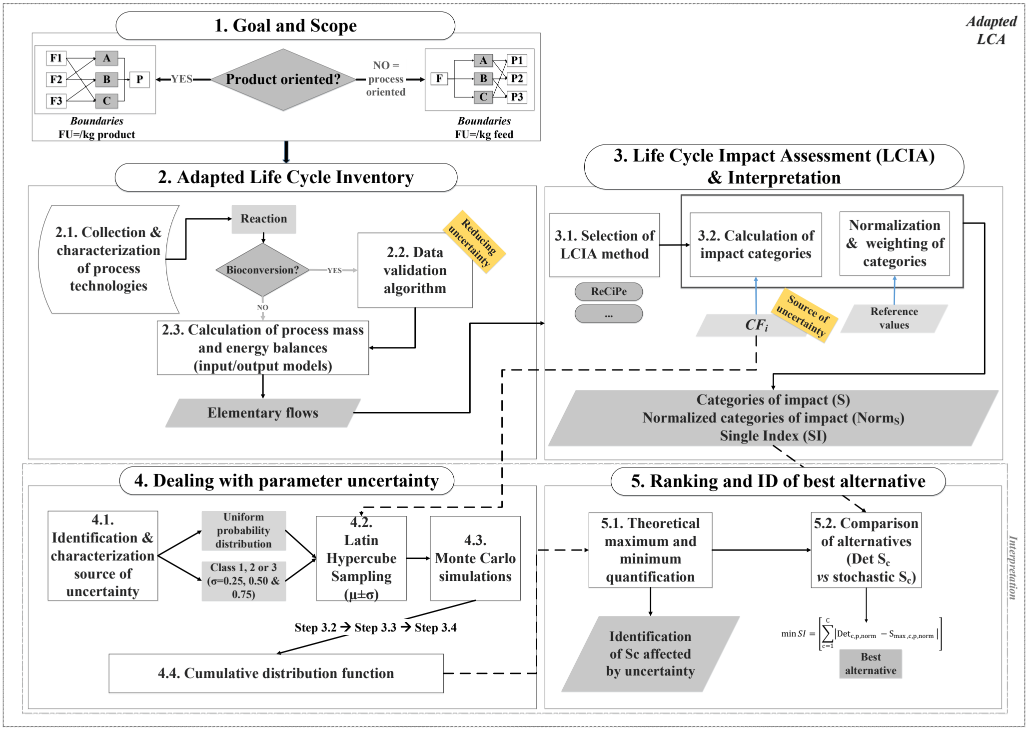

Figure 2.1: Schematic representation of the proposed E3BU methodology.

2.2.1 Step 1: Goal and Scope

This step aims at defining the system boundaries (processes/operations to be included in the LCA study) and the Functional Unit (FU). E3BU has been developed to guide the decision-maker to define if the problem to be solved is based on a product- or process-oriented approach in order to select the FU. Therefore, in order to assure equivalence among the systems, the following FU are recommended within E3BU:

- A *product-oriented approach* is suggested when the goal is to produce a certain product (or a set of products), and the decision-maker needs to evaluate several pathways for its production. This is the case of a retrofitting problem, where one wants to adapt or change the current plant so as to have additional manufacturing paths and/or to have diverse sources of feedstock being transformed in the plant. Therefore, the functional unit (FU) would be kg of product produced from the chosen feedstock.

- A *process-oriented approach* should be used when the decision-maker is targeting to assess a number of routes to produce a set of products from a given (previously chosen) feedstock and, thus, the issue is the establishment of a proper product portfolio. Therefore, it would result in an entirely new plant (or module); and the FU would be kg of feedstock being converted in the plant which is still reflecting the primary function of the plant.

2.2.2 Step 2: Adapted Life Cycle Inventory

The data collection and management section involves all steps related to data gathering and generation to be performed in the life cycle inventory (LCI). The required data consists of the mass and energy balances for all the operations composing the processing networks within the design space. The data needed can be provided by databases (such as Ecoinvent), real data and/or simulation. When real data and databases are unavailable, which often happens when considering bioprocesses, process simulation is needed. Therefore, in step 2 of E3BU, a stepwise procedure to fill this gap concerning the lack of bioprocess data for early stage design is proposed. This procedure reduces the uncertainty related to fluxes involved in the bioreaction. The steps included in step 2, as shown in Figure 2.1, are: *Step 2.1. Collection and characterization of process technologies; Step 2.2 Bioreaction validation algorithm; and, Step 2.3 calculation of mass and energy balances by simulation using input-output models.*

Step 2.1: Collection and characterization of process technologies

After clearly defining the boundaries of the environmental assessment to be conducted (i.e. defining it as a product- or process-oriented approach), the next step is the collection of possible conversion pathways. Therefore, the aim of this step is to guide the decision-maker towards the development of a database of process technologies describing the systems under study, therefore leading to the full description of the system and the collection of all the associated data required to perform the mass balances in the subsequent steps. Additionally, the possible combinations are graphically established in a process superstructure composing the design space, from which the best potential alternatives will be identified. The superstructure of technologies representing the object of the study is built of processing networks/pathways. A processing network consists of a number of processing steps connecting raw materials to products, such as pre-treatment, conversion, separation and purification. Therefore, a generic process modeling approach previously proposed by [108], [17] is here used to collect and manage the complexity of multidisciplinary and multi-dimensional data of different process alternatives within a processing network. The block model (Figure 2.2) consists of four parts described by representative balance equations: (i) mixing, (ii) reaction, (iii) waste separation, and (iv) product separation, where each one is specified by specific parameters. These input parameters and ratios per unit of inlet mass flowrate are, $\mu_{i,j,kk}$ – ratio of chemicals or utilities added, $\alpha_{i,kk}$ – direct consumption of utilities or chemicals, $SW_{i,kk}$ – waste separation fraction, $split_{i,kk}$– product separation fraction and, at last, $\gamma_{i,rr}$, representing the stoichiometry coefficients. The required process data (input parameters and ratios) can be collected through a comprehensive literature review combining different sources, such as, experimental, pilot and demonstration plant data, simulation results, or available stream tables or operating data of a provided flowsheet.

A multidimensional matrix (i.e. database) is then constructed where the data previously gathered is inserted and organized to represent the processing steps composing the different alternatives that are potentially available in the study. Hence, this is a robust

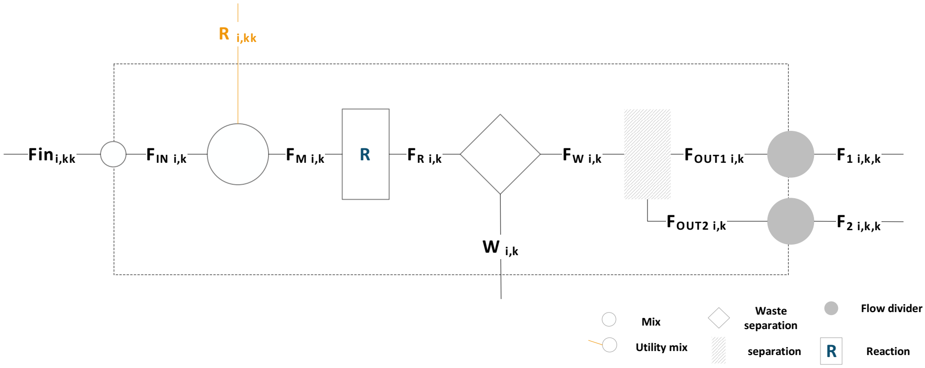

Figure 2.2: Generic input-output model. Adapted from [17].

way to standardize the input data gathered from different sources (all converted to the same format), making it easily accessible, reusable and expandable.

Step 2.2: Data validation algorithm

For early stage design of bioprocesses, the data is often unavailable, unrepresentative (data inaccuracy) or there are data gaps. Therefore, identifying data gaps or lack of representative data in the life cycle inventory such as pollutant flows or inter-process flows may be complicated at this conceptual phase. A more complete accounting of emissions may be obtained from the analysis with the closest processes and by analyzing the process reaction stoichiometry, where the law of conservation of mass helps to predict data gaps. It may still underestimate pollutant losses, but it is still superior compared to completely disregarding the mass balances [109]. As a result, in order to reduce uncertainty related to the fluxes involved in the reaction step, and thus, manage to decrease the uncertainty in the inventory stage, the bioconversion data collected needs to be validated. A systematic consistency analysis of experimental data is thus proposed to verify and, in some cases predict, the missing data to describe fully the reaction stoichiometry (the stoichiometric coefficients $\gamma_{i,rr}$). It is based upon elemental and degree of reduction balances, and their underlying concepts can be found in [110]. The workflow of this algorithm is represented in Figure 2.3.

Step A.1 and A.2 have as first input the data collected in step 2.1. These data frequently consists of experimental yield(s) of products along with the information about the microorganism used in the bioconversion. In step A.1, the yields collected (output step 2.1) are converted into C-mol of compound per C-mol of substrate; and, in step A.2, the degree of reduction of each component is estimated. Targeting to validate (or predict) the bioreaction stoichiometry, an investigation into the microorganism metabolic pathways and the growth media used is needed (step B.1) to predict a possible stoichiometry equation (step B.2). A generic equation, as presented in Eq. 2.1, will be used as an input model for calculation and optimization purposes, which intends to guide the decision-maker towards a fully determined and verified bioreaction stoichiometry.

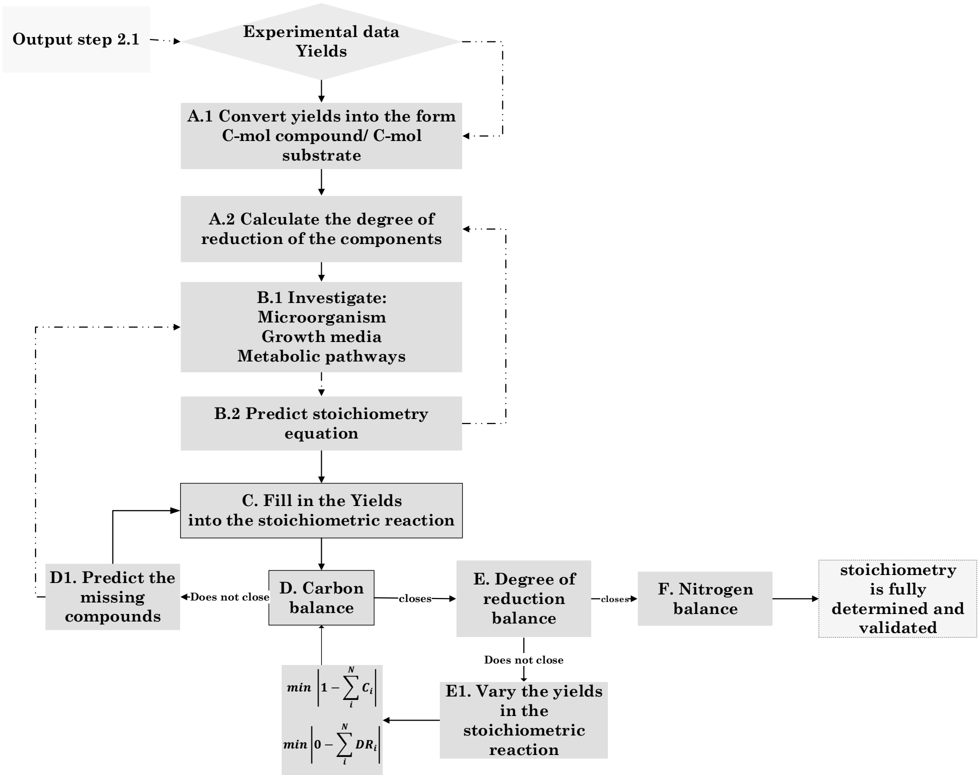

Figure 2.3: Algorithm for bioreaction data validation (the dash-dotted lines represent the information flow).

$$
\begin{aligned}
&-substrate - Y_{SN}NH_3 - Y_{SO}O_2 + Y_{SP1}P_1 + Y_{SP2}P_2 \\
&+ Y_{SP3}P_3 + ... + Y_{SC}CO_2 + Y_{SX}X + Y_{SW}H_2O = 0
\end{aligned}
\tag{2.1}
$$

where, P_1, P_2 and P_3 represent the products (metabolites) of the fermentation, and Y_{SP} represents the yield of carbon containing compounds (represented by C-mol) per C-mol of substrate. Note that the yield of the non-carbon containing compounds is represented in terms of mol per C-mol of substrate. In step C, the output of step A.1 is inserted into the equation (output step B.2) and hence, steps D, E and F are performed and mathematically formulated as follows in Eqs. 2.2, 2.3 and 2.4, respectively.

$$E_m Y_{sm} = 1 \leftrightarrow -1 + \sum_{i=1}^{M} x_{cm_1} \cdot Y_{sm_1} = 0 \tag{2.2}$$

$$E_k K = 0 \leftrightarrow -1 \cdot k_s + \sum_{i=1}^{M} k_{m_1} \cdot Y_{sm_1} = 0 \tag{2.3}$$

$$E_k Y_{SN} = 0 \leftrightarrow -1 + \sum_{i=1}^{M} x_{Nm_1} \cdot Y_{sm_1} = 0 \tag{2.4}$$

Equations 2.2 to 2.4 are then translated into the following matrices,

$$\begin{bmatrix} x_{Cm_1} & x_{Cm_2} & \cdots & x_{Cm_M} \\ k_{m_1} & k_{m_2} & \cdots & k_{m_M} \\ x_{Nm_1} & x_{Nm_2} & \cdots & x_{Nm_M} \end{bmatrix} \cdot \begin{bmatrix} Y_{Sm_1} \\ Y_{Sm_2} \\ \vdots \\ Y_{Sm_M} \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 1 \end{bmatrix} \tag{2.5}$$

where, M represents the number of metabolites in Eq. 2.2 to 2.5; x_{cm_i} and x_{Nm_i} specify the carbon and nitrogen content of the given metabolite m_i, respectively. The constant k_{m_i} represents the degree of reduction per C-mol of the metabolite m_i; and, Y_{sm_i} as mentioned earlier, identifies the molar yield of metabolite m_i (C-mol) per C-mol of substrate. If the carbon or degree of reduction balance does not close (step D and E), multiplication of the matrices differs from the last column on the right in Eq. 2.5, and then the reported yields are to be investigated and varied satisfying Eqs. 2.6 and 2.7. Thus, the verified stoichiometry will be the one that presents the minimum least squares difference regarding the carbon and degree of reduction balance, as presented in Eqs. 2.6 and 2.7.

$$min \mid 1 - \sum_{i}^{M} C_i \mid \tag{2.6}$$

$$min \mid 0 - \sum_{i}^{M} K_i \mid \tag{2.7}$$

Therefore, the output of this step is the verified stoichiometry, which is one of the required inputs for the calculation of mass and energy balances.

Step 2.3: Calculation of mass balances and energy balances

After collecting all the process parameters representing the technologies and verifying the stoichiometry, all the data needed to solve the block model equation is collected. Therefore, by using a mathematical solver, the processes are simulated providing all the data requirements for the next step.

2.2.3 Step 3: Life Cycle Impact Assessment

The aim of this step is to assess the environmental impact of the processing networks within the design space, by establishing a link between the product/process that is investigated and its corresponding categories of impact.

Selection of LCIA method

In this step, the LCIA method for characterization of environmental impacts is selected according to ISO 14040 standards. There are several LCIA methods that can be applied (ReCiPe, CML 2002, Eco-indicator 99, EDIP97, etc.) and they diverge in the impact categories, the selection of indicators, and in the geographical focus. The most suitable method to be applied is case-dependent and the International Reference Life Cycle Data System (ILCD) Handbook [111] provides guidance and further details on the adequacy of the method.

Calculation of impact categories & single indicator

The deterministic environmental category of impact (Det_c) for a certain category c is obtained by aggregating all the characterized flows by category using the following equation.

$$Det_c = \sum_i CF_{i,c} \times F_i \tag{2.8}$$

Where $i = \{1, , I\}$ corresponds to the components present in the system, the $CF_{i,c}$ represent characterization factors that convert component flows i into impact categories c, and F_i is the material flux of component i. Having selected the LCIA method, the indicators and characterization factors are pre-selected and therefore used in the subsequent steps. Therefore, depending on the classification method selected, the inventory is then characterized into C impact categories. It is important to note that, the science-based characterization factors ($CF_{i,c}$) are based on models that are usually simplified versions of more complex models within the various impact categories. Different databases may have different estimations or experimental values for the science-based characterization factors that are used to convert mass balance inventory into appropriate categories of midpoint impact. Differences may derive from geographical conditions, from data sources or measurement errors. They provide useful indications for relative comparisons but they are not suitable for absolute or damage assessment to the environment or to human health since they carry significant uncertainty. Furthermore, in this step normalization could be used to express impact indicator data in a way that can be compared among impact categories [112]. This procedure normalizes the indicator results by dividing them by a selected reference value. After normalization, the impact categories can be aggregated into an overall dimensionless score by a weighting technique incorporated into an overall single indicator, *SI*, as shown in Eq. 2.9.

$$SI = \sum_i^C w_c \times Det_{norm,c} \tag{2.9}$$

Where, w_c refers to the weighting reference, which can either be global, local or regional, and c represents the impact category being estimated.

2.2.4 Step 4: Dealing with parameter uncertainty - Monte Carlo technique

The characterization and propagation of parameter uncertainty into the potential environmental impacts is a central feature of the E3BU methodology (see the workflow in Figure 2.1, Step 4). To that purpose, the Monte Carlo technique has been applied.

Step 4.1: Characterization of uncertainty

Appropriate characterisation of uncertainties in *CFs* require data sets with proper statistical information such as accuracy, confidence intervals and/or standard deviation. Due to lack of statistical information in databases (e.g. ReCiPe, IMPACT2002), the expert review method is used. Expert review is a commonly used approach for uncertainty analysis in engineering studies [113], [114]. Three classes of uncertainties for *CFs* were defined as follows: the class 1 uncertainty refers to 25% variation, the class 2 refers to 50% variation, and the class 3 refers to 75% variation around the reported (mean) values of *CFs*. The assignment of uncertainty classes for each $CF_{i,c}$ is done based on the availability and variability of the number of observations regarding their reported values (measurements). Then, it has been assumed that uncertainty in $CF_{i,c}$ follows a uniform distribution (a common assumption when there is limited data to identify an underlying distribution). Moreover, with these assumptions, the lower and upper bound of a uniform distribution are calculated as follows: the *lower bound*=$(1-\%var)\times$ *mean value* and the *upper bound*=$(1+\%var)\times$ *mean value* [115]. The mean value of $CF_{i,c}$ is collected from available databases.

Step 4.2: Latin Hypercube Sampling

The Latin Hypercube Sampling (*LHS*) method is used to sample from the parameter space [114]. For the sampling step, one needs to *a priori* specify the total sample number, *N*. After the sampling, one obtains a sampling matrix with *N* rows and *p* columns, where *N* is the total number of samples and *p* refers to the number of uncertain parameters for which the sampling is performed $\{CF_{i,cat_1},...,CF_{I,cat_P}\}$, as shown in Eq. 2.10. The summary table with the mean values, uncertainty classes and lower and upper bounds are given in Appendix A, Table A.3.

$$LHS_{class1,2or3} = \begin{bmatrix} ss_{1,1} & \dots & ss_{1,P} \\ \vdots & \ddots & \vdots \\ ss_{N,1} & \dots & ss_{N,P} \end{bmatrix} \tag{2.10}$$

Step 4.3: Monte Carlo simulations

In this step, the model equation (Eq. 2.8) describing the calculation of Det_c for each impact category is solved using parameter values from the sampling matrix (usually called

Monte Carlo simulations). Performing N calculations with the model leads to a distribution of the model output values (i.e. S values) as result of propagation of the joined parameter uncertainties in the input (i.e. $CF_{i,c}$). The distribution of outputs, as shown in Eq. 2.11, will be analyzed by means of an empirical cumulative distribution function (CDF) for all categories c, and for each one of the uncertainty classes attributed in Step 4.1., and used for interpretation in the next step.

$$output_{class1,2or3} = \begin{bmatrix} Det_{1,1} & \dots & Det_{1,C} \\ \vdots & \ddots & \vdots \\ Det_{N,1} & \dots & Det_{N,C} \end{bmatrix} \tag{2.11}$$

2.2.5 Step 5: Ranking and identification of best potential alternative

The objectives of this step are to obtain the ranking of alternatives regarding their environmental performance and finally identify the most environmentally friendly solution. In this step of $E3BU$, a probabilistic interpretation framework is used which interactively assists the decision-maker to compare and screen alternatives. It is described in detail in the following steps.

Step 5.1: Theoretical maximum and minimum

For each alternative, the empirical cumulative distribution functions of the potential environmental impacts are built for each uncertainty class (1, 2 and 3). The y-axis in CDF reads probability of x (the Det_c) being less than or equal to a certain value X, $P(Det_c \leq X)$, while the x-axis refers to actual values of the impact categories. The range of the x-axis indicates how large the uncertainty is (the larger the range of the x-axis, the larger the uncertainty). The shape of the CDF function (e.g. linear, S-shape), indicates the probability of observing X. A linear CDF means that input uncertainty propagates linearly to the outputs, while an S-shape CDF indicates that input uncertainties propagate in a non-linear fashion to the output [116]. By identifying a certain percentile, an estimate of the theoretical maximum and minimum is established for every impact category. In this work, the 90% confidence interval is used by reading the 95/5 percentiles in the CDF. These are used as theoretical thresholds representing the best and worst case scenario, $Det_c@5_{class1}$ and $Det_c@95_{class3}$, respectively. As shown in Figure 2.4, the theoretical minimum and maximum are identified by x_1 and X_3, once it gives the 'conservative' minimum and maximum among the uncertainty classes (the worst case scenarios).

Step 5.2. Comparison of alternatives – single indicator under uncertainty (*SI*)

In this step, the alternatives are to be compared and ranked according to their performance by following the algorithm shown in Figure 2.5.

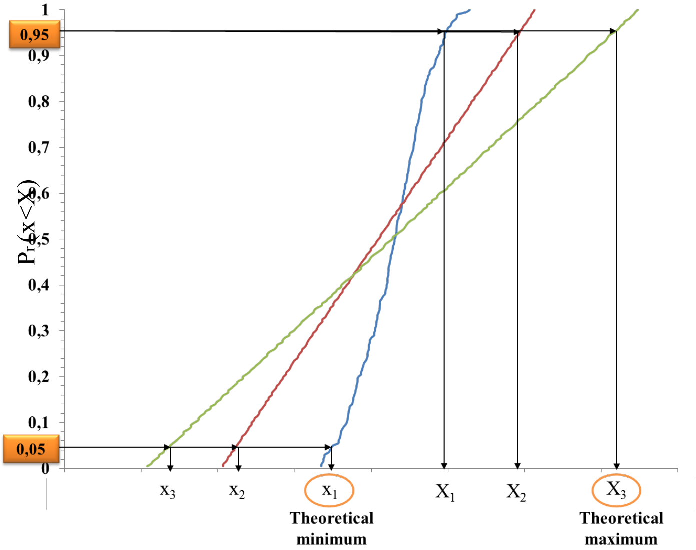

Figure 2.4: Theoretical minimum and maximum values established from the empirical cumulative distribution of generic impact categories. Blue, red and green, correspond to class 1, 2 and 3 uncertainty.

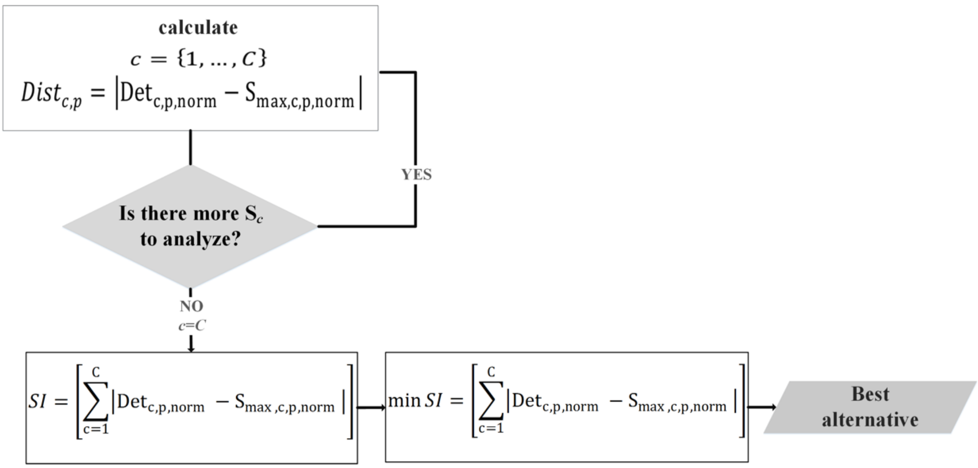

Figure 2.5: Algorithm for comparison, ranking and identification of the best alternative.

Firstly, for a certain impact category c, the alternative's performance is quantified by Eq. 2.12. It corresponds to the difference ('distance') between the category's nominal value given by the deterministic value obtained in Step 3.2 and the theoretical maximum established in Step 5.1. Both values are normalized, where the reference value is given by the difference between $T_{max,c}$ and $T_{min,c}$, which represent the theoretical maximum and minimum of a certain category of impact across all alternatives in the design space. $Det_{c,p}$ and $S_{max,c,p}$ stand for the deterministic value and the maximum value obtained through the CDF for a certain category c and for a given product p, respectively.

$$Dist_{c,p} =\mid Det_{c,p,norm} - S_{max,c,p,norm} \mid= \left(\frac{\mid Det_{c,p} - S_{max,c,p} \mid}{T_{max,c} - T_{min,c}}) \right) \tag{2.12}$$

The procedure is followed for each alternative until there are no more categories to analyze. Once there are no more categories c, to analyze for a certain product p, the normalized categories of impact are summed into a single score under uncertainty, *SI*, (see Eq. 2.9). Therefore, the identification of the best potential environmentally friendly solution is enabled, and it corresponds to the one that minimizes *SI*, as presented in Eq. 2.13. It is noted that the $Dist_{c,p}$ here indicates the extent of uncertainty on the calculated value. If the uncertainty is low, then the distance will be low, which is a desirable solution. This is due to the fact that the smaller is the difference between the deterministic value of the category and the theoretical maximum, the more trustworthy are the deterministic values for the categories of impact.

$$\begin{aligned} Best_{alt} &= minSI = min \left[\sum_{c=1}^{C} Dist_{c,p} \right] \\ &= min \left[\sum_{c=1}^{C} \mid Det_{c,p,norm} - S_{max,c,p,norm} \mid \right] = min \left[\sum_{c=1}^{C} \left(\frac{\mid Det_{c,p} - S_{max,c,p} \mid}{T_{max,c} - T_{min,c}} \right) \right] \end{aligned} \tag{2.13}$$

As motivational example, hypothetic alternatives A and B, for a generic set of three categories (Cat 1, Cat 2 and Cat 3), have the sum of 'distances' and the corresponding *SI* represented in Figure 2.6. As it can be seen from Figure 2.6, the smaller the distance between the deterministic value (Det_c) and the theoretical maximum (S_{max_c}), the higher the performance of that alternative regarding the set of categories c. By minimizing the 'distances', the algorithm attributes naturally/automatically more importance to the categories that carry higher uncertainty, because the greater the 'distance' the less trustworthy is the category of impact results. Therefore, alternative A is found to be the best alternative in this example.

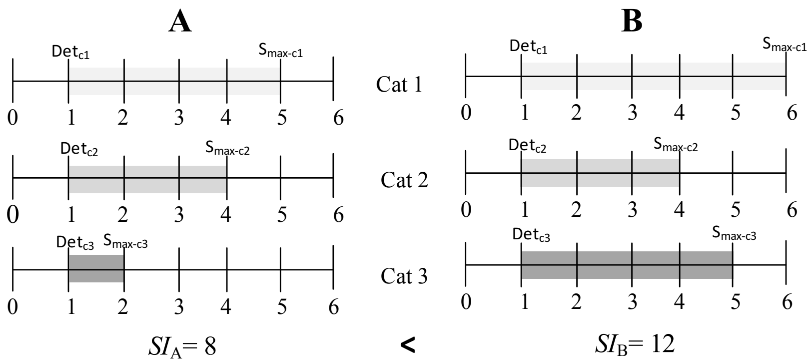

Figure 2.6: 'Distances' for hypothetical alternatives A and B. Det_c, $S_{max,c}$ and SI correspond to the normalized categories deterministic value, theoretical maximum and Single Indicator of A and B, $SI_{A,B}$, respectively.

2.3 Results & Discussion

2.3.1 Step 1: Goal and Scope

The goal of applying the *E3BU* methodology to the case study is to identify the best potential environmentally sustainable design alternative to add value to the glycerol side stream by converting it to high-value added products. The problem is looked at from a process-oriented point of view, since the decision-maker is targeting to assess a number of bioconversion paths to produce a set of products from glycerol. Therefore, the function is the valorization of 1 kg of crude glycerol, the functional unit being the inflow of 1 kg crude glycerol. Thus, as represented in Figure 2.7, the boundary limits are set up to be gate-to-gate, which includes the manufacturing process, the utilities scheme and waste disposal.

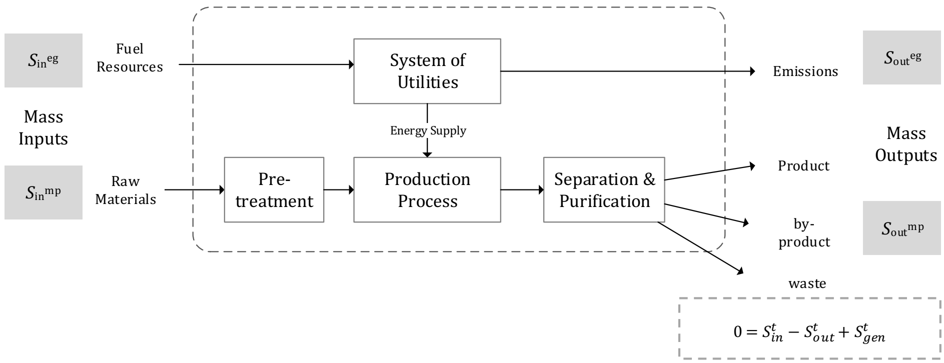

Figure 2.7: System boundaries: S_{in}^{eg}, S_{out}^{mp}, S_{in}^{mp} and S_{out}^{mp}, S_{in}^{eg}, S_{out}^{eg}, S_{in}^{mp},S_{out}^{mp}, represent the impact categories that enter and leave the energy generation process and, the S that enter and leave the manufacturing process, respectively. S_{in}^{t}, S_{out}^{t} and S_{gen}^{t} represent the total S that enter, leave or are generated inside the system boundaries, respectively.

2.3.2 Step 2: Data collection & Management

Collection and characterization of process technologies

The first step was to collect information for all technologies regarding glycerol conversion to value-added chemicals, through literature review of significant publications in the field. The study presented in this chapter includes: the purification and bioconversion of crude glycerol (obtained from the palm oil-based biodiesel plant) into six value-added products (ethanol, poly-3-hydroxybutyrate, D-lactic acid, succinic acid, propionic acid and, 1,3-propanediol), and their potential environmental impact under uncertainties, is studied. Table 2.2 summarizes the details and data sources of the glycerol-based biorefinery concepts.

Table 2.2: Glycerol biorefinery concepts (and data sources).

Product	**Bioconversion process**	**Data sources**
Ethanol	Glycerol fermentation by an engineered strain of *E. coli*	[117], [118]
PHB	Glycerol fermentation by an engineered strain of *C. necator*	[104], [119]
Lactic acid	Glycerol fermentation by an engineered strain of *E. coli*	[120], [121]
Succinic acid	Glycerol fermentation by an engineered strain of *E. coli*	[122]
Propionic acid	Glycerol fermentation by an engineered strain of *P. acidipropionici ACK-Tet*	[123], [124]
1,3PDO	Glycerol fermentation by an engineered strain of *K. pneumoniae*	[125], [126]

After collecting all the data needed, a superstructure representing the design space was constructed (see Figure 2.8). As mentioned before, the mass and energy balances were obtained based on the generic input-output block model, described in Figure 2.2. As a generic example, the succinic acid production is presented in Figure 2.9, by exemplifying the process as having the bioconversion and the separation and purification stages.

Bioprocess data validation algorithm

Targeting to reduce the uncertainty present at the conceptual phase of process design, a validation algorithm for the bioreaction stoichiometry is here applied to decrease the uncertainty related to the material flows (inventory) involved in the reaction step. Therefore, the data was validated and consolidated following the algorithm explained in detail in Step 2.2. (Figure 2.3); a short example for succinic acid is provided below. The metabolic pathways and experimental data for fermentation are provided in [122], and the resulting stoichiometric equation is as follows.

$$\begin{aligned} &-CH_{8/3}O - Y_{SN}NH_3 + Y_{SP1}CH_{3/2}O + Y_{SP2}CH_2O + Y_{SP3}CH_{4/3}O \\ &+ Y_{SC}CO_2 + Y_{SX}CH_{1.8}O_{0.5}N_{0.25} + Y_{SH_2O}H_2O = 0 \end{aligned} \tag{2.14}$$

Where SP_1, SP_2, SP_3 represent the production of succinic acid, acetate and pyruvate, respectively. After applying the validation algorithm for experimental data (Figure 2.3), the stoichiometry is completed and the yield coefficients are filled in accordingly,

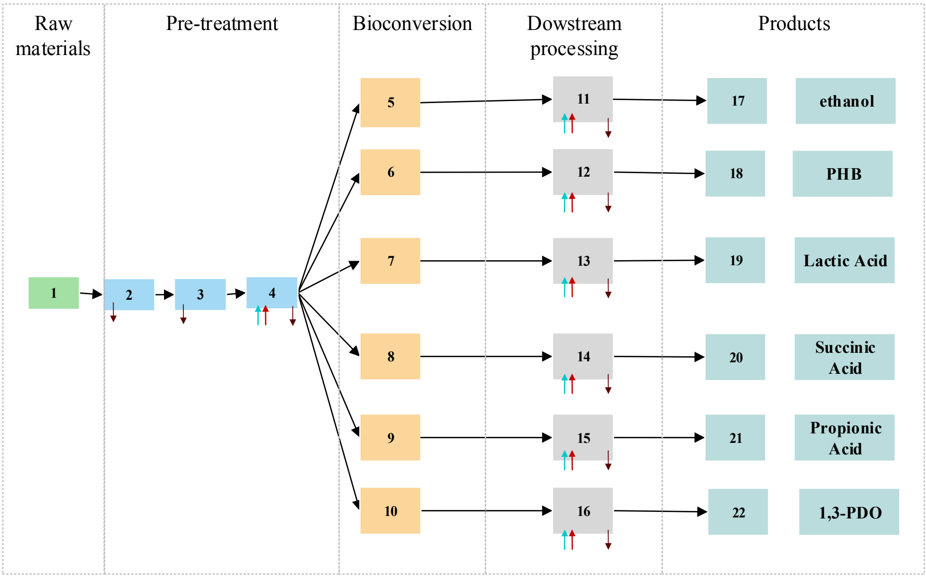

Figure 2.8: Superstructure representing the design space for the glycerol-based biorefinery concepts. Light blue, red and brown arrows represent cooling and heating utilities and waste generated, respectively.

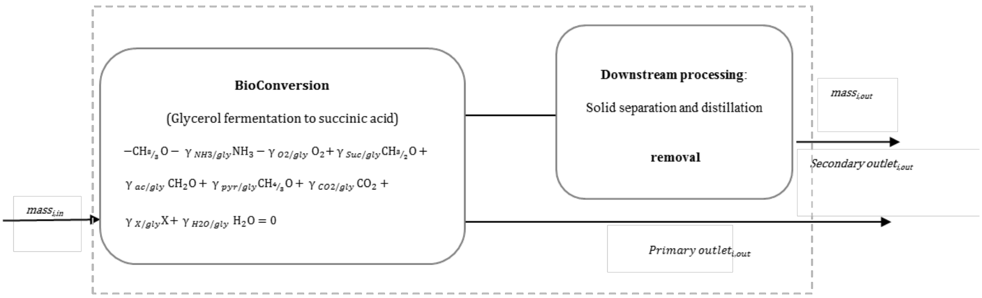

Figure 2.9: Generic example of the input-output calculation for the production of succinic acid

$$
\begin{aligned}
&- CH_{8/3}O - Y_{SN}NH_3 + 0.544CH_{3/2}O + 0.064CH_2O + 0.009CH_{4/3}O \\
&+ Y_{SC}CO_2 + 0.066CH_{1.8}O_{0.5}N_{0.25} + Y_{SH_2O}H_2O = 0
\end{aligned}
\tag{2.15}
$$

Since, the molar yields of carbon dioxide (Y_{SC}) and nitrogen (Y_{SN}) are still missing, therefore, the matrices for carbon and degree of reduction balances are prepared as shown in Eq. 2.16 and 2.17.

$$\begin{bmatrix} x_{C_{glyc}} & x_{C_{NH_3}} & x_{C_{HSuc}} & x_{C_{HAc}} & x_{C_{pyr}} & x_{C_{CO_2}} & x_{C_X} \\ x_{C_{glyc}} & x_{N_{NH_3}} & x_{N_{HSuc}} & x_{N_{HAc}} & x_{N_{pyr}} & x_{N_{CO_2}} & x_{N_X} \\ k_{glyc} & k_{NH_3} & k_{HSuc} & k_{HAc} & k_{pyr} & k_{CO_2} & k_X \end{bmatrix} \cdot \begin{bmatrix} -1 \\ Y_{SN} \\ Y_{SHSuc} \\ Y_{SHAc} \\ Y_{Spyr} \\ Y_{SC} \\ Y_{SX} \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix} \tag{2.16}$$

$$\begin{bmatrix} 1 & 0 & 1 & 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0.25 \\ 4.67 & 0 & 6.00 & 3.50 & 2 & 0 & 4.20 \end{bmatrix} \cdot \begin{bmatrix} -1 \\ Y_{SN} \\ 0.544 \\ 0.064 \\ 0.009 \\ Y_{SC} \\ 0.066 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix} \tag{2.17}$$

By solving the closed set of equations (Eq. 2.17), the result is that $Y_{SN} = 0.0132$ mol NH_3 per C-mol of glycerol consumed. From the degree of reduction balance exemplified in Eq. 2.18, Y_{SO} is also identified as follows.

$$-4.67 + 3.50 \times Y_{SHSuc} + 4.00 \times Y_{SAc} + 3.33 \times Y_{Spyr} + 4.20 \times Y_{SX} = 0 \tag{2.18}$$

The left-hand side of Eq. 2.18 is different from zero and equal to -2.20. Consequently, an electron donor has to be provided in order to have a closed degree of reduction balance. In reality, the glycerol fermentation here described is performed under microaerobic conditions [122]. Therefore, the electron donor is O_2 and its molar coefficient is, $Y_{SO} = 0.55$ mol O_2 per C-mol of glycerol substrate. Finally, the complete confirmed stoichiometry is shown in Eq. 2.19.

$$\begin{aligned} &- CH_{8/3}O - 0.0132NH_3 - 0.55O_2 + 0.544CH_{3/2} + 0.064CH_2O \\ &+ 0.009CH_{4/3} + 0.303CO_2 + 0.066CH_{1.8}O_{0.5}N_{0.25} = 0 \end{aligned} \tag{2.19}$$

The fermentation stoichiometry of the system is now fully determined and it is considered to be consistent and accurate. For the five remaining products, the same algorithm was followed and the results are presented in Table A.1, Appendix A.

Calculation of mass and energy balances

By knowing the full stoichiometry for the bio-reactions occurring in each of the pathways, the next stage was to verify the data collected (or estimated). As a result, the inventory regarding the fluxes of mass were found. Following the guidance provided in this step, the database consisting of the required process steps that compose the pathways in the superstructure, and the related coefficients are represented/reported in Table A.1.

2.3.3 Step 3: Life cycle impact assessment (LCIA)

The ReCiPe impact assessment method [127] was selected in accordance with the internationally accepted ISO 14000 standard. The deterministic categories of impact (S_c) are calculated, using the completed inventory data from the previous section, and following Eq. 2.18. The categories of impact are depicted in Figure 2.10.

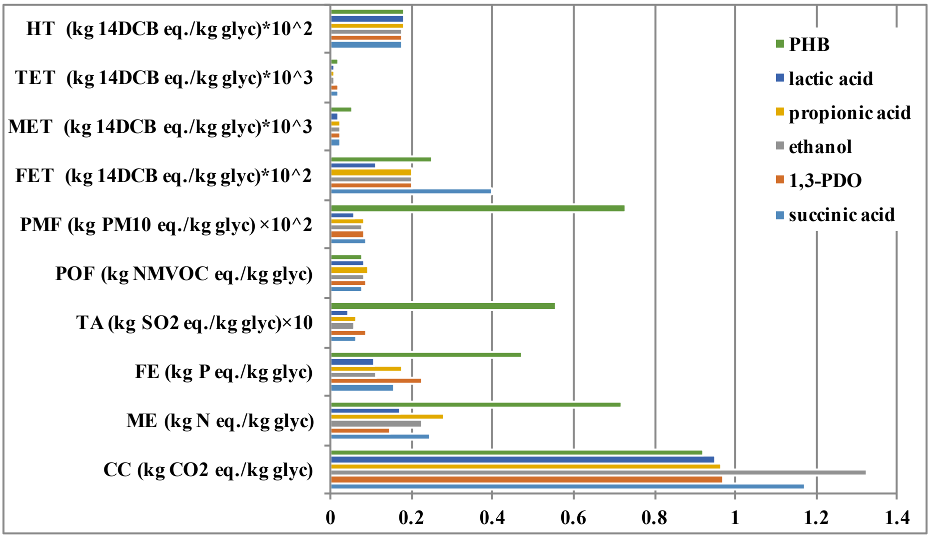

Figure 2.10: Deterministic midpoint categories of impact for the alternatives being tested per kg of glycerol.

The results have been validated based on a brief literature review. However, the results are discussed based only on three products and their corresponding Climate Change category of impact (CC). This is due to the following reasons: (i) the lack of environmental studies, to the best of our knowledge, on the glycerol valorization to value-added products; and, (ii) substantial differences in methodological choices and scope/background information of the available analyses (such as feedstock, energy types, downstream processing, etc.). Therefore, bio-based lactic acid, propionic acid and 1,3-Propanediol, are used as benchmark. It is important to note that, while in Figure 2.10, the categories of impact are reported per kg of glycerol, for comparison purposes, the CC values are now discussed and compared in terms of kg of CO_2 eq. per kg of product being produced as follows. The CC value for the lactic acid production obtained in this work (1.90 kg CO_2 eq./

kg lactic acid) is located in the range of values reported per kg of bio-based lactic acid stated in other studies for the same boundary conditions (1.80 and 1.94 kg CO_2 eq./kg in [128] and [129], respectively).In the case of the production of propionic acid, the value obtained in this study (2.84 kg CO_2 eq./ kg propionic acid) is located in the range of values being reported by Tufvesson and colleagues [130] (3.8 kg CO_2 eq./ kg propionic acid), considering approximately the same set of boundary conditions. Likewise, according to [131], the production of bio-based 1,3-propanediol leads to a reduction of emissions by 56% when compared to its petroleum based counterpart. The petro-based reference value is approximately 9.5 CO_2 eq./kg 1,3-PDO [132]. Therefore, the value obtained in this work (3.3 kg CO2 eq./kg 1,3-PDO) reports a difference of approximately 20% to the above-mentioned reference for bio-based 1,3-propanediol (4 CO_2 eq./kg 1,3-PDO). As also previously mentioned, due to different methodological choices and scope, differences in the obtained *CC* values were to be expected [133], [134].

2.3.4 Step 4: Monte Carlo technique: dealing with parameter uncertainty

After the mass and energy fluxes are collected, verified and inventoried, and following the estimation of the deterministic categories of impact, the next step is the first stage of the Monte Carlo method. For the identification of possible sources of uncertainty one starts by gathering the characterization factor (*CFs*) values. In this work, the nominal values of the characterization factors were retrieved from an open-source database (ReCiPe[127]). The upper and lower bound of the uniform distribution are established on the basis of the extent of variability reported across different databases; thus the expert review was used, and a low (25%), medium (50%) or high (75%) level of variation around the nominal values is assigned [115]. The same procedure is performed for all input components in the system within the defined boundaries. The next step is the sampling from the input uncertainty domain using Latin Hypercube Sampling. As a result, N=200 random estimates of each CF_i are created (p=*38*). A brief sample of the *CFs* for flux classification for some of the components in the system (input uncertainties) is shown in Table 2.3. It provides an example of (i) the characterization factors collected for two distinct products (methanol and ammonia) and for the respective categories of impact; and, (ii) the minimum and maximum values obtained after sampling using Latin Hypercube Sampling having three classes of uncertainty and the collected (nominal) values as the input uncertainty domain.

Table 2.3: Characterization factors: mean value collected from the reference database, minimum and maximum value according to uniform distribution and class 1, 2 and 3 uncertainty, respectively from left to right (see full table in Appendix A).

		Uniform distribution, class 1 uncertainty (µ±0.25)			Uniform distribution, class 2 uncertainty (µ±0.50)			Uniform distribution, class 3 uncertainty (µ±0.75)		
	Mean	**Min**	**Max**	**Std.**	**Min**	**Max**	**Std.**	**Min**	**Max**	**Std.**
Methanol EcotA	8.37E-04	6.28E-04	1.05E-03	2.09E-04	4.19E-04	1.26E-03	4.19E-04	2.09E-04	1.46E-03	6.28E-04
Methanol EcotT	6.08E-04	4.56E-04	7.60E-04	1.52E-04	3.04E-04	9.13E-04	3.04E-04	1.52E-04	1.06E-03	4.56E-04
Methanol HTP	1.17E-02	8.80E-03	1.47E-02	2.93E-03	5.87E-03	1.76E-02	5.87E-03	2.93E-03	2.05E-02	8.80E-03
Methanol POP	2.36E-01	1.77E-01	2.95E-01	5.90E-02	1.18E-01	3.54E-01	1.18E-01	5.90E-02	4.13E-01	1.77E-01
Ammonia AP	2.45	1.84	3.06	6.12E-01	1.23	3.68	1.23	6.13E-01	4.29	1.84
Ammonia EP	9.20E-02	6.90E-02	1.15E-01	2.30E-02	4.60E-02	1.38E-01	4.60E-02	2.30E-02	1.61E-01	6.90E-02

The output of this step is the domain definition of input uncertainty which is composed of an $N \times M$ space, where M refers to the $CF_{i,c}$ representing the total number of compounds (products, intermediates, raw material, etc.) in the system (from which sampling will be done). In the next step, by applying Eq. 2.8, the fluxes (F_i) are multiplied to each one of the 200 samples, for the c impact categories considered. Consequently, for a certain potential environmental impact category c, an empirical cumulative distribution function (CDF) was built, which will be used in the next stage of the methodology.

2.3.5 Step 5: Ranking and identification of best potential alternative

2.3.5.1 Theoretical minimum and maximum quantification

Several midpoint categories are analyzed through the probabilistic interpretation framework, providing a robust tool to evaluate and compare the environmental performance of the alternatives. As mentioned before, as part of the Monte Carlo method, and after estimating the S_c for each one of the samples, a CDF can be built for every impact category. The CDF of the model outputs is obtained by revising equation Eq. 2.8, where CF_i represents the sample space N instead of nominal values. As shown in Figure 5, $S@5_{class1}$ and $S@95_{class3}$, quantify the thresholds for best and worst case scenario, by quantifying the theoretical minimum ($T_{min,c}$) and maximum ($T_{max,c}$) across all the products, respectively. As an example, in Table 2.4 the CC and HT for the succinic acid production are compared under deterministic and uncertainty conditions (best and worst case scenarios). Where ($T_{max,c}$) and ($T_{min,c}$) represent the theoretical maximum and minimum of a certain category of impact across all alternatives in the design space, $Det_{c,p}$ and $S_{max,c,p}$ stand for the deterministic value and the maximum value obtained through the CDF for a certain category c and for a given product p, respectively. Lastly, $\frac{|Det_{c,p}-S_{max,c,p}|}{T_{max,c}-T_{min,c}}$ represents the normalized 'distance' for each category of impact c and for a given product p.

Table 2.4: CC and HT are compared under deterministic and uncertainty conditions (best and worst case scenarios) for the succinic acid production.

	CC (kg CO_2 eq./ kg of glyc)	**HT** (kg 14DCB eq./ kg of glyc)
$Det_{c,p}$	1.17	$1.76 \cdot 10^{-3}$
$S_{max,c,p}$	1.96	$2.90 \cdot 10^{-3}$
$T_{max,c}$	2.21	$2.94 \cdot 10^{-3}$
$T_{min,c}$	0.71	$1.35 \cdot 10^{-3}$
$\frac{\mid Det_{c,p} - S_{max,c,p} \mid}{T_{max,c} - T_{min,c}}$	0.18	0.72

2.3.6 Comparison of alternatives

As mentioned before, the goal is to be able to robustly rank and identify the potentially best environmentally sustainable alternative(s) to add value to the glycerol side stream.

Therefore, in this step, the alternatives' performance is quantified and analyzed by following the algorithm proposed in Figure 2.5, for each alternative and for each category of impact until there are no more categories to analyze. The difference ('distance') between the category's deterministic value obtained in Step 3.2 and the theoretical maximum established in Step 5.1. is estimated based on Eq.2.12. The normalized 'distances' were estimated for each category of impact c and for a given product p. As an example, in the last row of Table 2.4, the normalized 'distances' are presented for the CC and HT regarding the production of succinic acid. The same calculation was performed for the remaining categories and for all products in the database. The results are summarized in Table 2.5. The single indicator (SI) estimated based upon Eq. 2.13 leads to the ranking of the alternatives. The production of lactic acid stands out as the best potential environmentally sustainable option within the design space since it has the lowest SI under uncertainty (Table 2.5).

Table 2.5: Ranking of alternatives based on the SI under uncertainty

product	**Succinic acid**	**1,3-PDO**	**Propionic acid**	**Lactic acid**	**PHB**	**Ethanol**
$SI = \sum_{cc} \frac{\mid Det_{c,p} - S_{max,c,p} \mid}{T_{max,c} - T_{min,c}}$	3.00	3.65	2.75	2.77	2.47	4.97
ranking	4	5	3	1	6	2

Furthermore, a comparison was drawn between the SI ranking under uncertainty here proposed and the SI estimated with the deterministic categories values. To that purpose, three reference normalization and weighting systems for analysis of midpoint (EDIP97, EU-15 and equal contribution) presented in [112] were applied on the deterministic values obtained for all categories for all alternatives in the design space and the SI was estimated. Therefore, as presented in Figure 2.11, a deterministic ranking was obtained for each one of the weighting systems used. It is noteworthy that the ranking of alternatives based upon deterministic single score is highly dependent on the respective weighting system. However, by following the methodology proposed here, and further applying the three above-mentioned weighting systems, it was found that, in this case, the ranking of alternatives under uncertainty conditions is robust ('this work' in Figure 2.11). This is due to the fact that the approach in this work uses the accuracy of the estimation of the respective impact categories. Where the lower the 'distance' to the theoretical maximum implies that the deterministic estimate is more trustworthy, and automatically attributes higher weight to that same category. Therefore, this statistical approach ensures consistency and robustness.

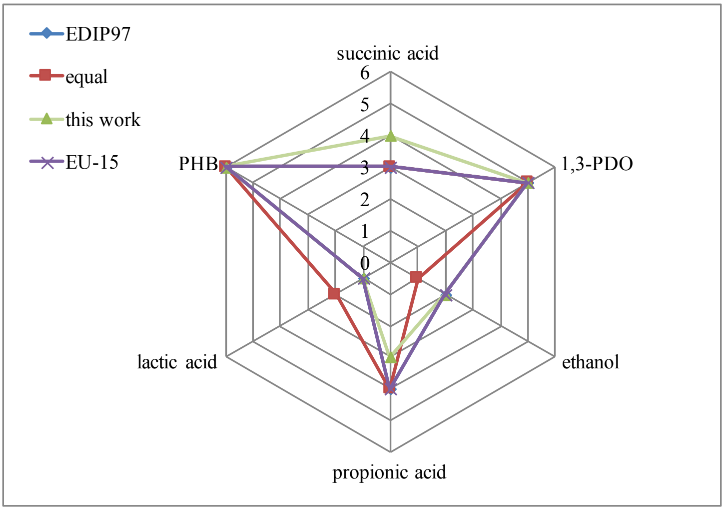

Figure 2.11: Ranking of alternatives by weighting system selected. 'this work' represents the consistent ranking of alternatives across the four weighting systems

2.4 Conclusions

A methodology for environmental evaluation under uncertainty was proposed aiming at ranking the alternatives within the design space and selecting/identifying the best potential processing network at the early stage of design. To achieve this, the methodology features the following: (i) a bioprocess validation algorithm, aiming at consistent bioprocess stoichiometry so that mass fluxes can be accurately calculated, reducing uncertainty in the LCI; (ii) identification and quantification of parameter uncertainties in particular focusing on the characterization factors for calculation of potential impact categories by applying the Monte Carlo technique; (iii) establishment of sound quantitative thresholds for alternatives comparison by incorporating a probabilistic interpretation; and lastly, (iv) ranking of the alternatives within the design space for identifying the potentially best environmentally sustainable alternative. The glycerol-based biorefinery concepts are found to be critically affected by uncertainties in the environmental assessment, and thus not considering uncertainty (uncertainty at the inventory stage and characterization factors) would lead to unreliable results. Following the methodology, lactic acid ranked best among the alternatives in the design space from the environmental sustainability point of view. Additionally, it is important to note that, through the application of the methodology, it was observed that the ranking obtained under uncertainty conditions is consistent and robust across different weighting systems, which is highlighted as an important contribution of this work. It is a significant contribution since it provides the decision-maker with the best potential alternative among the set of options and under a given degree of information accuracy (or uncertainty). In this way, uncertainty analysis can be used as a tool for robust and reliable estimation of the theoretical maximum and the ranking of alternatives towards more robust and environmentally friendly solutions. In short, the proposed methodology extended the state-of the-art by providing a customized approach that targets to achieve more robust analysis at the conceptual stage of bioprocess development by considering uncertainties in decision-making to support generation of environmentally sustainable solutions. Uncertainty analysis enabled a more detailed interpretation of results, then improving the transparency and robustness of the reached conclusions. However, further identification of additional sources of uncertainty needs to be acknowledged, quantified and characterized in order to provide robust results and sound alternatives.

CHAPTER 3

Economic risk assessment of early-stage designs for glycerol valorization

In this chapter, a systematic methodology is proposed to critically assess and screen among early stage design alternatives for glycerol conversion. Through deterministic sensitivity analysis it was found that variations in the product and feedstock prices, total production cost, fixed capital investment as well as discount rate, among others, have high impact on the project's profitability analysis. Therefore, the profitability was tested under uncertainties by using NPV and MSP as economic metrics. The robust ranking of solutions is presented with respect to minimizing the economic risk of the project being non-profitable (failure to achieve a positive NPV times the consequential profit loss). In Figure 3.1, a graphic description of this chapter is presented.

This chapter of the thesis is based upon the following article:

Economic Risk Assessment of Early Stage Designs for Glycerol Valorization in Biorefinery Concepts. L. Gargalo, C., Cheali, P., Posada, J.A., Gernaey, K. V. Sin, G *Industrial & Engineering Chemistry Research*, vol 55, no. 24, pp. 6801–6814. (2016)

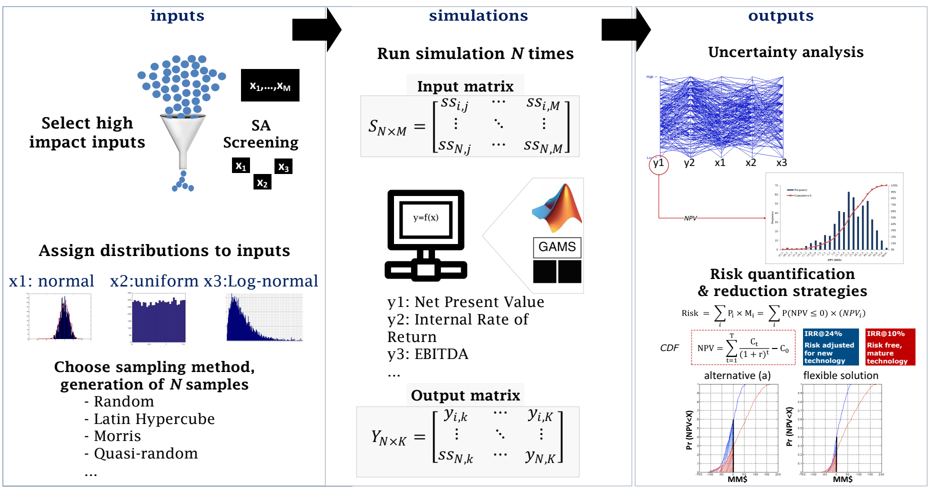

Figure 3.1: Graphic description of chapter 3.

Nomenclature

NPV	Net Present Value
C_t	Net cash inflow during the lifetime of the plant
C_0	Total initial investment costs
r	Discount rate (internal Rate of Return, IRR) (%)
FCI	Fixed capital investment
DCFR	Discounted cash-flow rate of return
LHS	Latin Hypercube Sampling
MSP	Minimum selling price
X_i	Input model variables
Y_k	Economic metrics
NPV_0	NPV at base case conditions
MSP_0	MSP at base case conditions
DSA	Deterministic Sensitivity Analysis
S_{NxM}	Matrix of samples generated through LHS from the uncertain domain
Y_{NxK}	Matrix of model outputs obtained through deterministic optimization
Pr_i	Probability of uncertain realization
M_i	Magnitude of loss in case of uncertain event realization
Std.	Standard deviation
DSP	Downstream processing
n	Exponent used in the seven-tenths rule
CEPCI	Chemical Engineering's Plant Cost Index
TPC	Total annual production cost
MACRS	Modified Accelerated Cost Recovery System
NPV@10	NPV estimated at dicount rate of 10%
NPV@24	NPV estimated at discount rate of 24%
MSP@10	MSP estimated at discount rate of 10%
MSP@24	MSP estimated at discount rate of 24%
P_i	Price of raw materials i, $i \in I_{rm}$
P_p	Price of products $i \in I_p$
P_{wd}	Price of waste disposal
$P_{i,ut}$	Price of utilities
$P_{i,rm}$	Price of raw materials
MACRS	Modified Accelerated Cost Recovery System

Indices

i	component i
k	utilities k

Sets

I	Total number of components i
K	Process technologies k
I_{ut}	Total components composing utilities
I_{rm}	Total components that are raw materials

Chemicals	
H_2	Hydrogen
1,3-PDO	1,3-propanediol
1,2-PDO	1,2-propanediol
PHB	Poly-3-hydroxybutyrate
HLac	Lactic acid
HSuc	Succinic acid
Prop	Propionic acid

3.1 Introduction

Earlier studies in our group have developed a systematic and robust methodology that aims to assist the user to manage the complexity of input data and their intrinsic uncertainties [17]. In this chapter, the methodology is extended by (i) identifying the sources of uncertainty which affect the economic performance the most using deterministic sensitivity analysis; (ii) proactively incorporating uncertainties through stochastic optimization and scenario-based analysis; (iii) quantitative and qualitative analysis of economic metrics; (iv) quantifying the risk of potential profit loss for the top-ranked alternatives taking into account time value of money; and, finally (v) exploring the implementation of flexible concepts as reduction strategy for the minimization of future risk. The study aims ultimately at providing a robust assessment and decision-making tool for the identification of optimal biorefinery concepts at the screening phase, under uncertainties with regards to technical and economic criteria. This systematic approach is applied to a significant case study focusing on value added products from glycerol.

As above-mentioned, in this study the aim is to identify and rank possible glycerol valorization concepts with regards to their economic performance, intending to implement such valorization concepts into the biodiesel plants as an add-on. This chapter is organized as follows: (i) the superstructure formulation and data collection (database) for the glycerol biorefinery and the economic model for the assessment are presented in the Materials and Methods section, followed by (iii) the Results section and (iv) Conclusions.

3.2 Materials & Methods

3.2.1 Glycerol-based value-added products

As having a comprehensive database is by itself very valuable, the database developed in Chapter 2 has been extended to include one additional biochemical pathway and chemical pathways for the conversion of glycerol (see Appendix B, Table B.1). The products added are: 1,2-propanediol, isobutanol, acrolein, H_2 and n-butanol. The main traits of the relevant processing technologies compiled from literature are summarized in Table 3.2. Additionally, the corresponding superstructure representing the glycerol-based biorefinery concepts was formulated (please see Appendix B, Figure B.1).

An extensive literature review has been done, gathering, to the best of my knowledge, the most significant contributions for the current set of products. Several building blocks for a wide range of applications (various bulk and niche chemicals) are included in the product portfolio. As an example: (i) poly-3-hydroxybutyrate (PHB), lactic acid and 1,3-propanediol, which are polymers building blocks for bio-polyesters, polylactic acid (PLA), polyethers, polyurethanes and plastics; and (ii) succinic acid, which can be used as food additive (natural flavor), excipient in pharmaceutical products (to control acidity) and also as a precursor of polyesters and thermoplastics (polybutylene terephthalate, PBT).

Important to note is, that the current product portfolio composing the database was selected based on the following criteria: (i) important reports on bio-based chemicals, such as the references [135], [9], [136], [137] where the main bio-based chemicals (value-added products) that could be co-produced with bio-energy/biofuel in integrated biorefineries are reported, in this case specifically checking for the chemicals that can be potentially obtained from glycerol; and furthrmore (ii) cross-checking this information with the availability and completeness of information for techno-economic assessment (given by previous studies and process simulations with sufficient detail).

Table 3.2: Glycerol-based biorefinery concepts investigated

Product	**Conversion technology & downstream processing**	**Production rate (ton/y)**	**Yield**	**Data sources**
Succinic acid	Glycerol fermentation by an engineered strain of *B. succinicis producens DD1* + reactive extraction w/ TOA and 1-octanol	10200	1.02 g/g glyc (0.80 mol/mol)	[106], [138]
1,3-Propanediol	Glycerol fermentation by an engineered strain of *K. pneumoniae* + reactive extraction w/ isobutyraldehyde	5500	0.55 g/g glyc (0.67 mol/mol)	[139], [140]
Propionic acid	Glycerol fermentation by an engineered strain of *P. acidopropionoci ACK-Tet* + reactive extraction w/ TO and ethylacetate	6796	0.68 g/g glyc (0.844 mol/mol)	[123]
PHB	Glycerol fermentation by an engineered strain of *C. necator* + blending w/ surfactant solution + hypochlorite digestion centrifugation + spray drying	3600	0.36 g/g glyc	[141]
1,2-Propanediol	Sequential processes of dehydrogenation-hydrogenation via hydroxyacetone	7740	0.744 g/g glyc	[142], [143]
Lactic acid	Glycerol fermentation by an engineered strain of *E.coli* + reactive extraction w/ TOA and DCE	7931	0.79 g/g glyc (0.81 mol/mol)	[121]
Isobutanol	Chemical conversion of glycerol to propanal via acrolein + methanol conversion to methanal + methanal and propanal condensed to methacrolein + hydrogentation of methacrolein to isobutanol	7300	0.73 g/g glyc	[144], [145]
H_2	Steam reforming of glycerol for hydrogen production over Ni/SiO_2 catalyst	659	0.07 g/g glyc	[144], [145]
n-Butanol	Glycerol anaerobic fermentation by an engineered strain of *C. pasteurianum* + vacuum stripping	3000	0.30 g/g glyc (0.37 mol/mol)	[106], [146], [147]
Ethanol	Glycerol fermentation by an engineered strain of *E.coli* + dehydration	5211	0.52 g/g glyc (1.02 mol/mol)	[117], [147]
Acrolein	Glycerol dehydration	4870	0.486 g/g glyc (0.80 mol/mol)	[148]

3.2.2 Techno-economic analysis: methods and assumptions

In order to make an investment decision, the foreseen profit from an investment must be evaluated relative to a quantitative measurement of profit with respect to the investment necessary to generate that profit. In this chapter, for the project evaluation, the economic model used is the discounted cash-flow rate of return (DCFR). This model is used to estimate the attractiveness of an investment. It uses future cash flow predictions and discounts them to get a present value estimate, which is then used to analyze the potential for investment. Therefore, it considers the time value of money, i.e., the DCFR takes into consideration that money to be received or paid at some time in the future is viewed as having less value than an equal amount received or paid today. Because the goal of investing is to increase the shareholder's wealth, an investment is worth undertaking if it creates value, and the investment creates value if it creates more value than it costs, considering the time value of money (discounted cash in- and out-flows). Therefore, a process to be economically viable/acceptable has to present a NPV higher than zero (at which point it breaks even, value created is equal to costs), which means that it is expected to generate more revenue than could be obtained by gaining the discount rate, representing the time value of money which is the amount that could be obtained by investing in other alternatives [149],[150]. Capturing the time dependency of cash-flows during the project is very important to investors firstly because not all the money has to be financed immediately, and secondly because the sooner the capital is repaid to the investors, the sooner it can be used to fund another investment [150]. This model is defined to be the interest rate at which all cash flows must be discounted in order for the net present value of the project to be equal to zero (breakeven). Therefore, it is based on the calculation of the net present value by setting a discount rate r, which is the interest rate that represents the minimum rate of return that the company is willing to accept for a new investment. The model also enables the calculation of minimum selling price to comprehensively assess and compare the process alternatives (Eqs. 3.1 to 3.8). Noteworthy is that this method is recommended when significant uncertainties are present and therefore risk is a challenge [151]. A brief description of the assumptions for the economic model is presented in the supplementary materials (Appendix B, section B.2) and a summary is presented in Table 3.3.

$$
\begin{aligned}
&NPV = \sum_{t}^{T} \frac{C_t}{(1+r)^t} - C_0 \\
&t = 1, ..., T \\
&C_t = \text{net cash inflow during the lifetime of the plant} \\
&C_0 = \text{total initial investment costs}
\end{aligned}
\tag{3.1}
$$

$$NPV = \text{Annual present value} - \textstyle\sum_{t=-2}^{T}(\text{Annual Fixed Investment Cost}) \tag{3.2}$$

$$\text{Annual present value (net present revenue)} = \textstyle\sum_{t=1}^{T}(\text{annual cash inflow} \times \dfrac{1}{(1+r)^t} \tag{3.3}$$
$$\dfrac{1}{(1+r)^t} = \text{discount factor}$$

$$\begin{aligned} &\text{annual cash inflow (net revenue)} = \text{total annual sales} \\ &-\text{total production cost} - \text{income tax} - \text{loan payment} \\ &= x_p \times P_p - \text{total production cost} - \text{income tax} - \text{loan payment} \end{aligned} \tag{3.4}$$

$$\text{total annual sales} = \text{production rate}_i(\text{ton/year}) \times \text{market price}_i(\$/\text{ton}) = \textstyle\sum_p x_p \times P_p \tag{3.5}$$

$$\text{total annual production cost} = \text{ variable operating costs} + \text{fixed operating costs} \tag{3.6}$$

$$\begin{aligned} &\text{variable operating costs (\$/year)} = \text{raw materials}_{i,rm}(\text{ton/year}) \times \text{market price}_{i,rm}(\$/\text{ton}) \\ &+\text{utilities}_{i,ut}(\text{ton/year}) \times \text{market price}_{i,ut}(\$/\text{ton}) + \text{waste disposal (ton/year)} \times \text{price (\$/ton)} \\ &+\text{repairs (\$/ton)} + \text{operating supplies (\$/year)} + \text{royalities (\$/year)} \\ &\text{variable operating costs (\$/year)} = \\ &\sum_k^K \sum_i^{I_{rm}} \phi_{i,k} \times P_{i_{rm}} + \sum_k^K \sum_i^{I_{ut}} R_{i_{ut},k} \times P_{i_{ut}} + \sum_k^K \sum_{i_w}^{I_w} x_{i_w,k} \times P_{wd} \\ &+\text{repairs (\$/ton)} + \text{operating supplies (\$/year)} + \text{royalities (\$/year)} \\ &k = 1, ..., K(\text{total number of technologies}) \\ &i_{ut} = 1, ..., I_{rm}(\text{total number of utilities}) \\ &i_{rm} = 1, ..., I_{ut}(\text{total number of raw materials}) \\ &i_w = 1, ..., I_w(\text{total number of wastes}) \\ &\text{for the factorial methodology see Appendix B, Table B.3} \end{aligned} \tag{3.7}$$

$$\begin{aligned} &\text{fixed operating costs} = \text{labor (operators} \times \text{ annual salary)} + \text{maintenance} \\ &+\text{property insurance and tax} \end{aligned} \tag{3.8}$$

Table 3.3: Summary of the assumptions used for the discounted cash-flow rate of return [149], [152], [153]

Parameter	**Assumption**
Plant life (years)	20
Discount Rate (m_{ar})	10%
Depreciation Period (Years)	10 (MACRS system)
Equity	40%
Interest	5%
Loan Term (Years)	10
Construction Period (Years)	2
% Spent in Year -1	60%
% Spent in Year 0	40%
Start-up Time (Years)	0.50
Product production/ Feedstock use (% of Normal)	50%
Variable Costs (% of Normal)	75%
Fixed Cost (% of Normal)	100%
Income Tax Rate	35%
Cost Year for Analysis	2014

3.3 Methodology

A comprehensive economic assessment is performed to characterize the uncertainty and incorporate it in the economic metrics for project evaluation. The economic assessment follows the algorithm in Table 3.4 below which includes the following: Step (1) - relevant economic metrics for the analysis are defined as well as the required input for the economic model; Step (2) - the output from step 1 is used to perform a deterministic analysis of economic metrics for each alternative; Step (3) - sensitivity analysis is applied to the results obtained in step 2 which provides a ranking of input data regarding their impact on the model; Step (4a) - using the most important parameters identified in step 3, an uncertainty analysis is performed on the economic metrics by first performing a Latin Hypercube Sampling (LHS) of the input uncertainty domain; Step (4b) - the optimization problem is solved for each LH sample, leading to the uncertainty mapping and analysis of solutions; Step (5A) - based on the uncertainty mapping, the top three product candidates are selected for further economic risk analysis; and, at last in Step (5B) risk mitigation strategies are proposed and evaluated. The application of these steps is further detailed and analyzed in the results section below.

Table 3.4: Algorithm for economic assessment under uncertainty.

Algorithm	Economic assessment under uncertainty
Step 1	Identify economic metrics (Y_k) and input model variables (X_i) $\Rightarrow X_i = \{x_1, x_2, ..., x_M\}$ $Y_k = \{y_1, y_2, ..., y_K\} = \{NPV, MSP, ...\}$
Step 2	Initialize model f $\rightarrow$deterministic solution (base case) $\Rightarrow Y_0 = \{NPV_0, MSP_0, ...\}$
Step 3	Sensitivity analysis of deterministic model: Identify model variables subject to uncertainty that have the highest impact on the model (θ_j) $\Rightarrow DSA = \frac{dy}{dx_1}, \frac{dy}{dx_2}, ..., \frac{dy}{dx_M}, \uparrow \frac{dy}{dx} \uparrow$impact of x $\in X$
Step 4A	Characterize θ_j by assigning probability distribution functions + generation of N samples with Latin Hypercube Sampling from the uncertainty domain of $\theta_M \Rightarrow S_{N,M} = \begin{bmatrix} ss_{i,j} & \dots & ss_{i,M} \\ \vdots & \ddots & \vdots \\ ss_{N,j} & \dots & ss_{N,M} \end{bmatrix}$
Step 4B	Deterministic optimization problem solved for each scenario $ss_{i,j}$ ($max f(x,y)$) $\rightarrow$Mapping and analysis of solutions (see Appendix B, section B.3) $\Rightarrow Z_{N,K} = \begin{bmatrix} y_{i,k} & \dots & y_{i,K} \\ \vdots & \ddots & \vdots \\ y_{N,k} & \dots & y_{N,K} \end{bmatrix}$
Step 5A	Risk-based economic analysis $\Rightarrow$Risk $= \sum_i P_i \times M_i = \sum_i P(NPV \leq 0) \times (NPV_i)$
Step 5B	Risk mitigation strategies $\Rightarrow$flexible multi-product network under uncertainty

3.4 Results

Step 1: Identify economic model and input model variables

As presented in Table 3.4, Step 1, instructs to select the economic model and metrics that the projects will be evaluated on, and they are referred to as Y_k, so as to identify the input variables to the model (X_i). As mentioned above, the economic model used in this work is the discounted cash-flow rate of return (DCFR). For the calculation of NPV, the question is which interest rate (represented by r in Eq. 3.1) is to be used to discount the cash-flows. This interest rate is usually set by the investors or management department and it represents the minimum rate of return that the company is willing to accept for a new investment, reflecting the company's adjustment to risk (more details in Appendix B). On the other hand, the user can also estimate the internal rate of return (IRR, which corresponds to the discount rate when NPV is set to zero) or minimum selling price (MSP) for which the project would break even (rearranging Eq.3.1) by using the goal-seek function and setting the NPV to zero, while maintaining all the other variables constant. This analysis is performed by using the NREL excel file ($http://www.nrel.gov/extranet/biorefinery/aspenmodels$) for the discounted cash-flow rate of return calculation after adapting it with the appropriate model assumptions for the present case study (see Table 3.3). To this end, the assumptions described in Table 3.3 together with the mean value of the remaining input variables are used to establish the base case (for the mean raw material cost and product selling price, see Table 3.5).

Step 2: Deterministic solution

In this step, the model is initialized to generate the base case and to estimate the first ranking of solutions, and therefore the economic metrics are calculated for the base case scenario. The problem is formulated and solved by estimating the Net Present Value (following Eqs. 3.1 to 3.8) for each of the processing networks (alternatives) using the nominal/average market prices of product and raw material (see Table 3.5).

Table 3.5: Product prices and respective standard deviations

Parameter	**Mean 2014** ($\$/kg$)	**Std.**	**Data points** ***ref.***
Crude glycerol (60 % w/w)	0.368	0.048	[154]
Succinic acid (HSuc)	2.0 [136]	0.23	[155]
Ethanol (EtOH)	0.707	0.137	[145], [152]
n-Butanol	1.558 [155]	0.421	[156]
H_2	0.536	0.138	[157]
1,2-Propanediol (1,2PDO)	1.662 [155]	0.28	[158]
Propionic acid	1.590 [155]	0.131	[130]
Polyhydroxybutyrate (PHB)	4.5 [155], [136]	0.197	[159]
Lactic acid (HLac)	2.0 [160]	0.041	[161]
Isobutanol	1.524 [155]	0.12	[155]
1,3-Propanediol (1,3-PDO)	2.02	0.35	[155], [162]
Acrolein	2.0 [148]	0.27	[156]

The capital investment was calculated based on the factorial methodology (in Appendix B, table B.3) and by dividing the processing routes/pathways into three sections: (1) glycerol separation and purification; (2) conversion step; and, (3) downstream processing (DSP). The capital investment for section (1) was calculated, as mentioned above, based on a medium-sized biodiesel plant in Europe [163], providing approximately 10 kton glycerol/year, corresponding to 10% (w/w) of the total annual biodiesel production rate (100 kton/year). The detailed equipment list and the equipment cost in \$2003 and the updated costs for \$2014, as well as the purchased, installed capital investment and total fixed capital investment can be found in the Appendix B, Table B.5. The total purchased capital investment for section (1) is 1.61 M\$, including the utilities system (Appendix B, Table B.4). For section (2) and (3), recovery and purification of products, the capital investment was calculated by a careful and independent calculation for all the products being produced based on a literature review, scaled to the production rate set by the verified stoichiometry. Table 3.6 presents the purchased equipment costs, the data sources and the remaining parts (calculated based on the factorial methodology). The purchased equipment costs were calculated based on the product specific references (base) and adapted to appropriate capacities (plant X), the purchase costs were updated to year 2014, as shown in Eq. 10 [164], [149]. The seven-tenths rule [164] was used as exponent (in Eq. 10) for scale up/down for all equipment except for the fermenters, where an exponent of 0.75 was used [165].

$$Cost_X^{2014} = \left[Cost_{base} \times \left(\frac{Capacity_X}{Capacity_{base}} \right)^n \right] \times \frac{CEPCI_{2014}}{CEPCI_{base}} \tag{3.9}$$

Where $Cost_X^{2014}$ represents the purchased cost for plant X calculated from the $Cost_{base}$ of a similar plant with similar functionality; $CEPCI_{2014}$ and $CEPCI_{base}$ represent the *Chemical Engineering's Plant Cost Index* (see Supplementary material, Figure B3) for 2014 and for the base year (reference year for each case), respectively. For the calculation of the fixed and variable operating costs, the capital investment (FCI) needs to be estimated prior to applying the factorial methodology (as presented in Appendix B, table B.3). It is important to stress that, as this work focused on systematically screening alternatives for glycerol based bio-products and their comprehensive uncertainty analysis at an early stage design, therefore rigorous simulations of shortlisted process candidates are considered to be out of scope of this work. It would be natural, however, at a later stage of the process development life cycle to perform more detailed process simulations for process design optimization and refinement of the cost estimation. The NPV and MSP estimated based on the nominal values are shown in Table 3.6. A first ranking of alternatives can be obtained, however as only the production of lactic acid presents a positive NPV, further analysis is needed especially on the high impact variables that might be subject to high degrees of uncertainty. It is important to mention that, like ethanol, isobutanol and n-butanol, the production of H_2 in the current project's setting is not profitable. Its market price should increase at least to its MSP level (see Table 3.6) in order for the project to break even. However, special attention should be payed to H_2 due to the fact that it is not straightforwardly transported or stored. Therefore, if along with the manufacture of high value-added product(s), synergies were to be explored and these fuels were to be produced and consumed inside the running plant (fulfilling part or all of its energetic needs), it would potentially result in a profitable project.

Table 3.6: Estimation of the purchased capital cost to be used for the factorial methodology (updated to 2014 prices by using the appropriate CEPCI) and remaining needed parameters. NPV and MSP are estimated at the conditions reported in Table 3.3

	E'* (MM$) [ref.]	FCI* (MM$)	TPC* ($/kg)	Utilities* (MM$/y)	Sales (MM$/y)	Product price ($/kg)	NPV@10 (MM$)	MSP@10 ($/kg)
Succinic acid	11.217 [166]	35.221	1.625	0.956	19.4	2.00	-2.72	2.18
1,3 PDO	5.347 [162]	22.278	2.045	1.971	10.6	2.02	-28.1	2.71
Propionic acid	4.747 [130], [166]	24.817	1.369	0.474	10.3	1.59	-16.4	1.94
PHB	15.020 [167]	45.903	3.643	1.948	15.4	4.50	-26.0	5.59
1,2 PDO	4.713 [143]	16.280	1.421	2.848	12.2	1.66	-6.0	1.79
Lactic acid	4.929 [166]	26.161	1.218	0.529	15.1	2.00	11.5	1.74
Isobutanol	6.705 [144]	21.107	1.471	0.921	11.5	1.524	-22.6	1.91
H2	5.551 [168]	21.627	1.445	1.666	3.4	0.536	-75.9	1.96
n-Butanol	5.202 [169]	22.615	3.172	1.434	4.4	1.558	-66.4	4.37
Ethanol	8.227 [152], [145]	30.022	1.708	0.551	3.5	0.707	-76.6	2.59
Acrolein	4.927 [148], [170]	27.314	3.133	0.761	9.3	2.00	-79.1	4.07

*it includes the separation and purification of crude glycerol. E - Purchased capital cost; FCI - Fixed capital investment; TPC - total product cost

Step 3: Deterministic Sensitivity Analysis

The investment and cash-flows are first calculated for the baseline conditions, and then the NPV is re-estimated by changing one variable at a time over the expected range of variability. This will express how sensitive the DCFR model is to variations in the input information. Therefore, this sensitivity analysis provides an idea about the degree of risk involved in forecasting the economic performance of the project and also indicates which input data have the highest impact. As an illustrative example, the sensitivity analysis is performed on the economic indicator NPV for the 1,2-PDO production from glycerol, when subjected to the variation of the input parameters, and it is presented in Table 3.7 and illustrated in Figure 3.2).

In Figure 3.2, the data categories are ordered so that the level of effect on the economic indicators decreases from top to bottom, i.e. the economic indicators on top of these figures correspond to the parameters that have relatively higher importance in the model. Product price, feedstock price and capital investment have been previously identified as important and common sources of uncertainty on the economic performance across different biorefinery types [175], [176],[177]. The effect of economies of scale can be perceived by the fact that increasing the plant capacity 20% has less impact on the NPV than the opposite decrease by 20%. It means that the fixed capital investment has a non-linear relationship with the NPV, i.e. the higher the plant capacity the less impact has the fixed

Table 3.7: – Key economic factors under variability for sensitivity analysis of the DCFR model.

	Data sources	Lower limit % of thee baseline	Base Case (1,2-PDO)	Upper limit % of the baseline
Product price	[150]	-20%	1.662 $\$/kg$	+20%
Feedstock price	[150]	-10%	0.368 $\$/kg$	+30%
Fixed Capital Investment	[171], [88]	-20%	16.280 $MM\$$	+50%
Discount rate	[150],[172] [this work]	8%	10%	24%
Plant life time	[this work]	10 years	20 years	30 years
Loan interest	[this work]	4%	5%	8%
Construction time	[this work]	1 year	2 years	3 years
Income tax rate	[173]	-20%	35%	+20%
Total Annual Production Cost (TPC)	[174] [this work]	-20%	1.421 $\$/kg$	+20%
Plant Capacity	[this work]	-20%	7740	+20%

capital investment on the NPV. The same effect is observed with the relationship total annual production cost *vs.* NPV.

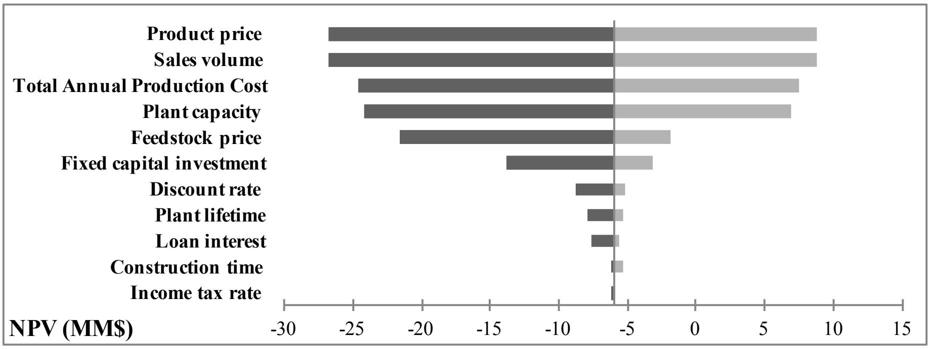

Figure 3.2: Sensitivity analysis of NPV to variations in key economic parameters for the production of 1,2-PDO. Dark grey represents a negative impact on the NPV and light grey represents a positive impact on the NPV

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In order to further investigate the yearly impact of the discount rate on the economic model, a complementary scenario analysis is presented in Figure 3.3. The figure shows the cumulative discounted cash-flows using the deterministic model varying only the discount rate (from 10% to 24%). The Figure 3.3 shows the discounted cash flow diagram generated using the deterministic model based on the 10 year Modified Accelerated Cost Recovery System (MACRS) depreciation method (see Table 3.3, and more details in Appendix B). The blue line represents the DCFR for a discount rate of 10% corresponding to a low risk project; and the red line represents the DCFR for a 24% discount rate, corresponding to a medium/high risk project (see Table 3.8). By analyzing Figure 3.3, one can see that at the 10 years' mark (depreciation period) the project at both discount rates starts to be profitable (NPV>0), however, at 24% the profit is barely visible since the investors set such a high rate of return to adjust for the possible risk the investment faces. The impact of the selected discount rate on the economic performance can be further analyzed by estimating the product minimum selling price (MSP) obtained by setting NPV to zero, for a constant discount rate. For example, the MSP for the 1,2-propanediol production at the conservative discount rate of 24% is 2.05 \$/kg, whereas for a discount rate of 10%, the MSP of 1,2-PDO is 1.79 \$/kg.

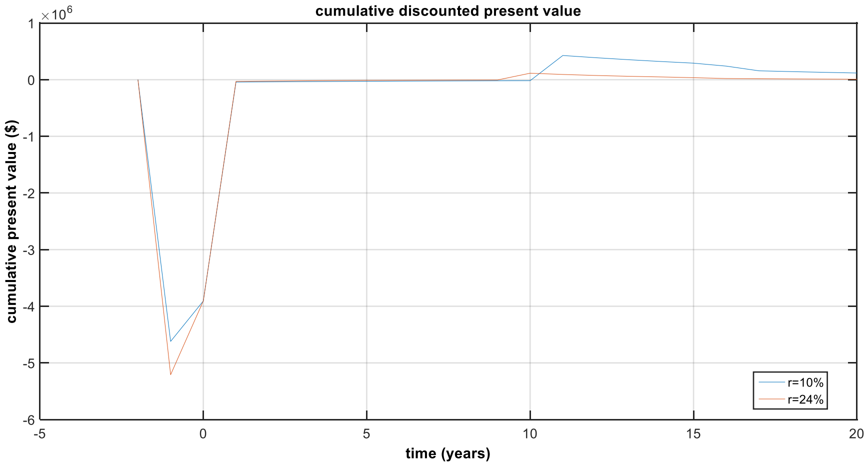

Figure 3.3: Cumulative discounted cash flow for 1,2-PDO production. Baseline assumptions + varying the internal rate of return for the investment: the red line represents 24% discount rate and the blue line represents 10% discount rate

Table 3.8: Suggested discount rate according to levels of risk per type of investment. Adapted from [149]

type of investment	**Risk level**	**r** (%/*year*)
Basis - safe corporate investment	Safe	4 – 8
New capacity for established corporate market position	Low	8 – 16
New product entering into established market, or new process technology	Medium	16 – 24
New product or process in a new application	High	24 – 32
Everything new, high R&D and market effort	Very high	32 – 48+

Step 4A: Uncertainty characterization and sampling from input uncertainty domain

Several sources of uncertainty on the economic model predictions were pointed out through deterministic sensitivity analysis as having high impact on the model predictions in Step 3. Therefore, the scenario considered for further analysis was built on (i) historical data on the raw materials and product market prices described through appropriate probability distribution functions; and, (ii) considering variability of the fixed capital investment over its typical range of variation (represented by a uniform distribution varying between -20 to +50%). There are several methods to get price forecasts, such as the ones discussed in [150], however obtaining consistent price information is a continuous challenge in this field/community, since companies cannot provide prices. Therefore, in this study, historical price data is chosen to define a scenario in which future price forecasts are sampled from historical price distributions. The historical trends of the products under consideration have been surveyed over the past 10 years and have been used to construct the historical price distributions for each product (Table 3.5). An example of the historical data price collection and their fitting through distribution functions, is presented in Figure 3.4, for the prices of crude glycerol and 1,2-PDO. The same procedure was performed for the remaining 10 products being considered here.

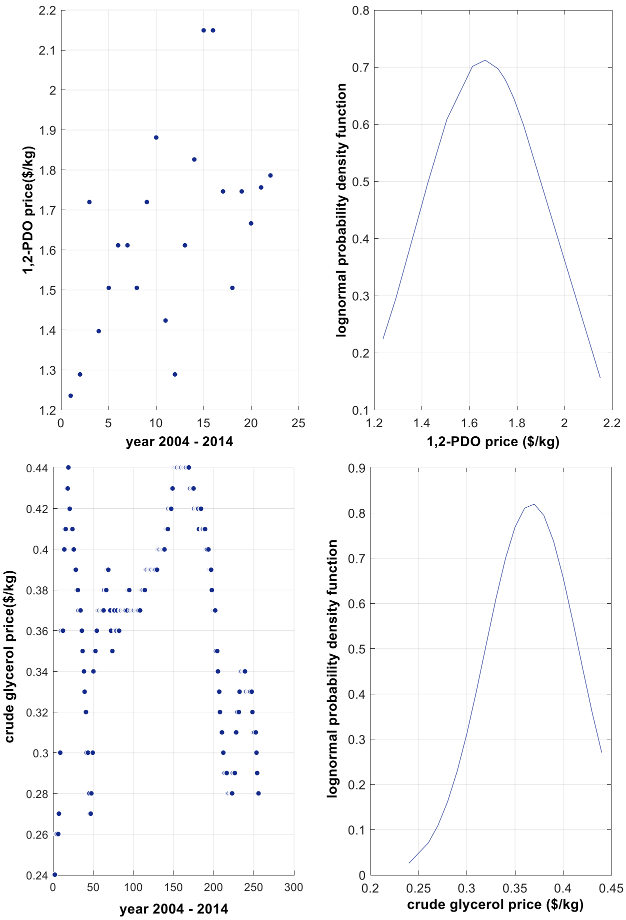

Figure 3.4: Historical price data collection (left) and their fitting through normal probability distribution functions (right). The 1^{st} and 2^{nd} row correspond to 1,2-PDO and glycerol, respectively. [178], [155], [154]

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Through Latin hypercube sampling with correlation structure/control [113] (see Appendix B, Table B.6), 500 future scenarios were generated for each of the input parameters. The remaining relevant sources of uncertainty were analyzed through scenario-based analysis in Step 4B.

Step 4B: Uncertainty mapping and analysis of solutions

In this step, a deterministic optimization problem is solved for each of the scenarios generated by Monte Carlo sampling performed in the previous step, where the consequences of the data uncertainty on the decision-making problem are studied and mapped. The result is a distribution of 500 optimal processing networks that are mapped and statically analyzed. The frequency of selection for each scenario is presented in Figure 3.5. The top-3 ranking alternatives are, lactic acid, succinic acid, and 1,2-PDO.

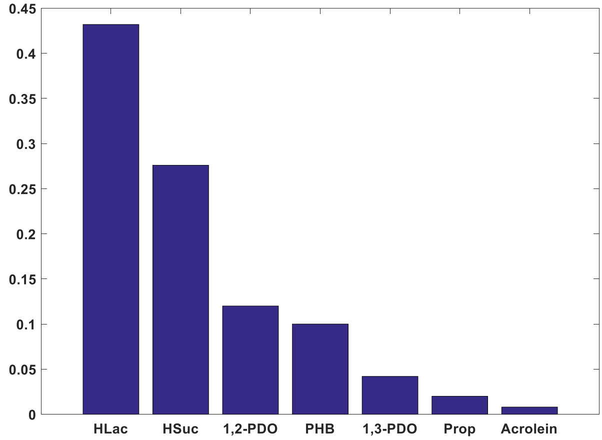

Figure 3.5: Network frequency of selection, where the top-3 selected are Lactic acid, Succinic acid and 1,2-PDO

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Figure 3.6 presents the parallel coordinate plot of the system under uncertainty. It allows a quick quantitative and qualitative visualization of results obtained from the optimization problem for each scenario generated by the Monte Carlo simulations. In this way the plot shows how input uncertainties affect the optimal decision. Hence, it presents the optimization results and the raw data corresponding to those uncertainty realizations. It displays high-dimensional datasets, where each y axis ('columns') represents one variable; there are 500 values for each y, corresponding to the 500 LH samples. These values are then joined, creating multiple polylines that represent the scenarios across variables. Variables ('columns') were normalized to a fixed range (0–100) which is equivalent to working with standardized variables (to avoid the influence of one variable onto the others due to scaling).

Furthermore, to take the uncertainties in a proactive way and further understand their impact on the ranking/mapping of solutions, three extra scenarios were built based on different assumptions of future uncertainties through the realization of Monte Carlo simulations. It is important to note that these scenarios were built on the base case where uniform distribution of capital investment and historical price data was used to

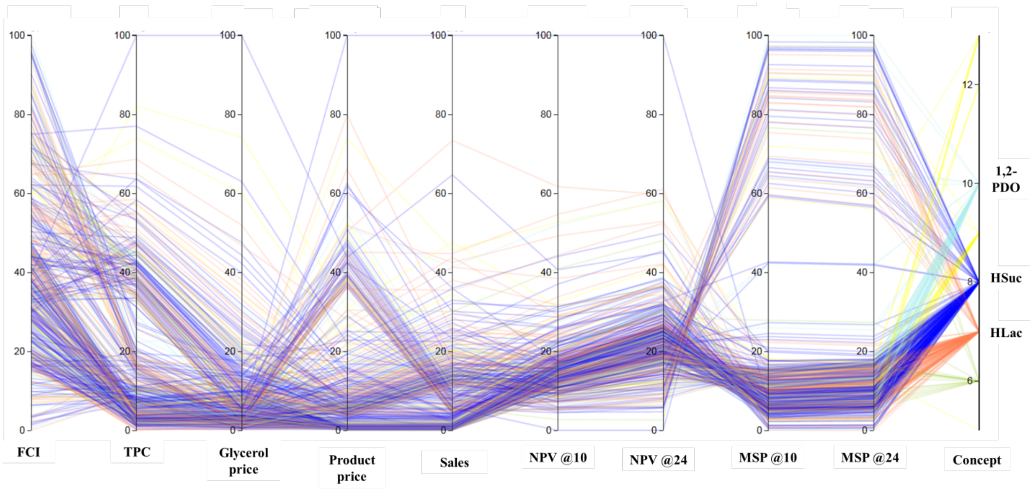


Figure 3.6: Parallel coordinate plot of the system under uncertainty. Orange, blue and light blue represent the top-4 best solutions: Lactic acid, succinic acid, 1,2-PDO and PHB. The yellow lines represent the remaining selected concepts

describe pre-identified uncertainties. The scenarios are: (i) the total production costs vary normally with 20% standard deviation, (ii) prices of selected top products crash to 80% of their average price, and, (iii) total sales volume decreases to 80% of its normal volume. The total production cost, essential for the estimation of the economic metrics, can vary for several reasons, such as raw materials, chemicals, utilities and solvents price variations, as well as labor and maintenance, among others. Therefore, scenario (i) considers the total production cost of each alternative in the base case to vary according to a normal distribution within its probable range of variation. The realization of uncertainties through the optimization problem is quantified and, in this scenario, lactic acid and succinic acid lead the top with 38% and 30%, followed by PHB and 1,2-PDO, with 16% and 10%, respectively. Further, if future developments take the prices of the top selected products identified in the base case scenario (scenario ii), to decrease to 80% of their average price, then the 1,2-PDO is selected for 34% of the samples, followed by lactic acid which is selected for 26%, 1,3-PDO and succinic acid with 16 and 13%, respectively. Finally, scenario (iii) is built on the assumption that the sales volume decreases to 80% of its average value. In this case, lactic acid is selected for 56% of the samples, followed by succinic acid and 1,2-PDO which are selected for 18% and 12%, respectively (please find the histograms corresponding to scenarios (i) to (iii) in Appendix B, Figures B.4 to B.6). Therefore, as expected from the deterministic sensitivity analysis performed in Step 3A, the results from scenario (ii) show that the ranking of solutions is highly dependent on the products' selling price. However, within the price scenario established (for the current and referenced price data, Table 3.5), the ranking of solutions is robust, which can be interpreted from the comparison of the rankings obtained in scenarios (i) and (iii) to the ranking obtained in case of the base case scenario.

Step 5A: Economic risk quantification

As mentioned earlier, risk is defined as the probability of occurrence times the consequence of that same event to occur. In this study, NPV is used as economic metric/indicator for project evaluation in order to support a risk-aware decision making. To this end, the risk is given by the probability of failing to achieve the targeted NPV ('being lower or equal to') times the magnitude of the consequence of that event occurring ('loss of profit'). The economic risk is defined by the probability of the project being non-profitable (NPV<0) times the consequence (loss of profit) as described in Eq. 3.10.

$$Risk = \sum_i P_i \times M_i = \sum_i P(NPV \leq 0) \times (NPV_i) \tag{3.10}$$

where i is the occurrence of the undesirable event, P_i is the probability of that event to occur and M_i is the magnitude of the consequence (in MM$) of the undesirable event. It is important to note that, in this study, the overall project to be undertaken represents the implementation of new technologies, and therefore the project discount rate is adjusted to offset risk and attract investors, therefore considered to be somewhere between medium to high, and so the minimum acceptable rate of return is set to be 24% (see Table 3.8). However, to also depict the effect of the company choices with respect to the level of discount rate used, the economic evaluation is here performed considering both discount rates of 10% and 24%. The cumulative distribution function of NPV is presented in Figure 3.7. The importance of incorporating cost uncertainties in the NPV calculations through stochastic modelling, has also been explored/demonstrated in [135] for analysis of biorefinery concepts. According to Eq. 3.10, the calculation of Risk is equal to the shaded area in the cumulative distribution function for NPV shown in Figure 3.7, where two curves are depicted in red and blue, representing NPV obtained at 24% and 10% internal rate of return, respectively. A summary of results is presented in Table 3.9.

Table 3.9: Summary of results for the calculation of economic risk for the top-3: lactic acid, succinic acid and 1,2-PDO.

	Lactic acid	**Succinic acid**	**1,2-PDO**
Frequency of selection	216/500	138/500	60/500
$Pr(NPV \leq 0)$ @10%	0.632	0.764	0.68
$Pr(NPV \leq 0)$ @24%	0.99	0.962	0.89
Risk @10% (MM$)	8.69	13.74	15.45
Risk @24% (MM$)	19.21	23.86	16.43
Net present revenue @10%	26.4	17.4	6.43
Risk 10%/net present revenue @10%	0.3291	0.787	2.403

Step 5B: Flexible multi-product glycerol-based biorefinery concepts

In this step, the aim is to identify the optimal trade-off between the operating flexibility and capital investment according to different uncertainty realizations of product prices.

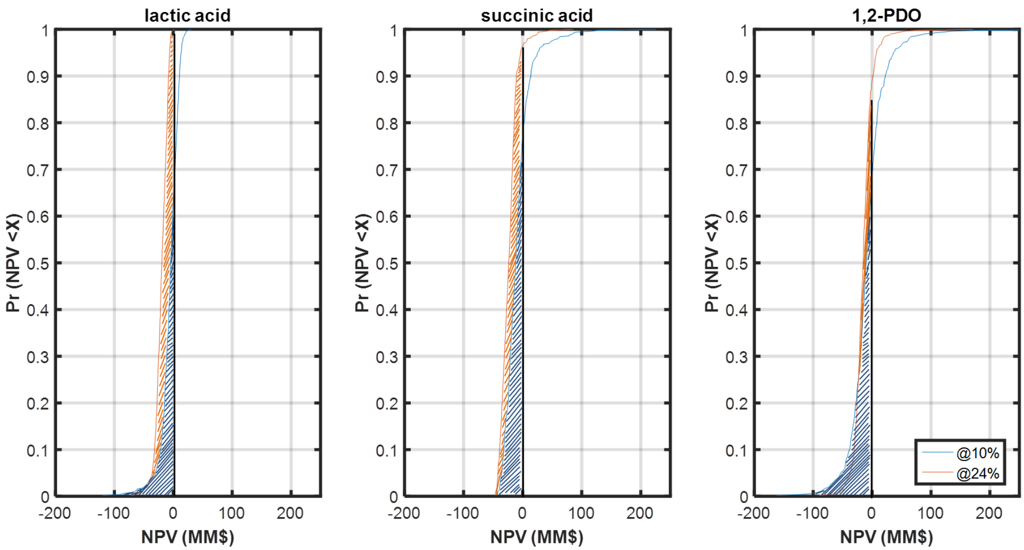


Figure 3.7: Cumulative distribution function for the lactic acid, succinic acid and 1,2-PDO production from glycerol. The highlighted area represents the risk of the project being non-profitable. Blue represents NPV obtained for a discount rate of 10%. Orange represents NPV obtained for a discount rate of 24%.

Therefore, as a risk mitigation strategy, a possible multi-product network (comb) was tested where lactic acid and succinic acid are produced depending on the market environment. Moreover, as previously mentioned, based on the large ratio risk/ net present revenue for the production of 1,2-PDO, its co-allocation combination with the production of lactic acid is economically unfeasible. Following the same principles as the economic risk estimated in step 5A, the risk was estimated for comb and it is reported in Table 3.10. There is a reduction in the quantified risk by about 20%, and consequentially the net present revenue to risk ratio has improved to be approximately 3.6 times the potential risk. Therefore, it indicates that a flexible multi-product network for the valorization of glycerol through the co-allocation of lactic acid and succinic acid is a promising solution to mitigate the effect of uncertainties in the techno-economic metrics. The multi-product network allows the products to be, in turn manufactured depending on favorable market demands and prices. A plant capable of switching between final products has advantages since it is then able to guarantee that it is continuously using the pathway that optimizes the profitability, considering the market demands, market prices and their corresponding volatilities. By mimicking the economic success story of the oil-based industry, a multi-product plant would be able to reduce the risk and therefore yield a more sustainable and competitive bio-based industry. Finally, the results support the argument that early-stage design of processes (concept screening phase) is significantly affected by uncertainties due to the scarcity and variability of the input data needed. Nevertheless, if reasonable approximations are used to describe the techno-economic reality and if carefully considering the potential (and probable) uncertainties, the methodology is still a powerful tool for removing unfeasible process-product pathways and, in this way, improve the effectiveness of decision making for screening of process concepts in the screening phase.

Table 3.10: Quantified risk for single- and multi-product combinations (estimated at discount rate of 10%)

Combination	**Risk10% (MM$)**	**Risk 10%/net present revenue @10%**
Lactic acid	8.69	0.33
Succinic acid	13.74	0.79
comb: lacitic acid + succinic acid	7.03	0.28

3.5 Discussion

A first ranking of solutions is given by solving the deterministic problem by maximizing the potential profit of the biorefinery concepts considering no variability on the input data (‘single point’ analysis). It was found that the lactic acid, succinic acid and 1,2-PDO are the top-3 ranked solutions when only using NPV nominal data. This is justified based on the balance between the product selling price and production capacity, fixed capital investment and the low variable operating costs when comparing to the remaining concepts. Various studies on glycerol conversion have been performed along the years [179], [180], [181], [148]; a few studies have considered techno-economic indicators, but noteworthy is that, to the best of my knowledge, up to now there are no studies on glycerol valorization concepts that are subjected to uncertainties on the input data. Vlysidis et al. [181] analyzed the coproduction of succinic acid to add value to the glycerol side stream of the biodiesel industry, where the co-production of succinic acid is forecasted to be a positive and potentially profitable solution to valorize glycerol. Posada (2011) [179] also performed a deterministic analysis of possible schemes for the conversion of glycerol to value-added products, assessed only based on the production cost. Both studies, being deterministic assessments for early stage screening and design of biorefinery concepts, present some shortcomings related to the possible lack of awareness of market fluctuations and technical variabilities. They embody a substantial risk concerning the selection of optimal process concepts, and so, long-term competitiveness and robustness cannot be guaranteed due to the variability, scarcity and uncertainty of input information. Therefore, in this work, a systematic study is performed by incorporating stochastic uncertainty in the techno-economic analysis, according to which the most suitable set of process concepts are identified. The input uncertainty on the feedstock and product prices was depicted based on the empirical historical data using appropriate probability distribution functions. The fixed capital investment variability was described by a uniform distribution of values around their typical predicted range of variation. Then, the input uncertainty was propagated to the objective function through Monte Carlo simulation enhanced with Latin Hypercube sampling. The obtained uncertainty mapping of solutions pointed to 1^{st} lactic acid and 2^{nd} succinic acid as the best potential alternatives regarding economic criteria (positive and high NPV), followed by 1,2-PDO. To further analyze the robustness of the ranking of alternatives under uncertainties, three additional scenarios were tested. As expected from the deterministic sensitivity analysis performed in Step 3A, the ranking of solutions is robust, and this can be concluded from the comparison of the rankings obtained in scenarios (i) and (iii) to the ranking obtained on the base case scenario which remains the same. The effect of the fixed capital investment variability was verified to have a significant impact on the project profitability and, consequentially, it substantially influences the optimal solution (decision-making) at the concept screening phase where a broad range of uncertainty is expected. Furthermore, the findings of this study pointing to lactic acid as the most suitable and robust candidate for the valorization of glycerol is corroborated by the existing commercial plants such as Corbion Purac, Natureworks and Galactic, among others, which are manufacturing lactic acid by fermentation of carbohydrates [9], [182]. Lactic acid is a bulk chemical and its demand has been reported to have an average annual growth rate of 10% [9], with a long history of uses in the the food, cosmetic and pharmaceutical sectors, and as a monomer for the production of biodegradable PLA (polylactic acid) [9]. The high growth rate of lactic acid demand lies fundamentally on the demand of PLA, the biodegradable polymer. It has approximately a demand of 25,000 ton/year (2013) and can reach up to 650,000 ton/year in 2025 [9]. On the other hand, succinic acid was also identified as a potential candidate for the glycerol valorization. This is also supported by commercial production plants such as: Reverdia producing 10 kton/y of Biosuccinium from renewable carbon sources (fermentable sugars) in Italy, since 2012 [183]; Succinity, a joint venture between Corbion Purac and BASF established in 2013, also operating a 10 kton/y plant in Spain since 2013; and, Myriant and Bioamber, with the same range of installed capacities, operating in Canada and North America, respectively [182]. Succinic acid (and its salts) has been predicted to be one of the future platform chemicals that can be derived from renewable resources and has significant potential as building block; for the production of biopolymers [184], to be used directly in food, pharmaceutical and cosmetic industries as well as due to its potential conversion into solvents and other current petro-based chemicals [138]. Finally, 1,2-PDO, having several applications in industry, for example in food and pharmaceuticals, is produced in industrial and USP grades, respectively. The world leader of bio based 1,2.-PDO production is ADM, followed by Oleon, manufacturing it from alternative carbohydrate sources such as glycerol, sorbitol and dextrose. Moreover, as mentioned in the above sections, several reports and review articles such as [182], [9], [185], have continuously identified lactic acid, succinic acid and 1,2-PDO, among others, reporting them as having strong market growth and highlighting their potential to be used as platform chemicals and their suitability as building blocks for the synthesis of a variety of chemicals through chemical conversion. Therefore, in light of this, a deeper analysis was undertaken into the top-3 concepts through economic risk analysis, i.e. the probability of NPV being lower than zero times the consequence of that event occurring. In other words, the economic risk will reflect the probability of the biorefinery concept under study to be non-profitable which corresponds to a NPV lower than zero. To this end, the glycerol valorization through the production of lactic acid, succinic acid and 1,2-PDO was compared based on the quantified economic risk of being non profitable. It was found that the lactic acid production from glycerol has a potential risk of profit loss of approximately 9 MM$ (estimated at discount rate of 10%), over a net present revenue of 26 MM$ (20 years of plant life time). In this case, the net present revenue, over 20 years of plant lifetime, is approximately 3 times the potential profit loss risk. On the other hand, succinic acid has a potential loss of 14 MM$, which represents around 80% of the potential net present revenue. Finally, based on the current data, 1,2-PDO has a high potential risk of profit loss of 16 MM$, representing a risk which is 2.4 times higher than the potential present revenue. In order to decrease the risk associated with the mentioned concepts, risk mitigation strategies can be applied. In this work, the flexible multi-product biorefinery is tested as a risk reduction strategy.

3.6 The impact of price correlations on economic assessment: Uncertainty & Global Sensitivity Analysis

This section of the thesis is based on the following article: *Uncertainty & sensitivity analysis of economic assessment of lactic acid production from crude glycerol – impact of price correlations.* Gargalo L.C., Carvalho, A., Gernaey K. V., Sin G. Proceedings of the 27th European Symposium on Computer Aided Process Engineering. Computer-Aided Chemical Engineering (in press).

In this section, global sensitivity analysis is used in order to fully comprehend the consequences of the expected price volatility, and their correlations, on the economic assessment and its predictions. Even though uncertainty and sensitivity analysis have become widespread tools to obtain relevant information about complex process models and despite searches in the avaiable literature, to my knowledge, this is the first study that addresses the impact of correlation between inputs on the sensitivity analysis of economic assessment, as all state of the art sensitivity analysis methods assume that inputs are independent [186], [114]. Therefore, in this section, the impact of the expected price volatility and correlations on the overall economic assessment is investigated, using lactic acid production from crude glycerol as case study (potentially best alternative identified in Step 4B). In particular, the goals are two-fold: (i) to understand the effect of the degree of pairwise correlation between input uncertainties on each other and on the outputs from the economic model (Net Present Value); and lastly, (ii) to estimate the first-order as well as independent variance-based sensitivity indices so as to identify which of the input uncertainties in the economic analysis affect the estimated NPV the most.

To assess how uncertainty in the output can be apportioned to input parameters, the variance of the model output(s) is decomposed into fractions that can be attributed to the inputs by estimating the variance-based sensitivity measures. Furthermore, in the literature two types of GSA can be distinguished, for the case of dependent and independent inputs, respectively. The latter is easier to tackle because there are effective computational methods to compute the sensitivity indices [187] [114]. However, the case of dependent inputs is more complex and the sensitivity indices can be estimated based upon parametric interpolation or non-model based methods [188]. In most chemical engineering model-based applications, e.g. for process design or control, in fact inputs are likely to be correlated, and therefore the importance of addressing the correlation properly when performing uncertainty and sensitivity analysis matters. Thus, considering the case of dependent inputs, the modeler is able to detect the inputs that contribute to the variation of the model output by themselves and also due to the relationships among each other. To estimate the aforementioned sensitivity indices, metamodeling [189] or sampling (Monte Carlo) [190] based techniques can be used. Here, the sampling algorithm developed by [188] is implemented in Matlab (R2015a), which uses a Monte Carlo method with permutation using Latin Hypercube Sampling and Iman Conover correlation control to compute the first order global sensitivity indices. For a given input uncertainty x_i, the Monte Carlo estimators for the first order and the independent sensitivity indices are given by the following equations,

$$S_i = \frac{V_i}{Var(Y)} = \frac{\frac{1}{N}\sum_{k=1}^{N} f(x_k) \times (f(x_k^i) - f(x'_k))}{Var(Y)} \tag{3.11}$$

$$S_{i-1}^{ind} = \frac{\frac{1}{N}\sum_{k=1}^{N} f(x_k) \times (f(x_k^{i-1}) - f(x'_k)}{Var(Y)} \tag{3.12}$$

where, $x_k^* = (x_k 1^*, ..., x_k n^*)$ is the k^{th} MC trial in the sample $x*$, $k \in [1, n]$ and $Var(Y)$ is the total variance predicted as the average of the total variances obtained with each sample $x*$. In Eq. 3.11, the Monte Carlo estimation of S_i - the first order sensitivity index for input i is shown. This is interpreted as the full first order sensitivity index, i.e. it includes the effect of the input x_i and its correlated part with other inputs $x \sim i$. In Eq. 3.12, the Monte Carlo estimation of S_i^{ind} is given which includes only the independent contribution of input x_i. These indices provide a comprehensive analysis of the importance of inputs on the model outputs, in particular the effect of x_i due to its correlation with other inputs or by itself. The same analysis can be extended to computation of the total sensitivity index, ST_i. For more details and the integral definitions of the sensitivity indices, the reader is referred to Mara et al. (2015) [188].

The economic model (DCFR) was implemented in Matlab (R2015a), and the sources of uncertainty investigated are $\{x_p, P_p, x_{rm_i}, P_{rm_i}, P_{ut_i}, FCI\}$ (Eqs. 3.1 to 3.8). However, special attention is paid to the effect on the economic model of correlation between the prices of lactic acid and glycerol. Using the above-mentioned algorithm, the correlated set of samples was generated and used for Monte Carlo simulations.

In Figure 3.8, it is observed that the mean value of the NPV is highly affected by the uncertainty on the input parameters. Furthermore, it is also perceived that the more positive the correlation between the LA and the glycerol price, the higher the mean value of the NPV and the lower the variance. As expected, the uncertainty on the model output decreases when the correlation between the prices is stronger, not only due to the decrease in the variation allowed but also due to the fact that the product price is approximately 5 times the glycerol price. As a stress test, considering that possible future developments take the market price of the LA to collapse to 50% of its average price, in Figure 3.9, one can see that the mean value of the NPV decreases drastically. Furthermore, the same pattern is observed, i.e. the more negative the correlation between the LA and the glycerol price, the lower the mean value of the NPV. This further confirms that the NPV, and the consequent project feasibility, is highly dependent on the product selling price.

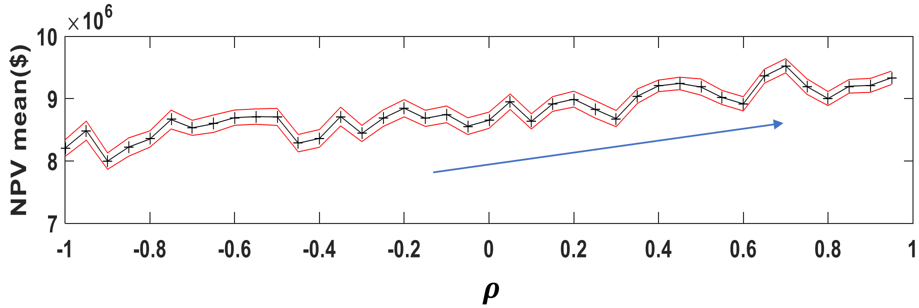


Figure 3.8: Mean value of the Net Present Value variation with the pairwise correlation between LA and glycerol prices (ρ)

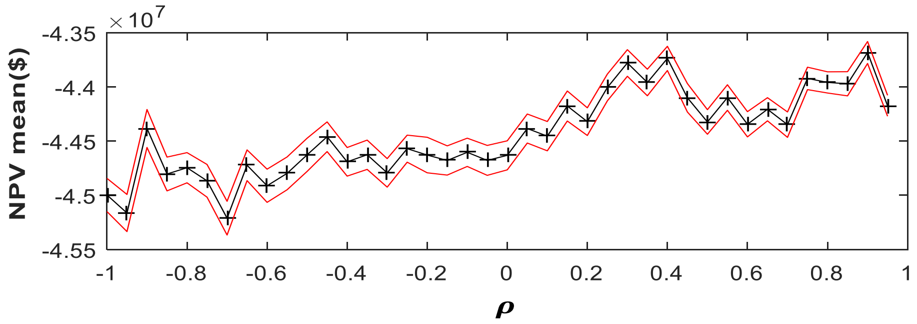


Figure 3.9: Mean value of the Net Present Value variation with the pairwise correlation between LA and glycerol prices (ρ). *Stress test*: lactic acid price crashes to 50% of its nominal value

The sensitivity indices of all input sources of uncertainty are depicted in Figure 3.10, considering the case where, as above, there is correlation between the LA and glycerol prices.

It is noteworthy that, when comparing the full first order indices presented in Figure 3.10(a) with the independent first order indices in Figure 3.10(b), one can see that the impact of the glycerol price on the variance of the NPV model is rather small when considered only by itself. However, through its correlation with the LA price, it has high importance for the variance of NPV. The LA price, on the other hand, has a high impact on the output variance mostly by itself, but also due to its correlation with the glycerol price. This clearly shows that the magnitude of the effects of the inputs heavily depends on the presence of correlation between them and should be included in adequate sensitivity analysis, otherwise the results of such analysis may be misleading. Furthermore, as presented in Figure 3.10 and highlighted in Table 3.11, one can see that the impact of input uncertainties on the output variance depends on the sign and on the magnitude

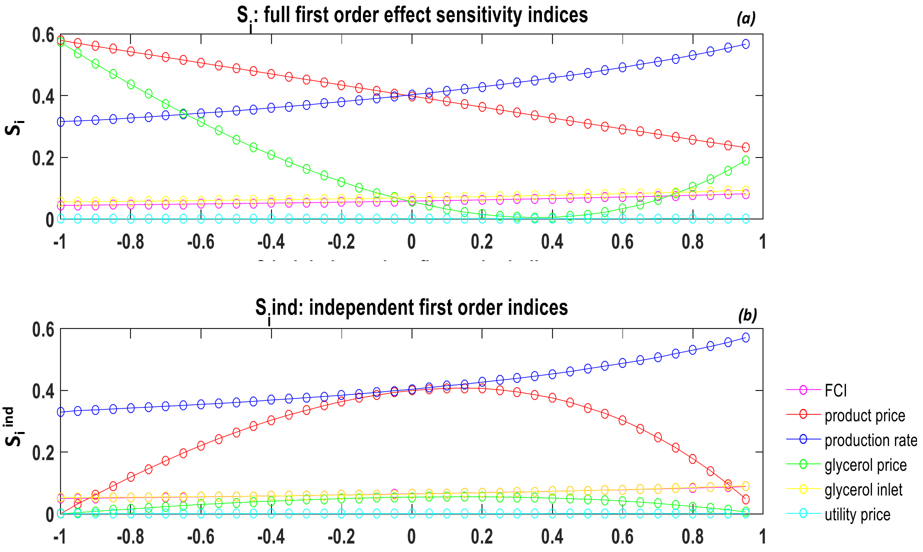


Figure 3.10: (a) full first order sensitivity indices; (b) independent first order sensitivity indices

of the correlation. In this case, negative correlation between product and glycerol price leads to lower mean value of NPV and relative importance of inputs on the model output variance.

Table 3.11: Highlight of the impact of magnitude and sign of correlation on the importance of inputs.

S_i	$\rho = 0$ **(base case)**	$\rho = -0.8$	$\rho = 0.8$
FCI	0.05	0.045	0.10
Product price	0.40	0.55	0.28
Production rate	0.40	0.32	0.56
Glycerol price	0.05	0.425	0.10
Glycerol inlet	0.05	0.045	0.10

For the base case where there is no correlation, the LA price and production rate have equally important contributions, while other inputs have negligible contributions. However, when a high negative correlation between LA and glycerol price is present, the glycerol price, which was unimportant in the base case, becomes a significant factor, followed by the production rate. Furthermore, for a high positive correlation a pattern similar to the base case is observed. The production rate has the highest impact on the model variance, and the effect of the glycerol price has a slightly larger contribution than in the base case. For engineering applications, it is noted that high variance in the estimated NPV is a cause for concern, as it essentially means that one does not know for sure what the true value of NPV is because the calculations are clouded due to the presence of uncertainty in the inputs. Therefore, knowing what inputs affect this output uncertainty can give a suggestion to manage/decrease this variance and the corresponding risk.

3.7 Conclusions

In this chapter, eleven gate-to-gate possible routes/technologies for the production of chemicals and biofuels from glycerol are analyzed. To this end, a systematic methodology for the detailed economic assessment has been proposed. This methodology accounts for the inherent presence of uncertainties in the input data/information, such as product and glycerol market prices and fixed capital investment. In this study, so as to depict potential future scenarios, it is assumed that future market price fluctuation will behave as in the past; thus, historical product and crude glycerol prices are used. However, as the methodology used is systematic, it can be iterated and solved for different price scenarios realizations, including the scenario where the prices are affected by increasing the availability of these products in the market, or any other price forecasting approach, for example the ones proposed in [150], [149]. The uncertainties portrayed are propagated to the model outputs by using Monte Carlo simulation enhanced with Latin Hypercube Sampling. The results have shown that the top-3 products that potentially carry lower economic risk are the conversion of glycerol into lactic acid, succinic acid and 1,2-PDO. Finally, the results support the development of an integrated multi-product concept through the production (co-allocation) of lactic acid and succinic acid according to the market environment observed. This seems to be a promising solution for the production of chemicals from the biodiesel by-product, potentially adding value and enhancing the bioindustry's overall robustness and sustainability. Furthermore, through global sensitivity analysis discussed in section 3.6, it has been shown that the predicted economic feasibility highly depends on the magnitude of the uncertainties. In particular, the stress test scenario has shown that the lactic acid price heavily impacts the mean NPV of the project. Additionally, as the aim of section 3.6 is first and foremost to understand how correlation between input uncertainties affects the model output, it was specifically analyzed how the correlation between lactic acid (LA) price and glycerol price affects the model output and how it impacts the importance of the other inputs on the model variance. It was observed that the economic feasibility depends upon both magnitude and sign of the correlation among input uncertainties. For engineering applications, high variance in the estimated NPV is a cause of concern since it essentially reflects that the true NPV value is unknown since the calculations are uncertain due to presence of uncertainty in the input data. Thus, any decision based on such high variance would be a risky decision. Therefore, this approach aims at providing information and powerful insights on the quality of the estimated NPV, helping to better assess economic feasibility under a broad range of uncertainties and ultimately give valuable suggestions to manage/decrease this variance and the corresponding risk of potential business failure.

CHAPTER 4

Framework for risk-based decision-support

In this chapter, a multi-level framework for techno-economic and environmental sustainability analysis through risk assessment is proposed for the early-stage design and screening of conceptual process alternatives. The alternatives within the design space are analyzed following the framework's work-flow, which targets to: (i) quantify the economic risk; (ii) perform the monetary valuation of environmental impact categories under uncertainty; (iii) quantify the potential environmental risk; (iv) measure the alternatives' eco-efficiency identifying possible trade-offs; and, lastly (v) propose a joint risk assessment matrix for the quantitative and qualitative assessment of sustainability at the decision-support level.

This chapter of the thesis is based upon the following article:

A framework for techno-economic & environmental sustainability analysis by risk assessment for conceptual process evaluation. L. Gargalo, C., Carvalho, A., Gernaey, K. V. & Sin, G. *Biochemical Engineering Journal*, vol 116, pp. 146–156. (2016)

Nomenclature

DCFR	Discounted cash-flow of return
NPV	Net Present Value
IRR	Internal rate of return
$Risk$@10	Economic risk estimated at IRR of 10%
$Risk$@24	Economic risk estimated at IRR of 24%
FU	Functional unit
LCIA	Life Cycle Impact Assessment method
S_c	Deterministic category of impact
$CF_{i,c}$	Characterization factor to convert inventory into environmental impact category
T	Production lifetime
w_c	Monetization factor
F_i	Flow reference of component i
LHS	Latin Hypercube Sampling
N	Number of LHS samples
j	Number of alternatives
p	Number of columns - number of parameters under uncertainty
$Risk_{econ,j}$	Economic risk associated to alternative j

P_i	Probability of a certain event
M_i	Magnitude of the consequence associated with the occurrence of a certain even
$Risk_{env,j}$	Environmental risk associated to alternative j
$REC_{n,j}$	Normalized economic risk
$REN_{n,j}$	Normalized environmental risk
$(REC'_{n,j}, REN'_{n,j})$	improved position of alternative j when eco-efficiency applies

Components

$1,3-PDO$	1,3-propanediol
$HSuc$	Succinic acid

4.1 Introduction

As previously mentioned, notwithstanding the many studies focused on the economic and environmental domains of sustainability, it should be noted that the majority of these studies measure sustainable performance solely under deterministic conditions, where uncertainty and the associated risk a decision carries, is disregarded. Accordingly,to the best of my knowledge, no other studies have proposed a combined techno-economic and environmental risk quantification matrix for sustainability assessment and decision-making. Therefore, this work proposes a step-by-step framework whose purpose is to identify the best potential alternative(s) that would sustainably create value with the least potential risk of economic and environmental impact. This is achieved by systematically integrating uncertainty and sustainability analysis into a risk assessment framework. The framework aims to establish a holistic view, by leading the user through the: (i) estimation of the deterministic economic and environmental metrics; (ii) use of Monte Carlo technique for propagation of uncertainties to the environmental and economic indicators; (iii) quantification of the economic risk; (iv) monetary valuation of environmental impact categories under uncertainty; (v) quantification of the potential environmental risk; and, (vi) use of the sustainability risk matrix as a visual tool for quantitative and qualitative analysis for decision-making. Moreover, performing qualitative analysis by making use of the sustainability risk assessment matrix (as a visual aid tool), it is a valuable advantage/benefit of the framework which facilitates exchange of information among experts and non-experts.

The rest of this chapter are structured as follows: (i) the framework section introduces a step-by-step explanation (user guide) of how to use the quantification of risk as an integrating decision-making tool; then (ii) the framework is highlighted through its application to the glycerol valorization to value added products namely 1,3-PDO and succinic acid; and finally, (iii) conclusions from the work are presented.

4.2 Framework for techno-economic environmental sustainability analysis by risk assessment

The main goal of the proposed framework is to systematically, at an early stage of process design, collect, evaluate and screen the alternatives within the design space, through a comprehensive sustainability analysis by risk assessment. As presented in Figure 4.1, the framework work-flow is composed of six steps: (1) problem definition; (2) data collection and management; (3A) deterministic techno-economic analysis; (3B) deterministic environmental analysis; (4) Monte Carlo technique for uncertainty analysis; (5) economic and environmental risk quantification; and, (6) risk assessment and decision-making. The framework is based on the combination of the two methodologies previously presented in Chapters 2 and 3, and in this chapter the analysis is further extended to incorporate quantitative and qualitative sustainability analysis by risk assessment.

As this framework is built upon the combination of the previously described methodologies, the reader is referred to the previous chapters for the detailed description of the common steps. (but the steps are briefly described through the application of the framework). Thus, in Table 4.2, a summary of details of each step and the correspondence to the previous methodologies is presented. The steps highlighted in Figure 4.1, Steps 5 and 6, are described in detail in the following sections.

Table 4.2: Details on the steps composing the framework.

Steps of the framework	**E3BU** (Chapter 2)	**Algorithm for techno-economic assessment under uncertainty** (Chapter 3)
Step 1	Step 1	-
Step 2	Step 2.1, Step 2.2 and Step 2.3	-
Step 3A.1	-	Step 2
Step 3A.2	-	Step 3
Step 3B	Step 3.1 and Step 3.2	-
Step 4.1	Step 4.1	Step 4.A
Step 4.2	Step 4.2 and Step 4.3	Step 4.B
Step 5.1	Described in this chapter	Step 5A
Step 5.2	Described in this chapter	Described in this chapter
Step 6	Described in this chapter	Described in this chapter

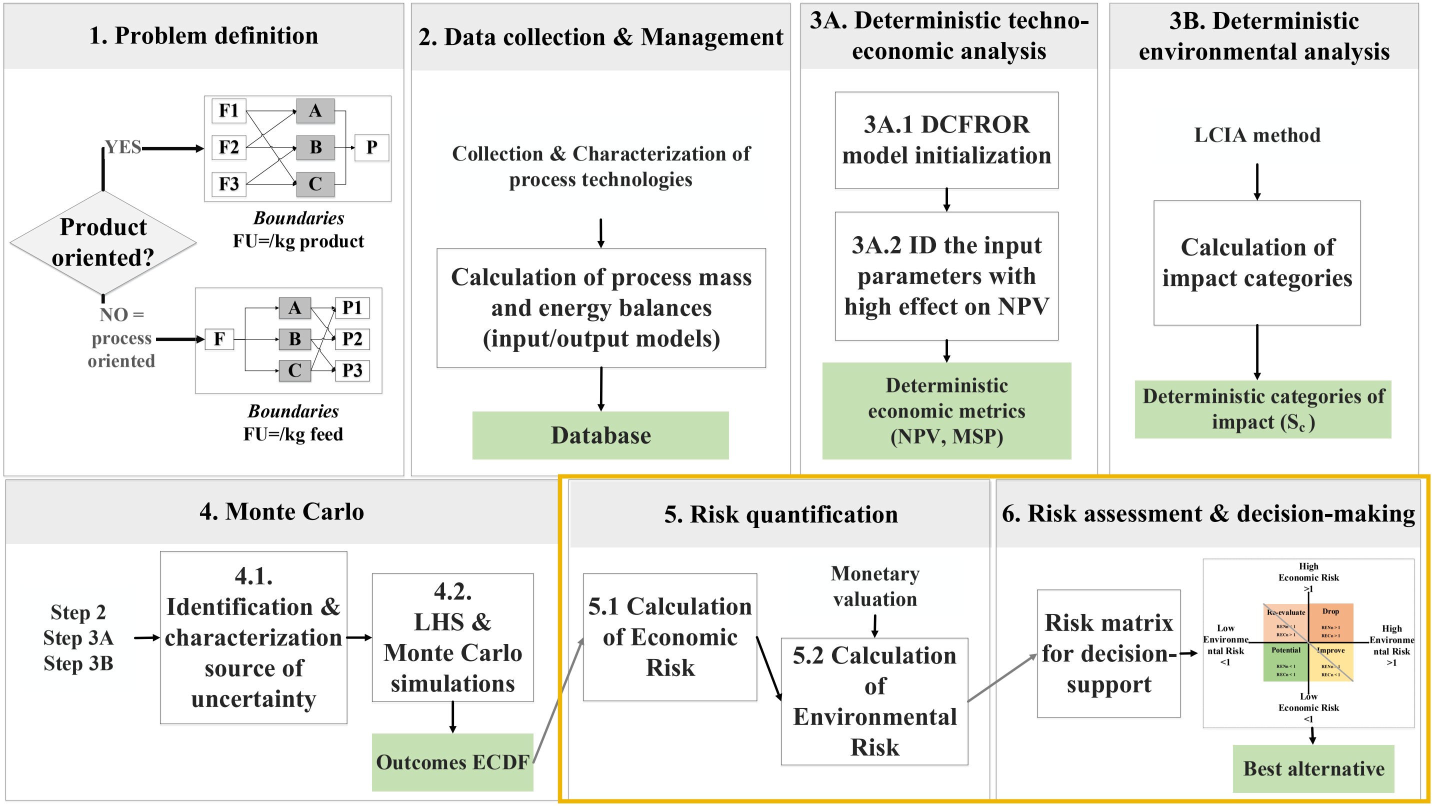


Figure 4.1: Schematic representation of the framework for sustainability risk assessment for early-stage of conceptual design and analysis. The steps described in detail in this chapter are highlighted in the orange box.

4.3 Step 5: Risk quantification

As shown in Figure 4.1, this step is composed of two sub-steps: the economic and environmental risk quantification.

4.3.1 Step 5.1: Economic risk quantification

As stated in Chapter 3, risk is estimated as the probability of occurrence of a certain event times the consequence of that same event to happen. In this work, the economic risk ($Risk_{econ}$) is quantified by the probability of failing to achieve the targeted NPV ('being lower or equal to') times the magnitude of the consequence of that happening ('loss of profit'). Therefore, the economic risk is given by the probability of the project being non-profitable ($NPV \leq 0$) times the loss of profit in the event of that happening (consequence). The respective mathematical description is presented in Eq. 3.10.

4.3.2 Step 5.2: Environmental risk quantification

In this study, the quantification of the environmental risk ($Risk_{env}$) of a certain alternative reflects the total amount that the decision-maker is willing to pay if the impact categories deviate from their deterministic value due to uncertainty on the CFs. Therefore, the $Risk_{env}$ is given by the probability of the category S_c being higher than the deterministic value multiplied by the consequence of that event happening. The magnitude of the consequence is estimated based on the monetary difference between the deterministic values and the realization of the conservative sample values (class 3 uncertainty, step 4.1) over the plant's production lifetime. Graphically, the individual risk incurred for each one of the impact categories S_C corresponds to the shaded area in the cumulative distribution function presented in Figure 4.2. The mathematical formulation is given by Eq. 4.1

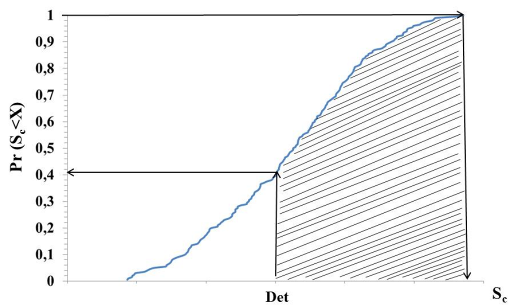


Figure 4.2: General representation of the cumulative distribution function for environmental categories of impact S_c, where Det corresponds to the deterministic value of the impact categories

$$
\begin{aligned}
Risk_{env} &= \sum_{t}^{T}\left(\sum_{c}^{C} Pr(S_c \leq Det_C)\times \mid Det_c - S_c \mid \times w_c\right) \\
&= \sum_{t}^{T}\left(\sum_{c}^{C}\left[\sum_{i} Pr(CF_i \geq Det_{CF_i})\times \mid Det_{CF_i} - CF_i \mid \times f_i\right]] \times w_c\right)
\end{aligned}
\tag{4.1}
$$

Where, S_c corresponds to the realization value of the category of impact c and Det_c corresponds to the deterministic value of the category of impact c (obtained previously in step 3B) and T reflects the production lifetime of the processing network under consideration. Lastly, w_c represents the monetary valuation factors used to convert midpoint or endpoint categories into a normalized and weighted monetary unit. Monetary valuation for direct comparison is the practice of converting measures of impacts into monetary units and is used to attribute economic value to non-market goods for which no market exists. Although advantages of such an approach have been pointed out by several authors such as Ahlroth (2014) [191], and the technique is being applied in cost benefit analysis, up to now monetary valuation has not been widely applied in environmental assessments, or more specifically in Life Cycle Assessment (LCA). However, it presents great potential for interpretation purposes and communication of environmental assessment results, due to the fact that decision-makers at the management level need a rough but clear presentation of results, and can easily relate to monetary units, for example if a trade off between two competing objectives is to be made. A summary of existing approaches for monetary valuation, built-in methods and key features is described in [192]. In this work, the weighting factors methodology selected is the one given by ECOVALUE08 [193], since our focus is on midpoint indicators and their well-defined cause-effect relationships between compound fluxes and the indicators to which they contribute to. Table 4.3 shows the weighting factors provided by ECOVALUE08.

Table 4.3: Midpoint weighting factors given by ECOVALUE08 [192],[193]. Values adjusted for inflation, \$2014.

Global warming [$\$/kgCO_2eq.$]	0.33
Acidification [$\$/kgSO_2eq.$]	5.06
Eutrophication [$\$/kgPO_4eq.$]	36.8
Photochemical oxidation formation [$\$/kgC_2H_4eq.$]	6.74
Human toxicity [$\$/kg1,4-DBeq.$]	2.03

4.4 Step 6: Risk assessment & decision-making

The main goal of this step is to rank and identify the potentially best alternative(s) regarding economic and environmental aspects through risk assessment for sustainability analysis. Therefore, a joined risk interpretation matrix is set as visual aid to facilitate a quantitative and qualitative interpretation of the quantified risk for decision support at early stage design. To this end, both economic and environmental risk are normalized as follows.

$$REC_{n,j} = Risk_{econ-norm,j} = \frac{Risk_{econ,j}}{(\sum_j Risk_{econ,j})/J} \tag{4.2}$$

$$REN_{n,j} = Risk_{env-norm,j} = \frac{Risk_{env,j}}{(\sum_j Risk_{env,j})/J} \tag{4.3}$$

where $(\sum_j Risk_{econ,j})$ and $(\sum_j Risk_{env,j})$ represent the sum of economic or environmental risk over the number J of alternatives considered within the design space, respectively.

Figure 4.3 presents the proposed qualitative matrix for decision-support, where, after normalization, the respective normalized risk position given by the pair $(REC_{n,j}, REN_{n,j})$, is set up for each alternative. The vertical and horizontal axes display the range of normalized economic risk and environmental risk, respectively. Due to the normalization, the center of both axes corresponds to 1. As proposed by [194], the distances of the products from the diagonal can be translated into differences between the respective eco-efficiency performance.

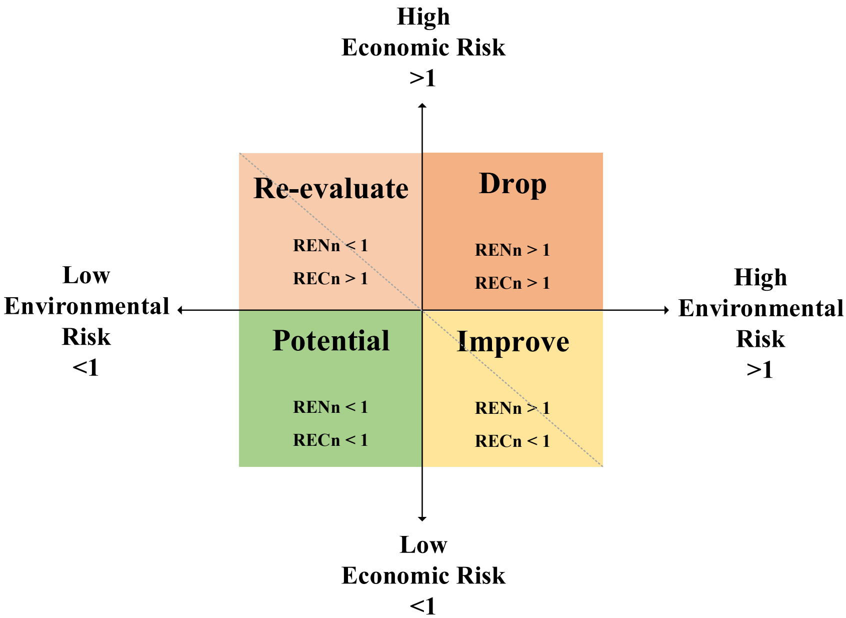


Figure 4.3: Sustainability risk assessment and interpretation matrix.

The visualization of results through the interpretation matrix provides not only a quick decision-making tool to select the potentially most sustainable alternative within the design space, but it is also an easy way to communicate results in an easily understandable way. To this end, the matrix is divided into four boxes both for qualitative ('which box does it fall in?') and quantitative interpretation ('higher or lower than 1?'). Therefore, from the qualitative point of view, and in clockwise direction: 'Drop' indicates that the alternatives that fall into this box are not promising and therefore they are recommended to be given up; 'Improve' categorizes the alternatives which have low economic risk, however the environmental risk assessment reflects that the process needs to be improved in order to decrease its environmental burden; 'Potential' presents high likelihood to be selected as best alternative since it has low economic risk and low environmental risk; and, finally, 'Re-evaluate' classifies the alternatives that have a potentially low environmental risk, but the economic risk is significant. In the latter case, improvements in the process could not only improve the economics but also its environmental assessment. In order to analyze the products' eco-efficiency, one starts by looking at the distances between the initial positions in the matrix and the diagonal line, i.e. the higher the distance to the diagonal line the lower the eco-efficiency. Furthermore, the ratio between the normalized environmental and economic risk (R_j) is estimated for each one of the products as given in Eq. 4.4. If is higher than 1 it means that the normalized environmental risk of the product is higher than the normalized economic risk. This ratio is used not only to analyze the systems' eco-efficiency but it is also useful to update the products' position in the matrix to an improved position, which represents a balance between the environmental and economic risk, i.e. it is located on the diagonal line. Thus, it allows a quick visualization of possible trade-offs when selecting a certain alternative.

$$R_j = \frac{REN_{n,j}}{REC_{n,j}} \tag{4.4}$$

The improved position is given by the pair $(REC'_{n,j}, REN'_{n,j})$ inspired by the procedure proposed in [194], which is based on the theorem of Pythagoras and on the cathetus theorem. Therefore, based on the sustainability analysis performed through the joined risk assessment, the user will be able to quickly assess which alternative stands out as potentially more sustainable, and also identify possible trade-offs.

4.5 Results

Step 1: Problem definition

The framework is highlighted through the application to the glycerol valorization, where the aim is to identify the best alternative to add value to crude glycerol, by the production of succinic acid or 1,3-propanediol as value-added products. Since the goal of the study is to identify the best potential product, the functional unit is the inflow of crude glycerol (1 kg of glycerol). The system boundaries are defined following a gate-to-gate approach as described in Figure 4.4, which includes the manufacturing process and the utilities scheme. An input flowrate of 4200 ton glycerol/year ($\approx$ 525 kg/h) is considered.

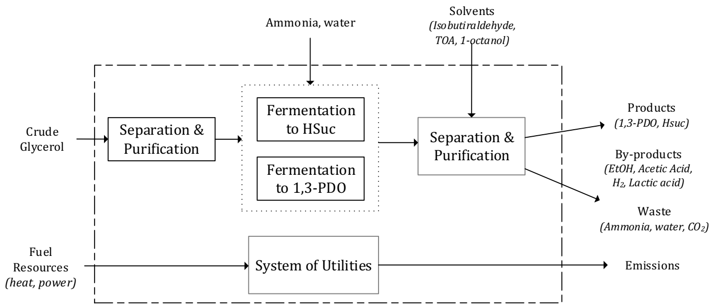


Figure 4.4: System boundaries to be included in the economic and environmental assessment.

Step 2: Data collection & management

As mentioned previously, all input data needed to perform the subsequent steps is collected and stored in a multidimensional matrix. The mass and energy balances were estimated based on the input data (please see Table C.1 in Appendix C) and following the generic block model equations (e.g. stoichiometry, conversion, mixing, product separation, waste separation) [108], [17]. Additionally, the techno-economic data required for Steps 3A and 4, such as nominal market prices of products and raw material(s) (see Table 4.4); and key assumptions for the economic model, are also collected and presented in Table C.2 in Appendix C. Regarding the data requirements of the environmental assessment, after selecting the LCIA methods, the characterization factors (CFs) are also collected and stored in the database. In this work the LCIA method selected is the ReCiPe method [127]. It is important to note that, having defined the LCIA method, the indicators and characterization factors are pre-selected and used in the subsequent steps.

Step 3A: deterministic techno-economic analysis

Step 3A.1: Economic model initialization

To generate the base case conditions and obtain the first ranking of solutions, the problem is solved maximizing the NPV of the processing networks within the design space. The summary of key input assumptions used in the economic model is presented in Table C.2. To this end, all the input data required for the calculation of Eqs. 3.1 to 3.8 [15], such as input parameters, have already been collected (e.g. market prices) or estimated (e.g. fixed and variable operating costs), as presented in Table 4.4. For the remaining process sections, the FCI was estimated based on literature review of all products and scaled to the production rate set by the verified stoichiometry. The purchased equipment costs were then estimated based on the product specific references (base) and adapted to appropriate capacities, and the respective costs were updated to year 2014, according to Eq.3.9.

Table 4.4: Data estimated and obtained in the economic model inintialization in Step 3A:1.

	Production rate (ton/year)	FCI* (MM$)	TPC* (MM$/y)	Utilities* (MM$/y)	Sales (MM$/y)	Product price ($/kg)	NPV10 (MM$)	MSP@10 ($/kg)
Succinic acid	2464	23.9	3.863	0.289	6.87	2.79	-3.3	2.98
1,3 PDO	2312	21.28	3.940	0.899	4.66	2.02	-6.7	2.43

Step 3A.2: Identification of input parameters with high impact on the model

The investment and cash-flows are firstly calculated for the baseline conditions, and then the NPV is re-estimated by changing one variable at a time over the expected range of variability of key economic factors (see Table 4.5). This will express how sensitive the DCFR model is, to variations in the input information. From Figure 4.5, it was concluded that (i) external input parameters such as feedstock price, product price, sales volume and fixed capital investment have a relatively high impact on the projected economic performance; and, (ii) the discount rate also has a significant impact on the economic model. Thus, in this study the above-mentioned sources of uncertainty are taken into account and analyzed further.

Table 4.5: Key economic factors under variability for sensitivity analysis of the DCFR model

	Data sources	Lower limit (% of the baseline)	Upper limit (% of the baseline)
Product price	[150]	-20%	+20%
Feedstock price	[150]	-10%	+30%
Fixed Capital Investment	[171], [88]	-20%	+50%
Discount rate	[150],[172] [this work]	8%	24%
Income tax rate	[173]	-20%	+20%
Sales volume	[149]	-20%	+20%

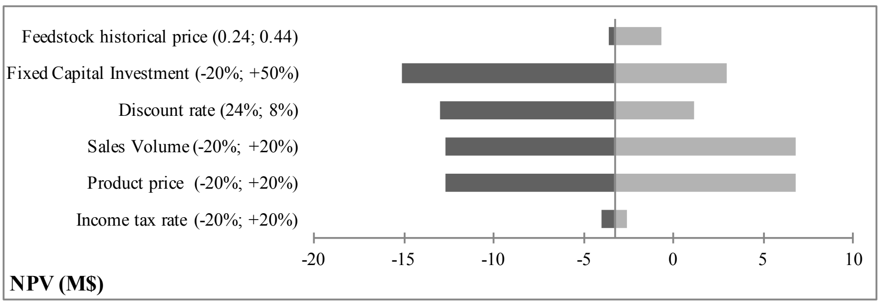


Figure 4.5: Sensitivity analysis of NPV to variations in key economic parameters.

Step 4: Monte Carlo technique

Step 4.1: characterization of sources of uncertainty

The external sources of uncertainty identified by the sensitivity analysis are now characterized using appropriate statistical distribution functions. Therefore, for further analysis, the scenario to be assessed was set-up based on (i) historical data on the raw materials and products market prices described through appropriate probability distribution functions; (ii) considering variability of the fixed capital investment over its typical range of variation; and, (iii) considering the variation of the sales volume by allowing it to vary in its probable range. Concerning the uncertainty in the LCIA, the $CF_{i,c}$ were identified as carrying substantial uncertainty. The input uncertainty domain is defined by the expert review method and assuming a uniform distribution as mentioned in Chapter 2.

Step 4.2: LHS Monte Carlo simulations

Trough Latin hypercube sampling with correlation structure/control [114], [113] 500 future scenarios (realizations of uncertainty) were generated for each of the input parameters from the input uncertainty domain. Therefore, the output of this step is composed by two $N \times p$ matrices, corresponding to input uncertainty identified in the techno-economic assessment and in the LCIA, where N represents the number of samples obtained with LHS and p represents the uncertain parameters. In order to identify the optimal processing networks, the optimization problem was formulated and solved, which led to 500 optimal solutions (Monte Carlo simulations) that are mapped and statistically analyzed. The frequency of selection of succinic acid and 1,3-propanediol is 0.84 and 0.16, respectively (also presented in Table 4.5).

Risk quantification

Economic risk quantification

In this study, as mentioned earlier, the economic risk is quantified by following Eq. 3.10. As identified in step 3A.2, the discount rate is an important source of uncertainty mostly set by management choices. In this case study, the project to be selected represents the implementation of a new technology, and therefore the project discount rate (IRR) is adjusted to offset risk and attract investors. It is, therefore, considered to be somewhere between medium to high, and so the minimum acceptable rate of return is set to be 24%. Thus, as also performed in Chapter 3, to represent the effect of the company choices with respect to the level of IRR used, the NPV is estimated considering both an IRR of 10% and 24% [149]. In Figure 4.6, two curves are depicted in red and blue, representing NPV obtained at 10% and 24% internal rate of return respectively, where the calculation of risk is equivalent to the shaded area under the cumulative distribution function of NPV as shown in Figure 4.6. A summary of the economic risk results is presented in Table 4.6.

Table 4.6: Summary of results for the calculation of economic risk for succinic acid and 1,3-PDO.

	Succinic acid	**1,3-PDO**
Frequency of selection	420/500	80/500
$Pr(NPV \leq 0)$ @10%	0.7857	0.8625
$Pr(NPV \leq 0)$ @24%	0.9119	0.95
Risk @10% (MM$)	41.22	62.68
Risk @24% (MM$)	48.40	65.24

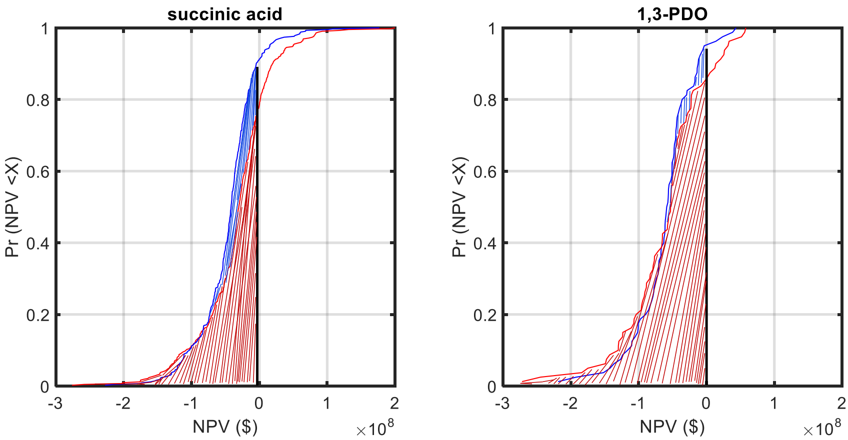


Figure 4.6: Cumulative distribution function for the succinic acid and 1,3-PDO production from glycerol. The highlighted area represents the risk of the project being non-profitable. Red represents NPV obtained for IRR@10%. Blue represents NPV obtained for IRR@24%.

Table 4.6 presents a summary of results and Figure 4.5 graphically presents the results obtained for the products under consideration, where we analyze the probability of NPV being lower than zero times the consequence of that event occurring. I.e., the economic risk will reflect the probability of the biorefinery concept under study to be non-profitable (non-viable) which corresponds to a NPV lower than zero. To this end, the crude glycerol valorization through the production of succinic acid is potentially the best investment alternative since it has a lower risk of being non-profitable than 1,3-PDO, representing a potential profit loss of 41 and 63 MM$ at a discount rate of 10%, respectively. Furthermore, in the case of selling the purified glycerol as the only product ("do nothing" alternative), the probability of NPV being lower than zero is equal to 1, and, therefore, this process is non-profitable for the full realization of uncertainty. The corresponding economic risk is 20 MM$, due to the lower capital investment required in comparison with the above-discussed alternatives. Also, it is important to note that, due to the fact that the market for refined/pharmaceutical grade of glycerol is nearly saturated, it is faced with global oversupply, and therefore there is a limited demand for purified glycerol [195], [196]. However, this fact was not taken into account in the estimation of risk for the "do nothing alternative", it was considered that all crude glycerol available is refined and sold.

Step 5.2: Environmental risk quantification

The environmental risk was quantified according to Eq.4.1, and using the monetary valuation factors in Table 4.3, where the built-in risk of each category is given by the probability of the category S_c being higher than the deterministic value multiplied by the consequence of that event happening. The empirical cumulative distribution function obtained as output of Step 4.2, and built based on the realization of conservative sample values (class 3 uncertainty, step 4.1), is used in order to read the cumulative probability needed for the estimation of risk for each category S_c. Then, the consequence is calculated based on the monetary difference between the deterministic values of each category and the realization of the conservative sample values over the plant's production lifetime. In this case study, the plant lifetime is taken to be consistent with the economic assumption lifetime of 30 years (Table C.2). However, since the first three years correspond to the plant construction (no production), 27 years is the entire period where the plant is operating and thus this is the time over which the environmental risk is quantified. The quantified environmental risk of 1,3-PDO and succinic acid is 47.7 and 53.9 MM\$/lifetime, respectively (shown also in Table 4.7). Therefore, based only on environmental risk and performance one can see that the production of 1,3-PDO stands out as being slightly better than the production of succinic acid.

Step 6: Combined risk assessment & decision-making

In order to assess the alternatives within the design space and identify the potentially best alternative, the proposed combined risk assessment matrix is used for decision-support. The position of both products in the matrix $(REC_{n,j}, REN_{n,j})$ is obtained by using the Eqs. 4.1 and 4.3; the results are summarized in Table 4.7 and shown in Figure 4.7. As shown in Figure 4.7, it is observed that the production of 1,3-propanediol is located in the 'Re-evaluate' box and the succinic acid production is located in the 'Improve' box. It is then clear that the potentially best alternative to be chosen for further investigation is the succinic acid production. However, the process needs to be improved in order to decrease its environmental burden and hence decrease its potential environmental risk. This is also highlighted by the R factor of the succinic acid alternative (see Table 4.7), which is higher than 1 showing that the normalized environmental risk has a greater impact that the normalized economic risk.

Figure 4.8 shows in detail the slight difference on the eco-efficiency of succinic acid over 1,3-PDO, where succinic acid presents itself more advantageously since the environmental benefit given by 1,3-PDO is evaluated not to be worth its additional economic risk. Moreover, the R_j and the improved positions $(REC_{n,j}, REN_{n,j})$ were estimated and shown in Table 4.7. The improved positions $(REC'_{n,j}, REN'_{n,j})$ represented in Figure 4.9, aim at establishing a balance between the economic and environmental risk, and therefore following the approach presented in the framework description, they are set upon the diagonal line. Finally, after analyzing the risk contributions of both products, one can deduce that choosing succinic acid is a safer choice, which potentially leads to a more sustainable solution for the glycerol valorization. This is also supported by existing com-

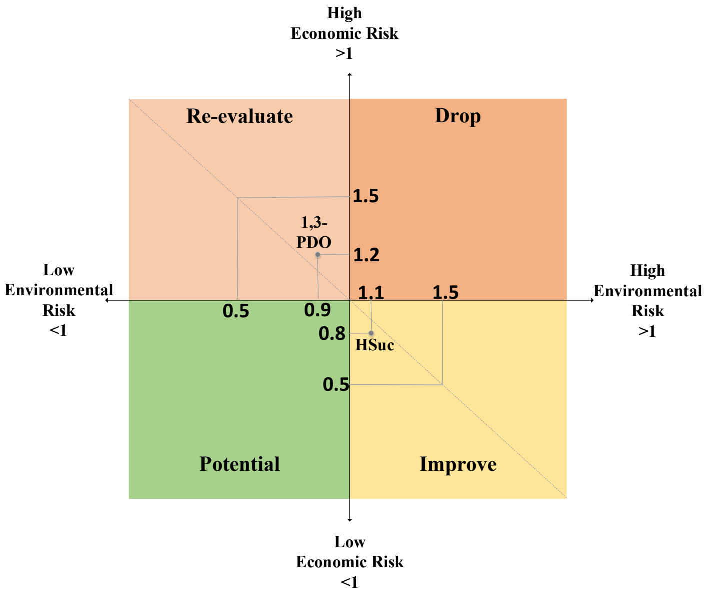


Figure 4.7: Sustainability risk assessment matrix, where 1,3-PDO and HSuc represent the product positions.

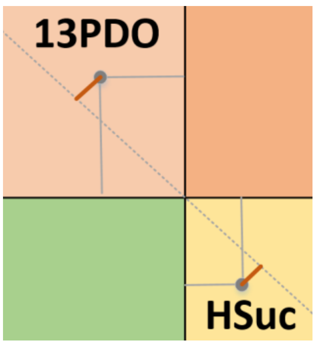


Figure 4.8: Detail of risk matrix to assess the alternatives' eco-efficiency.

mercial production plants such as: Reverdia producing 10 kton/y of Biosuccinium from renewable carbon sources (fermentable sugars) in Italy, since 2012 [183]; Succinity, a joint venture between Corbion Purac and BASF built in 2013, also having a 10kton/y working plant in Spain since 2013; and, Myriant and Bioamber, with the same range of installed capacities, operating in Canada and North America, respectively [197]. Succinic acid (and its salts) has been projected to be one of the future platform chemicals obtainable from renewable resources and has noteworthy potential as building block for the production of biopolymers [198], or to be used in food, pharmaceutical and cosmetic applications as well following its transformation into solvents and other existing petro-based chemicals [138].

Table 4.7: Summary results for the joint risk assessment.

	Succinic acid	1,3-PDO
$Risk_{env}$ $(MM\$/lifetime)$	53.85	47.66
$(REC_{n,j}, REN_{n,j})$	(0.80; 1.1)	(1.21; 0.88)
R	1.39	0.73
$(REC'_{n,j}, REN'_{n,j})$	(0.80; 1.13)	(1.24; 0.91)

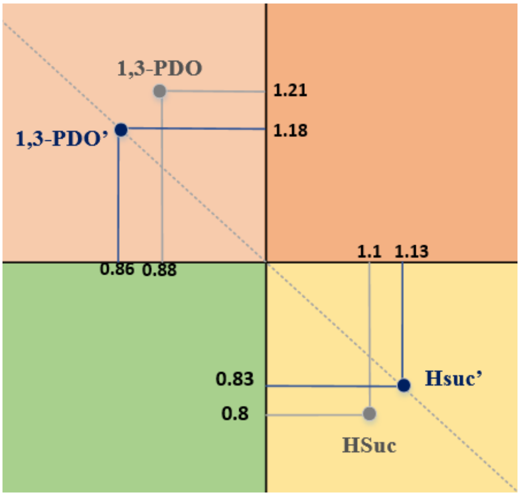


Figure 4.9: Combinatorial risk assessment matrix, where 1-3PDO' and HSuc' represent the improved positions.

Furthermore, it is important to note that, the uncertainty analysis and risk assessment results presented here depend on the framing of the problem which includes (i) sources of uncertainty identified, (ii) the uncertainty ranges defined (based on historical price range, internal company experiences, process expert/engineering insights, textbooks, etc). Therefore these results should be interpreted within that framing. However since the methodology is flexible, the uncertainty and risk analysis can be iterated as the user has more refined/updated information on sources/magnitude of uncertainties in the project development.

4.6 Conclusions

A flexible and systematic framework for a 'gate-to-gate' sustainability analysis incorporating techno-economic and environmental risk assessment is proposed as a decision-support tool to help rank the alternatives within the design space and identify the best potential conceptual process. To this end, the framework leads the user to actively: (i) identify techno-economic sources of uncertainty and, through uncertainty propagation; (ii) quantify the economic risk; (iii) perform the monetary valuation of environmental impact categories under uncertainty; (iv) quantify the potential environmental risk; (v) measure the alternatives' eco-efficiency identifying possible trade-offs; and, lastly (vi) use a sustainability risk assessment matrix for quantitative and qualitative assessment at the decision-support level also enabling information transfer to non-experts. The benefit given by the combined risk assessment matrix is a quick graphic analysis of all products within the design space; therefore after estimating the normalized position the user is able to visually identify the optimal solution. Enterprises are under increasing pressure to assess environmental, social, and economic impacts of the projects they evaluate. Thus, the proposed framework provides a meaningful measure of sustainability, being a useful and flexible way for companies to evaluate their processes and/or products from a quantitative and qualitative stand-point, enabling easier communication of feasibility assessments. In this way, the proposed framework provides the user with a useful and flexible tool for the decision-making support at the conceptual phase, which allows a quick assessment of results to facilitate decisions concerning which products to select or reject for further process development efforts. The framework has shown to be successful identifying the best potential alternative in the design space to sustainably add value to the glycerol side-stream.

Part II

Towards the sustainable design of biorefinery supply chains

CHAPTER 5

Supply chain design: the *GlyThink* model development and application

To further advance the development and implementation of glycerol based biorefinery concepts, it is critical to analyze the glycerol conversion into high value-added products in a holistic manner, considering both production as well as the logistics aspects related to the supply chain structure. To address the optimal design and planning of the glycerol-based biorefinery supply chain, in this chapter, a multi-period, multi-stage and multi-product Mixed Integer Linear Programming optimization model, called GlyThink, based upon the maximization of the Net Present Value (NPV) is proposed. The proposed model is able to identify operational decisions - including locations, capacity levels, technologies and product portfolio - as well as strategic decisions such as inventory levels, production amounts and transportation to the final markets. Several technologies are considered for the glycerol valorization to high value-added products. In Figure 5.1, a graphic description of this chapter is presented.

This chapter of the thesis is based upon the following article:

Supply chain optimization of integrated glycerol biorefinery: GlyThink model development and application. L. Gargalo, C., Cheali, P., Posada, J.A., Gernaey, K. V. Sin, G. *Industrial & Engineering Chemistry Research*, DOI:10.1021/acs.iecr.7b00908.

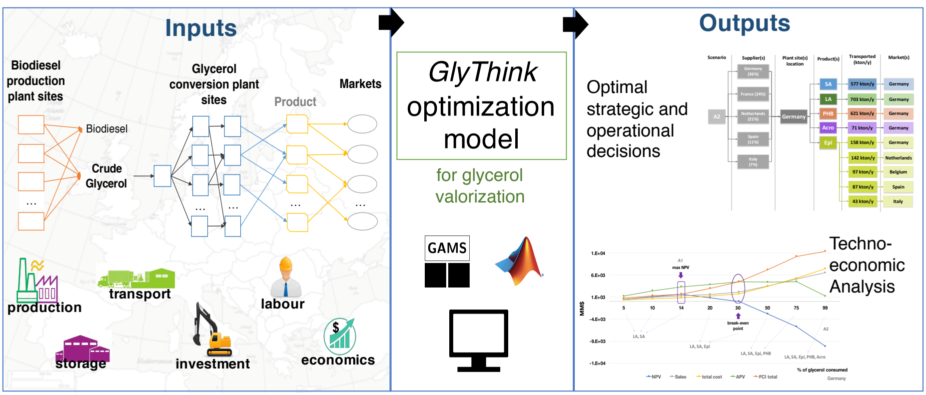


Figure 5.1: Graphic description of chapter 5.

Nomenclature

Subscript indices	
i	Components
k	Technologies
x	Plant site locations
t	Time periods
r	Reactions
q	Capacity levels
m	Final markets
z	Suppliers

Sets	
I	Set of all components i
I_p	Set of components i that are final products
I_{rm}	Set of components i that are raw materials
I_{ut}	Set of components i that are utilities and/or chemicals/solvents
I_r	Set of components i that are reactants
K	Set of all technologies k
K_{GP}	Set of technologies k used for the purification of raw materials
K_{conv}	Set of technologies k used for the conversion of raw materials to final products $i \in I_p$
K_{SP}	Set of technologies k used for the separation and purification of final products $i \in I_p$
X	Set of plant locations x
T	Set of time periods t
R	Set of reactions r
Q	Set of capacity levels q
M	Set of final markets m
Z	Set of all suppliers z

Parameters

Technology	
$\phi_{i,z,t}$	Raw materials i available from supplier z in time period t
$\alpha_{i,k}$	Specific utility consumption of i in k
$\theta_{i,k,r}$	Conversion of reactant i in technology k where r occurs
$\gamma_{i,k,r}$	Reaction stoichiometry for every component i in technology k and reaction r
$\mu_{i,k}$	Fraction of chemicals/solvents mixed with process stream of i in technology k
$SW_{i,k}$	Fraction of i that is separated as waste in k

Technology capacity and cost	
$H^{min}_{k,q}$	Minimum capacity for each capacity level q for technology k
$H^{max}_{k,q}$	Maximum capacity for each capacity level q for technology k
$slope_{k,q,x}$	Linearization constant for technology k and interval q
$b_{k,q,x}$	Intercept value for the linearized interval q for technology k
c^{max}_k	Maximum cost of technology k

wc_t	Operating supplies cost at time period t
ms_t	Maintenance cost at time period t

Transportation

$D_{p,m,t}$	Demand of product p in market m in time period t
L	Total load of transport mode per trip traveled
pR	Cost of rail freight per ton.km
$d_{x,m}$	Distance of market m from plant site location i

Cost related parameters

pRM	Price of raw materials $i \in I_{rm}$
pUT_i	Price of utilities per component $i \in I_{ut}$
pST_p	Storage price per final product $i \in I_p$
pP_i	Price of final product $i \in I_p$
ω	Interest rate (%)
φ	Tax rate (%)
γ_t	Capital depreciation in time period t

Decision variables

Continuous variables

$F^{in}_{i,k,x,t}$	Inflow of components i into technology k in plant location x in time period t
$F_{i,k,x,t}$	Outflow of components i from technology k in plant location x in time period t
$U_{i,k,x,t}$	Flow of utilities i added in technology k in plant location x in time period t
$Pr_{i,k,x,t}$	Flow of components i produced/consumed in technology k in plant location x in time period t
$Ftr_{i,x,m,t}$	Transported flow of component $i \in I_p$ from plant location x to final markets m in time period t
$W_{i,k,x,t}$	Flow of components i separated as waste in technology k in plant location x in time period t
$RawM_{i,z,x,t}$	Flow of raw materials i from supplier z to plant location x in time period t
$Cost_{k,x,t}$	Cost of technology k in plant location x in time period t
$C_{k,q,x,t}$	Cost of technology k in each capacity interval q in time period t
$h'_{k,q,x,t}$	Disaggregated flowrate variable of technology k with capacity interval q in time period t

Integer variables

$T_{x,m,t}$	Number of trips performed by truck from plant site location x to markets m in time period t
$T_{z,x,t}$	Number of trips performed by truck from supplier z to production plant site x in time period t

Binary variables

$y_{k,q,x,t}$	=1 if technology k with capacity q is installed in location x in time period t

Boolean variables

$Y_{k,x,t}$	=1 if technology k with capacity q is installed in location x in time period t

Auxiliary variables for the objective function

NPV	Net Present Value
CF_t	Cash flow in time period t
NE_t	Net earnings in time period t
$FCI_{k,x,t}$	Fixed capital investment of technology k in plant location x and time period t
CD_t	Capital depreciation in time period t

5.1 Introduction

This chapter focuses on the optimization of the supply chain for the optimal operation of an integrated biorefinery based upon the conversion of glycerol to high value-added products. This study differs from previous studies in the field, by proposing the *GlyThink* model, a MILP multi-product, multi-period (planning horizon over a discrete set of time periods) and multi-stage (decisions on multiple parts/stages of the supply chain) tool. Hence, this chapter introduces the following novel contributions: (i) a mathematical formulation based upon the proposed superstructure for the maximization of the economic performance across the entire value chain (maximizing Net Present Value), by using detailed cash flow analysis with taxation and capital depreciation, transportation and operating costs; (ii) the model appropriately estimates the fixed capital investment for the facilities by employing disjunctive programming to linearize the power-law exponential cost function and reformulating it to a mixed integer linear programming problem; and, (iii) the model identifies, at an early stage of design, the optimal operational decisions, including crude glycerol suppliers, plant site location(s), capacity levels, technologies and product portfolio; furthermore, strategic decisions such as inventory levels, production amounts and transportation to the final markets are also supported.

The remainder of the chapter is organized as follows. In section 5.2 an overview of the GlyThink model is provided, highlighting the problem statement; in section 5.3 the mathematical formulation of the optimization problem is formally introduced. Section 5.4 introduces the case study, and in section 5 the case study results and the discussion are presented. Lastly, key conclusions are drawn and 'take home' messages are formulated in section 5.6.

5.2 Overview of the *GlyThink* model

The overall network of the integrated glycerol biorefinery supply chain is illustrated in Figure 5.2, where both upstream and downstream parts of the supply chain are highlighted. Within the network presented, there are six significant sections as follows: 1) transport of biomass to the biodiesel production sites; 2) glycerol production in the biodiesel plants; 3) transportation of crude glycerol to the glycerol conversion plant site(s); 4) glycerol purification; 5) conversion, product separation and purification; 6) distribution of the products to the final markets.

The *GlyThink* model focuses on the downstream part of the network presented in Figure 5.2. This is due to the fact that: (i) glycerol is an immediate by-product of

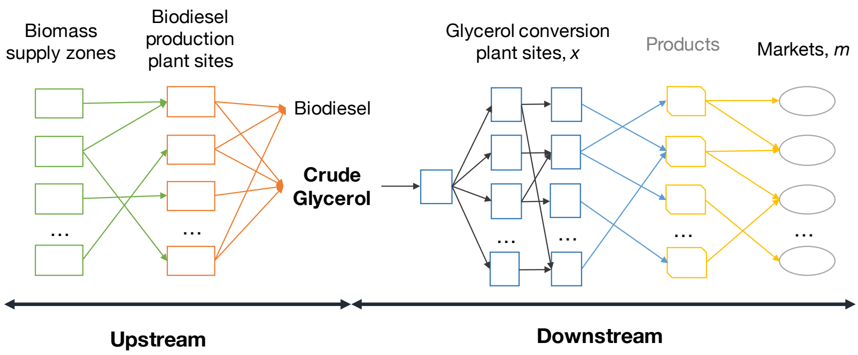


Figure 5.2: Structure of the multi-stage nature of the glycerol to value-added products supply chain network.

the biodiesel industry, being produced independently of the raw material used for the biodiesel manufacture; and, (ii) it is nowadays a surplus product, with low market value due to overproduction [15]. Therefore, one of the main goals of this work is to - at the early stage of design - identify and critically analyze the optimal integrated glycerol-based biorefinery supply chain for the valorization of glycerol into high value-added products. As presented in Figure 5.3, the GlyThink model was developed by integrating technology selection and operation, geographical information, capital investment models, economic models and optimization techniques. The corresponding problem can be formally stated as follows.

Overall, given:

- a possible superstructure of the integrated glycerol-based biorefinery supply chain combining crude glycerol acquisition, plant site locations, upgrading technologies and distribution logistics;
- the planning time period, corresponding to the typical biorefinery lifetime in terms of years;
- a set of crude glycerol suppliers and a maximum supply available per supplier;
- crude glycerol composition;
- a set of potential products to be produced from glycerol;
- a set of available production, separation and purification technologies and corresponding yields;
- a set of potential locations for the construction of the biorefinery(ies);
- a set of potential markets and corresponding demands;
- distances between nodes of the supply chain structure;
- crude glycerol and product prices;

- labor cost dependency on production capacity;
- transportation capacity and related costs;
- upper and lower bounds for each technology's capacity level;
- process and economic models (such as fixed capital investment calculation); and,
- financial data (such as interest and tax rates).

The goal is to maximize the Net Present Value associated with the integrated glycerol biorefinery supply chain and determining the following operational and strategic decision variables:

- Location of glycerol suppliers and related logistics;
- The number, capacities, locations (single- or multi-plant), and technologies for the biorefinery plants;
- Glycerol inflow consumed for each selected biorefinery;
- Product portfolio, production scale and storage levels at the plant locations for each time period; and,
- Product quantities to be delivered from plants to the demand sinks.

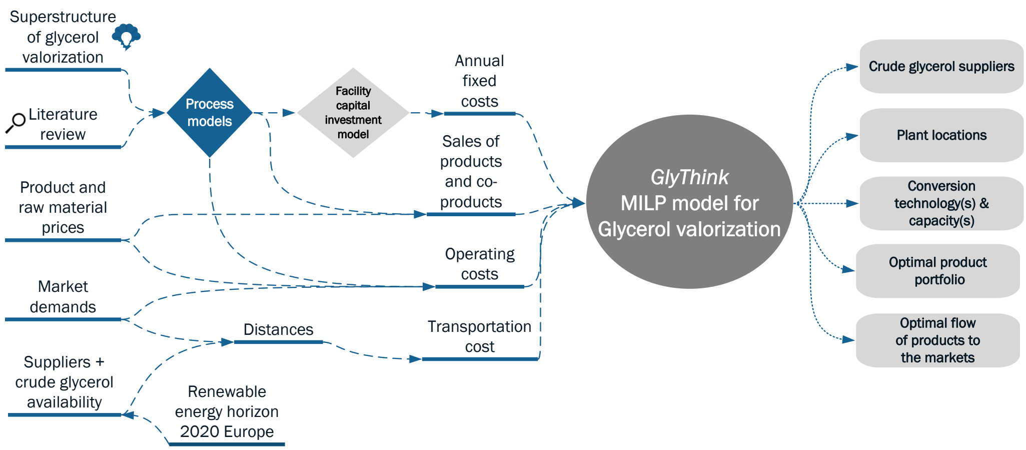


Figure 5.3: Components and expected outcomes of the *GlyThink* model.

5.3 Mathematical Formulation

The *GlyThink* model is formulated as a multi-period, multi-product and multi-stage mixed integer linear program (MILP), aiming at maximizing the Net Present Value associated with the optimal integrated glycerol biorefinery supply chain. From this moment on, SC will be used as a simplified terminology for the integrated glycerol biorefinery supply chain. Constraints are set up concerning: the supply of glycerol to the plant site location(s), production capacity, mass balances, technology(s) for the conversion of glycerol into the final products, operating costs, transportation capacities, and demand satisfaction. The mathematical model is described in detail below. The full nomenclature, including definitions of all sets, variables, and parameters of the model, is given at the beginning of this chapter.

5.3.1 Constraints

The operational planning model regarding plant capacity, production, transportation and mass balance relationships is considered together with the constraints of these activities due to the supply chain structure. Thus, the corresponding constraints and relationships are grouped into six classes, and these are: mass balances, selection of conversion technology and plant location, supply, demand satisfaction, technology capacity and cost, and non-negativity constraints. Each class is presented in more detail below.

Mass balances

The mathematical formulation regarding the mass balances has been adapted from a previous work developed in our group [87], where generic process models enables the description of every technology within the superstructure trough a sequence of tasks that follow the same modeling structure. The overall mass balance for each component i in technology k at plant site location x at each time period t is set by Eq. (5.1). For each technology k at site location x and time period t, the inflow of i ($F^{in}_{i,k,x,t}$) plus the amount of i produced ($Pr_{i,k,x,t}$), must be equal to the amount of i separated as waste ($W_{i,k,x,t}$) plus the output flow ($F_{i,k,x,t}$) to be delivered to the customers or to be stored in location x.

$$\begin{aligned} &\sum_{z}^{Z} RawM_{i,z,x,t} + \sum_{k}^{K_{conv}} Pr_{i,k,x,t} + \alpha_{i,k} \cdot \sum_{k}^{K} U_{i,k,x,t} = \\ &\sum_{k}^{K_{GP} \cup K_{SP}} W_{i,k,x,t} + \sum_{k}^{K_{SP}} F_{i,k,x,t}, \forall i \wedge Ix \wedge t \in T \end{aligned} \tag{5.1}$$

Furthermore, in this equation (5.1), K_{conv} represents the set of technologies used for the conversion of raw materials into value-added products, and finally K_{SP} , represents the set of technologies to be used for the separation and purification of the above-mentioned products. Also, $\alpha_{i,k}$ is the fraction of a chemical or utility mixed with the process stream (iI_{ut}), being 1 if the utility/chemical/solvent i is directly added to the flow stream (e.g. direct steam, and 0 otherwise (e.g. cooling water).

The amount of component i produced or consumed in the conversion technologies, $Pr_{i,k,x,t}$, is given in Eq. (5.2).

$$\sum_{k}^{K_{conv}} Pr_{i,k,x,t} = \sum_{k}^{K_{conv}} \sum_{r}^{R} \sum_{rct}^{Rct} \gamma_{i,k,r} \cdot \theta_{rct,k,r} \cdot F^{in}_{rct,k,x,t}, \quad \forall i \in I \wedge x \in X \wedge t \in T \tag{5.2}$$

where, $\gamma_{i,k,r}$ and $\theta_{rct,k,r}$ represent reaction stoichiometry for each component i in technology k and reaction r, and conversion of key reactant i in technology k where r occurs, respectively. The total amount of chemicals or utilities consumed/added i is obtained as a fraction of the total flow in the technologies k and it is given in Eq. (5.3) as follows.

$$\sum_{k}^{K} U_{i,k,x,t} = \mu_{i,k} \cdot \sum_{i}^{I \notin I_{ut}} F^{in}_{i,k,x,t}, \forall i \in I_{ut} \wedge x \in X \wedge t \in T \tag{5.3}$$

where, $\mu_{i,k}$ is the fraction of chemicals/solvents $i \in I_{ut}$ mixed with the process stream in technology k.

Supply

In constraint (5.4), the inflow of component $i \in I_{rm}$ into plant site location x coming from supplier z in time period t, $RawM_{i,z,x,t}$, is enforced to be lower than or equal to the total amount of i available from supplier z in time period t ($\phi_{i,z,t}$).

$$\sum_{x}^{X} RawM_{i,z,x,t} \leq \phi_{i,z,t}, \forall i \in I_{feed} \wedge z \in Z \wedge t \in T \tag{5.4}$$

$$\sum_{x}^{X} \sum_{z}^{Z} RawM_{i,z,x,t} \leq \sum_{z}^{Z} \phi_{i,z,t}, \forall i \in I_{feed} \wedge t \in T \tag{5.5}$$

$$\sum_{i}^{I_{feed}} RawM_{i,z,x,t} \leq L \cdot T_{z,x,t}, \forall x \in X \wedge z \in Z \wedge t \in T \tag{5.6}$$

Furthermore, constraint (5.5) imposes that the maximum flow of raw material i delivered to all locations x coming from all suppliers z cannot exceed the total amount of raw materials i available from all suppliers z in time period t. Finally, constraint (5.6) sets the total flow of raw materials to be delivered to the plant site locations x to be lower or, at most, equal to the available transportation capacity over the planning time period.

Selection of conversion technology and plant location

A binary variable, $y_{k,q,x,t}$, is introduced in constraints (5.7) and (5.8) to impose the selection of technologies k, with capacity level q, in biorefinery location x, and time period t. The capacity level q refers to each one of the regions considered in the linearization of the capital investment.

$$\sum_{x}^{X} y_{k,q,x,t} \geq 1, \forall k \in K \wedge q \in Q \wedge t \in T \tag{5.7}$$

$$\sum_{x}^{X} y_{k,q,x,t} \leq N_x, \forall k \in K \wedge q \in Q \wedge t \in T \tag{5.8}$$

where $y_{k,q,x,t}$ is equal to 1 if technology k with capacity level q is built at location x and time period t; and N_x corresponds to the total number of plant site locations available for the construction of the biorefineries. Constraint (5.7) and constraint (5.8) state that at least one and at most N_x locations can be simultaneously selected for the construction of the biorefinery(ies). Also, as stated in constraint (5.9), if at time period t, technology k with capacity level q is selected to be built at plant site location x, then it is assumed that it must be selected/open during all time periods greater than t.

$$y_{k,q,x,t+1} \geq y_{k,q,x,t}, \forall k \in K \wedge x \in X \wedge q \in Q \wedge t \in T-1 \tag{5.9}$$

Demand satisfaction

$$Ftr_{i,x,m,t} + \sum_{k}^{K} St_{i,k,x,t} \leq \sum_{k}^{K} F_{i,k,x,t}, \forall i \in I_p \wedge x \in X \wedge m \in M \wedge k \in K_{SP} \wedge t \in T \tag{5.10}$$

$$\sum_{x}^{X} Ftr_{i,x,m,t} \leq D_{p,m,t}, \forall i \in I_p \wedge m \in M \wedge t \in T \tag{5.11}$$

$$\sum_{x}^{X} \sum_{m}^{M} Ftr_{i,x,m,t} \leq \sum_{m}^{M} D_{p,m,t}, \forall i \in I_p \wedge m \in M \wedge t \in T \tag{5.12}$$

$$Ftr_{p,x,m,t} \leq L \cdot T_{p,x,m,t}, \forall x \in X \wedge m \in M \wedge \in T \tag{5.13}$$

Constraint (5.10) sets the maximum limit of product being transported to the markets m, $Ftr_{p,x,m,t}$, as the maximum amount of product p being produced at plant site x in time period t, where the $St_{i,k,x,t}$ is the amount of product i to be stored at location x. Constraint (5.11) enforces that, the amount of product p delivered to a market m must not exceed the demand in that same market m. Furthermore, constraint (5.12) imposes that the maximum flow of product p delivered to all markets m cannot exceed the total demand of product p in all markets m. Finally, constraint (5.13) sets the product flow delivered to the markets ($Ftr_{p,x,m,t}$) to be lower or, at most, equal to the available transportation capacity over the planning time period.

Technology capacity and cost

The fixed capital investment (FCI) is one of the most critical costs associated to biocrefinery design and implementation [15]. It is beneficial for the capacity of the installed technologies k to be a continuous variable, which commonly involves knowledge of the plant's costs as a function of its capacity, which might be given by a non-linear equation such as the power law presented in Eq. (5.14).

$$Cost_x = cost_{base} \cdot (\frac{capacity_x}{capacity_{base}})^n \tag{5.14}$$

In such a power law, the exponent n usually varies around 0.7. Therefore, in this work, to account for economies of scale of the technologies, the power law has been used to estimate the capital costs based upon the investment costs of a reference case ($cost_{base}$ and $capacity_{base}$), where exponents of 0.75 and 0.7 were used for biochemical and chemical processing plants, respectively [15]. As a linear programming model is efficient, we employ a piecewise linear function of the non-linear power law, which specifies a set of capacity levels q. This disjunctive formulation is used to linearize the power law equation that relates the capital costs against capacity, and it is presented in Eq.(5.15).

$$\begin{bmatrix} Y_{k,x,t} \\ \forall q \in Q \begin{bmatrix} y_{k,q,x,t} \\ Cost_{k,x,t} = b_{k,q,x} + slope_{k,q,x} \cdot H^{'}_{k,x,t} \\ H^{'min}_{k,q} \leq H^{\prime}_{k,x,t} \leq H^{'max}_{k,q} \end{bmatrix} \end{bmatrix} \forall \begin{bmatrix} \neg Y_{k,x,t} \\ Cost_{k,x,t} = 0 \end{bmatrix}, \forall k \in K \wedge x \in X \wedge t \in T \tag{5.15}$$

This disjunction portrays that the linear equation to determine the capital cost of the technology k depends on its capacity. The Boolean variable $Y_{k,x,t}$ is used to activate each term of the disjunction. In this way, if a certain capacity is selected, the corresponding segment of the capital cost function is selected and the binary variable $y_{k,q,x,t}$ is 1. To appropriately model the disjunction presented in Eq.(5.15), the convex hull technique following reference [199] is used and the respective algebraic equations are obtained. These are presented below.

$$\sum_{q}^{Q} y_{k,q,x,t} \leq 1, \forall k \in K \wedge x \in X \wedge t \in T \tag{5.16}$$

$$H^{\prime}_{k,x,t} = \sum_{i}^{I_p} F_{i,k,x,t}, \forall i \in I_p \wedge k \in K \wedge x \in X \wedge t \in T \tag{5.17}$$

$$H^{\prime}_{k,x,t} = \sum_{q}^{Q} h^{\prime}_{k,q,x,t}, \forall k \in K \wedge x \in X \wedge t \in T \tag{5.18}$$

$$Cost_{k,x,t} = \sum_{q}^{Q} C_{k,q,x,t}, \forall k \in K \wedge x \in X \wedge t \in T \tag{5.19}$$

$$H^{min}_{k,q} \cdot y_{k,q,x,t} \leq h^{\prime}_{k,q,x,t} \leq H^{max}_{k,q} \cdot y_{k,q,x,t}, \forall k \in K \wedge q \in Q \wedge x \in X \wedge t \in T \tag{5.20}$$

$$C_{k,q,x,t} = b_{k,q,x} \cdot y_{k,q,x,t} + slope_{k,q,x} \cdot h^{\prime}_{k,q,x,t}, \forall k \in K \wedge q \in Q \wedge x \in X \wedge t \in T \tag{5.21}$$

$$C_{k,q,x,t} \leq c^{max}_{k} \cdot y_{k,q,x,t}, \forall k \in K \wedge q \in Q \wedge x \in X \wedge t \in T \tag{5.22}$$

In summary, if a segment of the disjunctive terms is selected, then the related Boolean variable $Y_{k,x,t}$ is true and the correlated binary variable $y_{k,q,x,t}$ must be 1. For all other remaining instances, the Boolean and binary variables are false and 0, respectively. Therefore, as the upper boundaries are given by constraints (5.20) and (5.22) for the segments that are not selected, the associated continuous disaggregated variables are 0. Furthermore, the variables that can have values higher than 0 are the ones obtained for the disjunctive term selected/identified. Furthermore, Eqs. (5.18) and (5.19) state that the continuous variables are equal to the disaggregated variables for the disjunctive term chosen, and their relationships are described through these disaggregated variables by constraints (5.17) and (5.18), which are only active when the related binary variables are 1.

Decision variables

Binary and non-negativity constraints on the decision variables are stated as follows in constraints (5.23) and (5.24), respectively.

$$y_{k,q,x,t} \in \{0,1\} \tag{5.23}$$

$$\begin{aligned} &F_{i,k,x,t}, F^{in}_{i,k,x,t}, U_{i,k,x,t}, Ftr_{p,x,m,t}, St_{i,k,x,t}, \\ &Pr_{i,k,x,t}, W_{i,k,x,t}, Cost_{k,x,t}, C_{k,q,x,t}, h'_{k,q,x,t}, T_{p,x,m,t}, T_{z,x,t} \geq 0 \end{aligned} \tag{5.24}$$

5.3.2 Objective function

As measure of economic performance, the total Net Present Value (NPV) of the supply chain is selected as the objective function. The NPV is estimated as the sum of yearly cash-flows discounted to the present year, at a specified interest rate, as presented in the following Eq. (5.25).

$$\begin{aligned} &NPV = \sum_{t}^{T} \frac{CF_t}{(1+\omega)^t} = \\ &\sum_{t}^{T} \frac{NE_t}{(1+\omega)^t} - C_0 = APV - C_0 = \\ &\sum_{t}^{T} \left[\frac{1}{(1+\omega)^t} \cdot (S_t - PC_t - Lc_t - TrC_t - SC_t - WC_t - TI_t) \right] + C_0 \cdot \left(\frac{sv}{(1+\omega)^t} - 1 \right) \end{aligned} \tag{5.25}$$

where, ω represents the interest rate. S_t and PC_t, represent the revenue (product sales) and production cost, respectively; Lc_t, TrC_t, and SC_t, represent the labor costs, transportation cost and storage cost, respectively; CD_t and WC_t, represent the capital depreciation and working capital, respectively. TI_t and C_0 stand for the taxable income and total initial capital investment, and they are given by the following equations:

$$TI_t = \varphi \cdot [S_t - PC_t - Lc_t - TrC_t - SC_t - CD_t] \tag{5.26}$$

$$FCI_{k,x,t} = 6.7 \cdot \sum_{q}^{Q} C_{k,q,x,t}, \forall q \in Q \wedge k \in K \wedge x \in X \wedge t \in T \tag{5.27}$$

$$C_0 = \sum_{x}^{X}\sum_{k}^{K} FCI_{k,x,t=1} + \sum_{t}^{T}\left[\sum_{x}^{X}\sum_{k}^{K} FCI_{k,x,t} - \sum_{x}^{X}\sum_{k}^{K} FCI_{k,x,t-1}\right], \\ \forall k \in K \wedge x \in X \wedge t \in T \tag{5.28}$$

Where, in Eq. (5.27) the purchased capital investment is converted into delivered capital investment as suggested in [149]. Moreover, C_0 includes the capital investment made at the beginning (t=1), and additional capital investment increments related to possible/potential expansions of production capacity in t time period(s). In this way the model is flexible allowing for potential future expansions of production capacity, if required, for example, to accommodate the realization of uncertainty, such as in product demand. Finally, the Net Present Value is fully given by the Eq.(5.29).

$$\begin{aligned}
NPV = \sum_{t}^{T} & \left[\frac{(1-\varphi)}{(1+\omega)^t} \right. \\
& \cdot \left[\sum_{x}^{X}\sum_{m}^{M}\sum_{k}^{K_{SP}}\sum_{i}^{I_p} Ftr_{i,x,m,t} \cdot pP_i - \sum_{x}^{X}\sum_{k}^{K_{PG}}\sum_{i}^{I_{feed}} F^{in}_{i,k,x,t} \cdot pRM_i \right. \\
& - \sum_{x}^{X}\sum_{k}^{K_{conv}\cup K_{SP}}\sum_{i}^{I_p} U_{i,k,x,t} \cdot pUT_i - op \cdot ns \cdot avSal_t \cdot \sum_{x}^{X}\sum_{k}^{K_{PG}}\sum_{i}^{I_{feed}} F^{in}_{i,k,x,t} \\
& - \sum_{x}^{X}\sum_{m}^{M}\sum_{i}^{I_p} \left[T_{i,m,x,t} \cdot \left(2 \cdot d_{x,m} \cdot (fc + trMa) + \left(\frac{2 \cdot d_{x,m}}{sp} + lut \right) \cdot dw \right) \right] \\
& \sum_{x}^{X}\sum_{m}^{M}\sum_{i}^{I_p} \left[T_{z,x,t} \cdot (2 \cdot d_{z,m} \cdot (fc \cdot pF + trMa) + \left(\frac{2 \cdot d_{z,m}}{sp} + lut \right) \cdot dw) \right] - 2 \cdot trGE_t \\
& \left. - \sum_{x}^{X}\sum_{k}^{K_{SP}}\sum_{i}^{I_p} St_{i,k,x,t} \cdot pSt_i - (wc_t + ms_t) \cdot C_0 \right] \\
& \left. + \frac{\varphi}{(1+\omega)^t} \cdot \gamma_t \cdot C_0 \right] + \left(\frac{sv}{(1+\omega)^t} - 1 \right) \cdot C_0
\end{aligned} \tag{5.29}$$

5.4 Case study description

The above-mentioned mathematical formulation corresponding to the *GlyThink* model was implemented in GAMS and solved to global optimality with CPLEX 12. *GlyThink* was applied to the case study on the valorization of crude glycerol in Europe to a number of value-added products. The case study is thereby aiming at identifying the optimal (i) set of suppliers, (ii) plant site location(s), (iii) product portfolio and, (iv) products distribution network (supply chain structure).

5.4.1 Supply chain characterization

In 2007, the European Commission council implemented a 10% compulsory minimum target for the share of renewable energy in transportation by 2020 [200] [201].

In the EU-28, the total energy consumed for all road transport modes amounted to 353 Mtoe in 2014 [202]. Thereby, assuming that in 2020 the renewable energy target will be fulfilled solely by biodiesel, which is currently the most consumed biofuel in Europe [105], it sets the glycerol availability in Europe to $4.10 \times 10^6 ton/year$. In this section, we identify the plant site candidates as the current top-5 major producers (and consumers) of biodiesel in Europe, and they are assumed to be stable markets [203]: Germany, France, The Netherlands, Spain and Italy. Being the top-5 major producers of biodiesel, these locations are also considered to be the potential suppliers for the acquisition of glycerol, whose availability is presented in Table 5.4. The typical composition for the crude glycerol stream obtained from the biodiesel process is assumed to be approximately 61 wt% glycerol, 32.59 wt% methanol, 2.62 wt% $NaOCH_3$, 1.94 wt% fats, and 2.8 wt% ash [204].

Table 5.4: Availability of crude glycerol per supplier*

Supliers	**Crude glycerol availability (ton/year)**
Germany	1.48×10^6
France	9.76×10^5
Netherlands	8.77×10^5
Spain	4.72×10^5
Italy	2.95×10^5

*obtained considering that the biodiesel produced in Europe is solely from these locations

The range of value-added products has been primarily identified in previous work [15] and is here expanded through literature review and based on their potential scale-up potential, aiming at being illustrative of the potential of the glycerol based biorefinery. Therefore, the most extensive processing network, to the best of my knowledge, with 12 processing pathways to produce a variety of biofuels and value-added bioproducts is proposed. As presented in Figure 5.4, the twelve unique products are: ethanol, poly-3-hydroxybutyrate, lactic acid, succinic acid, propionic acid, 1,3-PDO, 1,2-PDO, hydrogen, acrolein, n-butanol, isobutanol and epichlorohydrin. Moreover, the products are produced by applying different technologies, which are included in this case study, through the definition of different process conversions, separation and purification technologies (see Table 5.5).

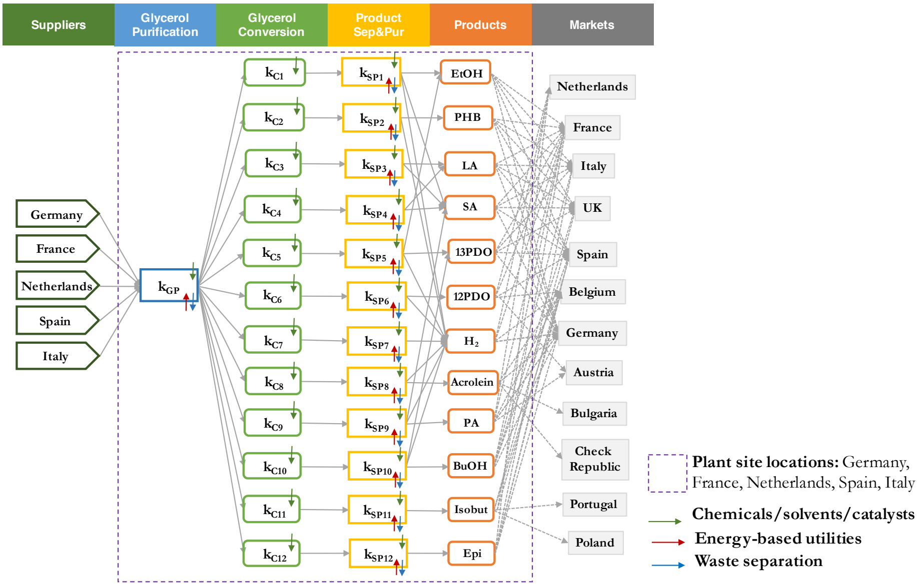


Figure 5.4: Superstructure of connections for the potential glycerol-based integrated biocrefinery. Where k_{GP} represents the glycerol separation and purification; k_{C1} to k_{C12} represents the conversion technologies; and, k_{SP1} to k_{SP12} represents the separation and purification technologies

Table 5.5: Products and corresponding technologies under study. Extended based on [15]

Product	**Technology description**	**Product Yield (g/ g glyc)**	**by-products**
1,3-propanediol (1,3-PDO)	Glycerol fermentation by an engineered strain of *K. pneumoniae* + reactive extraction w/ isobutyraldehyde hydrophilic alcohol/salt mixture (ethanol/K_2HPO_4) [162]	0.55	EtOH, AA, CO_2, H_2, biomass
Propionic acid (PA)	Glycerol fermentation by an engineered strain of *P. acidopropionoci* $ACK - Tet$ + reactive extraction w/ TO and ethylacetate [123]	0.68	SA, AA,CO_2, H_2, $biomass$
Polyhydroxybutyrate (PHB)	Glycerol fermentation by an engineered strain of *C. necator* + blending w/ surfactant solution + hypochlorite digestion centrifugation + spray drying [141]	0.68	CO_2, H_2, biomass
1,2-propanedio (1,2-PDO)	sequential processes of dehydrogenation-hydrogenation via hydroxyacetone [142] [143]	0.774	H_2, H_2O, EG
Lactic acid (LA)	Glycerol fermentation by an engineered strain of *E.coli* + reactive extraction w/ TOA and DCE [121]	0.79	SA, FA, AA, CO_2, biomass
Succinic acid (SA)	Glycerol fermentation by an engineered strain of *B succinis producens DD1* + reactive extraction w/ TOA and 1-octanol [106],[205]	1.02	LA, CO_2, biomass
Isobutanol (Isob)	Chemical conversion of glycerol to propanal via acrolein + methanol conversion to methanal + methanal and propanal condensed to methacrolein + hydrogenation of methacrolein to isobutanol [144],[145]	0.73	CO_2, H_2O
Hydrogen (H_2)	Steam reforming of glycerol for hydrogen production over Ni/SiO2 catalyst [179],[168]	0.66	CO_2, CO, CH_4
n-Butanol (BuOH)	Glycerol anaerobic fermentation by an engineered strain of *C. pasteurianum* + vacuum stripping [106],[146],[147]	0.30	13PDO, H_2,H_2O, CO_2, biomass
Ethanol (EtOH)	Glycerol fermentation by an engineered strain of *E.coli* + dehydration [117],[147]	0.52	SA, H_2, CO_2, biomass
Acrolein (Acro)	Glycerol dehydration [148]	0.49	AC, H_2O
Epichlorohydrin (Epi)	Glycerol hydrochlorination [206]	0.79	NaCl, H_2O

5.4.2 Market Demands

The market demands for the above-mentioned twelve products were collected from reports, publications and public communications. To be as much representative of the European market as possible, a total of 5 top markets were identified for each product and the corresponding demands were collected, and they are summarized in Table5.6. The transportation costs regarding the transport of products to the markets depends on the distance and the transportation mode and its corresponding cost. In this work, we consider cross-country product delivery, thus the transportation mode used is by truck. The storage of non-sold products is centralized, and the distances between the production plant sites and the markets is assumed to be the distance point to point between the center of the countries, respectively. They are reported in the matrix of distances presented in Table D.1 in Appendix D.

Table 5.6: Market demands for each product, corresponding main assumptions and respective references.

Products	Markets	Demand per market (10^3 ton/year)	Assumptions	Refs
PHB	Germany	8.82×10^3	Potential addressable market is replacement of polypropylene (PP) and polyethylene	[182] [197], [207]
	France	4.97×10^3		
	Italy	3.37×10^3		
	United Kingdom	2.64×10^3		
	Spain	2.60×10^3		
Ethanol	Germany	1.20×10^6	Ethanol used as biofuel	[197] [203]
	United Kingdom	7.89x102		
	France	6.71×10^2		
	Spain	2.96×10^2		
	Italy	2.84×10^2		
Lactic acid	Germany	5.36×10^3	Production of PLA, with an addressable market as replacement of polystyrene (PS), polypropylene (PP) and PET. this market represents 39% of the total market of lactic acid	[197] [197], [207], [208]
	France	3.02×10^3		
	Italy	2.05×10^3		
	United Kingdom	1.60×10^3		
	Spain	1.85×10^3		
Succinic acid	United Kingdom	2.56×10^2	Production of PLA, with an addressable market is as Addressable markets are given by plasticizers, BDO, polyester polyols, alkyl resins, PBS and PBST	[207], [209], [210]
	Spain	2.52×10^2		
	Germany	8.54×10^2		
	Italy	4.81×10^2		
	France	3.26×10^2		
1,3-Propanediol	Germany	1.22×10^3	For the production of PTT, which is a biodegradable replacement for PET	[197],[207]
	France	6.87×10^2		
	Italy	4.66×10^2		
	United Kingdom	3.65×10^2		
	Spain	3.60×10^2		
1,2-Propanediol	Germany	4.90×10^2	Top-5 major propylene glycol producers a biodegradable replacement for PET	[182] [154]
	Netherlands	80		
	France	80		
	Spain	95		
	Belgium	50		
H_2	Germany	2.44×10^6	16% of the world demand corresponds to western Europe, top-5 distribution based on the GDP of the individual countries	[211], [212]
	France	1.78×10^6		
	Netherlands	5.54×10^5		
	Belgium	3.36×10^5		
	Austria	2.77×10^5		

Table 5.7: *cont.* of Table 5.6.

Products	Markets	Demand per market (10^3 ton/year)	Assumptions	Refs
Acrolein	Bulgaria	$9.15x10^2$	Addressable market is acrylic acid and the demand was given in total for eastern and western Europe, the top-5 distribution was given based on the GDP of the individual countries	[211],[213], [214]
	Germany	$6.35x10^2$		
	Belgium	$3.20x10^2$		
	France	$2.75x10^2$		
	Czech Republic	55		
Propionic acid	Germany	67.5	Propionic acid demand in the world, where 16% is for Europe. GDP was used to find the top-5 consumers	[215]
	France	49.3		
	Netherlands	15		
	Belgium	92.7		
	Austria	7.65		
n-Butanol	Germany	$2.19x10^2$	European demand of n-butanol	[216], [217], [211]
	United Kingdom	$1.58x10^2$		
	France	$1.65x10^2$		
	Italy	35.3		
	Spain	82		
Isobutanol	Belgium	$2.19x10^2$	Isobutanol is used as a precursor of terephtalic acid, which is s a precursor of PE. The same distribution as the one for plastics in Europe	[218],[219]
	Portugal	$1.58x10^2$		
	Spain	$1.65x10^2$		
	Poland	35.3		
	United Kingdom	82		
Epichlorohydrin	Germany	$1.58x10^2$	Addressable market is the production of epoxy resins. For this, bisphenol A (BPA) is used along with epichlorohydrin. 30% of the consumption of BPA is for the production of epoxy resins. World demand of BPA and the respective percentage for Europe. Top-5 consumers of BPA assumed to be the same for epichlorohydrin	[220], [9], [221]
	Netherlands	$1.42x10^2$		
	Belgium	96.7		
	Spain	86.8		
	Italy	42.7		

5.4.3 Economic Analysis

As mentioned before, the discounted cash flow analysis model was employed to estimate the NPV over the biorefinery lifetime of 20 years (planning time period), where the investors owned 100% equity. This model, based upon the Eqs. (5.26) to (5.29) presented in section 5.3.2, is estimated as the sum of a time series of cash flows discounted to the present year over a 10% interest rate (minimum rate of return). Capital depreciation is recorded for tax purposes as a portion of the fixed capital investment obtained by following and IRS (Internal Revenue Service) schedule. In this work, the Modified Accelerated Cost Recovery System (MACRS) for ten years is used as tax depreciation system, in which the capitalized cost of property is salvaged over a specific time by yearly deductions for depreciation. Income tax is paid on taxable income with at a 35% tax rate where we assume that losses after start-up are not forwarded. Finally, the working capital is assumed to be 5% of the fixed capital investment. Table 5.8 presents the market prices of each product considered in the design space (see superstructure in Figure 5.4). Furthermore, the techno-economic models respective to each technology were collected and are reported in previous work [15]; a summary of the information used as reference regarding capacity and economics is presented in Table D.2 in Appendix D.

Linearization of capital investment

As previously mentioned, since linear programming is computationally efficient, the non-linear power-law function (Eq. 5.14) is linearized by using a disjunctive formulation, which

Table 5.8: Products market spot prices.

Product	Selling price ($/kg) [*ref*]	Product	Selling price ($/kg) [*ref*]
SA	2.0 [15]	H_2	0.536 [15]
1,3-PDO	2.02 [15]	n-BuOH	1.558 [15]
PA	1.590 [15]	EtOH	0.707[15]
PHB	4.5 [15]	Acrolein	2.0 [15]
1,2-PDO	1.662 [15]	Epichlorohydrin	1.992 [206]
LA	2.0 [15]	Isobutanol	1.524 [15]

is transformed sequentially into mixed integer linear programming (see section 5.2.2). To improve the resolution of the capital cost estimation, we propose three capacity levels for the processing technologies introduced in this work, namely (ton/year): (i) small (5,000 to 40,000); (ii) medium (40,000 to 200,000); and, (iii) large (200,000 to 600,000), as proposed in [222] for a biorefinery of similar size. Within each level there is a linear relationship between the capacity and capital investment, where the slope represents the unit variable capital-related costs and the intercept value stands for the fixed capital-related costs. The greater the plant capacity, the larger will be the fixed capital investment costs, although the unit variable capital investment costs will be lower. In Figure 5.5, an example is shown for the piecewise linear estimation of purchased capital investment for the production of succinic acid. Finally, following the same procedure, the data regarding the disjunctive relationships between purchased capital investment (PCI) and capacity (Cap) for all production technologies are presented in Table 5.9. As previously mentioned, the reference data needed to estimate the linear regression parameters is reported in D.2 in Appendix D.

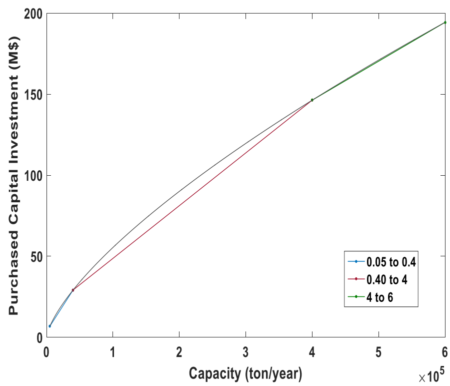


Figure 5.5: Capital investment estimation corresponding to the succinic acid case at small, medium and large capacity levels. The original cost curve is presented in black.

Table 5.9: Data for the estimation of the purchased capital investment (PCI) through disjunctive relationships, where $PCI(MM\$) = slope_q \cdot Cap(ton/y) + intercept_q$.

Product	Capacity interval (ton/year)					
	Small (5000 to 40000)		Medium (40001 to 400000)		Large (400001 to 600000)	
	$slope_1$	$intercept_1$	$slope_2$	$intercept_2$	$slope_3$	$intercept_3$
EtOH	8.56E-04	3.70	4.87E-04	18.5	3.79E-04	61.7
PHB	2.06E-03	8.90	1.17E-03	44.5	9.13E-04	148.7
LA	3.74E-04	1.62	2.13E-04	8.07	1.66E-04	26.98
SA	7.05E-04	3.04	4.01E-04	15.2	3.12E-04	50.83
1,3-PDO	5.34E-04	2.31	3.04E-04	11.5	2.37E-04	38.51
1,2-PDO	3.26E-04	1.84	1.66E-04	8.25	1.22E-04	25.63
H_2	2.15E-03	12.2	1.10E-03	54.5	8.09E-04	169.3
Acrolein	4.71E-04	2.66	2.40E-04	11.9	1.77E-04	37.05
PA	4.05E-04	1.75	2.30E-04	8.72	1.79E-04	29.18
n-BuOH	8.66E-04	3.74	4.93E-04	18.7	3.84E-04	62.43
Isobutanol	4.83E-04	2.73	2.46E-04	12.2	1.81E-04	39.78
Epichlorohydrin	4.12E-04	2.32	2.09E-04	10.4	1.55E-04	32.35

5.5 Results and Discussion

In this section, the results are presented regarding the application of the *GlyThink* model for the identification of the optimal integrated glycerol biorefinery supply chain. So as to understand the sensitivity of the strategic and operational decisions, as well as the project feasibility and economic performance, a group of scenarios were set up for analysis as represented in Figure 5.6.

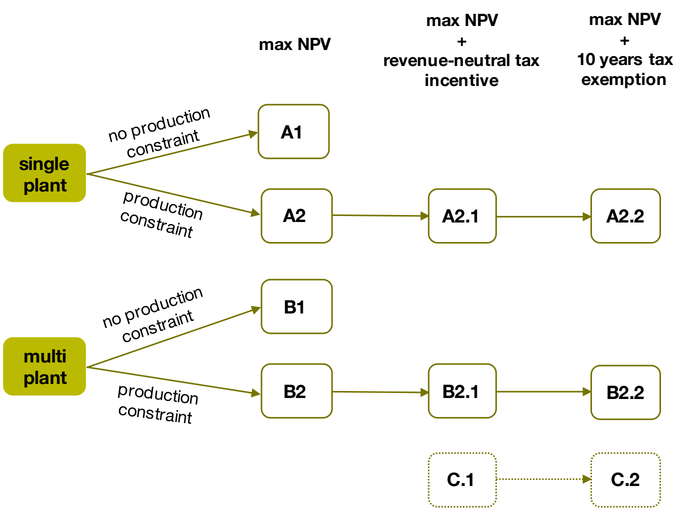


Figure 5.6: Formulation of scenarios analyzed.

The scenarios pictured in Figure 5.6 were built to understand the influence of: (i) constraining the model to a certain production capacity, and (ii) having the SC structure based upon a single plant site location or on multiple locations. They are described as follows:

- Scenario A1: leads to the optimization of the supply chain network allowing the model to determine the amount of glycerol converted into products per plant site location, if only one plant location is allowed, so that NPV is maximized;

- Scenario A2: the optimization problem set in A1 is further constrained to convert the total amount of glycerol available ($4.10 \times 10^6 ton/year$) if only one plant location is allowed to be selected, so that NPV is maximized;

- Scenario B1: leads to the optimization of the supply chain network allowing the model to identify a combination of best plant site locations (allowing the selection of more than one plant), by also determining the optimal amount of glycerol converted into value added products, so that NPV is maximized;

- Scenario B2: the optimization problem set in B1 is further constrained to convert the total amount of glycerol available ($4.10 \times 10^6 ton/year$), also allowing the selection of more than one plant, so that NPV is maximized.

So as to understand the effect of possible government policies in the economic performance and feasibility, as well as in the strategic and operational decisions, the following scenarios were built:

- Scenario A2.1: leads to the identification of the optimal SC structure through the optimization problem set in scenario A2 and having the government *revenue neutral* incentive of $0.11 per kg of bio-based building block chemical, which has been implemented in several states in the U.S. [223];

- Scenario A2.2: identify the optimal SC structure through the optimization problem set in scenario A2 and having the government incentive based upon the example of Malaysia, which has been giving *10 years of full tax exemption* for biobased industries [224],[225].

- Scenario B2.1: identify the optimal SC structure through the optimization problem set in scenario B2 and having the government *revenue neutral* incentive of $0.11 per kg of bio-based building block chemical;

- Scenario B2.2: identify the optimal SC structure through the optimization problem set in scenario B2 and having the government incentive of *100% tax exemption* for 10 years;

- Scenario C.1: identify the optimal SC structure through the optimization problem set in scenario A2 by constraining the model to consume the glycerol amount obtained at the break-even point and having the government *revenue neutral* incentive;

- Scenario C.2: identify the optimal SC structure through the optimization problem set in scenario A2 by constraining the model to consume the glycerol amount obtained at the break-even point and having the government incentive of *tax exemption for 10 years.*

Comparison between scenarios A1 & A2

In this section the results aim to illustrate: (i) how the optimal configuration and profitability of the supply chain network depend on the facility location; and, (ii) the effect of the amount of glycerol converted on the economic performance and feasibility. The NPV obtained for scenarios A1 and A2, along with the corresponding potential plant site locations for the installation of the glycerol integrated biorefinery, are depicted in Figure Figure 5.7.

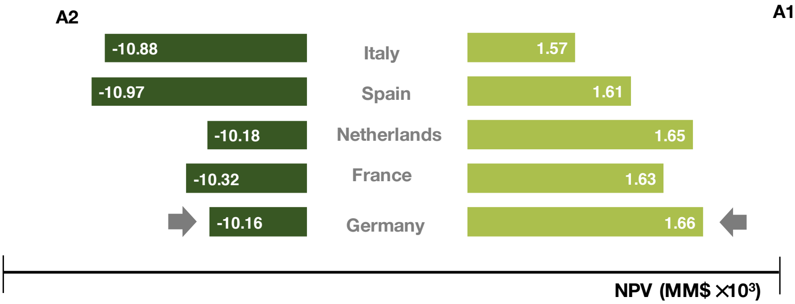


Figure 5.7: NPV obtained for all plant locations for A1 (light green, right) and A2 (dark green, left).

The glycerol converted in all potential plant site locations is approximately 14% (5.60×10^5 ton/year) of the total amount of glycerol available in Europe (4.10×10^6 ton/year). This leads to a consistent optimal product portfolio composed by the production of SA and LA, where the revenue is able to absorb the costs. Thus, positive yearly cash-flows are obtained for all locations within scenario A1, consequently leading to positive NPVs. In Figure 5.7, one can see that the optimal location to build the plant site seems to be in Germany with a NPV of $1.66 \times 10^3 MM\$$, closely followed by the Netherlands and France. As an example, the SC structure based upon Germany as the plant site location is presented in Figure 5.8.

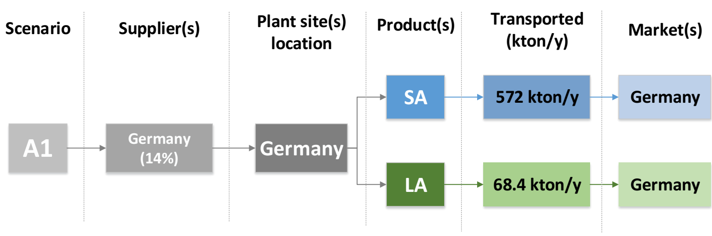


Figure 5.8: SC structure of the integrated glycerol biorefinery located in Germany obtained through scenario A1.

Through scenario A2, as presented in Figure 5.9, when converting the total amount of glycerol available ($4.10 \times 10^6 ton/year$), it leads to solutions with negative NPVs - meaning that they are not economically feasible - for the SCs based upon all locations.

Even though the optimal SC obtained for all locations presents negative NPV, Germany still stands out as the best alternative due to the (i) higher product demands observed for this market, and (ii) the reduced implied transportation costs. The negative values of NPV result from the increased inflow of glycerol to be compulsory converted, leading to the production of additional products besides SA and LA (identified as the most profitable products in 5.8) because these products have reached their full integrated capacity (level 3 of capacity for both LA and SA production units, as presented in Table 5.9). Therefore, to be able to convert the total amount of glycerol, the product portfolio is extended to include PHB, acrolein and epichlorohydrin as presented in Figure 5.9 (for Germany as an example). All in all, scenario A2 presents in fact an unfeasible solution since the increased production due to the full conversion of the glycerol available, requires higher investment and production costs, which are not balanced by the revenue obtained.

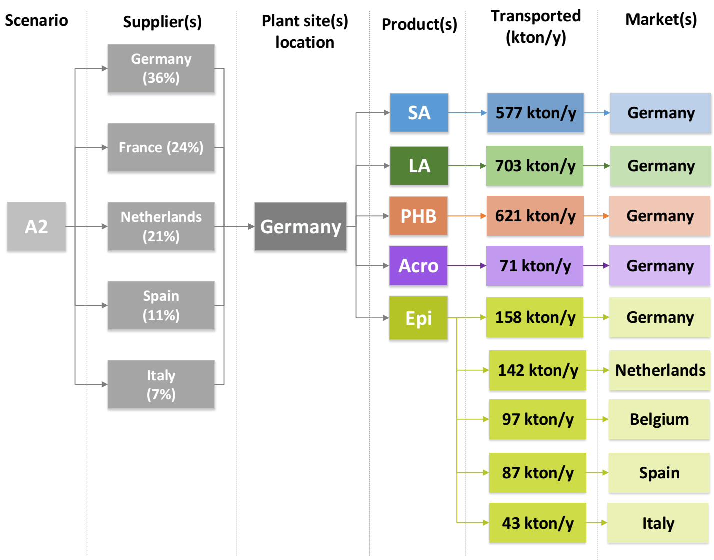


Figure 5.9: SC structure of the integrated glycerol biorefinery located in Germany obtained through scenario A2.

Comparison of scenarios B1 & B2

As mentioned above, in scenarios B1 and B2, the model is free to choose the best combination of plant sites to maximize the NPV of the integrated glycerol biorefinery SC. The NPV values corresponding to the optimal solutions obtained with scenarios B1 and B2 are presented in Figure 5.10, corresponding to a glycerol inflow of 2.15×10^6 ton/year and 4.10×10^6 ton/year (total available), respectively.

The SC structures are presented in Figures 5.11 and 5.12, for scenarios B1 and B2, respectively. B1 identifies the optimal SC as resulting of the combination of four plant sites whose locations are: Germany, France, the Netherlands and Italy. As presented in Figure 5.11, the total fraction of glycerol that is converted is approximately 53% of the

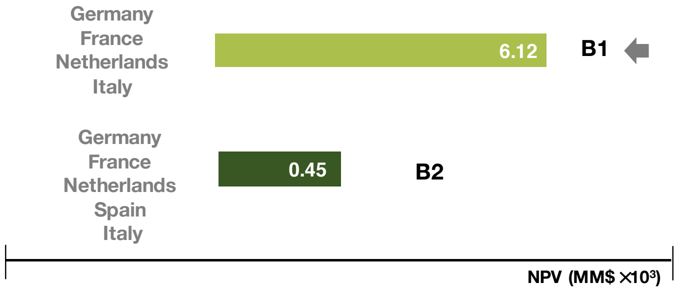


Figure 5.10: NPV of the optimal SC obtained with B1 (light green) and B2 (dark green).

total amount available in Europe per year, being mostly sourced by their own markets except for the plant site in Italy which acquires glycerol not only in Italy but also from France. Moreover, the product portfolio obtained in scenario B1, enforces the fact that SA and LA are the potentially the most profitable products. Also, although there are higher investment costs as a consequence of building more plant sites, the revenue of opening plants closer to the markets compensates the investment costs and NPV is maximized in such a scenario. This is observed by the fact that the demand of SA is being fully satisfied in Germany, France, and UK markets, along with 94% satisfaction in Italy. Also, as presented in Figure Figure 5.11, the LA obtained as co-product of the SA production in each plant is sent, as expected, to the closest market to the corresponding plant sites.

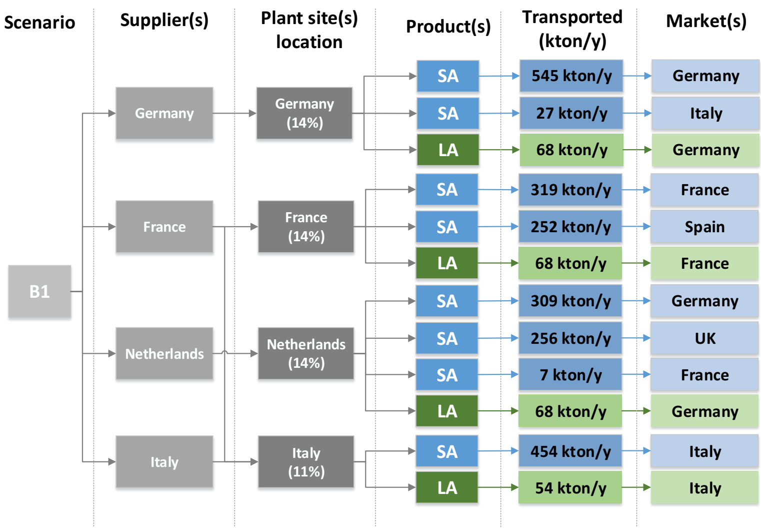


Figure 5.11: SC structure of the integrated glycerol biorefinery obtained through scenario B1, resulting in a combination of 4 plant site locations in Europe.

The SC structure obtained through scenario B2 has a low positive NPV, and the corresponding SC structure is presented in Figure 5.12. In order to maximize the NPV but consuming all glycerol available, a combination of the possible five possible locations is set up in order to have the production closer to the demand markets; where Germany consumes 45% of the glycerol available, followed by France consuming 15% and the remaining plants consuming from 14% to 11% of the total glycerol available. The co-production of SA and LA stand out once more as the most profitable solution since the demand of SA in Germany, France, Spain, Italy and UK is being fully satisfied, and the LA co-produced along with SA is sent to the markets closest to the production plants. However, since the SA production capacity has been reached and its demand in the markets has been fully satisfied, the product portfolio is further extended to include the production of PHB and epichlorohydrin in the plants closer to their markets for these products so as to fulfill the glycerol capacity. These products are selected due to their high selling price, but they are for example not chosen in scenario's A1 and B1 due to their high associated investment and production costs (specially due to the separation and purification stages).

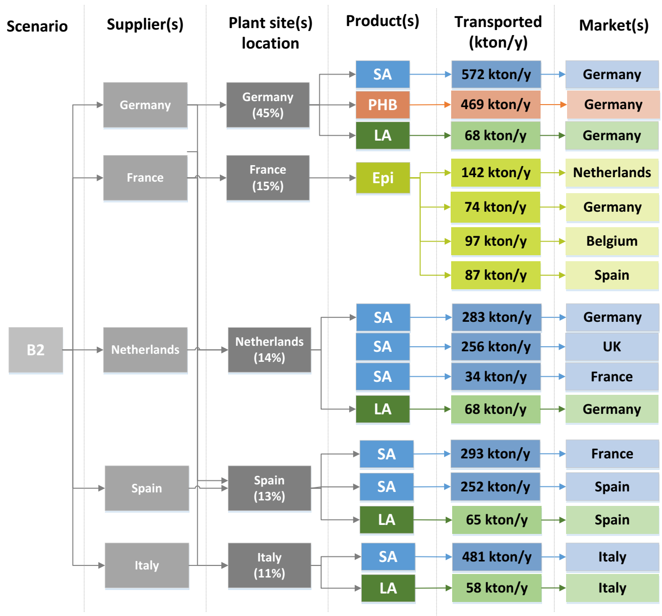


Figure 5.12: SC structure of the integrated glycerol biorefinery obtained through scenario B2, resulting in a combination of 4 plant site locations in Europe.

Comparison of scenarios A & B

As observed in Figures 5.7 and 5.10, the optimal solution is given by the SC structure obtained through the multi-plant scenario B1 since it provides the highest NPV among all scenarios within scenarios A and B. This is due to the fact that the revenue attained is higher than the incurred costs related to the production and fixed capital investment. Furthermore, it is worth noticing that throughout the scenarios discussed, SA and LA are consistently selected as part of the product portfolio (see Figures 5.8, 5.9, 5.11 and 5.12). This results from the combination of favorable conditions, such as the high SA yield, the fact that LA is produced as a co-product of SA production, and their high selling price which allow the revenue attained to compensate the investment, production and the logistic costs. Additionally, SA and LA have also been identified as the best potential products to be produced from glycerol in an earlier techno-economic study where the SC was not considered, where SA and LA were identified as two of the products having the lower associated economic risk [15].

A more detailed analysis of the operating cost for all discussed scenarios is presented in Figures 5.13 (A1-Germany, A2-Germany, B1 and B2). Common to all scenarios, is the fact that the production cost (glycerol purchase and utilities) has the most significant cost share, ranging from 58% to 61% in A1 and A2, to 65% in B1 and B2 due to the total conversion of glycerol. Furthermore, the cost of utilities associated with the purification of crude glycerol is approximately 4 to 5% of the total utilities cost for all scenarios considered. Therefore, if the degree of purity of the crude glycerol inflow increases, the costs associated to its purification will decrease, but the impact on the overall production costs will not be substantial. The transportation cost has a rather small contribution to the total cost of the supply chain, in particular for the cases where the model is not constrained to convert all glycerol due to full satisfaction of market demands farther away from the plants, in which case A1 and B1 would become unfeasible solutions (negative NPV). However, as expected, the transportation cost is more significant for the cases where the model is constrained to consume the total glycerol (A2 and B2), since more markets have to be served in order to fulfill the glycerol capacity, and as a consequence transport distance increases. Similarly, in these scenarios, the storage cost becomes important, since the high production capacity leaves by-products such as H_2 in storage, which is not worth of delivering due to its low selling price and related transportation cost. Also, the higher the investment, the higher the importance of the operation and maintenance (O&M) cost, since it directly depends on the FCI. The difference between the revenue and costs is higher in A1 and B1, and therefore, as expected, the taxable income and the tax paid are both higher for these scenarios.

Sensitivity analysis of the NPV to the variation of the glycerol conversion

The sensitivity analysis has been performed to understand the influence of the glycerol conversion on the economic feasibility of the project (NPV). Therefore, as an example the single plant located in Germany is represented in Figure 5.14.

As presented in Figure 5.14, the optimal NPV is obtained for the SC structure that converts approximately 14% of the glycerol available in Europe, and its structure has been previously depicted in Figure 5.8. Also, the sum of discounted cash-flows, here represented through the Annual Present Value (APV in Eq. 5.26, green line in Figure 5.14), is rising with the increasing glycerol conversion, attaining its maximum along with the optimal NPV, which occurs when the net earnings are also at their maximum (given by the difference between the revenue and the total costs). From this moment on, the NPV steadily decreases, reaching zero (break-even point) at around 30% glycerol conversion, where the APV equals the total fixed capital investment (tFCI, orange line). The SC structure corresponding to the break-even point is presented in Figure 5.15, where the

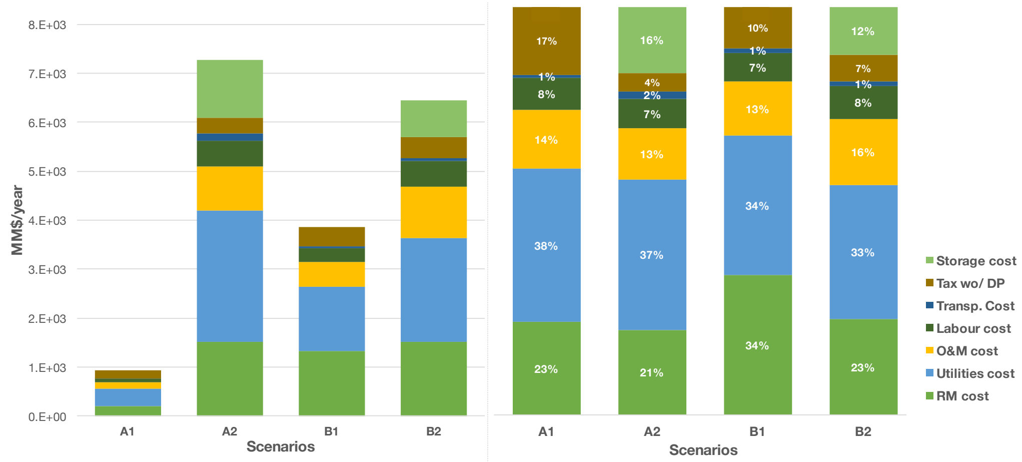


Figure 5.13: Break-down of costs in terms of their corresponding impact on the total cost of the SC obtained in scenarios A1, A2, B1 and B2; where on the left this is represented in terms of monetary units and on the right it is presented as percentage of the total costs.

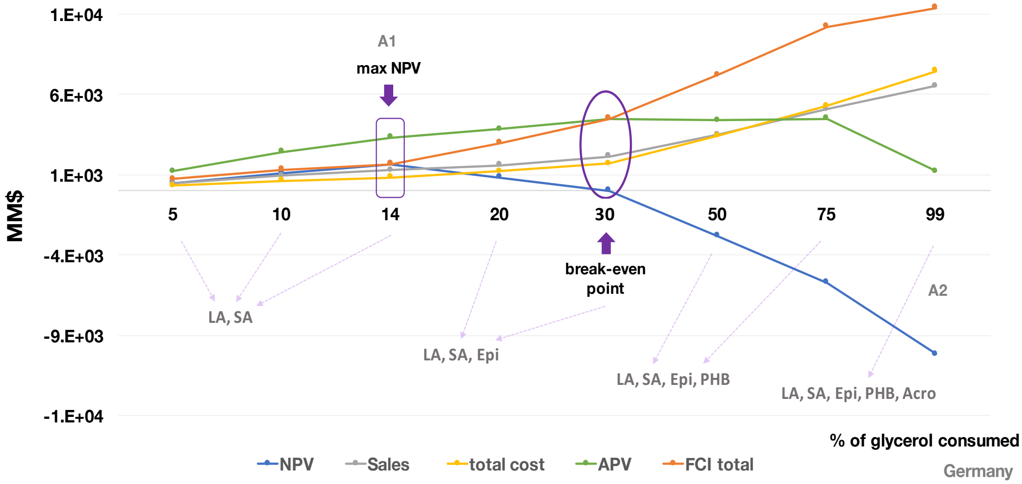


Figure 5.14: Sensitivity analysis of the NPV to the variation of the glycerol conversion, for the integrated glycerol biorefinery SC based upon a single plant located in Germany. NPV, Sales, total cost, APV and tFCI, represented in dark blue, grey, yellow, green and orange, respectively.

SC structure changes from the optimal one by adding the epichlorohydrin production.

Furthermore, from the break-even point on, the increase in sales due to increased production capacity does not compensate the extra costs incurred, leading to low net earnings, and corresponding low APV. Additionally, the fixed capital investment (tFCI, orange line) increases greatly, finally heading to a vast decline in NPV. The SC structure identified through scenario A2, corresponding to approximately total conversion of the

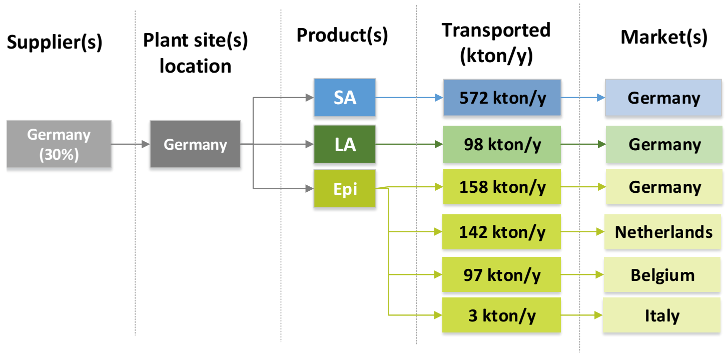


Figure 5.15: SC structure of the integrated glycerol biorefinery located in Germany obtained at the break-even point between costs and revenue.

glycerol available, it has also been presented previously in Figure 5.9. Therefore, by analyzing Figures 5.8, 5.9 and 5.15 one can see that the SA production capacity is at its maximum limit in all three SC structures. It is then followed by an expansion on the LA production capacity when moving from scenario A1 towards scenario A2, where it also reaches its maximum capacity. Therefore, there is an investment in the production of other value added products (epichlorohydrin, acrolein and PHB) to attain the total conversion of glycerol inflow, where the optimal configuration leads to highly negative NPV.

Sensitivity analysis of the NPV to the product prices

In this section, a sensitivity analysis of the NPV value was performed so as to understand the potential effect of price variation on the projects economic feasibility and overall profitability. Therefore, Figure 5.16 presentes the results corresponding to a price variation of - 50% to 150% of the original prices applied for the products on which the supply chain is primarily based upon, the SA and LA.

As observed in Figure 5.16, the NPV fluctuates with the price variation in all scenarios tested. Common to all cases is the fact that, when the SA and LA prices crash to 50%, as expected and previously explained, the SC structure turns heavily to the production of PHB and epichlorohydrin, being the products with the higher selling price and relatively high demand. However, important to note is that the least affected scenario is scenario A1, due to the fact that its SC structure is based upon the single-plant (in Germany) having the lowest flexibility. However, scenario B2 is the one that shows to be the most impacted by price fluctuation, showing to be more flexible and capable of adapting to changes in external conditions. Thus, when facing high selling prices of SA and LA, B2 reacts with by expanding the production capacity, thus modifying the SC structure from Figure 5.12, replacing the production of PHB and epichlorohydrin by additional production (and distribution) of LA in Germany, France and the Netherlands.

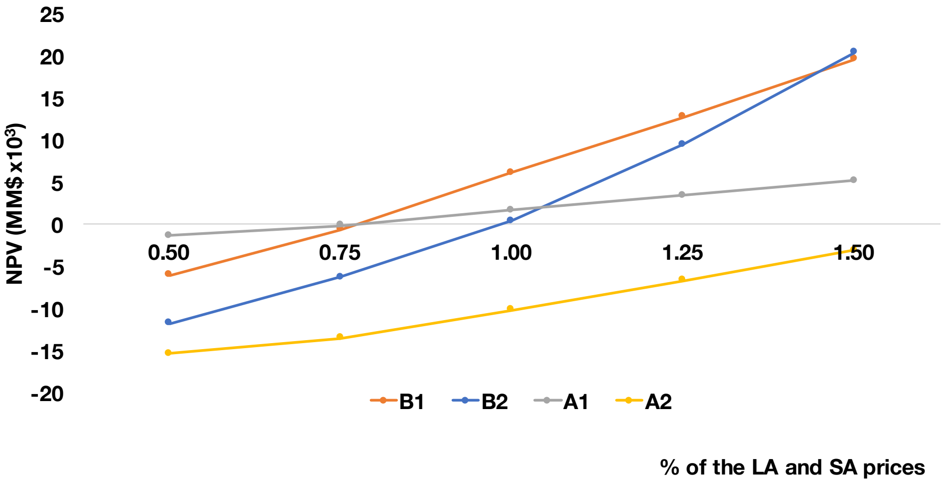


Figure 5.16: Sensitivity analysis of the NPV to the variation of LA and SA prices, with a range of variation from 50% to 150% of the original prices.

The impact of potential government incentives

In this section, the impact of government incentives on the economic feasibility and the obtained SC structure is analyzed. Furthermore, the cases where there is total conversion of glycerol, corresponding to scenario A2 and B2, are here re-tested under conditions involving potential government incentives. In Table 5.10 a summary of the scenarios analyzed in this work is presented. However, the NPV obtained with the revenue neutral incentive (A2.1) for the single-plant SC when converting the total glycerol available (A2.1) is still highly negative and the structure obtained is identical to the SC structure presented in Figure 5.9. This is thereby demonstrating that converting such an amount of glycerol in a single plant is not economically feasible, even when considering potential government incentives, due to the fact that the production, investment and logistic costs are very high when compared to the revenue attained. Furthermore, the tax exemption incentive is not suitable to be applied in this case (A2.2) due to the fact that the total yearly costs are always higher than the revenue, which leads to a situation with zero taxable income on which tax should be paid.

Furthermore, a meaningful improvement of the NPV is detected when applying both incentives to the multi-plant SC structure when the total glycerol is being converted (B2.1 and B2.2). Here it is observed that, as expected, the tax exemption incentive leads to higher NPV. The obtained SC structure for B2.1 is identical to the one for scenario B2 presented in Figure 5.12. The SC structure corresponding to the scenario B2.2 is different, and presented in Figure 5.17. The latter differs significantly from B2 by moving the production of epichlorohydrin from France to Germany and moving the PHB production from Germany to France (satisfying this market instead). For the glycerol conversion obtained at the break-even point, both incentives (C.1 and C.2) lead to positive NPV, which is evidence that the government support could be fundamental for the growth of a

Table 5.10: Summary table of the scenarios tested to highlight the effect of potential government incentives.

Scenarios	NPV ($\times 10^3 MM\$$)	Products	SC structure
A1	1.66	LA, SA	Figure 5.8
A2	-10.2	LA, SA, Acro, PHB, Epi	Figure 5.9
A2.1	-7.58	LA, SA, Acro, PHB, Epi	Figure 5.9
A2.2	-	-	-
B1	6.12	LA, SA	Figure 5.11
B2	0.45	LA, SA, Acro, PHB, Epi	Figure 5.12
B2.1	3.54	LA, SA, Acro, PHB, Epi	Figure 5.12
B2.2	4.22	LA, SA, Acro, PHB, Epi	Figure 5.17
C.1	1.00	LA, SA, Epi	Figure 5.16
C.2	1.22	LA, SA, Epi	Figure 5.16

robust bio-based industry. The SC structures obtained for C.1 and C.2 are identical to the SC structure obtained at the break-even point as represented in Figure 5.15. However, on the longer term, as the past experience with lignocellulosic biofuels industry has shown, for a bio-based production concept to be successful, it has to stand out on its terms and be cost-competitive against other competing producers in the market place especially since government incentives are temporary and may expire once the volatile political environment changes.

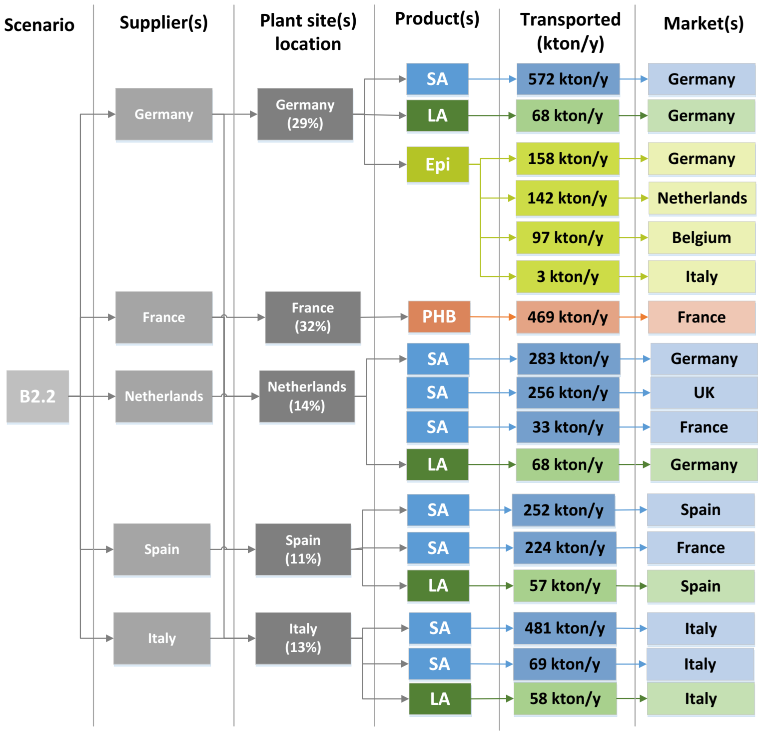


Figure 5.17: SC structure of the integrated glycerol biorefinery obtained through scenario B2.2, resulting in a combination of 5 plant site locations in Europe

Many factors related to supply chain analysis of the glycerol biorefinery can be studied with the help of the *GlyThink* supply chain model. Sensitivity analysis has indicated that the economic feasibility and profitability of any given supply chain is subject to external disturbances such as price volatility among others. In future studies, we will comprehensively investigate the effect/impact of inherent uncertainties [15], such as demand and product prices, volatility in glycerol feedstock price and the impact of additional plants on the price changes, on the integrated glycerol biorefinery SC, in order to explore and fully understand the impact of external factors on the economic and overall sustainability.

5.6 Conclusions

A novel MILP multi-period, multi-stage model (*GlyThink*) is proposed for the identification of the optimal supply chain network of glycerol conversion into value-added products, maximizing the Net Present Value as the objective function. Optimal decisions regarding design, operation and strategy provided by the model include supply chain network layout, facility location and sizing, technology selection, yearly production planning and cross-country logistics. The *GlyThink* model was demonstrated on a superstructure build based on 5 possible plant site locations, 12 available conversion technologies, 12 available separation and purification technologies, 12 unique products, and 5 markets were identified for each one of the products. The analysis was performed over a number of scenarios where it has been observed that: (i) throughout all scenarios tested the product portfolio is primarily composed of SA and LA, produced in an integrated fashion which makes sense from an engineering point of view given that they are co-products and have relatively higher selling prices; (ii) when the model is constrained to convert as much as possible of glycerol, the production of SA and LA reaches their maximum and the portfolio is further supplemented with the production of PHB and epichlorohydrine; (iii) the production cost is the most significant share of the total manufacturing costs of the SC; (iv) a SC structure based upon a multi-plant site integrated biorefinery leads to an improved economic performance, where the optimum is given by the combination of four locations (Germany, France, Netherlands and Italy); and finally, (v) both government incentives tested have shown to lead to improvement of the NPV of the SC proving that government support could be important for the growth of a bio-based economy. All in all, *GlyThink* aims at being a decision-making tool through supply chain optimization, leading to the identification of optimal glycerol integrated biorefinery concepts at the early-stage of design, by maximizing the economic performance and identifying the optimal product portfolio, alongside with supporting the most efficient strategic and design decisions. Furthermore, accompanying studies will investigate the economic feasibility of the integrated glycerol biorefinery SC when taking into account the presence of inherent uncertainties on significant input parameters, such as, among others, product demand and product prices.

CHAPTER 6

Optimal design and planning of sustainable glycerol-based biorefinery supply chains under uncertainty

In this chapter, a decision-making framework is proposed to holistically optimize the design and planning of the glycerol-based biorefinery supply chains under uncertainties. This framework presents a multi-layered strategy composed of different steps, and it is strongly based on optimization techniques, detailed economic and environmental assessment, and multi-objective optimization in a stochastic environment. To maximize the business value, the economic objective is measured by the Net Present Value (NPV), whereas the environmental performance is measured by the estimation of a Single Indicator (SI) through the application of LCA methods, in this case the ReCiPe method. The proposed framework ultimately leads to the identification of the optimal design and planning decisions for the development of environmentally conscious biorefinery supply chains, where the consequences of external economic uncertainties on the environmental objective function are analyzed and the trade-offs identified. The effectiveness of the presented approach is demonstrated through its application to the realistic case study of the glycerol-based biorefinery in Europe.

This chapter of the thesis is based upon following article:

Optimal design and planning of sustainable glycerol-based biorefinery supply chains under uncertainty. L. Gargalo, C., Carvalho, A., Gernaey, K. V. & Sin, G. Submitted. (2017)

Nomenclature

Subscript indices	
i	Components
k	Technologies
x	Plant site locations
t	Time periods
r	Reactions
q	Capacity levels

m	Final markets
z	Suppliers

Sets

I	Set of all components i
I_p	Set of components i that are final products
I_{rm}	Set of components i that are raw materials
I_{ut}	Set of components i that are utilities and/or chemicals/solvents
I_r	Set of components i that are reactants
K	Set of all technologies k
K_{GP}	Set of technologies k used for the purification of raw materials
K_{conv}	Set of technologies k used for the conversion of raw materials to final products $i \in I_p$
K_{SP}	Set of technologies k used for the separation and purification of final products $i \in I_p$
X	Set of plant locations x
T	Set of time periods t
R	Set of reactions r
Q	Set of capacity levels q
M	Set of final markets m
Z	Set of all suppliers z

Parameters

Technology

$\phi_{i,z,t}$	Raw materials i available from supplier z in time period t
$\alpha_{i,k}$	Specific utility consumption of i in k
$\theta_{i,k,r}$	Conversion of reactant i in technology k where r occurs
$\gamma_{i,k,r}$	Reaction stoichiometry for every component i in technology k and reaction r
$\mu_{i,k}$	Fraction of chemicals/solvents mixed with process stream of component i in technology k
$SW_{i,k}$	Fraction of component i that is separated as waste in k

Technology capacity and cost

$H_{k,q}^{min}$	Minimum capacity for each capacity level q for technology k
$H_{k,q}^{max}$	Maximum capacity for each capacity level q for technology k
$slope_{k,q,x}$	Linearization constant for technology k and interval q
$b_{k,q,x}$	Intercept value for the linearized interval q for technology k
c_k^{max}	Maximum cost of technology k
wc_t	Operating supplies cost for time period t
ms_t	Maintenance cost for time period t

Transportation

$D_{p,m,t}$	Demand of product p in market m in time period t
L	Total load of transport mode per trip traveled
pR	Cost of rail freight per ton.km
$d_{x,m}$	Distance of market m from plant site location i

Cost related parameters

pRM	Price of raw materials $i \in I_{rm}$
pUT_i	Price of utilities per component $i \in I_{ut}$
pST_p	Storage price per final product $i \in I_p$
pP_i	Price of final product $i \in I_p$
ω	Interest rate (%)
φ	Tax rate (%)
γ_t	Capital depreciation in time period t —

LCA related parameters

$CF_{i,c}$	Characterization factor to convert inventory of component i into impact category c
n_c	Normalization factor for impact category c
$\lambda_{cs_{i,k}}$	Emissions of component i linked to the separation and purification per unit of reference component flow in technology k
$\lambda_{sl_{i,k}}$	Emissions of component i linked to the usage of solvents/ chemicals/ catalysts per unit of reference component flow in technology k
$\lambda_{en_{i,k}}$	Emissions of component i linked to the usage of energy per unit of reference component flow in technology k
$\lambda_{pl_{i,k}}$	Emissions of component i linked to the product loss in the separation and purification per unit of reference component flow in technology k

Decision variables

Continuous variables

$F^{in}_{i,k,x,t,s}$	Inflow of components i into technology k in plant location x in time period t and in scenario s
$F_{i,k,x,t,s}$	Outflow of components i from technology k in plant location x in time period t in scenario s
$U_{i,k,x,t,s}$	Flow of utilities i added in technology k in plant location x in time period t in scenario s
$Pr_{i,k,x,t,s}$	Flow of components i produced/consumed in technology k in plant location x in time period t
$Ftr_{i,x,m,t,s}$	Transported flow of component $i \in I_p$ from plant location x to final markets m in time period t in scenario s
$W_{i,k,x,t,s}$	Flow of components i separated as waste in technology k in plant location x in time period t in scenario s
$RawM_{i,z,x,t,s}$	Flow of raw materials i from supplier z to plant location x in time period t in scenario s
$LCI_{i,t}$	Life cycle inventory of component i in time period t
$F_{b,k,x,t}$	Flow reference of product b being manufactured in unit k in plant x in time period t
$F^{in}_{g,k,x,z,t}$	Inflow of glycerol g from supplier z into the pre-treatment unit k in plant x in time period t
$Cost_{k,x,t}$	Cost of technology k in plant location x in time period t
$C_{k,q,x,t}$	Cost of technology k in each capacity interval q in time period t
$h'_{k,q,x,t}$	Disaggregated flow rate variable of technology k with capacity interval q in time period t

Integer variables

$T_{x,m,t,s}$	Number of trips performed by truck from plant site x to markets m in time period t in scenario s
$T_{z,x,t,s}$	Number of trips performed by truck from supplier z to plant site x in time period t in scenario s

Binary variables	
$y_{k,q,x,t}$	=1 if technology k with capacity q is installed in location x in time period t

Auxiliary variables for the objective function	
NPV	Net Present Value
$CF_{t,s}$	Cash flow in time period t in scenario s
$NE_{t,s}$	Net earnings in time period t in scenario s
$FCI_{k,x,t}$	Fixed capital investment of technology k in plant location x and time period t
$CD_{t,s}$	Capital depreciation in time period t in scenario s
S_c	Impact category c
SI	Single indicator for environmental assessment
b	Representative of all 1^{st} variables
b_s	Representative of all 2^{nd} variables

6.1 Introduction

As discussed in the Introduction section of this thesis, the primal objective function used for the design and planning of biorefinery supply chain networks under uncertainties is based on economic metrics. In the works where both the economic and environmental objectives are present and tested under uncertainties, the environmental indicator is only given by CO_2 emissions. Among these, the most frequently used are single-period optimization problems, maximizing the total profit or minimizing the total costs. Moreover, studies covering the full supply chain including design and planning decisions all the way from the feedstock supplier, technology and capacity selection, and delivery to the final markets, are limited. Therefore, our contribution arises from these identified research gaps, by providing a holistic multi-level decision-making framework, strongly based on optimization techniques, detailed economic and environmental assessment, and multi-objective optimization under stochastic environment. The proposed integrated framework ultimately leads to the identification of the optimal design and planning decisions for the development of environmentally conscious biorefinery supply chains, where the consequences of external economic uncertainties on the economic and environmental objective function are analyzed and the trade-offs identified.

The remainder of the chapter is organized as follows. Section 6.2 introduces and describes in detail the framework proposed in this work for the design and planning of glycerol supply chains. The results and the discussion are presented in Section 6.3. Lastly, key conclusions are drawn and ‘take home’ messages are formulated in Section 6.4.

6.2 Framework for design and planning of supply chains under uncertainty

The main goal of this work is to identify and critically analyze the optimal integrated glycerol-based biorefinery supply chain for the valorization of glycerol into high value-added products. Therefore, in this section, the integrated framework for the design, planning and analysis of glycerol-based biorefinery supply chains under uncertainties is proposed and presented in Figure 6.1.

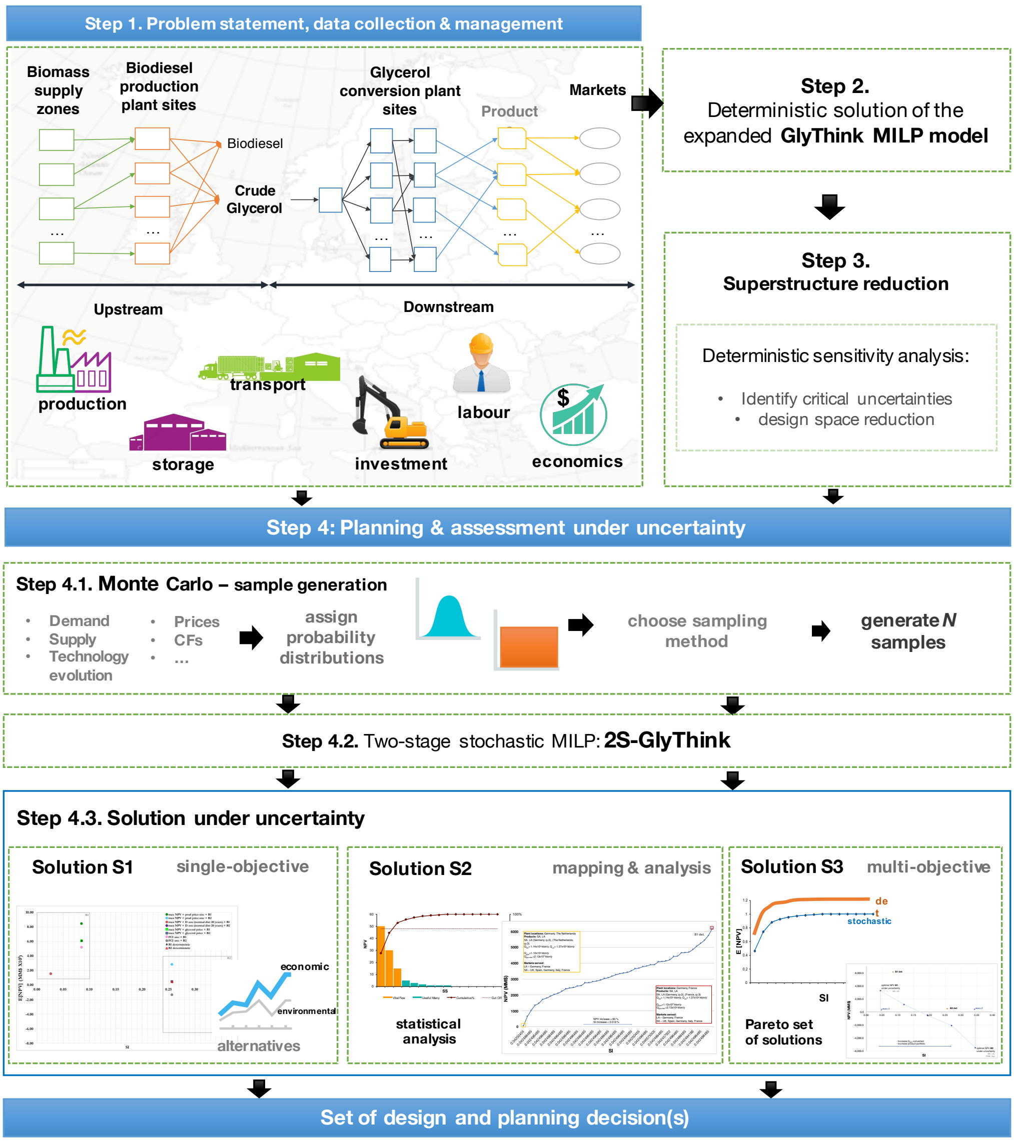


Figure 6.1: Framework for optimal early-stage design and planning of biorefinery supply chains under uncertainty.

6.2.1 Step 1: Problem statement, data collection and management

In this step of the methodology, the problem is identified by stating the goals, objectives and the scope of the study. Glycerol is an immediate by-product of the biodiesel industry, being produced independently of the type of raw material used for the biodiesel manufacture. Since it is nowadays a surplus product, with low market prices, it may lead to a potential environmental problem as it cannot be directly disposed into the environment [15]. Thus, in this work, the aim is to optimize the supply chain of the glycerol-based biorefinery, which is defined by a three-echelon SC (supplier-plant-market) as presented in Figure 6.2. It includes five stages and they are as follows: 1) transportation of crude glycerol from the biodiesel production plants to the glycerol conversion plant site(s); 2) glycerol purification process; 3) process of glycerol conversion into value added products; 4) product separation and purification process; and, 5) distribution of the products to the final markets.

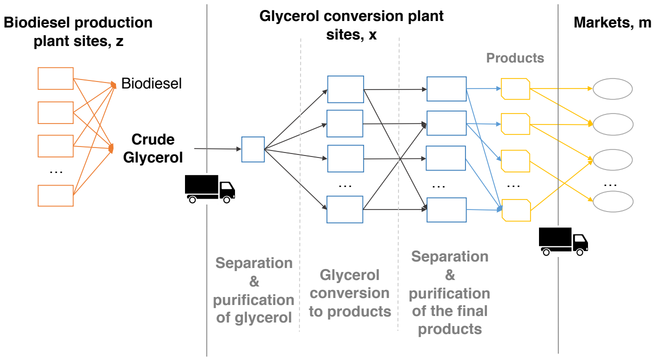


Figure 6.2: Three-echelon glycerol-based biorefinery supply chain (suppliers-plants-markets).

As stated, the objective of this study is to maximize the Net Present Value, while accounting for the environmental impact associated with the glycerol-based integrated biorefinery supply chain under uncertainties, by determining the design and planning decision variables. Furthermore, a key aspect is how to assess the alternatives in the design space also regarding environmental considerations. In this work, the single indicator is used as comparison metric, which is estimated based upon the LCA principles. As described in the literature review (Introduction section), its calculation follows the four main LCA steps [107]. In this study, the boundaries of analysis for the LCA are limited to the sphere of the supply chain defined in Figure 6.2, which includes the 5 stages described. Correspondingly, the required data to estimate the environmental impact categories is collected, which consists of the mass and energy balances for all the operations included in the system boundaries [226]. In summary, the data concerning the characterization of technologies, logistics and characterization factors of LCA is collected and the superstructure reflecting all possible alternatives is generated. Therefore, this is the main input for the next step of the proposed methodology.

6.2.2 Step 2: Deterministic formulation

To address the optimal design and planning of the glycerol-based biorefinery supply chain, a multi-period, multi-stage and multi-product Mixed Integer Linear Programming optimization model, called *GlyThink* has been proposed in chapter 5. In this step, the *GlyThink* model is extended to include the environmental impact assessment calculations. The complete description of the model and the corresponding mathematical formulation is presented in chapter 5, section 5.2 and 5.3. As stated, in this work, the *GlyThink* model is extended to include the estimation of the environmental impact. The mathematical description of the life cycle assessment of the SC (formulated in this chapter) is firstly obtained by estimating the life cycle inventory of the SC activities/operations, whose related emissions can be expressed as a function of continuous decision variables of the model. Thus, the energy consumption, chemicals, solvents and catalysts used are cataloged and quantified, alongside with wastes released to the environment. The mathematical description of the SC activities and operations as shown in Figure 6.2 is presented in Eq. 6.1.

$$
\begin{aligned}
&LCI_{i,t} = \sum_{z}^{Z}\sum_{x}^{X}\sum_{k}^{K} \lambda_{tr,i} \cdot \frac{F^{in}_{g,k,x,z,t}}{L} \cdot 2 \cdot D_{z,x} \cdot AvCons + \\
&\sum_{z}^{Z}\sum_{x}^{X}\sum_{k}^{K} \left(\lambda_{cs_{i,k}} + \lambda_{sl_{i,k}} + \lambda_{en_{i,k}}\right) \cdot F^{in}_{g,k,x,z,t} + \\
&\sum_{x}^{X}\sum_{k}^{K} \lambda_{en_{i,k}} \cdot F_{b,k,x,t} + \\
&\sum_{t}^{T}\sum_{x}^{X}\sum_{k}^{K} \left(\lambda_{cs_{i,k}} + \lambda_{sl_{i,k}} + \lambda_{en_{i,k}} + \lambda_{pl_{i,k}}\right) \cdot F_{p,k,x,t} + \\
&\sum_{x}^{X}\sum_{i}^{I_p}\sum_{m}^{M} \lambda_{tr,i} \cdot \frac{Ftr_{i,x,m,t}}{L} \cdot 2 \cdot D_{x,m} \cdot fc, \\
&\forall i \in I_p \wedge k \in K \wedge q \in Q \wedge x \in X z \in Z \wedge t \in T \wedge
\end{aligned}
\tag{6.1}
$$

In this equation $\lambda_{tr,i}$, $\lambda_{cs_{i,k}}$, $\lambda_{sl_{i,k}}$, $\lambda_{en_{i,k}}$ and $\lambda_{pl_{i,k}}$ represent the life cycle inventory entries (released emissions) per stage related to the flow of the component used as reference. For example, $\lambda_{en_{i,k}}$ represents the emissions of component i linked to the usage of energy per unit of reference component flow in technology k at plant x in time t. The remaining details of the parameters are described in the nomenclature section. The next step is to convert the gathered data into a meaningful group of environmental impact categories. This is achieved by using damage models that connect the emissions to their consequent environmental damage.

$$S_c = \sum_{i}^{I_c} LCI_i \times CF_{i,c} \tag{6.2}$$

Consequently, in this study, these are then normalized and weighted in order to be aggregated into a single indicator (single indicator, SI).

$$SI = \sum_{c}^{C} S_c \cdot w_c \tag{6.3}$$

where, w_c are the weighting factors. Since the LCIA method has been decided upon in the Step 1 of the methodology, the $CF_{i,c}$ and the w_c values are then correspondingly selected.

The output of this step is the deterministic solution of the extended *GlyThink* model which will be used for comparison with the model solution after the superstructure reduction performed in the next step of the framework.

6.2.3 Step 3: Superstructure reduction

The aim of Step 3 of the methodology is to decrease the complexity of the optimization problem in order to decrease the computational effort, so that a stochastic model can be run. This is attained by reducing the superstructure that will be further handled and optimized through stochastic modeling (in Step 4). To this end, the first stage is to select the sources of uncertainty that one knows, through literature research and/or expert knowledge on similar problems, that might affect significantly the feasibility and optimality of the network. In this study, the input sources that might carry uncertainty are categorized into endogenous or exogenous sources, where endogenous refer to process design and technical performance, while exogenous stands for all parameters that the engineer do not control or predict in advance. The former might be derived from the data collection step, if data is obtained from different sources, for example regarding the estimation of the fixed capital investment. The exogenous sources of uncertainty are given by the intrinsic variability, such as price forecast and market demands, among others. After identifying the potential sources of uncertainty, the impact of the propagation of input uncertainties to the model outputs of interest, such as the economic objective function and the environmental criteria, is quantified. This is achieved through a comprehensive scenario-based sensitivity analysis, which applies the extended deterministic model presented in Step 2. Analyzing the influence of the input variation of the uncertain parameters on the: (i) the objective functions (economic -NPV and environmental- LCA); and, (ii) SC design, one can ascertain a set of SC structures (links) that are consistently not selected under extreme variation of the parametric uncertainties. In this way, the superstructure can be reduced by removing the links that are not utilized, leaving only the links corresponding to the SC structures that are most frequently selected. Henceforth, the outcome of this step is twofold: (i) the identification of parameters that have high impact on the model outputs (uncertainty domain); and, (ii) a reduced superstructure obtained by eliminating the links that are not used when subject to extreme variation of uncertainty factors.

6.2.4 Step 4: Planning and assessment under uncertainty

This part of the methodology intends to provide the user with a tool to deal with inherent uncertainty by explicitly incorporating it into the decision-making. To this end, in step 4.1 NS samples are generated that represent NS possible future uncertain events; in step 4.2, the two-stage stochastic model is developed; and, in step 4.3, a thorough assessment is proposed in the form of three solution approaches for the decision under uncertainty (S1, S2 and S3).

6.2.4.1 Step 4.1: Monte Carlo technique

The sources of uncertainty identified in the step 3 as being the ones having more effect on the model outputs and SC structures, are now represented in terms of probability distribution functions (e.g. normal, log-normal, uniform, etc.), with characteristic parameters (e.g. mean and standard deviation for normal distribution). When possible, the probability density functions are built upon historical data. However, this information is often not available in the early stage of process design, especially regarding new biotechnological routes. Therefore, in these circumstances, expert knowledge is used, where typical ranges of variation are inferred and uncertainty classes are assigned. Furthermore, possible correlation between the input sources of uncertainty are analyzed, and if present they are defined by estimating the pairwise covariance from an historical data set. Henceforth, the uncertainty domain obtained in step 3 is used as input data for the Monte Carlo sampling, where Latin Hypercube sampling with Iman and Conover rank correlation control is used, leading to a set of samples (representing future equally probable uncertain events). This set of samples is employed as discretization points to approximate the probability integral in the objective function of the optimization problem under uncertainty presented in the next step of the framework.

6.2.4.2 Step 4.2: Stochastic mathematical formulation - *2S-GlyThink* model

In this step of the framework, uncertainty is explicitly incorporated by reformulating the extended version of the *GlyThink* model chapter 5 developed in Step 2, into a two-stage stochastic optimization problem, called *2S-GlyThink*. Decisions concerning the design and planning of the biorefinery supply chain are made in two stages: the 1^{st} stage decisions ('here-and-now') are taken before the exact realization of uncertainty; and the 2^{nd} stage decisions are made after the realization of uncertainty ('wait-and-see'), being therefore adjustable to its occurrence, also called recourse or corrective actions. In this work, the 1st stage decisions are the initial production capacities of the plants and their capacity expansions over the time horizon, thus directly associated with the fixed investment of the project which has to be taken in the beginning of the time horizon. The 2^{nd} stage decisions consist of planning decision variables, such as inflow of raw materials, production levels and flow of products to the market sinks, and they are depicted in Figure 6.3.

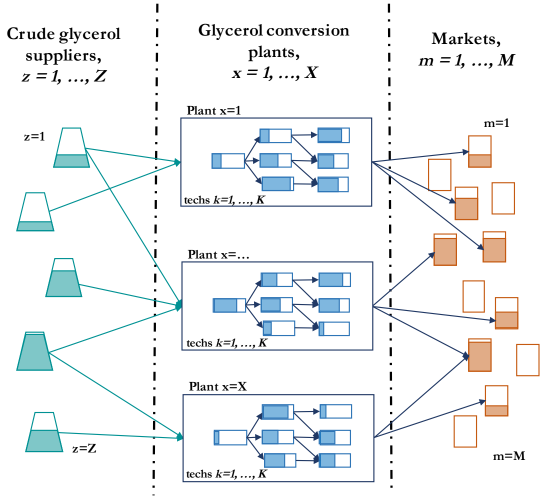


Figure 6.3: Exemplification of the planning decisions as 2^{nd} variables to be identified through solving the *2S-GlyThink* model.

To achieve this, the *2S-GlyThink* model is formulated as a multi-period, multi-product and multi-stage (three-echelon) MILP, targeting at maximizing the NPV of the corresponding SC structure. The following sections describe in length the variables and constraints of the 2S-*GlyThink* model. The mathematical formulation of the *2S-GlyThink* model, is developed so as to allow the flow delivered between the suppliers and plant site locations, production levels, and flows transported to the markets, and associated costs to change with time and with uncertain event realization. The model constraints are grouped into 1^{st} stage constraints that include (6.4) to (6.13) and 2^{nd} stage constraints which includes constraints (6.14) to (6.23). The economic objective function is presented in Eq. (6.25). The definitions of the sets, variables and parameters are given at the beginning of this chapter.

1^{st} ***stage constraints***

A binary variable, $y_{k,q,x,t}$, is introduced in constraints (6.4) and (6.5) to impose the selection of technologies k, with capacity level q, in biorefinery location x, and time period t.

$$\sum_{x}^{X} y_{k,q,x,t} \geq 1, \forall k \in K \wedge q \in Q \wedge t \in T \tag{6.4}$$

$$\sum_{x}^{X} y_{k,q,x,t} \leq N_x, \forall k \in K \wedge q \in Q \wedge t \in T \tag{6.5}$$

where $y_{k,q,x,t}$ is equal to 1 if technology k with capacity level q is built at location x and time period t; and corresponds to the total number of plant site locations available for the construction of the biorefineries. Constraint (6.4) and constraint (6.5) states that at least one and at most N_x locations can be simultaneously selected for the construction of the biorefinery(ies). Also, as stated in constraint (6.6), if at time period t, technology k with capacity level q is selected to be built at plant site location x, then it is assumed that it must be selected/open during all time periods greater than t.

$$y_{k,q,x,t+1} \geq y_{k,q,x,t}, \forall k \in K \wedge x \in X \wedge q \in Q \wedge t \in T-1 \tag{6.6}$$

The convex hull technique has been used to linearize the power law equation for the estimation of the fixed capital investment, as proposed in chapter 5. The obtained algebraic equations are as follows.

$$\sum_{q}^{Q} y_{k,q,x,t} \leq 1, \forall k \in K \wedge x \in X \wedge t \in T \tag{6.7}$$

$$\sum_{q}^{Q} h'_{k,q,x,t} = \frac{1}{NS} \cdot \sum_{s}^{NS} \sum_{i}^{I_p} F_{i,k,x,t,s}, \forall s \in NS \wedge i \in I_p \wedge k \in K \wedge x \in X \wedge t \in T \tag{6.8}$$

$$H_{k,q}^{min} \cdot y_{k,q,x,t} \leq h'_{k,q,x,t} \leq H_{k,q}^{max} \cdot y_{k,q,x,t}, \forall k \in K \wedge q \in Q \wedge x \in X \wedge t \in T \tag{6.9}$$

$$C_{k,q,x,t} = b_{k,q,x} \cdot y_{k,q,x,t} + slope_{k,q,x} \cdot h'_{k,q,x,t}, \forall k \in K \wedge q \in Q \wedge x \in X \wedge t \in T \tag{6.10}$$

$$C_{k,q,x,t} \leq c_k^{max} \cdot y_{k,q,x,t}, \forall k \in K \wedge q \in Q \wedge x \in X \wedge t \in T \tag{6.11}$$

$$FCI_{k,x,t} = 6.7 \cdot \sum_{q}^{Q} C_{k,q,x,t}, \forall q \in Q \wedge k \in K \wedge x \in X \wedge t \in T \tag{6.12}$$

$$\begin{aligned} C_0 = \sum_{x}^{X} \sum_{k}^{K} FCI_{k,x,t=1} + \sum_{t}^{T} \left[\sum_{x}^{X} \sum_{k}^{K} FCI_{k,x,t} - \sum_{x}^{X} \sum_{k}^{K} FCI_{k,x,t-1} \right], \\ \forall k \in K \wedge x \in X \wedge t \in T \end{aligned} \tag{6.13}$$

Firstly, only one segment q per technology k at location x in time period t can be selected, as presented in Eq. (6.7). In Equation (6.8), the continuous variable representing the flow rate in k is disaggregated for each segment q, $h'_{k,q,x,t}$. This is set to be the expected average of the total flow of components leaving technology k, at location x and in time period t, over the range of uncertainties $s \in NS$. The disaggregated variable representing the cost, $C_{k,q,x,t}$ is estimated as presented in Eq. (6.10). Lastly, upper and lower limits are set for the disaggregated variables as presented in (6.9) and (6.11) for the flow and cost, respectively. For all other remaining instances, the Boolean and binary variables are false and 0, respectively. Therefore, as the upper boundaries are given by constraints (6.9) and (6.11) for the segments not selected, the associated continuous disaggregated variables are 0; and, the variables that can have values higher than 0 are the ones obtained for the disjunctive term selected. Furthermore, Eqs. (6.8) and (6.12) state that the continuous variables are equal to the disaggregated variables for the disjunctive term chosen, and their relationships are described through these disaggregated variables by constraints (6.8), which is only active when the related binary variables are 1.

2^{nd} ***stage constraints***

The mass balance must hold for each node within the network. Therefore, the overall mass balance for each component i in technology k at plant site location x at each time period t and scenario s is set by Eq. (6.14). For each technology k at site location x in time period t and scenario s, the inflow of i ($F^{in}_{i,k,x,t,s}$) plus the amount of i produced ($Pr_{i,k,x,t,s}$), must be equal to the amount of i separated as waste ($W_{i,k,x,t,s}$) plus the output flow ($F_{i,k,x,t,s}$) to be delivered to the customers or to be stored in location x.

$$\begin{aligned} &\sum_{z}^{Z} RawM_{i,z,x,t,s} + \sum_{k}^{K_{conv}} Pr_{i,k,x,t,s} + \alpha_{i,k} \cdot \sum_{k}^{K} U_{i,k,x,t,s} = \\ &\sum_{k}^{K_{GP} \cup K_{SP}} W_{i,k,x,t,s} + \sum_{k}^{K_{SP}} F_{i,k,x,t,s}, \\ &\forall i \in I \wedge x \in X \wedge t \in T \wedge s \in NS \end{aligned} \tag{6.14}$$

Furthermore, in Eq. (6.14), K_{conv} represents the set of technologies used for the conversion of raw materials into value-added products, and finally K_{SP} , represents the set of technologies to be used for the separation and purification of the above-mentioned products. Also, $\alpha_{i,k}$ is the fraction of a chemical or utility mixed with the process stream (iI_{ut}), being 1 if the utility/chemical/solvent i is directly added to the flow stream (e.g. direct steam, and 0 otherwise (e.g. cooling water). The amount of component i produced or consumed in the conversion technologies, $Pr_{i,k,x,t}$, is given in Eq. (6.15).

$$\begin{aligned} &\sum_{k}^{K_{conv}} Pr_{i,k,x,t,s} = \sum_{k}^{K_{conv}} \sum_{r}^{R} \sum_{rct}^{Rct} \gamma_{i,k,r} \cdot \theta_{rct,k,r} \cdot F^{in}_{rct,k,x,t,s}, \\ &\forall i \in I \wedge x \in X \wedge t \in T \wedge s \in NS \end{aligned} \tag{6.15}$$

where, $\gamma_{i,k,r}$ and $\theta_{rct,k,r}$ represent the reaction stoichiometry for each component i in technology k and reaction r, and conversion of key reactant i in technology k where r occurs, respectively. The total amount of chemicals or utilities consumed/added i is obtained as a fraction of the total flow in the technologies k and it is given in Eq. (6.16) as follows.

$$\begin{aligned} &\sum_{k}^{K} U_{i,k,x,t,s} = \mu_{i,k} \cdot \sum_{i}^{I \notin I_{ut}} F^{in}_{i,k,x,t,s}, \\ &\forall i \in I_{ut} \wedge x \in X \wedge t \in T \wedge s \in NS \end{aligned} \tag{6.16}$$

where, $\mu_{i,k}$ is the fraction of chemicals/solvents $i \in I_{ut}$ mixed with the process stream in technology k.

In constraint (6.17), the inflow of component $i \in I_{rm}$ into plant site location x coming from supplier z in time period t and in scenario s, $RawM_{i,z,x,t,s}$, is enforced to be lower or equal to the total amount of i available from supplier z in time period t ($\phi_{i,z,t}$).

$$\sum_{x}^{X} RawM_{i,z,x,t,s} \leq \phi_{i,z,t}, \forall i \in I_{feed} \wedge z \in Z \wedge t \in T \wedge s \in NS \tag{6.17}$$

$$\sum_{x}^{X}\sum_{z}^{Z} RawM_{i,z,x,t,s} \leq \sum_{z}^{Z} \phi_{i,z,t}, \forall i \in I_{feed} \wedge t \in T \wedge s \in NS \tag{6.18}$$

$$\sum_{i}^{I_{feed}} RawM_{i,z,x,t,s} \leq L \cdot T_{z,x,t,s}, \forall x \in X \wedge z \in Z \wedge t \in T \wedge s \in NS \tag{6.19}$$

Furthermore, constraint (6.18) imposes that the maximum flow of raw material i delivered to all locations x coming from all suppliers z cannot exceed the total amount of raw materials i available from all suppliers z in time period t. Finally, constraint (6.19) sets the total flow of raw materials to be delivered to the plant site locations x to be lower or, at most, equal to the available transportation capacity over the planning time period.

Constraint (6.20) sets the maximum limit of product being transported to the markets m, $Ftr_{p,x,m,t,s}$, as the maximum amount of product p being produced at plant site x in time period t and scenario s, where the $St_{i,k,x,t,s}$ is the amount of product i to be stored at location x, in time period t and scenario s. Constraint (6.21) enforces that, the amount of product p delivered to a market m must not exceed the demand in that same market m. Furthermore, constraint (6.22) imposes that the maximum flow of product p delivered to all markets m cannot exceed the total demand of product p in all markets m. Finally, constraint (6.23) sets the product flow delivered to the markets ($Ftr_{p,x,m,t,s}$) to be lower or, at most, equal to the available transportation capacity over the planning time-period.

$$\begin{aligned} &Ftr_{i,x,m,t,s} + \sum_{k}^{K} St_{i,k,x,t,s} \leq \sum_{k}^{K} F_{i,k,x,t,s}, \\ &\forall i \in I_p \wedge x \in X \wedge m \in M \wedge k \in K_{SP} \wedge t \in T \wedge s \in NS \end{aligned} \tag{6.20}$$

$$\sum_{x}^{X} Ftr_{i,x,m,t,s} \leq D_{p,m,t,s}, \forall i \in I_p \wedge m \in M \wedge t \in T \wedge s \in NS \tag{6.21}$$

$$\sum_{x}^{X}\sum_{m}^{M} Ftr_{i,x,m,t,s} \leq \sum_{m}^{M} D_{p,m,t,s}, \forall i \in I_p \wedge m \in M \wedge t \in T \wedge s \in NS \tag{6.22}$$

$$Ftr_{p,x,m,t,s} \leq L \cdot T_{p,x,m,t,s}, \forall x \in X \wedge m \in M \wedge t \in T \wedge s \in NS \tag{6.23}$$

Furthermore, the environmental impact assessment calculations presented in Eqs. (6.1) to (6.3) are reformulated in order to include uncertainty in the material flows, but it is not necessary to repeat the equations here.

Objective Function

As previously mentioned, in this work, the measure of economic performance is given by the Net Present Value (NPV) as the objective function of the supply chain, and it is presented as follows. The NPV_s is estimated as the sum of yearly cash-flows discounted to the present year, at a specific interest rate (ω), as presented in Eq.(6.24).

$$\begin{aligned}
&NPV_s = \sum_{t}^{T} \frac{CF_{t,s}}{(1+\omega)^t} = \\
&\sum_{t}^{T} \frac{NE_{t,s}}{(1+\omega)^t} - C_0 = APV_s - C_0 = \\
&\sum_{t}^{T} \left[\frac{1}{(1+\omega)^t} \cdot [S_{t,s} - PC_{t,s} - Lc_{t,s} - TrC_{t,s} - SC_{t,s} - WC_t - \right. \\
&\left. [\varphi \cdot (S_{t,s} - PC_{t,s} - Lc_{t,s} - TrC_{t,s} - SC_{t,s} - CD_t)] \right] + C_0 \cdot \left(\frac{sv}{(1+\omega)^t} - 1 \right), \forall s \in NS
\end{aligned} \tag{6.24}$$

where, $S_{t,s}$ and $PC_{t,s}$, represent the revenue (product sales) and production cost, respectively; $Lc_{t,s}$, $TrC_{t,s}$, and $SC_{t,s}$, represent the labor costs, transportation cost and storage cost, respectively; CD_t and WC_t, represent the capital depreciation and working capital, respectively. $TI_{t,s}$ and C_0 stand for the taxable income and total initial capital investment.

Finally, the NPV_s is fully given by Eq.(6.25).

$$\begin{aligned}
&NPV_s = \sum_{t}^{T} \left[\frac{(1-\varphi)}{(1+\omega)^t} \right. \\
&\cdot \left[\sum_{x}^{X} \sum_{m}^{M} \sum_{k}^{K_{SP}} \sum_{i}^{I_p} Ftr_{i,x,m,t,s} \cdot pP_{i,s} - \sum_{x}^{X} \sum_{k}^{K_{PG}} \sum_{i}^{I_{feed}} F^{in}_{i,k,x,t,s} \cdot pRM_{i,s} \right. \\
&- \sum_{x}^{X} \sum_{k}^{K_{conv} \cup K_{SP}} \sum_{i}^{I_p} U_{i,k,x,t,s} \cdot pUT_i - op \cdot ns \cdot avSal_t \cdot \sum_{x}^{X} \sum_{k}^{K_{PG}} \sum_{i}^{I_{feed}} F^{in}_{i,k,x,t,s} \\
&- \sum_{x}^{X} \sum_{m}^{M} \sum_{i}^{I_p} \left[T_{i,m,x,t,s} \cdot \left(2 \cdot d_{x,m} \cdot (fc + trMa) + \left(\frac{2 \cdot d_{x,m}}{sp} + lut \right) \cdot dw \right) \right] \\
&\sum_{x}^{X} \sum_{m}^{M} \sum_{i}^{I_p} \left[T_{z,x,t,s} \cdot (2 \cdot d_{z,m} \cdot (fc \cdot pF + trMa) + \left(\frac{2 \cdot d_{z,m}}{sp} + lut \right) \cdot dw) \right] - 2 \cdot trGE_t \\
&\left. - \sum_{x}^{X} \sum_{k}^{K_{SP}} \sum_{i}^{I_p} St_{i,k,x,t,s} \cdot pSt_i - (wc_t + ms_t) \cdot C_0 \right] \\
&\left. + \frac{\varphi}{(1+\omega)^t} \cdot \gamma_{k,x,t} \cdot C_0 \right] + \left(\frac{sv}{(1+\omega)^t} - 1 \right) \cdot C_0
\end{aligned} \tag{6.25}$$

6.2.5 Step 4.3: Solution under uncertainty

In this step of the methodology, three solution approaches for an informed decision under uncertainty are given to decision-maker (S1, S2 and S3). These solutions are based upon: (S1) the stochastic single-objective optimization maximizing the NPV of the SC; (S2) detailed analysis, by mapping the SC structures of all solutions obtained from the implementation of the Monte-Carlo method; and, (S3) the stochastic multi-objective optimization, maximizing the NPV and minimizing the environmental impact of the supply chain.

Solution S1 – stochastic single-objective optimization

The main goal of the mathematical formulation is to maximize the expected value of the Net Present Value (NPV) as presented in Eq. (6.26). The MILP formulation can be expressed as follows:

$$\begin{aligned} \underset{b,b_s,y}{\text{maximize}} \quad & E[NPV(b,b_s,y,\theta)] \\ \text{subject to} \quad & (6.4) \text{ to } (6.23) \end{aligned} \tag{6.26}$$

where, b represents 1^{st} stage decision variables, b_s represents 2^{nd} stage variables (planning) that are scenario dependent and y stands for the binary variables. θ is the vector of uncertain data and the $E[NPV(b,b_s,y,\theta)]$ is the expected value of the objective function NPV over the θ space. The estimation of the expected value of the objective function (in this case, NPV) requires the evaluation of a multidimensional probability integral. Thus, in large problems the evaluation of this integral might result in a heavy and complex procedure, requiring a high computational effort. Therefore, a common way to tackle this in stochastic programming is based upon the Monte Carlo sampling method for the approximation of the expected value of the objective function called Sample Average Approximation [227]. Where, as above-mentioned, the generated set of samples are employed as discretization points to approximate the probability integral. This is exemplified in Eq. (6.27), where the expected value of the objective function *E[NPV]* is approximated by the expected value of the resulting distribution. Where pr_s is the probability of occurrence of a certain scenario s and *NS* is the total number of scenarios s.

$$E[NPV(b,b_s,y,\theta)] \approx \sum_{s}^{NS} (pr_s \cdot NPV(b,b_s,y,\theta_s)) = \frac{1}{NS}\sum_{s}^{NS} NPV(b,b_s,y,\theta_s) \tag{6.27}$$

Therefore, the optimization problem is finally expressed as,

$$\begin{aligned} \underset{b,b_s,y}{\text{maximize}} \quad & E[NPV(b,b_s,y,\theta)] = \frac{1}{NS}\sum_{s=1}^{NS} NPV(b,b_s,y,\theta_s) \\ \text{subject to} \quad & (6.4) \text{ to } (6.23) \end{aligned} \tag{6.28}$$

Given the (fixed) sample s to *NS*, the function $E[NPV(b,b_s,y,\theta)]$ is deterministic, thus deterministic optimization algorithms can be used to solve the problem.

6.2.5.1 Solution S2 – SC structure mapping and analysis

In this solution approach, the consequences of named uncertainties on the SC structure and, on the objective function, are mapped and analyzed. To this end, the deterministic optimization problem formulated in Step 2, is solved for each one of the samples generated in Step 4.1, as described by the problem formulation presented below in Eq.(6.29). This falls under the 'wait and see' category of optimization problems, since it is built on the premise that the decision-making will wait and be made upon the realization of the uncertain event. A distribution of the objective function values is achieved, i.e. a different objective function value is obtained for every sample, to which corresponds to a certain design and planning SC structure. The application of this solution approach enables the analysis of the robustness of the SC structure, which provides information about how sensitive a selected SC structure is against future uncertainties.

$$\begin{aligned} \underset{B,y}{\text{maximize}} \quad & NPV_s, \forall s \in NS \\ \text{subject to} \quad & (6.4) \text{ to } (6.23) \end{aligned} \tag{6.29}$$

6.2.5.2 Solution S3 – multi(bi)-objective

The overall bi-objective formulation can be expressed as follows:

$$\begin{aligned} \underset{b,b_s,y}{\text{maximize}} \quad & E\{[NPV]; -SI\} \\ \text{subject to} \quad & (6.4) \;\text{ to }\; (6.23) \end{aligned} \tag{6.30}$$

The solution of this problem is given by a set of Pareto alternatives representing the optimal trade-offs between the two objectives, in order to manage the environmental consequences. In this study, these solutions are obtained via ϵ-constraint method as defined in Ehrgott (2004) [228] that leads to the solution of the following single-objective function for various instances of the parameter ϵ:

$$\begin{aligned} \underset{b,b_s,y}{\text{maximize}} \quad & E\{[NPV]\} \\ \text{subject to} \quad & (6.4) \;\text{ to }\; (6.23) \\ & SI \leq \epsilon \\ & \epsilon^{min} \leq \epsilon \leq \epsilon^{max} \end{aligned} \tag{6.31}$$

where ϵ^{min} and ϵ^{max} represent the lower and upper limits within which the ϵ must fall are given by the optimization of each separate objective function (economic-NPV and environmental- LCA). Therefore, ϵ^{min} is obtained following the mathematical formulation presented below in Eq. (6.32).

$$\begin{gathered} \left(\underline{b}, \underline{b_s}, \underline{y}\right) = \underset{b,b_s,y}{\text{argmin}}\{SI\} \\ \text{subject to } (6.4) \text{ to } (6.23) \end{gathered} \tag{6.32}$$

where, $(\underline{b}, \underline{b_s}, \underline{y})$ stand for, $1s^{st}$ stage decision variables, 2^{nd} decision variables and binary variables that correspond to the optimal SC structure when maximizing the expected value of SI as objective function. The ϵ^{max} is obtained when maximizing the expected value of NPV of the supply chain, and it is obtained through the formulation presented in Eq. (6.33).

$$\begin{aligned} (\bar{b}, \bar{b_s}, \bar{y}) &= \underset{b,b_s,y}{\operatorname{argmax}}\{E[NPV]\} \\ \text{subject to} &\qquad (6.4) \text{ to } (6.23) \end{aligned} \tag{6.33}$$

where, $(\bar{b}, \bar{b_s}, \bar{y})$ stand for, $1s^{st}$ stage decision variables, 2^{nd} decision variables and binary variables that correspond to the optimal SC structure when maximizing the expected value of the economic objective function (NPV).

6.3 Results & Discussion

6.3.1 Step 1: Problem definition, data collection & management

This work, aims to identify the optimal supply chain of the glycerol-based integrated biorefinery in Europe under multi-level uncertainties. To this end, the starting point is to characterize the superstructure of alternatives obtained in chapter 5 for the glycerol conversion to chemicals and biofuels. However, in this study, this superstructure is focused to only include bio-based chemicals, based upon a price screening and based upon the fact that, through deterministic assessment, biofuels have not been selected as an economically sustainable alternative for the glycerol valorization [15]. Therefore, the superstructure of alternatives used is presented in Figure 6.4. Included in this network are: several alternative suppliers, plant site locations, technologies (and corresponding products), and demand sinks. The products included in the superstructure are: polyhydroxybutyrate (PHB), lactic acid (LA), succinic acid (SA), 1-2-propanediol (1,2-PDO), 1,3-propanediol, (1,3-PDO), acrolein (Acro) and epichlorohydrin (Epi). The corresponding processing technologies are described in Table 6.4. The total glycerol availability in Europe is 4.10×10^6 ton/year as discussed in chapter 5. The suppliers are given by the top-5 major producers (and consumers) of biodiesel currently in Europe, and they are: Germany, France, The Netherlands, Spain and Italy (see chapter 5). The glycerol available per supplier is given in chapter 5 Table 5.4. The market demands for the above-mentioned products were collected from reports, publications and public communications. To be as much representative of the European market as possible, a total of 5 top markets were identified for each product and the corresponding demands were collected. They are reported in chapter 5, Table 5.6. The product prices needed for the economic analysis are presented in Table 5.8. Furthermore, regarding the data required for the environmental assessment, the ReCiPe [229] was the life cycle impact assessment method (LCIA) selected [54], thus all impact categories and characterization factors needed to convert the material flows into impact categories are defined, along with the normalization and weighting factors.

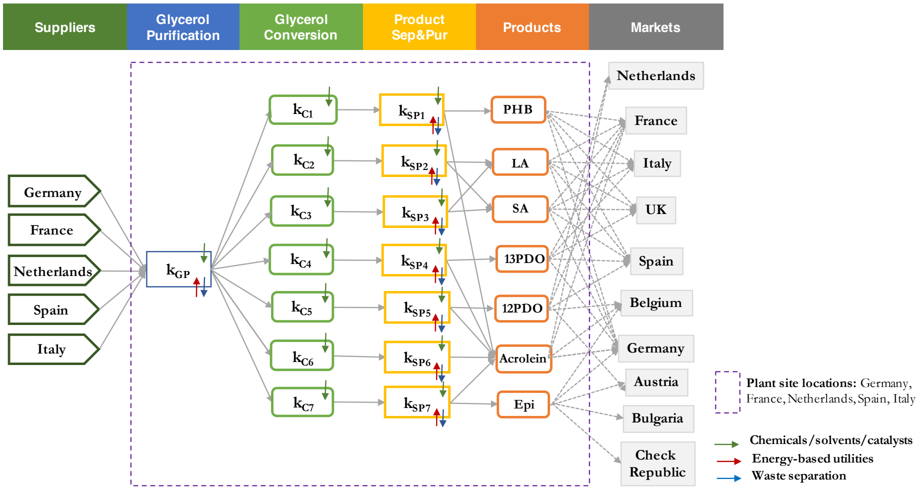


Figure 6.4: Superstructure representing the alternatives in the design space.

Table 6.4: Process description for all the alternatives in the superstructure.

Symbol	Product	Description
k_{C_1} & k_{SP_1}	Polyhydroxybutyrate (PHB)	Glycerol fermentation by an engineered strain of *C. necator* to Polyhydroxybutyrate (PHB) + blending w/ surfactant solution + hypochlorite digestion centrifugation + spray drying [141]
k_{C_2} & k_{SP_2}	Lactic acid (LA)	Glycerol fermentation by an engineered strain of *E.coli* to Lactic acid (LA) + reactive extraction w/ TOA and DCE [121]
k_{C_3} & k_{SP_3}	Succinic acid (SA)	Glycerol fermentation by an engineered strain of *B. succinis producens DD1* to Succinic acid (SA) + reactive extraction w/ TOA and 1-octanol [106], [205]
k_{C_4} & k_{SP_4}	1,3-propanediol (1,3-PDO)	Glycerol fermentation by an engineered strain of *K pneumoniae* to 1,3-propanediol (1,3-PDO) + reactive extraction w/ isobutyraldehyde hydrophilic alcohol/salt mixture (ethanol/K_2HPO_4) [162],[139],[140]
k_{C_5} & k_{SP_5}	1,2-propanediol (1,2-PDO)	Sequential processes of dehydrogenation-hydrogenation via hydroxyacetone to 1,2-propanediol (1,2-PDO) [142] [143]
k_{C_6} & k_{SP_6}	Acrolein	Glycerol dehydration [148]
k_{C_7} & k_{SP_7}	Epichlorohydrin (Epi)	Glycerol hydrochlorination to Epichlorohydrin (Epi) [206]

6.3.2 Step 2: Deterministic solution

The deterministic optimization problem defined in Step 2 is here solved. As proposed in chapter 5, two scenarios were built to understand the influence of constraining the model to a certain production capacity. They are described as follows:

- Scenario B1: leads to the optimization of the supply chain network allowing the model to identify a combination of best plant site locations (allowing the selection of more than one plant), by also determining the optimal amount of glycerol converted into value added products, so that NPV is maximized;
- Scenario B2: the optimization problem set in B1 is further constrained to convert the total amount of glycerol available (4.10×10^6 ton/year), also allowing the selection of more than one plant, so that NPV is maximized.

The main characteristics of the optimal SC structures obtained for B1 and B2 are described in Table 6.6, also presented in chapter 5 in Figures 5.11 and 5.12, respectively.

Table 6.5: Details on the deterministic solutions: B1 and B2.

Scenarios	NPV (MM$ $\times 10^3$)	SI	SC structure main characteristics
B1	6.115	0.085	Plant site locations: Germany, France, The Netherlands, Italy Suppliers: Germany, France, The Netherlands, Italy Products: SA, LA Markets served: LA – Germany, France, Italy SA – UK, Spain, Germany, Italy, France $Q_{glyc} = 2.13x10^3$ kton/year
B2	0.452	0.257	Plant site locations: Germany, France, The Netherlands, Italy, Spain Suppliers: Germany, France, The Netherlands, Italy, Spain Products: SA, LA, PHB, Epi Markets served: LA – Germany, Italy, Spain SA – UK, Spain, Germany, Italy, France PHB – Germany Epi – Germany, The Netherlands, Belgium, Spain

6.3.3 Step 3: Superstructure reduction

This step has a two-fold objective: (i) to identify the parameters that have the highest impact on the objective function; and, (ii) to provide the user with a reduced superstructure by analyzing the SC structures obtained when subjecting the supply chain model to extreme variations of the input parameters, so as to reduce the problem complexity. To this end, a scenario-based sensitivity analysis is performed based on the deterministic single-objective optimization of the NPV. The sources of uncertainty identified are based on most common uncertainty sources studied in the works presented in the literature reviewed in Table 1.3. Therefore, in this work, the sources of uncertainty under analysis are: product demand, glycerol price, product price, and technology evolution (FCI and glycerol conversion). According to the sources of uncertainty identified, a relevant set of scenarios was built as presented in Figure 6.5.

The set of scenarios represented in Figure 6.5 were developed so as to analyze the impact of extreme variation of the parameter values on the (a) objective function- NPV; (b) consequences of external techno-economic uncertainties on the environmental impact - SI; and, (c) SC structure and product portfolio selected. The scenarios description is as follows:

- Pp-Sc1: variation of 0.50 and 1.50 of the original price value regarding all products, to represent extreme cases of price variation.
- Pp-Sc2: variation of 0.50 and 1.50 of the original price value regarding the most frequently selected products: SA, LA, PHB and Epi. To represent extreme cases of price variation of the products selected in the deterministic solution of B2.

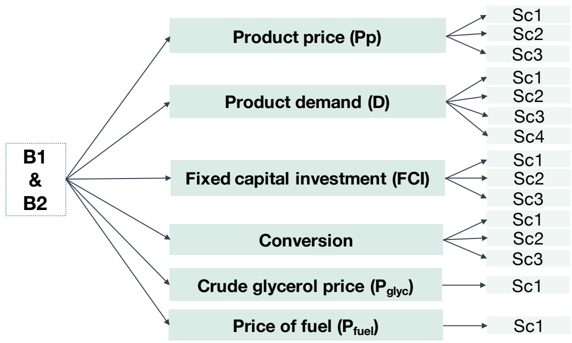


Figure 6.5: Scenarios analyzed through the deterministic sensitivity analysis.

- Pp-Sc3: variation of 0.50 and 1.50 of the original price value regarding the most frequently selected products: SA and LA. To represent extreme cases of price variation of the products selected in the deterministic solution of B1.
- D-Sc1: variation of 0.50 and 1.50 of the original demand value regarding all products, to represent extreme cases of demand variation.
- D-Sc2: variation of 0.50 and 1.50 of the original demand value regarding the most frequently selected products: SA, LA, PHB and Epi. To represent extreme cases of price variation of the products selected in the deterministic solution of B2.
- D-Sc3: variation of 0.50 and 1.50 of the original demand value regarding the most frequently selected products: SA and LA. To represent extreme cases of price variation of the products selected in the deterministic solution of B1.
- D-Sc4: variation of demand following a normal distribution [230], [231] (with 10% standard deviation and original value as expected value) for the twenty years of plant life time. This represents a more realistic scenario of demand variation along the plant life time.
- FCI-Sc1: variation of 0.50 and 1.50 of the original FCI value regarding all products, to represent extreme cases of price variation.
- FCI-Sc2: variation of 0.50 and 1.50 of the original FCI value regarding the most frequently selected products: SA, LA, PHB and Epi. To represent extreme cases of price variation of the products selected in the deterministic solution of B2.
- FCI-Sc3: variation of 0.50 and 1.50 of the original FCI value regarding the most frequently selected products: SA and LA. To represent extreme cases of price variation of the products selected in the deterministic solution of B1.
- Conv-Sc1: variation of 0.50 and 1.50 of the original conversion value of all products, to represent extreme cases of price variation.
- Conv-Sc2: variation of 0.50 and 1.50 of the original conversion value of the most selected products: SA, LA, PHB and Epi. To represent extreme cases of price variation of the products selected in the deterministic solution of B2.
- Conv-Sc3: variation of 0.50 and 1.50 of the original conversion value of the most selected products: SA and LA. To represent extreme cases of price variation of the products selected in the deterministic solution of B1.

- Pglyc-Sc1: variation of 0.50 and 1.50 of the original crude glycerol price, in order to represent extreme cases of price variation.
- pFuel-Sc1: variation of 0.50 and 1.50 of the original fuel price, used for the transportation by truck.

The deterministic sensitivity analysis results obtained by the single-objective optimization maximizing the NPV of the supply chain are graphically represented in Figure 6.6 for B1 conditions, and in Figures E.1 and E.2 for B2 conditions. Furthermore, all corresponding SC structures were analyzed, and a summary of the main characteristics of the scenarios that show the highest variation of the NPV are summarized in Table 6.6 below.

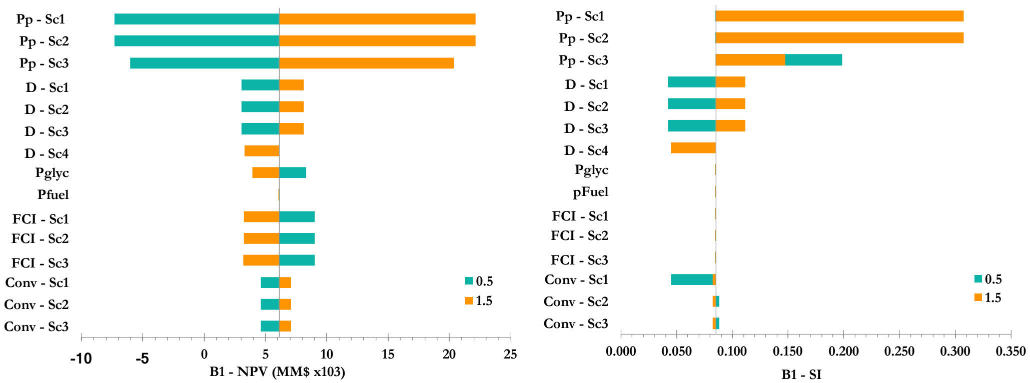


Figure 6.6: Sensitivity analysis of the NPV (left), SI (right) and corresponding SC structure to parameter variation, corresponding to B1 conditions.

Hence, significant insights on the consequences of these techno-economic uncertainties on the NPV, SI and corresponding SC structures are discussed as follows.

Influence on the NPV

The analysis of Figures 6.6 (left hand side) and E.1, shows that the sources of uncertainty that have the highest impact on the NPV are: product price, product demand and FCI. In more detail, by analyzing the NPV of the scenarios Pp-Sc1, Pp-Sc2 and Pp-Sc3 under B1 and B2 conditions, it can be observed that the Pp-Sc1 and Pp-Sc2 scenarios have approximately the same impact, i.e., the variation of all prices and the variation of prices of the products SA, LA, Epi and PHB lead to the same results, which supports the fact that in fact these are the most relevant products to be included in the design space. Similar conclusions are reached by looking at the scenarios where the demand and the FCI are under parametric variation.

Influence on the SI

As can be observed in Figures 6.6 (right hand side) and E.2 for scenarios corresponding to B1 and B2, respectively, through the analysis of the SI, both product price and demand uncertainties have a significant impact on the SC structures, and on the corresponding SI, under B1 and B2 conditions. Whereas in case of B1 conditions, the variation of the FCI only affects the NPV (Figure 6.6), where there is no variation on the SI of the corresponding solutions, i.e., the SC structure obtained through deterministic analysis is robust regarding the effects of the variation of the FCI. However, under B2 conditions, when varying the FCI corresponding to the most frequently selected products (observed in FCI-Sc1 and FCI-Sc2, on Figure E.2), the SI is slightly changed. This is due to the fact that, to compensate for the higher fixed investment costs of these products, and to fulfill the demand for full conversion of the available glycerol, the production of SA and LA is decreased and the production of PHB increased, which leads to higher environmental impact. The augmented environemental impact is due to the higher consumption of utilities in the separation and purification stages of the PHB production, leading to higher carbon footprint and terrestrial acidification potential. This is explained by the fact that production of PHB is a heavier consumer of utilities than the production of SA, LA and Epi. All in all, higher variation of the NPV and SI is observed in scenario B2 conditions (Figure E.1 and E.2), since in this case the production is constrained to convert the total amount of glycerol available in Europe at a given year; while, in scenario B1 (Figure 6.6, left and right hand side) the production can be adjusted to the uncertain events in order to reach an optimal solution.

Table 6.6: Summary of the main characteristics of the SC structures corresponding to the highest variation of NPV. Where Pp and D stand for product price and demand, respectively.

Scenarios	$\Delta\theta$	NPV (MM\$ $\times 10^3$)	SI	SC structure main characteristics
Pp-Sc1+B1	-50%	-7.329	0.084596	Plant site locations: Germany, France, Netherlands, Spain Suppliers: Germany, France, Netherlands, Spain Products: LA, SA Markets served: LA – Germany, France, Spain SA - Germany, France, Spain, UK, Italy
	50%	22.129	0.30779	Plant site locations: Germany, France, Netherlands, Spain, Italy Suppliers: Germany, France, Netherlands, Spain, Italy Products: LA, SA, Epi, PHB Markets served: LA - Germany, France, Spain, Italy SA - Germany, France, Spain, UK, Italy PHB – Germany Epi – The Netherlands, Belgium
Pp-Sc1+B2	-50%	-21.01	0.25621	Plant site locations: Germany, France, Netherlands, Spain, Italy Suppliers: Germany, France, Netherlands, Spain, Italy Products: LA, SA, Epi, PHB Markets served: LA – Germany, Italy, Spain SA - Germany, France, Spain, UK, Italy PHB – Germany Epi – Germany, The Netherlands, Belgium, Spain
	50%	22.129	0.30779	Plant site locations: Germany, France, Netherlands, Spain, Italy Suppliers: Germany, France, Netherlands, Spain, Italy Products: LA, SA, Epi, PHB Markets served: LA – Germany, Italy, Spain, France SA - Germany, France, Spain, UK, Italy PHB – Germany Epi –The Netherlands, Belgium

Table 6.7: *cont.* Table 6.6.

Scenarios	$\Delta\theta$	NPV (MM\$ $\times 10^3$)	SI	SC structure main characteristics
D-Sc3 + B	-50%	3.05	0.04235	Plant site locations: France, Netherlands Suppliers: France, Netherlands Products: LA, SA Markets served: LA – Germany, France SA - Germany, The Netherlands, UK, Spain, Italy
	50%	8.136	0.11161	Plant site locations: Germany, France, Netherlands, Spain, Italy Suppliers: Germany, France, Netherlands, Spain, Italy Products: LA, SA Markets served: LA – Germany, France, Italy, Spain SA - Germany, France, Spain, Italy
D-Sc3 + B2	-50%	-6.152	0.3778	Plant site locations: Germany, France, Netherlands, Spain, Italy Suppliers: Germany, France, Netherlands, Spain, Italy Products: LA, SA, PHB, Epi Markets served: LA – Germany, Spain SA - Germany, France, Spain, Italy, UK PHB – Germany, France Epi – Germany, The Netherlands, Belgium, Spain, Italy
	50%	5.069	0.12077	Plant site locations: Germany, France, Netherlands, Spain, Italy Suppliers: Germany, France, Netherlands, Spain, Italy Products: LA, SA, Epi Markets served: LA – Germany, Spain, Italy, Spain SA - Germany, France, Spain, Italy Epi – Germany, The Netherlands, Belgium, Spain, Italy

Based upon the previous analysis, the superstructure has been reduced based on the following considerations: (i) the set of products selected is constant (see Table 6.6) and it is composed of SA, LA, PHB and Epi, thus the links corresponding to other products (technologies and markets) have been excluded; also, (ii) by analyzing the SC structures in Table 6.6, one can see a pattern of the most frequently selected links between production plants and markets. These are the ones kept in the reduced superstructure. Thus, having these facts into consideration, the initial superstructure as presented in Figure 6.4 has been reduced to the one presented in Figure 6.7. Furthermore, since the products and the corresponding links identified as optimal in the deterministic solution for scenarios B1 and B2 have been kept as part of the reduced superstructure (see Table 6.5), the deterministic solution corresponding to B1 and B2 scenarios after superstructure reduction are equal to the SC structures obtained for B1 and B2 before the superstructure reduction (which characteristics have been reported in Table 6.5). In this way, validating the reliability of the reduced superstructure obtained, which will be the starting point of the step 4.

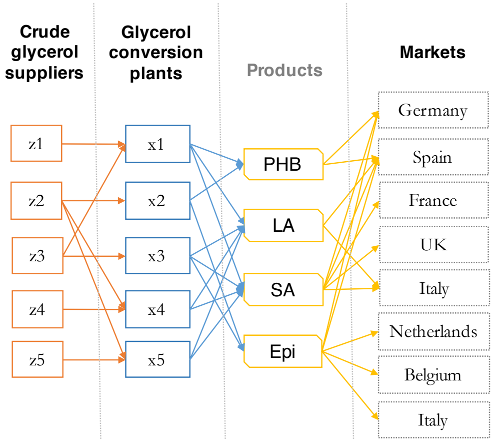


Figure 6.7: Reduced superstructure obtained through scenario sensitivity analysis (original superstructure is represented in Figure 6.4.)

6.3.4 Step 4: Planning and assessment under uncertainty

Step 4.1: Monte Carlo technique

The uncertain data identified through deterministic sensitivity analysis as having high impact on the economic and environmental performance are considered for further analysis in the following steps. The application of this technique has been described in detail in in [15]. For the uncertainty on the prices, the premise is that the product price will vary in the future in the same manner as it did in the past. To this end, historical price data trends of the products under consideration have been surveyed over the past 10 years and used to construct the historical price distributions for each product [15]. Also, the presence of correlation between the price data was investigated and quantified by estimating the pairwise covariance. For the uncertainty on the product demand, it is assumed that it follows a normal distribution with 10% standard deviation [230], [231], along the 20 years of the biorefinery plant life time. Furthermore, through Latin Hypercube Sampling NS future uncertainty events were generated, where the rank correlation control method proposed by Iman Conover is used in order to reflect the correlation between the uncertain parameters in the generated future scenarios.

Step 4.2: Solution under uncertainty

Solution S1 - stochastic single-objective optimization

In solution S1, the problem corresponding to the formulation of the stochastic single-objective optimization presented in Eq. (6.28) is solved for different sources of uncertainty. As identified in Step 4.1, the uncertainty domain to be tested is composed of the product price and product demand uncertainties. Therefore, scenarios were built to test the effect of sources of uncertainty, independently and combined, on the economic objective function, under B1 and B2 conditions. The generated scenarios are the following:

- Pp + B1: uncertainty on the product price, under B1 conditions.

- Pp + B2: uncertainty on the product price, under B2 conditions.

- D + B1: uncertainty on the product demand, under B1 conditions.

- D + B2: uncertainty on the product demand, under B2 conditions.

- Pp + D + B1: uncertainty on the product demand and product price, under B1 conditions.

- Pp + D + B2: uncertainty on the product demand and product price, under B2 conditions.

The results obtained by solving the stochastic single-objective optimization for each one of the scenarios above are depicted in Figure 6.8 and reported in Table 6.8, and compared to the deterministic solutions.

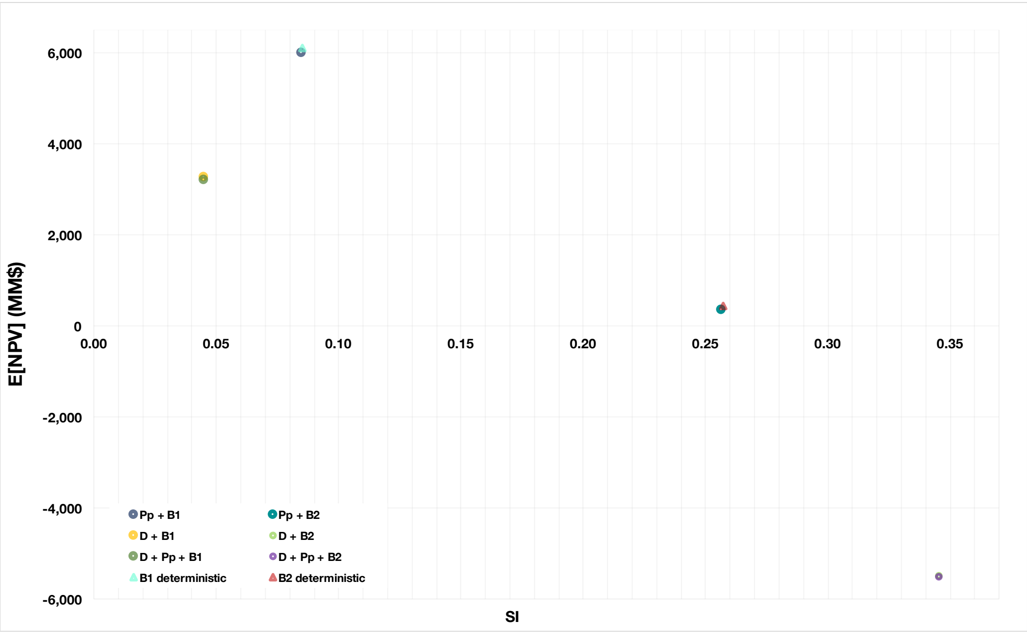


Figure 6.8: Results of the solution S1, where the E[NPV] is estimated through SAA for different uncertainty conditions. The triangles represent the deterministic solutions.

Table 6.8: Stochastic solutions for the scenarios generated (S1).

Scenarios	NPV (MM$)	SI	SC structure
Pp + B1	6011	0.0846	Plant site locations: Germany, France, The Netherlands, Italy Suppliers: Germany, France, The Netherlands, Italy Products: SA, LA Markets served: LA – Germany, France, Italy SA – UK, Spain, Germany, Italy, France Q_{glyc}= 2.13×10^3 kton/year
D + B1	3286.1	0.04459	Plant site locations: Germany, France Suppliers: Germany, France Products: LA, SA Markets served: LA – Germany, France SA - Germany, France, Spain, UK, Italy
Pp + D + B1	3230.3	0.04458	Same as scenario (D + B1)
B1 det.	6115	0.085	Plant site locations: Germany, France, The Netherlands, Italy Suppliers: Germany, France, The Netherlands, Italy Products: SA, LA Markets served: LA – Germany, France, Italy SA – UK, Spain, Germany, Italy, France Q_{glyc}= 2.13×10^3 kton/year
Pp + B2	373.6	0.25611	Plant site locations: Germany, France, The Netherlands, Italy, Spain Suppliers: Germany, France, The Netherlands, Italy, Spain Products: SA, LA, PHB, Epi Markets served: LA – Germany, Italy, Spain SA – UK, Spain, Germany, Italy, France PHB – Germany Epi – Germany, The Netherlands, Belgium, Spain
D + B2	-5493.7	0.34542	Plant site locations: Germany, France, Netherlands, Spain, Italy Suppliers: Germany, France, Netherlands, Spain, Italy Products: LA, SA, PHB, Epi Markets served: LA – Italy, Spain SA - Germany, France, Spain, Italy, UK PHB – Germany, France Epi – Germany, The Netherlands, Belgium, Spain, Italy
Pp + D + B2	-5525.8	0.34542	Same as scenario (D + B2)
B2 det.	452	0.257	Plant site locations: Germany, France, The Netherlands, Italy, Spain Suppliers: Germany, France, The Netherlands, Italy, Spain Products: SA, LA, PHB, Epi Markets served: LA – Germany, Italy, Spain SA – UK, Spain, Germany, Italy, France PHB – Germany Epi – Germany, The Netherlands, Belgium, Spain

The results presented in Figure 6.8 and Table 6.8 have shown that the demand has a high impact on the objective function (NPV), and that the product price uncertainty further decreases the NPV of the project. In the B1 case, since the model has an additional degree of freedom compared to scenario B2, the model is flexible enough to adjust the production in face of uncertainty. In the present case, the demand uncertainty leads to a decrease in the production and accordingly a decrease in the environmental impact. Whereas under B2 conditions, the NPV drops significantly when compared to the deterministic counterpart not being flexible with regards to the inflow of glycerol. Thus, under demand uncertainty, the optimal NPV is obtained when increasing the production of PHB and correspondingly decreasing the production of SA and LA. This is accompanied by an increase in the environmental impact since the production of PHB is a heavier consumer of utilities at the separation and purification stages than the other products. Furthermore, it can be observed that following the realistic scenario when both sources of uncertainty play a role in the market environment (scenario Pp + D+ B1 and B2 in Table 6.8 and Figure 6.8), the NPV of the project decreases, for both B1 and B2. In summary, since the combination of both uncertainties composes a realistic scenario, and given that it has high impact of the model outcomes, this will be the scenario that will be analyzed in detail in the next solution approach, S2.

Solution S2 – SC structure mapping and analysis

In this step, a deterministic optimization problem corresponding to the solution of the problem formulated in Eq. (6.29), is solved for each one of the scenarios generated by the Monte Carlo sampling performed in Step 4.1. Immediate consequences of the data uncertainty on the decision-making problem are statistically analyzed. The result is composed of a distribution of 50 optimal (NS) NPV and SI values (points) that are mapped and statistically analyzed. Every point solution of sample s is characterized by an SC structure, reflecting design and planning decisions. Moreover, so as to decrease the computational effort (by reducing the number of equations), the SI calculation is reduced to include only two of the categories of impact. To this end, a significance test was performed so as to pinpoint which are the two categories that weigh more in the single indicator (SI) for both the B1 and B2 deterministic cases (see Appendix E, Figure E.6). Therefore, the scenario where both product price and product demand are sources of uncertainty is here analyzed in more detail through S2, under conditions corresponding to scenarios B1 and B2. The results regarding the B2 scenario are presented in Appendix E, Figures E.3 and E.4. The results concerning scenario B1 are discussed in detail below.

In Figure 6.9 the optimal NPV obtained for the optimization problem resulting of each Monte Carlo sample is presented. Comparing to the B1 base case (deterministic) it is observed that the probability of NPV being lower than the deterministic B1 result is 98% (Figure 6.10), where the average (3.28×10^3 MM\$) corresponds to 46% of the deterministic NPV (see Table 6.5). This is due to the adjustment of the planning decisions to the uncertainty realization characterizing the scenarios s, where the market demand instability and reduced product price, leads to a lower optimal inflow of glycerol converted (1120 kton/y), when compared to the optimal nominal inflow identified in the B1 base case (2126 kton/y) as presented in Figure 6.9. Also, as depicted in Figures 6.9 and 6.10, the maximum NPV reached is approximately 80% higher than the minimum NPV reported. This mainly results from the increase in the product market price in the markets when moving from left to right in Figure 6.9, which also justifies the slight change in the markets served. Furthermore, as above-mentioned, there is a significant difference between the expected deterministic NPV and the stochastic solution, thus carrying economic risk. Therefore, it is critical to consider the inherent presence of uncertainties and its potential effect on the optimal SC structure and corresponding inflow of crude glycerol.

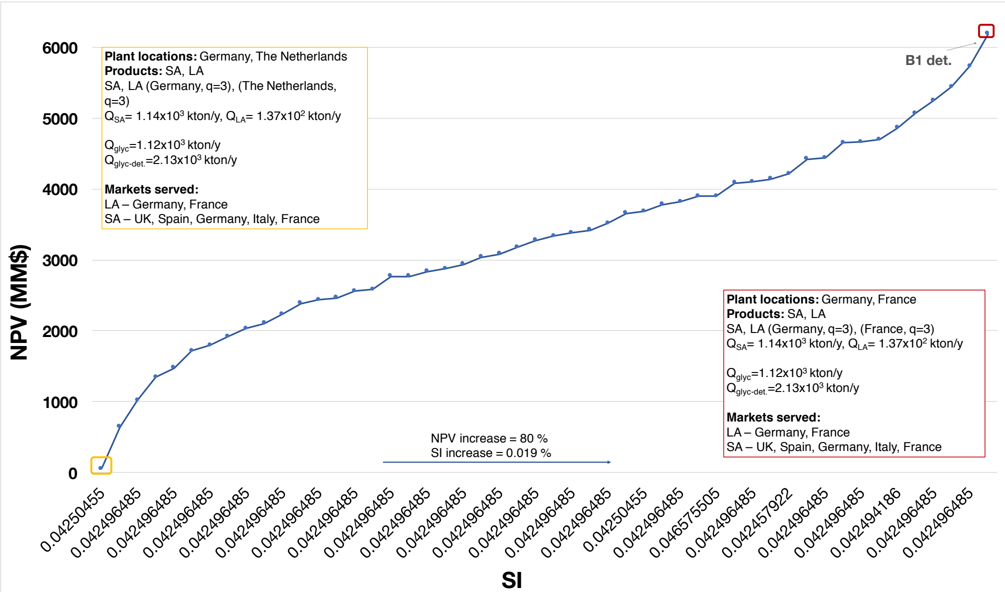


Figure 6.9: NPV variation for all scenarios along with the highlighting of some significant SC structures and their characteristics for B1.

The alternative that presents a high probability of having a positive NPV and thus having the project being approved, even under market uncertainty, is scenario B1. This is due to the fact that B1 has an extra degree of freedom when compared to B2, where B1 is capable of adjusting the inflow of glycerol, and thus the production, according to the market environment, which leads to positive NPV's. In contrast, the SC structures obtained under B2 conditions are economically unfeasible for all uncertainty realizations (see Figure E.3), as expected from the results obtained by applying solution approach S1.

Therefore, a more detailed analysis was performed into the topology of the obtained solutions under B1 conditions. The main characteristics and the frequency of selection are presented in Table 6.9. It is observed that the topology-1 (Top-1) is selected in 96% of the events, which is characterized by having the plants located in Germany and France for the production of SA and LA. These production plants are also characterized by the maximum level of production capacity (q=3), which is stable in 90% of the uncertainty realizations (see Figure E.5). Thus, Top-1 is considered to be a robust solution under the stochastic conditions. This conclusion is further supported by the results obtained through solution approach S1.

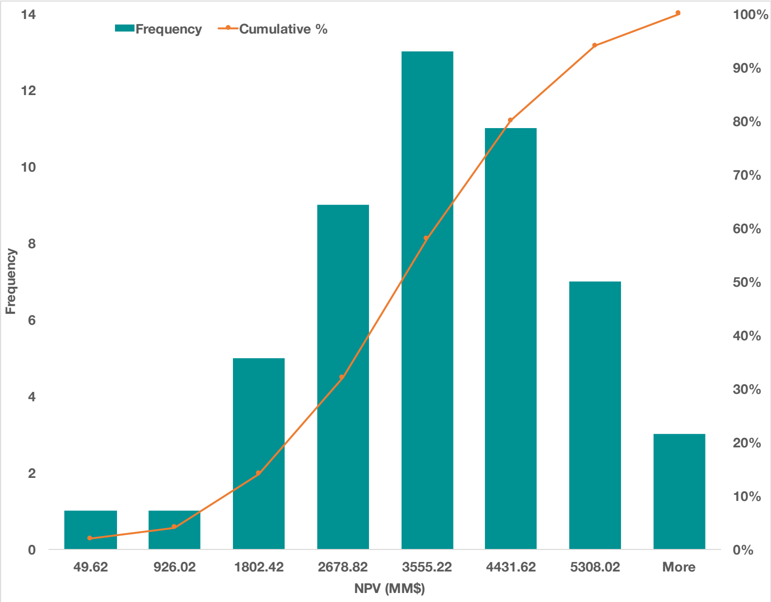


Figure 6.10: Cumulative probability distribution of the NPV and frequency of selection of the corresponding SC structures for B1.

Table 6.9: SC topology and corresponding frequency of selection.

Topologies	Frequency of selection	Technology	Suppliers	Plant site location	Markets
Top-1	96%	Glycerol conversion to SA and LA (k_{C_3} & k_{SP_3} in Table 6.4) (q=3)	Germany, France	Germany France	Germany: LA - Germany SA - UK, Germany, Italy France: LA - France SA - Spain, France, Germany, Italy
Top-2	4%	Glycerol conversion to SA and LA (k_{C_3} & k_{SP_3} in Table 6.4) (q=3)	Germany, The Netherlands	Germany The Netherlands	Germany: LA - Germany, France SA - Germany, France, Italy The Netherlands: LA - Germany SA - UK, Spain, France, Germany

Overall, this theoretical analysis performed on the glycerol-based biorefinery supply chain (based on the SC description provided in the step 1 of the framework), suggested that an economically feasible project could be obtained based upon a decentralized setup of plants located in Germany and France for the production of SA and LA. This corresponds to an expected NPV of approximately 3.28 $\times 10^3$ MM$, under stochastic conditions, for the conversion of 2.13 $\times 10^3$ kton of glycerol/year. Therefore, economies of scale are observed when comparing to the analysis carried out in chapter 3, which led to the production of LA as the best alternative in a small scale biorefinery, converting only 10 kton glycerol/year, with a NPV of 11.2 MM$. Noteworthy is that, in case the user acquires better or more sound information, the model developed in chapter 5, and further extended in this chapter, is flexible and can be solved for different or additional constraints, reflecting other market environments and/or business models.

Furthermore, it is important to note that the stress test performed on the prices of LA and SA, where these crash to 50% of their original value, has demonstrated that it might have drastic consequences on the feasibility of the project, potentially leading to a negative NPV (see Table 6.6). This further emphasizes the need to better understand the correlation between the product price patterns and demand, considering the increase or decrease products availability in the market. Hence, more investigation into the dynamics between the availability of a product in the market and its consequent price is recommended as future work, by, for example, applying the recognized theory of supply and demand, as the first step towards understanding how market prices are defined and how they shape production and consumption decisions.

Solution S3 – stochastic multi(bi)-objective optimization

The aim of this solution approach, as formulated in Eq. (6.31), is to identify the existing trade-offs between the economic (NPV) and environmental (SI) performances, in this way providing control over the variability of the SI. The first step is to estimate the lower bound and the upper bound for the SI. The lower bound (ϵ^{min}) is obtained by solving Eq. (6.32). The SI upper bound (ϵ^{max}) is obtained by solving Eq. (6.33), where SI corresponds to the optimal NPV obtained for the B1 scenario under product price and product demand uncertainties. The optimization problem, as stated in Eq.(6.31) was then solved for several instances between ϵ^{min} and ϵ^{max} values, leading to the Pareto solutions portrayed in Figure 6.11.

All the optimal solutions that take into account the NPV and SI objectives lie on the Pareto curve. Therefore, the solutions above the curve in Figure 6.11 are suboptimal solutions, and all solutions below this curve are infeasible. The trend of this Pareto curve reveals a clear tradeoff, where a gain in NPV leads to a lower environmental performance. This is due to the fact that, NPV is increased when the inflow of glycerol and corresponding production is raised. The increase in the production leads to a higher environmental burden since the production emissions are augmented. As it can be observed in Figure 6.11, the minimum environmental burden is obtained for the conversion of 8 kton/y, producing 5 kton/y of epichlorohydrin, with NPV of -124 MM$. The stochastic maximum leads to the production of SA and LA, by consuming 1121 kton/y with NPV of 3230 MM$. Additionally, the deterministic Pareto front is also shown. As expected, the NPV of the deterministic set of solutions is slightly higher than under uncertainty. This is especially noticed between the maximum NPV achievable through deterministic and uncertainty conditions, where the deterministic maximum dominates the stochastic solution by approximately 90%.

Furthermore, an additional analysis was carried out in order to understand the variation of the NPV and the SI when the optimization problem is moving from the B1 conditions to B2 conditions, and results are presented in Figure 6.12. The $\epsilon^{max,2}$ is the SI corresponding to the maximum NPV obtainable under stochastic B2 conditions, where

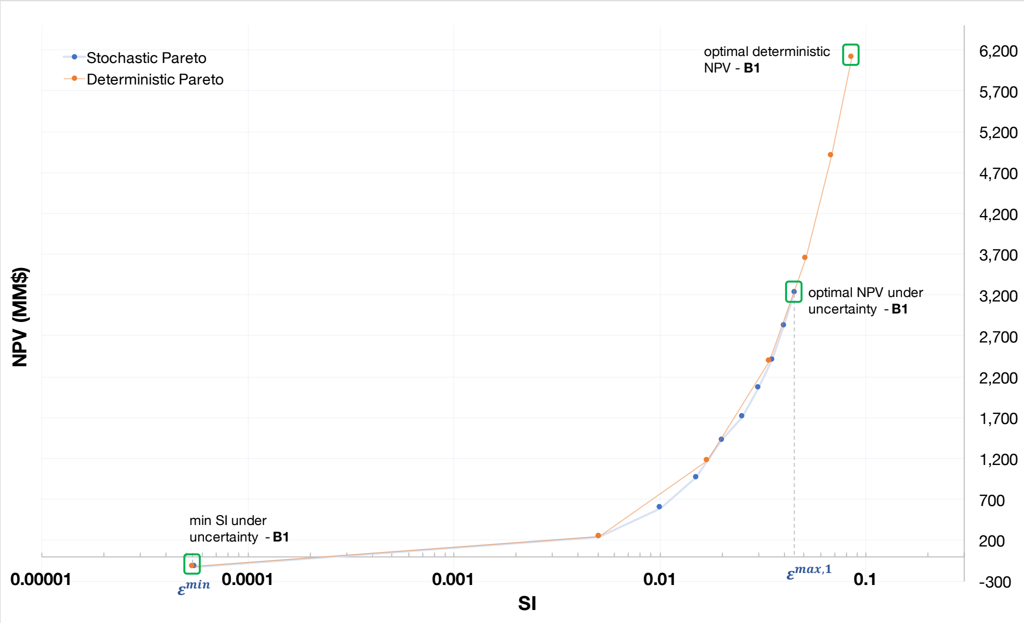


Figure 6.11: Pareto front of optimal solutions, highlighting the trade-offs observed between the NPV and SI under demand and product price uncertainties. $\epsilon^{max,1}$ represents the maximum value of SI obtained maximizing the NPV of the supply chain, under B1 conditions. ϵ^{min} is the SI corresponding to the minimum SI obtainable under B1 conditions.

the problem is constrained to convert the total glycerol available in Europe in a given year.

As observed in Figure 6.12, there is a strong trend when moving from $\epsilon^{max,1}$ to $\epsilon^{max,2}$, where the NPV of the optimal SC structure is declining along with an increase in the SI values. This is due to the fact that the amount of glycerol converted is increasing, thus moving away from the optimal value corresponding to the $\epsilon^{max,1}$. This is accompanied by significant changes in the optimal SC structure given by the increase in the SA and LA production, along with the production of Epi and PHB, whose production is increased until all glycerol is converted (optimal SC structure at B2 conditions). Moreover, as expected from previous solutions S1 and S2, there is a significant reduction on the NPV from the deterministic to the stochastic solution, where the deterministic solution is always above the stochastic solutions depicted. This is a clear argument on the importance of not overlooking the inherit presence of uncertainties, especially regarding the market uncertain circumstances.

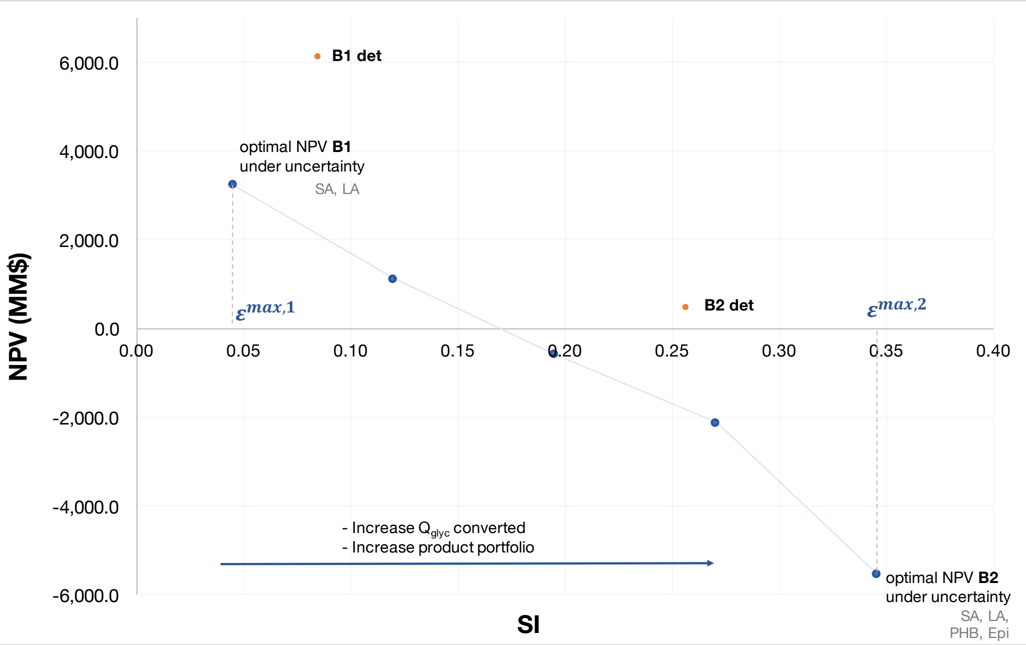


Figure 6.12: Set of solutions corresponding to the monitoring of the environmental impact, under product price and product demand uncertainty. $\epsilon^{max,1}$ represents the maximum value of SI obtained maximizing the NPV of the supply chain, under B1 conditions. $\epsilon^{max,2}$ stands for the SI corresponding to the maximum NPV obtainable under B2 conditions.

6.4 Conclusions

A novel decision-making framework to holistically optimize the design and planning of the glycerol-based biorefinery supply chains under uncertainties is proposed in this work. The set of optimal decisions regarding design, operation and strategy provided by the multi-layered framework, including supply chain network layout, facility location and sizing, technology selection, yearly production planning and cross-country logistics. The framework was demonstrated on a superstructure build based on 5 possible plant site locations, 7 available conversion technologies, 7 available separation and purification technologies, 7 unique products, and 5 markets were identified for each one of the products. The results have shown that: (i) market uncertainties highly affect the economic and environmental performances of the optimal SC structure when compared to the nominal threshold; (ii) under market uncertainty, the economic performance is maximized for the case where the SC is flexible and not constrained to convert all glycerol available (scenario B1); (iii) the set of SC structures obtained under stochastic conditions are robust,where, with 96% frequency of selection, the optimal SC structure is characterized by a decentralized production of SA and LA in the production plants located in Germany and France, despite given future uncertainties; and, (iv) the multi-objective optimization results in Pareto-optimal curves that reveal the tradeoff between the economic and environmental dimensions of the glycerol-based biorefinery supply chains with higher economic profit associated with increased environmental impact. All in all, the proposed framework is expected to serve as a decision-making tool through supply chain optimization, leading to the identification of the optimal design and planning decisions for the development of environmentally conscious glycerol biorefinery supply chains. Furthermore, despite the fact that it has been developed for the optimal design and planning of glycerol-based biorefinery supply chains, the proposed framework is flexible and adaptable to other biorefineries similar in nature.

CHAPTER 7

Overall conclusions & suggestions for future research

For each chapter in this thesis, the conclusions and relevant future work are described. In this last chapter, these considerations are brought together, along with suggestions that could be considered to extend and further improve this work in the future.

Part I: Process design, optimization and analysis

A methodology for the environmental evaluation of early stage process concepts (E3BU) under uncertainties has been developed in Chapter 2 to assess and rank potential bioconversion routes for the valorization of glycerol. This methodology, built upon the LCA principles, deals with the inherit presence of uncertainties in the life cycle inventory (LCI) and in the life cycle impact assessment (LCIA). This is achieved by (i) firstly, proposing a data validation algorithm to provide consistent mass fluxes, and therefore reduce the uncertainty in the data collection step (LCI); and, (ii) secondly, by using the Monte Carlo technique to bring on board the inbuilt uncertainty on the characterization factors used for the conversion of material flows into environmental burdens (LCIA). This enabled the establishment of sound quantitative thresholds for the comparison of alternatives under uncertainties, which has proven to be a consistent and robust way of ranking the alternatives across different weighting systems. Following this methodology, lactic acid has ranked best, thus being the most environmentally friendly solution among the set of alternatives used as starting point (ethanol, succinic acid, 1,3-PDO, PHB, propionic acid and lactic acid). Therefore, it has been shown that the methodology extended the state-of-the-art by providing a robust analysis at the conceptual design stage of biotechnological processes by considering and dealing with uncertainties in the decision-making. Although built to aid/support the challenges faced in this thesis while developing process understanding concerning the conversion of glycerol into bioproducts, this methodology is applicable and it provides valuable insights on the assessment of new biotechnological routes at the concept screening stage. Furthermore, this methodology could be further improved and expanded to include the characterization of other sources of uncertainty such as uncertainty regarding the efficiency of separation and purification technologies, in order for a more accurate and robust screening of alternatives.

In Chapter 3, an extended superstructure of eleven gate-to-gate possible early stage pathways for the production of chemicals and biofuels from glycerol is evaluated in terms of their economic feasibility. Therefore, in order to do this, a systematic methodology for the detailed economic assessment under uncertainties has been proposed, that can be used for all types of applications as guiding tool for robust evaluation of process concepts. Where, in order to portray future scenarios, exogenous and endogenous sources of uncertainty such as market prices (including a description of possible correlations) and the fixed capital investment, are characterized and incorporated into the analysis. As in Chapter 2, the Monte Carlo technique is used to propagate the uncertainties on the input data into the model outputs, such as Net Present Value, thus enabling the estimation of the associated economic risk through a probabilistic interpretation framework. This has shown to be an efficient tool to rank alternatives from a gate-to-gate perspective, which led to a top-3 list of products/processes that potentially carry lower economic risk. The top-3 list of alternatives is composed of the conversion of glycerol into lactic acid, succinic acid and 1,2-PDO. Furthermore, as risk is a direct effect of variability/uncertainty, a global sensitivity analysis was performed so as to better understand the quality of the estimated NPV. This global sensitivity analysis is thereby helping to better assess economic feasibility under a broad range of uncertainties and ultimately give valuable suggestions to manage/decrease this variance and the corresponding risk of potential business failure. It was observed that economic feasibility, and its variance, highly depends upon: (i) the product selling price; and, (ii) both magnitude and sign of the correlation among input uncertainties. Additionally, the results have also shown that there are effective strategies for the mitigation of the economic risk associated to the project of converting glycerol into value added products, such as (i) the development of a multi-product plant, allocating the production depending on the market environment, such as in the case of co-producing lactic and succinic acid; and, (ii) by installing the glycerol conversion plant as an add-on into a running biodiesel plant. Therefore, as to further improve/advance this work, a comprehensive analysis on potential synergies would be of significant value, for example by (a) exploring potential relationships between the glycerol conversion module and local running plants; (b) applying mass and energy integration; and, (c) using 'in house' by-products with low economic value, such as H_2, as energy carriers. In this way one could possibly identify promising solutions that can potentially enhance the bioindustry's robustness and overall sustainability.

The framework presented in Chapter 4 has been built as a natural extension of the methodologies proposed in previous chapters. The target of this approach is to provide an holistic picture associated to a certain decision on a 'gate-to-gate' dimension of analysis. To this end, based upon the monetization of both economic and environmental risks, every alternative has an associated pair of coordinates which will give its position within the risk assessment matrix. The main benefit of this approach is given by the visual aid enabled by the risk assessment matrix that, not only facilitates a trade-offs aware decision-making, but also eases the communication of results between different management levels. A further enhancement of this work could be achieved by coupling this tool with multiple criteria decision making (MCDM), which is a flexible method used in of operational research that deals with finding optimal results in complex scenarios including several criteria, conflicting objectives and performance indicators [232].

Part II: Towards the sustainable design of biorefinery supply chains

In Part II, the boundaries of design and analysis are broadened so as to include the supply/value chain in order to consolidate the knowledge on the glycerol-based biorefinery. In Chapter 5, the *GlyThink* model was developed for the identification of the optimal glycerol-based biorefinery supply chain, maximizing the Net Present Value as the objective function. Therefore, *GlyThink* was built as a multi-period, multi-stage and multi-product MILP model that is able to identify operational decisions, including locations, capacity levels, technologies and product portfolio; as well as strategic decisions such as inventory levels, production amounts and transportation flows to the final markets. The superstructure of alternatives for the conversion of glycerol to value-added products was extended based upon Chapter 3, and the locations for the suppliers, production plants and demand sinks are based on realistic data characterizing the European market. The results have shown that the optimal NPV is obtained by establishing a multi-plant supply chain for the glycerol-based integrated biorefinery, built upon four plant site locations (Germany, France, the Netherlands and Italy). Moreover, the optimal product portfolio is strongly based on the production of succinic acid and lactic acid, as expected from the analysis performed in Chapter 3, followed by epichlorohydrin and poly-3-hydroxybutyrate (PHB). It has also been showed that government incentives could be very important for the healthy growth of a bio-based economy. So as to improve this work, the *GlyThink* model could be further extended to allow the selection and possible combination of different transportation modes. Lastly, Chapter 6 aims at providing a decision-support tool towards the design and planning of biorefinery supply chains under uncertainties. It leads to the identification of a set of optimal design and planning decisions for the development of environmentally conscious biorefinery supply chains, where the consequences of external economic uncertainties on the environmental objective function are analyzed and the potential trade-offs identified. The main goal of this chapter is to identify and critically analyze the optimal integrated glycerol-based biorefinery supply chain for the valorization of glycerol into high value-added products. The results have mainly shown that: (i) market uncertainties such as demand highly affect the economic and environmental performances of the optimal SC structure when compared to the deterministic threshold; (ii) the economic performance is maximized for the case where the inflow of glycerol into the SC is flexible and according to the market environment, where the optimal is obtained for the decentralized production of SA and LA in the production plants located in Germany and France; (iii) there are tradeoffs between the economic and environmental dimensions of the glycerol-based biorefinery supply chains revealed by the Pareto-optimal curves.

A suggestion for further development of this work would be to overcome the great challenge posed by the faulty knowledge of product price and demand. A deeper understanding of the market could be obtained by developing a price and demand forecasting model that, through for example the use of machine learning techniques as suggested by [233], would portray the correlation product price and demand by using historical data. Furthermore, extending the superstructure by including the upstream supply chain of the glycerol/biodiesel production in Europe would bring very interesting and strong insights on the optimal design and strategy for the establishment of a sound symbiotic integrated biorefinery, for the production of biofuels and value-added bioproducts. In this way, it would be possible to: (i) assess the impact of sources of uncertainty characteristic to the upstream, such as biomass yield and biomass supply; and, (ii) expand the analysis to include the valorization of additional upstream supply chain by-products. Moreover, to move towards the sustainable development and implementation of the glycerol biorefinery supply chains, the social dimension should be considered as an additional objective function by, for example, quantifying indicators such as job creation and GDP growth.

Furthermore, despite the fact that all methods and tools derived in this thesis have been developed to address the optimal design and planning of the glycerol-based biorefinery, they are flexible and applicable to other biorefineries that are similar in nature.

APPENDIX A

Chapter 2

Table A.1: Database of early-stage design of glycerol-based biorefinery concepts.

Product	**PS**	**Mixing** $\mu_{i,k}(\alpha_{i,k}=1)$ **(kg/kg glycerol)**		**Stoichiometry** $\gamma_{i,k}(\theta_{i,k}=0.985)$ **(C-mol/ C-mol glycerol)**	**Waste Separation** $(SW_{i,k})$		**Product Separation** $(Split_{i,k})$		**Description**
Glycerol purification to 88% or/and 98%*	2	-	-	-	-	-	Esters Methanol Glycerol	0.452 0.108 0.997	Methanol separation, to be redirected to the biodiesel process
	3	NaOH	0.009	-	$NaOCH_3$ Protein/ solids	0.99 0.99			Solid settling and separation
	4	-	-	-	esters Methanol H_2O Glycerol $NaOCH_3$	0.99 0.997 0.913 0.0217 0.9	-	-	Methanol and solids separation
Ethanol	5	H20 NH_3	29.7 0.0041	$-CH_{8/3}O - 0.0124NH_3 + 0.67CH_3O_{1/3} + 0.042CH_{6/4}O + 0.158H_2 + 0.242CO_2 + 0.05CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HSuc CO_2 H_2	0.999 0.999 0.999 0.999 0.999	-	-	Glycerol bioconversion to EtOH + separation and dehydration
PHB	6	NH_3 H_2O NaOCl Enzyme	0.038 30.1 0.41 0.62	$-CH_{8/3}O - 0.115NH_3 + 0.502CH_2O_{1/2} + 0.116H_2 + 0.039CO_2 + 0.459CH_{1.8}O_{0.5}N_{0.25} = 0$	solids H_2O CO_2	0.999 0.999 0.999	-	-	Glycerol bioconversion to PHB + H_2O_2 washing, evaporation and spray drying
Lactic Acid	7	H_2O NH_3 O_2 TOA DCE	14.2 0.003 0.133 0.0296 2.22	$-CH_{8/3}O - 0.009NH_3 + 0.045CH_2O + 0.008CH_{3/2}O + 0.859CH_2O + 0.006CH_2O_3 + 0.045CO_2 + 0.037CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HForm HSuc HAc CO_2 TOA DCE	0.999 0.999 0.999 0.999 0.999 0.999 0.999 0.999	-	-	Glycerol bioconversion to D-lactic acid + reactive extraction
Succinic Acid	8	H_2O NH_3 TOA 1-octanol O_2	28.8 0.0044 0.341 2.63 0.341	$-CH_{8/3}O - 0.0132NH_3 - 0.55O_2 + 0.544CH_{3/2}O + 0.064CH_2O + 0.009CH_{4/3}O + 0.303CO_2 + 0.066CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HLac NH_3 TOA 1-octanol CO_2	0.999 0.999 0.998 0.999 0.9568 0.9568 0.999	-	-	Glycerol bioconversion to succinic acid + reactive extraction
Propionic Acid	13	H2O NH_3 TOA Ethylacetate	11.3 0.008 0.928 11.4	$-CH_{8/3}O - 0.0235NH_3 + 0.7086CH_2O_{2/3} + 0.0523CH_2O + 0.088CH_{3/2}O_3 + 0.057CO_2 + 0.224H_2 + 0.094CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HAc HSuc Ethylacetate TOA $CO2$	0.999 0.97 0.81 0.998 0.994 0.999 0.999	-	-	Glycerol bioconversion to propionic acid + reactive extraction
1,3-PDO	9	Isobut. NH_3 H_2O	8.93 0.006 13.8	$-CH_{8/3}O - 0.014NH_3 + 0.594CH_{8/3}O_{2/3} + 0.112CH_2O + 0.0436CH_{2/3}H_2O_{1/3} + 0.193CO_2 + 0.276H_2 + 0.0575CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HAc EtOH CO_2 H_2 Isobut.	0.999 0.999 0.4 0.99 0.998 0.998 0.998	-	-	Glycerol bioconversion to 1,3-PDO + reactive extraction

Table A.2: List of components.

Symbol	Component	CAS
comp1	glycerol (1,2,3-propenetriol)	56-81-5
comp2	glycerol -biodiesel mass allocation + only gas natural as fossil + palm oil	56-81-5
comp3	12PDO (propylene glycol)	57-55-6
comp4	acrolein	107-02-8
comp5	methylesters - biodiesel + only gas natural as fuel + palm oil	79-20-9
comp6	esters -methyacetate	79-20-9
comp7	ethanol	64-17-5
comp8	succinic acid	110-15-6
comp9	PHB	107-89-1
comp10	lactic acid	10326-41-7
comp11	13PDO	504-63-2
comp12	acetic acid	64-19-7
comp13	propionic acid	79-09-4
comp14	butanol	71-36-3
comp15	isobutanol	78-83-1
comp16	epychlorohydrine	106-89-8
comp17	formic acid	000064-18-6
comp18	methanol	000067-56-1
comp19	co2	000124-38-9
comp20	N2	7727-37-9
comp21	isobutiraldehyde	78-84-2
comp22	1-octanol	111-87-5
comp23	H2O2	7722-84-1
comp24	methane, biogenic	74-82-8
comp25	methane, fossil	74-82-8
comp26	ethylene glycol	107-21-1
comp27	formaldehyde	50-00-0
comp28	acetaldehyde	75-07-0
comp29	NH3	7664-41-7
comp30	H2	1333-74-0
comp31	Nox - N2O	10024-97-2
comp32	2,3 Butanediol	513-85-9
comp33	dichloroethane	107-06-2
comp34	NaOCl	7681-52-9
comp35	ethylacetate	141-78-6
comp36	TOA	1116-76-3
comp37	oleyc acid	112-80-1
comp38	SO2	007446-09-5

Table A.3: Database of CFs and uncertainty: uniform distribution class 1 to class 3.

		uniform class 1			uniform class 2			uniform class 3		
compound_cat	Mean value (of LCIA characterization factor)	Minimum value	Maximum value	Std deviation	Minimum value	Maximum value	Std deviation	Minimum value	Maximum value	Std deviation
Comp1_EcotA	1.2E-04	8.8E-05	1.5E-04	2.9E-05	5.9E-05	1.8E-04	5.9E-05	2.9E-05	2.1E-04	8.8E-05
Comp1_EcotT	1.6E-04	1.2E-04	2.0E-04	4.1E-05	8.2E-05	2.5E-04	8.2E-05	4.1E-05	2.9E-04	1.2E-04
Comp2_AP	4.6E-04	3.4E-04	5.7E-04	1.2E-04	2.3E-04	6.9E-04	2.3E-04	1.2E-04	8.0E-04	3.4E-04
Comp2_GWP	7.2E-01	5.4E-01	9.0E-01	1.8E-01	3.6E-01	1.1E+00	3.6E-01	1.8E-01	1.3E+00	5.4E-01
Comp2_EP	2.9E-05	2.2E-05	3.6E-05	7.2E-06	1.5E-05	4.3E-05	1.5E-05	7.2E-06	5.1E-05	2.2E-05
Comp2_PMP	1.7E-04	1.3E-04	2.2E-04	4.3E-05	8.6E-05	2.6E-04	8.6E-05	4.3E-05	3.0E-04	1.3E-04
Comp2_POP	7.5E-04	5.6E-04	9.3E-04	1.9E-04	3.7E-04	1.1E-03	3.7E-04	1.9E-04	1.3E-03	5.6E-04
Comp2_FDP	1.5E-05	1.1E-05	1.9E-05	3.8E-06	7.5E-06	2.3E-05	7.5E-06	3.8E-06	2.6E-05	1.1E-05
Comp3_EcotA	1.7E-03	1.3E-03	2.1E-03	4.3E-04	8.6E-04	2.6E-03	8.6E-04	4.3E-04	3.0E-03	1.3E-03
Comp3_EcotT	4.3E-03	3.2E-03	5.4E-03	1.1E-03	2.2E-03	6.5E-03	2.2E-03	1.1E-03	7.5E-03	3.2E-03
Comp3_POP	7.7E-01	5.8E-01	9.7E-01	1.9E-01	3.9E-01	1.2E+00	3.9E-01	1.9E-01	1.4E+00	5.8E-01
Comp4_EcotA	4.6E+01	3.4E+01	5.7E+01	1.1E+01	2.3E+01	6.8E+01	2.3E+01	1.1E+01	8.0E+01	3.4E+01
Comp4_EcotT	6.7E+01	5.0E+01	8.4E+01	1.7E+01	3.4E+01	1.0E+02	3.4E+01	1.7E+01	1.2E+02	5.0E+01
Comp4_HT	4.2E+00	3.1E+00	5.2E+00	1.0E+00	2.1E+00	6.3E+00	2.1E+00	1.0E+00	7.3E+00	3.1E+00
Comp5_AP	4.1E-03	3.1E-03	5.2E-03	1.0E-03	2.1E-03	6.2E-03	2.1E-03	1.0E-03	7.2E-03	3.1E-03
Comp5_GWP	6.5E+00	4.8E+00	8.1E+00	1.6E+00	3.2E+00	9.7E+00	3.2E+00	1.6E+00	1.1E+01	4.8E+00
Comp5_EP	2.6E-04	2.0E-04	3.3E-04	6.5E-05	1.3E-04	3.9E-04	1.3E-04	6.5E-05	4.6E-04	2.0E-04
Comp5_PMP	1.6E-03	1.2E-03	1.9E-03	3.9E-04	7.7E-04	2.3E-03	7.7E-04	3.9E-04	2.7E-03	1.2E-03
Comp5_POP	6.7E-03	5.0E-03	8.4E-03	1.7E-03	3.4E-03	1.0E-02	3.4E-03	1.7E-03	1.2E-02	5.0E-03
Comp5_FDP	1.4E-04	1.0E-04	1.7E-04	3.4E-05	6.8E-05	2.0E-04	6.8E-05	3.4E-05	2.4E-04	1.0E-04
Comp6_EcotA	6.2E-03	4.6E-03	7.7E-03	1.5E-03	3.1E-03	9.3E-03	3.1E-03	1.5E-03	1.1E-02	4.6E-03
Comp6_EcotT	1.7E-02	1.3E-02	2.1E-02	4.2E-03	8.5E-03	2.5E-02	8.5E-03	4.2E-03	3.0E-02	1.3E-02
Comp6_POP	1.0E-01	7.5E-02	1.3E-01	2.5E-02	5.0E-02	1.5E-01	5.0E-02	2.5E-02	1.8E-01	7.5E-02
Comp7_EcotA	2.3E-04	1.7E-04	2.9E-04	5.7E-05	1.2E-04	3.5E-04	1.2E-04	5.7E-05	4.0E-04	1.7E-04
Comp7_EcotT	2.1E-04	1.6E-04	2.6E-04	5.2E-05	1.0E-04	3.1E-04	1.0E-04	5.2E-05	3.6E-04	1.6E-04
Comp7_HT	7.4E-04	5.5E-04	9.2E-04	1.8E-04	3.7E-04	1.1E-03	3.7E-04	1.8E-04	1.3E-03	5.5E-04
Comp7_POP	6.7E-01	5.1E-01	8.4E-01	1.7E-01	3.4E-01	1.0E+00	3.4E-01	1.7E-01	1.2E+00	5.1E-01
Comp10_EcotA	1.3E-02	9.6E-03	1.6E-02	3.2E-03	6.4E-03	1.9E-02	6.4E-03	3.2E-03	2.2E-02	9.6E-03
Comp10_EcotT	2.0E-02	1.5E-02	2.5E-02	5.1E-03	1.0E-02	3.1E-02	1.0E-02	5.1E-03	3.6E-02	1.5E-02

		uniform class 1			uniform class 2			uniform class 3		
compound_cat	Mean value (of LCIA characterization factor)	Minimum value	Maximum value	Std deviation	Minimum value	Maximum value	Std deviation	Minimum value	Maximum value	Std deviation
Comp11_EcotA	8.0E-04	6.0E-04	1.0E-03	2.0E-04	4.0E-04	1.2E-03	4.0E-04	2.0E-04	1.4E-03	6.0E-04
Comp11_EcotT	1.3E-03	9.5E-04	1.6E-03	3.2E-04	6.3E-04	1.9E-03	6.3E-04	3.2E-04	2.2E-03	9.5E-04
Comp12_EcotA	2.5E-02	1.9E-02	3.1E-02	6.2E-03	1.2E-02	3.7E-02	1.2E-02	6.2E-03	4.4E-02	1.9E-02
Comp12_EcotT	4.4E-02	3.3E-02	5.5E-02	1.1E-02	2.2E-02	6.7E-02	2.2E-02	1.1E-02	7.8E-02	3.3E-02
Comp12_POP	1.6E-01	1.2E-01	2.1E-01	4.1E-02	8.2E-02	2.5E-01	8.2E-02	4.1E-02	2.9E-01	1.2E-01
Comp13_EcotA	3.5E-02	2.6E-02	4.3E-02	8.6E-03	1.7E-02	5.2E-02	1.7E-02	8.6E-03	6.0E-02	2.6E-02
Comp13_EcotT	4.0E-02	3.0E-02	5.0E-02	1.0E-02	2.0E-02	6.0E-02	2.0E-02	1.0E-02	7.0E-02	3.0E-02
Comp13_POP	2.5E-01	1.9E-01	3.2E-01	6.3E-02	1.3E-01	3.8E-01	1.3E-01	6.3E-02	4.4E-01	1.9E-01
Comp14_EcotA	3.3E-03	2.5E-03	4.2E-03	8.3E-04	1.7E-03	5.0E-03	1.7E-03	8.3E-04	5.8E-03	2.5E-03
Comp14_EcotT	1.5E-03	1.1E-03	1.9E-03	3.8E-04	7.6E-04	2.3E-03	7.6E-04	3.8E-04	2.7E-03	1.1E-03
Comp14_HT	3.1E-02	2.3E-02	3.8E-02	7.7E-03	1.5E-02	4.6E-02	1.5E-02	7.7E-03	5.4E-02	2.3E-02
Comp14_POP	1.1E+00	7.9E-01	1.3E+00	2.6E-01	5.2E-01	1.6E+00	5.2E-01	2.6E-01	1.8E+00	7.9E-01
Comp15_EcotA	4.0E-03	3.0E-03	5.0E-03	1.0E-03	2.0E-03	6.1E-03	2.0E-03	1.0E-03	7.1E-03	3.0E-03
Comp15_EcotT	2.4E-03	1.8E-03	2.9E-03	5.9E-04	1.2E-03	3.5E-03	1.2E-03	5.9E-04	4.1E-03	1.8E-03
Comp15_HT	1.5E-02	1.1E-02	1.8E-02	3.7E-03	7.3E-03	2.2E-02	7.3E-03	3.7E-03	2.6E-02	1.1E-02
Comp15_POP	6.1E-01	4.6E-01	7.6E-01	1.5E-01	3.0E-01	9.1E-01	3.0E-01	1.5E-01	1.1E+00	4.6E-01
Comp16_EcotA	1.9E-01	1.4E-01	2.3E-01	4.7E-02	9.3E-02	2.8E-01	9.3E-02	4.7E-02	3.3E-01	1.4E-01
Comp16_EcotT	1.2E-01	9.3E-02	1.6E-01	3.1E-02	6.2E-02	1.9E-01	6.2E-02	3.1E-02	2.2E-01	9.3E-02
Comp16_HT	1.3E+01	9.5E+00	1.6E+01	3.2E+00	6.3E+00	1.9E+01	6.3E+00	3.2E+00	2.2E+01	9.5E+00
Comp17_EcotA	1.3E-02	9.8E-03	1.6E-02	3.3E-03	6.5E-03	2.0E-02	6.5E-03	3.3E-03	2.3E-02	9.8E-03
Comp17_EcotT	6.7E-03	5.0E-03	8.3E-03	1.7E-03	3.3E-03	1.0E-02	3.3E-03	1.7E-03	1.2E-02	5.0E-03
Comp17_POP	5.4E-02	4.1E-02	6.8E-02	1.4E-02	2.7E-02	8.1E-02	2.7E-02	1.4E-02	9.5E-02	4.1E-02
Comp18_EcotA	8.4E-04	6.3E-04	1.1E-03	2.1E-04	4.2E-04	1.3E-03	4.2E-04	2.1E-04	1.5E-03	6.3E-04
Comp18_EcotT	6.1E-04	4.6E-04	7.6E-04	1.5E-04	3.0E-04	9.1E-04	3.0E-04	1.5E-04	1.1E-03	4.6E-04
Comp18_HT	1.2E-02	8.8E-03	1.5E-02	2.9E-03	5.9E-03	1.8E-02	5.9E-03	2.9E-03	2.1E-02	8.8E-03
Comp18_POP	2.4E-01	1.8E-01	3.0E-01	5.9E-02	1.2E-01	3.5E-01	1.2E-01	5.9E-02	4.1E-01	1.8E-01
Comp19_GWP	1.0E+00	7.5E-01	1.3E+00	2.5E-01	5.0E-01	1.5E+00	5.0E-01	2.5E-01	1.8E+00	7.5E-01
Comp20_EP	1.0E+00	7.5E-01	1.3E+00	2.5E-01	5.0E-01	1.5E+00	5.0E-01	2.5E-01	1.8E+00	7.5E-01
Comp22_EcotA	1.0E-01	7.5E-02	1.3E-01	2.5E-02	5.0E-02	1.5E-01	5.0E-02	2.5E-02	1.8E-01	7.5E-02
Comp22_EcotT	6.8E-03	5.1E-03	8.5E-03	1.7E-03	3.4E-03	1.0E-02	3.4E-03	1.7E-03	1.2E-02	5.1E-03
Comp24_GWP	2.2E+01	1.7E+01	2.8E+01	5.6E+00	1.1E+01	3.3E+01	1.1E+01	5.6E+00	3.9E+01	1.7E+01
Comp24_POP	1.0E-02	7.6E-03	1.3E-02	2.5E-03	5.1E-03	1.5E-02	5.1E-03	2.5E-03	1.8E-02	7.6E-03

		uniform class 1			uniform class 2			uniform class 3		
compound_cat	Mean value (of LCIA characterization factor)	Minimum value	Maximum value	Std deviation	Minimum value	Maximum value	Std deviation	Minimum value	Maximum value	Std deviation
Comp25_GWP	2.5E+01	1.9E+01	3.1E+01	6.3E+00	1.3E+01	3.8E+01	1.3E+01	6.3E+00	4.4E+01	1.9E+01
Comp25_POP	1.0E-02	7.6E-03	1.3E-02	2.5E-03	5.1E-03	1.5E-02	5.1E-03	2.5E-03	1.8E-02	7.6E-03
Comp26_EcotA	4.6E-04	3.4E-04	5.7E-04	1.1E-04	2.3E-04	6.8E-04	2.3E-04	1.1E-04	8.0E-04	3.4E-04
Comp26_EcotT	2.6E-03	1.9E-03	3.2E-03	6.4E-04	1.3E-03	3.9E-03	1.3E-03	6.4E-04	4.5E-03	1.9E-03
Comp26_HT	1.6E-02	1.2E-02	2.0E-02	3.9E-03	7.9E-03	2.4E-02	7.9E-03	3.9E-03	2.8E-02	1.2E-02
Comp26_POP	6.3E-01	4.7E-01	7.9E-01	1.6E-01	3.2E-01	9.5E-01	3.2E-01	1.6E-01	1.1E+00	4.7E-01
Comp27_EcotA	9.7E-02	7.3E-02	1.2E-01	2.4E-02	4.9E-02	1.5E-01	4.9E-02	2.4E-02	1.7E-01	7.3E-02
Comp27_EcotT	4.7E-02	3.5E-02	5.9E-02	1.2E-02	2.3E-02	7.0E-02	2.3E-02	1.2E-02	8.2E-02	3.5E-02
Comp27_HT	1.1E+01	8.5E+00	1.4E+01	2.8E+00	5.7E+00	1.7E+01	5.7E+00	2.8E+00	2.0E+01	8.5E+00
Comp27_POP	8.8E-01	6.6E-01	1.1E+00	2.2E-01	4.4E-01	1.3E+00	4.4E-01	2.2E-01	1.5E+00	6.6E-01
Comp28_EcotA	4.6E-02	3.4E-02	5.7E-02	1.1E-02	2.3E-02	6.8E-02	2.3E-02	1.1E-02	8.0E-02	3.4E-02
Comp28_EcotT	6.0E-02	4.5E-02	7.5E-02	1.5E-02	3.0E-02	9.0E-02	3.0E-02	1.5E-02	1.1E-01	4.5E-02
Comp28_HT	4.0E-01	3.0E-01	5.1E-01	1.0E-01	2.0E-01	6.1E-01	2.0E-01	1.0E-01	7.1E-01	3.0E-01
Comp29_AP	2.5E+00	1.8E+00	3.1E+00	6.1E-01	1.2E+00	3.7E+00	1.2E+00	6.1E-01	4.3E+00	1.8E+00
Comp29_EP	9.2E-02	6.9E-02	1.2E-01	2.3E-02	4.6E-02	1.4E-01	4.6E-02	2.3E-02	1.6E-01	6.9E-02
Comp29_PMP	3.2E-01	2.4E-01	4.0E-01	8.0E-02	1.6E-01	4.8E-01	1.6E-01	8.0E-02	5.6E-01	2.4E-01
Comp31_AP	5.6E-01	4.2E-01	7.0E-01	1.4E-01	2.8E-01	8.4E-01	2.8E-01	1.4E-01	9.8E-01	4.2E-01
Comp31_GWP	3.0E+02	2.2E+02	3.7E+02	7.5E+01	1.5E+02	4.5E+02	1.5E+02	7.5E+01	5.2E+02	2.2E+02
Comp31_EP	3.9E-02	2.9E-02	4.9E-02	9.8E-03	2.0E-02	5.9E-02	2.0E-02	9.8E-03	6.8E-02	2.9E-02
Comp31_PMP	2.2E-01	1.7E-01	2.8E-01	5.5E-02	1.1E-01	3.3E-01	1.1E-01	5.5E-02	3.9E-01	1.7E-01
Comp31_POP	1.0E+00	7.5E-01	1.3E+00	2.5E-01	5.0E-01	1.5E+00	5.0E-01	2.5E-01	1.8E+00	7.5E-01
Comp33_EcotA	1.9E-02	1.5E-02	2.4E-02	4.8E-03	9.7E-03	2.9E-02	9.7E-03	4.8E-03	3.4E-02	1.5E-02
Comp33_EcotT	4.1E-02	3.1E-02	5.1E-02	1.0E-02	2.0E-02	6.1E-02	2.0E-02	1.0E-02	7.1E-02	3.1E-02
Comp33_HT	1.6E+01	1.2E+01	2.0E+01	4.0E+00	8.0E+00	2.4E+01	8.0E+00	4.0E+00	2.8E+01	1.2E+01
Comp35_EcotA	3.4E-03	2.6E-03	4.2E-03	8.5E-04	1.7E-03	5.1E-03	1.7E-03	8.5E-04	5.9E-03	2.6E-03
Comp35_EcotT	4.1E-03	3.0E-03	5.1E-03	1.0E-03	2.0E-03	6.1E-03	2.0E-03	1.0E-03	7.1E-03	3.0E-03
Comp35_HT	8.1E-02	6.1E-02	1.0E-01	2.0E-02	4.0E-02	1.2E-01	4.0E-02	2.0E-02	1.4E-01	6.1E-02
Comp37_EcotA	8.4E-04	6.3E-04	1.0E-03	2.1E-04	4.2E-04	1.3E-03	4.2E-04	2.1E-04	1.5E-03	6.3E-04
Comp37_EcotT	3.1E-07	2.3E-07	3.8E-07	7.6E-08	1.5E-07	4.6E-07	1.5E-07	7.6E-08	5.3E-07	2.3E-07
Comp38_AP	1.0E+00	7.5E-01	1.3E+00	2.5E-01	5.0E-01	1.5E+00	5.0E-01	2.5E-01	1.8E+00	7.5E-01
Comp38_PMP	2.0E-01	1.5E-01	2.5E-01	5.0E-02	1.0E-01	3.0E-01	1.0E-01	5.0E-02	3.5E-01	1.5E-01
Comp38_POP	8.1E-02	6.1E-02	1.0E-01	2.0E-02	4.1E-02	1.2E-01	4.1E-02	2.0E-02	1.4E-01	6.1E-02

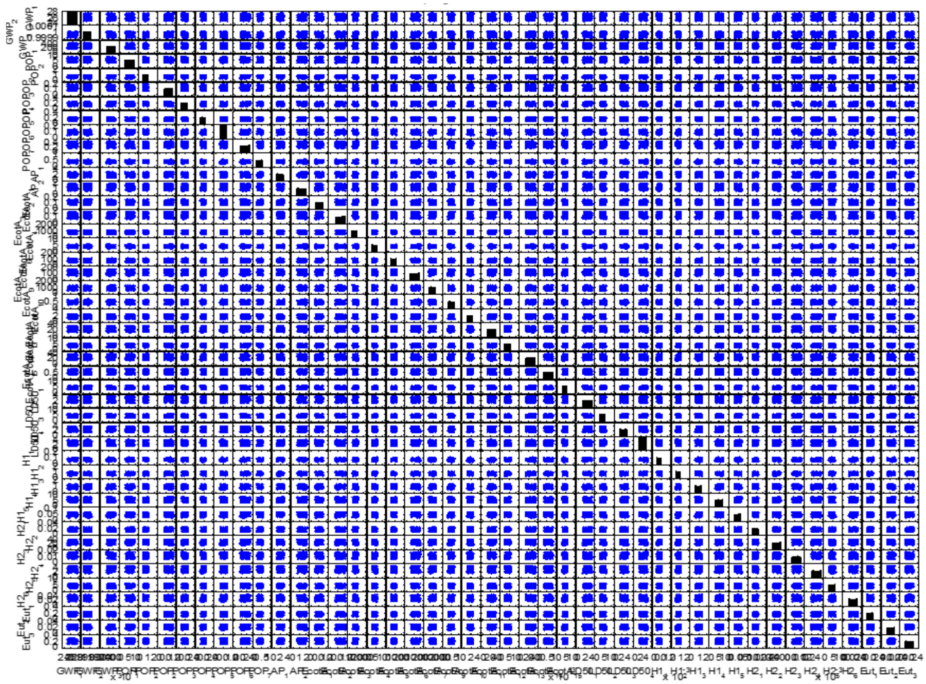


Figure A.1: CFs sampling.

APPENDIX B

Chapter 3

Description of process alternatives

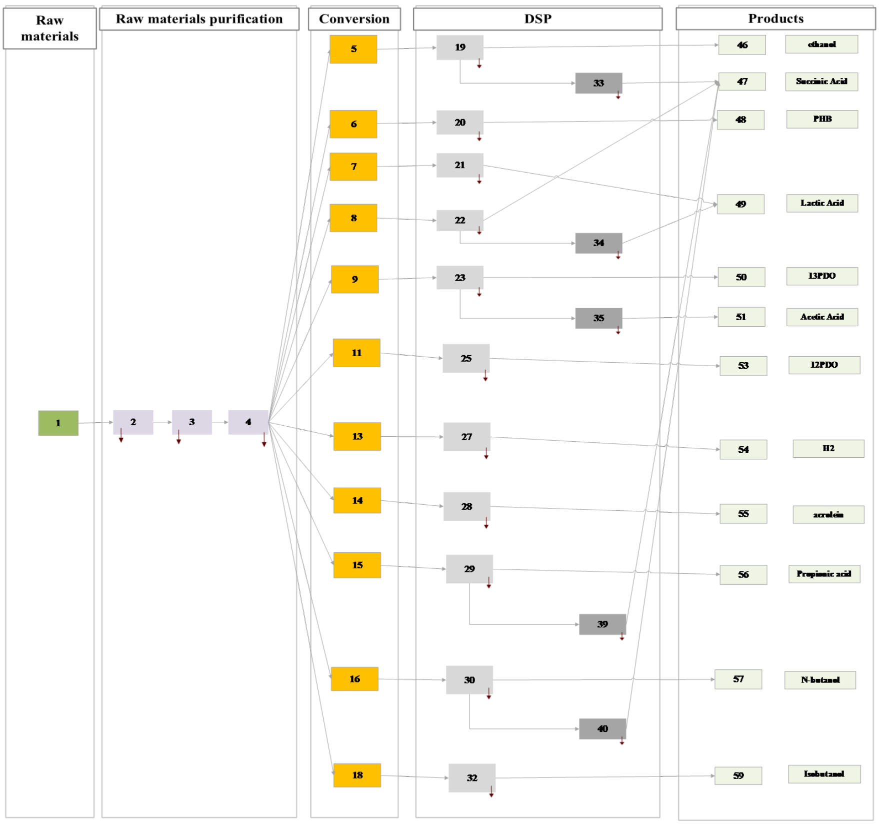


Figure B.1: Design space representation by superstructure (for details see Table B.1)

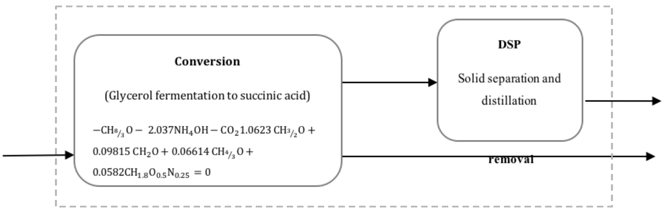


Figure B.2: Generic input-output model. Example based on the production of succinic acid from glycerol by fermentation.

Table B.1: Database of early-stage design of glycerol-based biorefinery concepts.

Product	PS	Mixing $\mu_{i,k}(\alpha_{i,k}=1)$ (kg/kg glycerol)		Stoichiometry $\gamma_{i,k}(\theta_{i,k}=0.985)$ (C-mol/ C-mol glycerol)	Waste Separation $(SW_{i,k})$		Product Separation $(Split_{i,k})$		Description
Glycerol purification to 88% or/and 98%*	2	-	-	-	-	-	Esters Methanol Glycerol	0.452 0.108 0.997	Methanol separation, to be redirected to the biodiesel process
	3	NaOH	0.009	-	$NaOCH_3$ Protein/ solids	0.99 0.99			Solid settling and separation
	4	-	-	-	esters Methanol H_2O Glycerol $NaOCH_3$	0.99 0.997 0.913 0.0217 0.9	-	-	Methanol and solids separation
Ethanol	5	H20 NH_3	29.7 0.0041	$-CH_{8/3}O - 0.0124NH_3 + 0.67CH_3O_{1/3} + 0.042CH_{6/4}O + 0.158H_2 + 0.242CO_2 + 0.05CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HSuc CO_2 H_2	0.999 0.999 0.999 0.999 0.999	-	-	Glycerol bioconversion to EtOH + separation and dehydration
PHB	6	NH_3 H_2O NaOCl Enzyme	0.038 30.1 0.41 0.62	$-CH_{8/3}O - 0.115NH_3 + 0.502CH_2O_{1/2} + 0.116H_2 + 0.039CO_2 + 0.459CH_{1.8}O_{0.5}N_{0.25} = 0$	solids H_2O CO_2	0.999 0.999 0.999	-	-	Glycerol bioconversion to PHB + H_2O_2 washing, evaporation and spray drying
Lactic Acid	7	H_2O NH_3 O_2 TOA DCE	14.2 0.003 0.133 0.0296 2.22	$-CH_{8/3}O - 0.009NH_3 + 0.045CH_2O + 0.008CH_{3/2}O + 0.859CH_2O + 0.006CH_2O_3 + 0.045CO_2 + 0.037CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HForm HSuc HAc CO_2 TOA DCE	0.999 0.999 0.999 0.999 0.999 0.999 0.999 0.999	-	-	Glycerol bioconversion to D-lactic acid + reactive extraction
Succinic Acid	8	H2O NH_4OH TOA 1-octanol	28.8 0.0044 0.341 2.63	$-CH_{8/3}O - 2.037NH_4OH - CO_2 + 1.0623CH_{3/2}O + 0.09815CH_2O + 0.06614CH_{4/3}O + 0.0582CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HLac NH_3OH TOA 1-octanol CO_2	0.999 0.999 0.998 0.999 0.9568 0.9568 0.999	-	-	Glycerol bioconversion to succinic acid + reactive extraction
Propionic Acid	13	H2O NH_3 TOA Ethylacetate	11.3 0.008 0.928 11.4	$-CH_{8/3}O - 0.0235NH_3 + 0.7086CH_2O_{2/3} + 0.0523CH_2O + 0.088CH_{3/2}O_3 + 0.057CO_2 + 0.224H_2 + 0.094CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HAc HSuc Ethyalcetate TOA $CO2$	0.999 0.97 0.81 0.998 0.994 0.999 0.999	-	-	Glycerol bioconversion to propionic acid + reactive extraction
1,3-PDO	9	Isobut. NH_3 H_2O	8.93 0.006 13.8	$-CH_{8/3}O - 0.014NH_3 + 0.594CH_{8/3}O_{2/3} + 0.112CH_2O + 0.0436CH_{2/3}H_2O_{1/3} + 0.193CO_2 + 0.276H_2 + 0.0575CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HAc EtOH CO_2 H_2 Isobut.	0.999 0.999 0.4 0.99 0.998 0.998 0.998	-	-	Glycerol bioconversion to 1,3-PDO + reactive extraction
n-Butanol	14	NH_3 H_2O		$-44C_3H_8O_3 - 3NH_3 + 3C_4H_7O_2N + 18C_4H_{10}O + 4C_3H_{82}O_2 + 36CO_2 + 36H_2 + 10H_2O + 0.0575CH_{1.8}O_{0.5}N_{0.25} = 0$	X 1,3-PDO CO_2 H_2	0.999 0.999 0.998 0.998	-	-	Glycerol bioconversion to n-Butanol + vacuum stripping
Isobutanol	15	H_2O H_2 Methanol oxygen	4.5 0.2 1 1.5	$-C_3H_8O_3 + C_3H_4O + 2H_2O = 0$ $-C_3H_4O - H_2 + C_3H_{6O} = 0$ $CH_4 - O_2 + CH_2O + H2_O = 0$ $-CH_2O - C_3H_6O + C_4H_{6O} + H_2O = 0$ $-C_4H_6O - 2H_2 + C_4H_{10}O = 0$	Methanol Methanal Propanal Methacrolein	0.999 0.999 0.999 0.999	-	-	glycerol to propanal via acrolein + methanol conversion to methanal + methanal and propanal condensed to methacrolein + hydrogentation of methacrolein to isobutanol
1,2-PDO	10	H_2O H_2	4 0.3	$-C_3H_8O_3 - 2H_2 + C_3H_8O_2 + H_2O = 0$	H_2O C-based compounds	0.999 0.999	-	-	Sequential dehydrogenation-hydrogenation via hydroxiacetone
Acrolein	12	H_2O	15	$-C_3H_8O_3 + C_2H_O + H_2 + H_2O + CO = 0$ $-C_3H_8O_3 + C_3H_4O + 2H_2O = 0$ $-C_3H_8O_3 + CO + C_xH_y = 0$ $-C_3H_8O_3 + 3C + H_2O + H_2 = 0$	CO H2 C-based compounds	0.999 0.999 0.999	-	-	Glycerol dehydration
H_2	11	H_2O	0.1	$-C_3H_8O_3 - 3H_2O + 3CO_2 + 7H_2 = 0$	CO_2	0.999	-	-	Steam Reforming of Glycerol over Ni/SiO_2 Catalyst

Economic model and assumptions

Discount rate

A regularly used profitability measurement/standard/benchmark is the minimum acceptable/attractive rate of return (mar). It is a rate of earning that must be achieved by an investment in order for it to be acceptable to the investor. The term mar, minimum acceptable rate of return per year, can be set based on (a) the highest rate of earning on safe investments such as corporate bonds, government bonds and loans (the reasoning behind is that, any investment in a project must show earnings at a rate that is at least equal to the highest safe alternative opportunity available to a company or corporation); and, (b) the cost of capital. Then, mar is adjusted to account for the uncertainties associated with a new project. Uncertainties are related to future behavior of the overall economy due to the uncertain future of price and demand for a particular product, and this risk is further increased whenever most of the capital is invested in equipment and plant construction, because the capital is not liquid, i.e. it not easily recoverable if needed. Therefore, the practice is to adjust the mar in order for it to reflect the risk, where the basic rate is sufficiently increased to make it attractive considering the risk, arriving at a mar which can be used in project evaluations. Table 3 presents the suggested values for mar, reflecting situations from medium risk to very high risk [149]. The discounted cash flow rate of return (DCFR) is the return attained from an investment in which all cash-flows and investments are discounted, i.e. DCFR is a measure of the maximum interest rate that the project could pay and still break even by the end of the project life. It is solved by setting the Net Present Value (NPV) to zero, and solving for the discount rate that satisfies the resulting equation. Clearly, if the NPV equals zero the mar used is the DCFR (discounted cash flow rate of return). As guidance, mar is a good starting point because the discounted cash flow rate of return will be greater than the mar used. When the NPV is favorable, the DCFR will necessarily be favorable and it will correspond to the actual rate of the investment, if NPV is below zero, then the project is not favorable and the rate of return will be lower than the minimum acceptable rate of return (mar) [149]. In this work, the overall project to be undertaken represents the implementation of new technologies not yet proven at a commercial scale, and therefore the project risk is considered to be somewhere between medium to high, and so the mar is set to be 24%.

Equity, Construction Start-up time

It is assumed that the plant will be 40% equity financed, where the loan is taken for ten years with 8% interest. Additionally, the plant is considered to be built within three years (1 for engineering planning and two years for construction), where the principal investment is paid in stages over these three years together with the respective interest [152]. According to Perry and Green [234], the start-up should be approximately 25% of the construction time, for a reasonably complex plant. In this case study, the startup-time is 0.50 years (0.25×24 months). Moreover, a typical rate of 50% of the production capacity is considered to be achieved during that period, while sustaining 75% and 100% of variable and the fixed costs, respectively.

Depreciation, Plant Life Taxes

For this analysis, to estimate the capital depreciation for the calculation of federal taxes to be paid, the IRS Modified Accelerated Cost Recovery System (MACRS) is the most frequently used [149], [152]. It is a combination of the declining-balance method and the straight-line method. The declining-balance method is used until the depreciation charge becomes less than it would be under the straight-line method, at which point the MACRS switches to charge the same as the straight-line method [153]. The plant's lifetime is considered to be 20years, in which during the first 10 years of operation, no income tax is paid since the depreciation and loan interest deductions are bigger than the net income. After that period, the federal corporate tax rate used is 35% [152].

Capital Investment Production Cost

For currently existing technologies, like fairly old chemical processes, the comparison to historical data is a relatively easy and reliable method to estimate capital investment [164], [88]. However, in the case of new technologies, it presents additional challenges since historical data are nonexistent or not accessible [164]. Moreover, when analyzing new technologies, the latest product and raw materials prices, along with equipment and utilities costs are mandatory [164]. In this work, we go one step further, and say that the volatility of market prices, the inaccuracy of capital investment, errors and technical imprecisions, need also to be accounted for, when performing economic assessment of new technologies. Regardless of the great number of uncertainties surrounding new technologies, the basic data needed to perform an economic analysis is well-established, which includes material and energy balances and major pieces of equipment. Production costs are the costs required for producing a product, and they can be expressed per units produced or on a time basis [149],[152], [164],. They are divided into variable and fixed production costs (**Table B3**). Opposite to variable costs, the fixed costs are independent of the plant capacity. The capital cost, one of the most important parts of the fixed cost, is classified into two parts, the fixed capital investment (mostly tangibles) and the working capital. Since the fixed-capital investment may take up to 80% of the production costs, it may determine the economic feasibility of a certain technology. Peters, Timmerhaus and Wets (2003) [149] described seven methods to estimate the fixed capital investment (FCI), which vary mostly due to: (a) available detailed information; and, (b) level of accuracy obtained with the analysis. In this work, the fixed capital investment (direct and indirect costs) is estimated based on the factorial methodology (**Table B2**), which is based on percentages of delivered equipment cost (DEq.). The DEq. is estimated by using the power relationship (six/seven-tenths rule). This rule is widely used for approximations of equipment and even total process costs when cost data is not available for the particular size or capacity [149],[164]. The total capital investment (TCI) is given by the sum of the FCI and the working capital. Working capital is the capital invested in maintaining plant operations, by retaining the money needed for covering for one or two months of salaries, few months of raw materials supplies and other operating supplies. It is regularly renewed with income from sales and stays at approximately the same throughout the plant's lifetime [152], [164],[149].

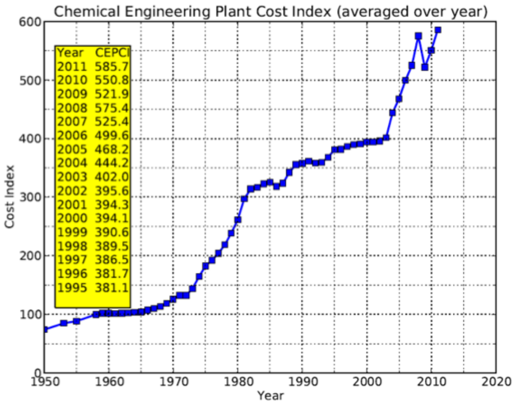


Figure B.3: NChemical Engineering Plant Cost Index (averaged over year) [235].

Table B.2: Factorial methodology for estimation of capital investment based on the delivered equipment cost [152], [149].

	Fraction of delivered equipment cost
Direct costs	
Purchased equipment, E'	*E'*
Delivery, fraction of E'	0.10 x E'
Subtotal: delivered equipment, DEq.	(1+0.10) x E'
Purchased equipment installation	0.47 x DEq.
Instrumentation & Controls (installed)	0.36 x DEq.
Piping (installed)	0.68 x DEq.
Electrical systems (installed)	0.11 x DEq.
Buildings (including services)	0.18 x DEq.
Yard improvements	0.10 x DEq.
Service facilities (installed)	0.70 x DEq.
Total direct costs	2.60 x DEq.
Indirect costs	
Engineering and supervision	0.33 x DEq.
Construction expenses	0.41 x DEq.
Legal expenses	0.04 x DEq.
Contractor's fee	0.22 x DEq.
Contigency	0.44 x DEq.
Total Indirect Costs	1.44 x DEq.
Fixed capital investment (FCI)	total indirect costs + total direct costs
Working capital (WC)	0.05 x FCI
Total capital investment (TCI)	FCI + WC

Table B.3: Factorial methodology to estimate the fixed and variable costs [152], [149].

Item	Default factor [149]	Basis
Variable costs		
Raw materials		
Operating labor		
Operating supervision	0.15	of operating labor
Utilities		
Maintenance and repairs	0.06	of FCI
Operating supplies	0.0035	of maintenance and repairs
Laboratory charges		operating labor
Royalities	0.0035	of c_0
Fixed costs		
Taxes (property)	0.02	of FCI
Financing (interest)		of FCI
Insurance	0.01	of FCI
Rent		of FCI
Depreciation	Calculated based on MACRS method	
Plant overhead, general	0.6	of labor, supervision and maintenance
Manufacturing cost	Plant overhead + fixed costs + variable costs	
General expenses		
Administration	0.2	of labor, supervision and maintenance
Distribution and selling	0.05	of c_0
Research and development	0.04	of c_0
Total Product Cost without Depreciation	c_0	

Table B.4: Price of utilities [149].

Utility	**Price**
Electricity	0.045 $/kWh
Cooling water	4.40/1000 $/kg
Process water	0.08/1000 $/kg
Waste water disposal	0.53/1000 $/kg
Non-hazardous waste disposal	36.00/1000 $/kg
Skilled labor	33.67 $/h

Table B.5: Equipment list and costs for section (1) – glycerol separation and purification. 1.7 conversion factor between the purchased and installed cost.

Equipment list Section (1)	*2003$*	*2014$*
glycerol storage tank	*2.20E+04*	*5.48E+04*
pumps storage	8.80E+03	2.19E+04
glycerol/methanol tank	6.00E+03	1.49E+04
methanol dist. tower preheater	4.00E+03	9.96E+03
methanol dist. tower preheater	9.50E+04	2.36E+05
dist. reboiler	5.00E+03	1.24E+04
dist. condenser	1.30E+04	3.24E+04
fatty acid storage tank	1.00E+04	2.49E+04
NaOH mix feeder	5.00E+03	1.24E+04
glycerol NaOH mix tank	6.00E+03	1.49E+04
glycerol dist tower	1.60E+04	3.98E+04
glycerol dist reboiler	2.60E+04	6.47E+04
glycerol dist post condenser	2.00E+03	4.98E+03
2 pumps	1.30E+04	3.24E+04
utilities system	1.03E+04	2.57E+04
Total purchased cost	1.61 MM$	
Total installed cost	2.73 MM$	

The optimization formulation

$$\max_{x} NPV \tag{B.1}$$

Subject to the following constraints:

(i) process models: material balances according to the generic block model;

Raw materials,

$$F_{i,k}^{out} = \phi_{i,k} \tag{B.2}$$

Mixing,

$$\begin{aligned} R_{i,k} &= \mu_{i,k} \times \sum_{i,k} F_{i,k,kk} \\ F_{i,k}^{M} &= \sum_{k} F_{i,k,kk} + \alpha_{i,k} \times R_{i,k} \end{aligned} \tag{B.3}$$

Waste separation,

$$\begin{aligned} F_{i,k}^{out} &= F_{i,k}^{R} \times (1 - SW_{i,k}) \\ F_{i,k}^{waste} &= F_{i,k}^{R} - F_{i,k}^{out} \end{aligned} \tag{B.4}$$

Reaction,

$$F_{i,k}^{R} = F_{i,k}^{M} + MW_i \times \sum_{rr} \frac{\gamma_{i,rr} \times \theta_{react,rr} \times F_{i,k}^{M}}{MW_{react}} \tag{B.5}$$

Product separation,

$$\begin{aligned} F_{i,k}^{out1} &= F_{i,k}^{out} \times Split_{i,k} \\ F_{i,k}^{out2} &= F_{i,k}^{out} \times (1 - Split_{i,k}) \end{aligned} \tag{B.6}$$

(ii) Process flow constraints: flow constraints;

$$\begin{aligned} & F_{i,k,kk}^{1} \leq F_{i,k}^{out1} \times Sp \\ & F_{i,k,kk}^{2} = F_{i,k}^{out2} \times (S - Sp) \\ & F_{i,k} = \sum_{k} (F_{i,k,kk}^{1} - F_{i,k,kk}^{2}) \\ & \sum_{k} F_{i,k,kk}^{1} = F_{i,k}^{out1} \\ & \sum_{k} F_{i,k,kk}^{2} = F_{i,k}^{out2} \\ & \sum_{i} F_{i,k}^{out} = F_{k}^{max} \end{aligned} \tag{B.7}$$

(iii) Structural constraints:
Raw materials, PS1, PS2, PS3, PS4,

$$y_1 \leq 1; y_2 \leq 1; y_3 \leq 1; y_4 \leq 1 \tag{B.8}$$

PS5: conversion,

$$y_5 + y_6 + y_7 + y_8 + y_9 + y_{10} + y_{11} + y_{12} + y_{13} + y_{14} + y_{15} \leq 1 \tag{B.9}$$

PS6: separation and purification,

$$y_5 + y_6 + y_7 + y_8 + y_9 + y_{10} + y_{11} + y_{12} + y_{13} + y_{14} + y_{15} \leq 1 y_{16} \rightarrow y_{27}; y_{19} \rightarrow y_{28}; y_{24} \rightarrow y_{29}; y_{25} \rightarrow y_{30} \tag{B.10}$$

PS7: Products,

$$y_{31} + y_{33} + y_{34} + y_{35} + y_{37} + y_{38} + y_{39} + y_{40} + y_{41} + y_{42} \leq 1 \tag{B.11}$$

(iv) big-M formulation,

$$F_{i,k}^{out} \leq M \times y_k R_{i,k} \leq M \times y_k y_k \leq M \times \sum_{i} F_{i,k}^{out} \sum_{i} F_{i,k}^{in} = M \times y_k \tag{B.12}$$

Uncertainty characterization

Table B.6: Correlation control matrix.

	Glycerol	Succinic acid	Ethanol	n-butanol	H_2	1,2-PDO	Propionic acid	PHB	Lactic acid	Isobutanol	1,3-PDO	Acrolein
Glycerol	1	0.999	-0.761	0.688	0.487	-1	-0.472	-1	0.595	0.5	0.12	0.457
Succinic acid	1	1	-0.749	0.674	0.503	-1	-0.455	-1	-0.293	-0.432	0.446	0.741
Ethanol	-0.761	-0.749	1	-0.994	1	1	0.931	1	-0.265	-0.614	0.669	0.5
n-butanol	0.688	0.674	-0.994	1	-0.299	-1	-0.965	-1	-0.534	0.678	0.6	0.891
H_2	0.487	0.503	1	-0.299	1	-1	0.541	-1	-0.209	0.002	0.681	0.047
1,2-PDO	-1	-1	1	-1	-1	1	1	-1	0.619	0	0.232	0.398
Propionic acid	-0.472	-0.455	0.931	-0.965	0.541	1	1	-1	-0.573	-0.037	0.6	0.012
PHB	-1	-1	1	-1	-1	-1	-1	1	0.481	-0.517	-0.198	0.863
Lactic acid	0.595	-0.293	-0.265	-0.534	-0.209	0.619	-0.573	0.481	1	-0.3	0.725	0.213
Isobutanol	0.5	-0.432	-0.614	0.678	0.002	0	-0.037	-0.517	-0.3	1	-0.559	-0.38
1,3-PDO	0.12	0.446	0.669	0.6	0.681	0.232	0.6	-0.198	0.725	-0.559	1	0.427
Acrolein	0.457	0.741	0.5	0.891	0.047	0.398	0.012	0.863	0.798	-0.38	0.427	1

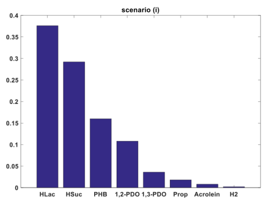


Figure B.4: Network frequency of selection for scenario (i).

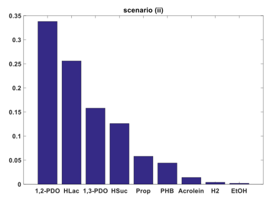


Figure B.5: Network frequency of selection for scenario (ii).

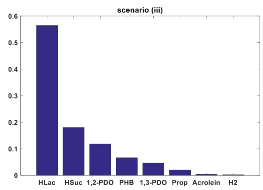


Figure B.6: Network frequency of selection for scenario (iii).

APPENDIX C

Chapter 4

Table C.1: Database of early-stage design of glycerol-based biorefinery concepts.

Product	**PS**	**Mixing** $\mu_{i,k}(\alpha_{i,k}=1)$ **(kg/kg glycerol)**		**Stoichiometry** $\gamma_{i,k}(\theta_{i,k}=0.985)$ **(C-mol/ C-mol glycerol)**	**Waste Separation** $(SW_{i,k})$		**Product Separation** $(Split_{i,k})$		**Description**
Glycerol purification to 88% or/and 98%*	2	-	-	-	-	-	Esters Methanol Glycerol	0.452 0.108 0.997	Methanol separation, to be redirected to the biodiesel process
	3	NaOH	0.009	-	$NaOCH_3$ Protein/ solids	0.99 0.99			Solid settling and separation
	4	-	-	-	esters Methanol H_2O Glycerol $NaOCH_3$	0.99 0.997 0.913 0.0217 0.9	-	-	Methanol and solids separation
Succinic Acid	8	H_2O NH_3 TOA 1-octanol O_2	28.8 0.0044 0.341 2.63 0.341	$-CH_{8/3}O - 0.0132NH_3 - 0.55O_2 + 0.544CH_{3/2}O + 0.064CH_2O + 0.009CH_{4/3}O + 0.303CO_2 + 0.066CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HLac NH_3 TOA 1-octanol CO_2	0.999 0.999 0.998 0.999 0.9568 0.9568 0.999	-	-	Glycerol bioconversion to succinic acid + reactive extraction
1,3-PDO	9	Isobut. NH_3 H_2O	8.93 0.006 13.8	$-CH_{8/3}O - 0.014NH_3 + 0.594CH_{8/3}O_{2/3} + 0.112CH_2O + 0.0436CH_{2/3}H_2O_{1/3} + 0.193CO_2 + 0.276H_2 + 0.0575CH_{1.8}O_{0.5}N_{0.25} = 0$	X H_2O HAc EtOH CO_2 H_2 Isobut.	0.999 0.999 0.4 0.99 0.998 0.998 0.998	-	-	Glycerol bioconversion to 1,3-PDO + reactive extraction

Table C.2: Summary of the assumptions used for the discounted cash-flow rate of return.

Parameter	**Assumption**
Plant life (years)	30
Discount Rate (m_{ar})	10%
Depreciation Period (Years)	5 (MACRS system)
Equity	40%
Interest	8%
Loan Term (Years)	10
Construction Period (Years)	3
% Spent in Year -2	8%
% Spent in Year -1	60%
% Spent in Year 0	32%
Start-up Time (Years)	0.50
Product production/ Feedstock use (% of Normal)	50%
Variable Costs (% of Normal)	75%
Fixed Cost (% of Normal)	100%
Income Tax Rate	35%
Cost Year for Analysis	2014

APPENDIX D

Chapter 5

Table D.1: Matrix of distances between the plant site and the markets (information obtained in Google Maps)

(km)	Germany	France	Netherlands	Spain	Italy
Germany	383.5	1032.7	467.3	2058.7	1376.3
France	1032.7	529.5	853.9	1001.6	1298
Italy	1376.3	1298	1621.9	1974.1	410
UK	1471.5	1428	1017.3	2311.3	2472.5
Spain	2058.7	1001.6	1753.9	471	1974.1
The Netherlands	467.3	853.9	131.4	1753.9	1621.9
Belgium	543.2	658	224.7	1549.7	1467.2
Austria	685.6	1308.4	1024.6	2242	933.9
Bulgaria	1972.8	2390.9	2412.9	3270.6	1962.5
Czech Republic	529.4	1313	932.4	2416.9	1371.1
Poland	755.9	1710	1023.5	2716.8	3053.9
Portugal	2397.3	1340.2	2092.6	477.8	2389.5

Table D.2: Reference capacity and reference purchased capital investment.

Product	Reference capacity (ton/year)	Purchased capital investment (MM$)
Succinic acid (SA)	10200	11.217 (21)
1,3-propanediol (13pdo)	5500	5.347 (21)
Propionic acid (PA)	6796	4.747 (21)
Polyhydroxybutyrate (PHB)	3600	15.020 (21)
1,2-propanediol (12pdo)	7740	4.713 (21)
Lactic acid (LA)	7931	4.929 (21)
Isobutanol (Isob)	7300	6.705 (21)
Hydrogen (H2)	659	5.551 (21)
n-Butanol (BuOH)	3000	5.202 (21)
Ethanol (EtOH)	5211	8.227 (21)
Acrolein (Acro)	4870	4.927 (21)
Epichlorohydrin (epi)	100000 (22)	166 (23)

APPENDIX E

Chapter 6

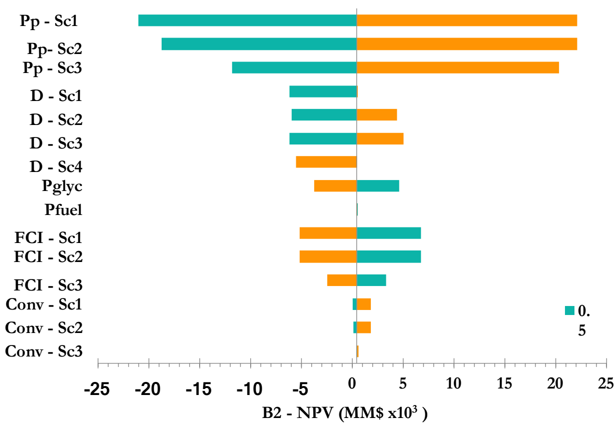


Figure E.1: Sensitivity analysis of the NPV and corresponding SC structure to parameter variation, corresponding to B2 conditions.

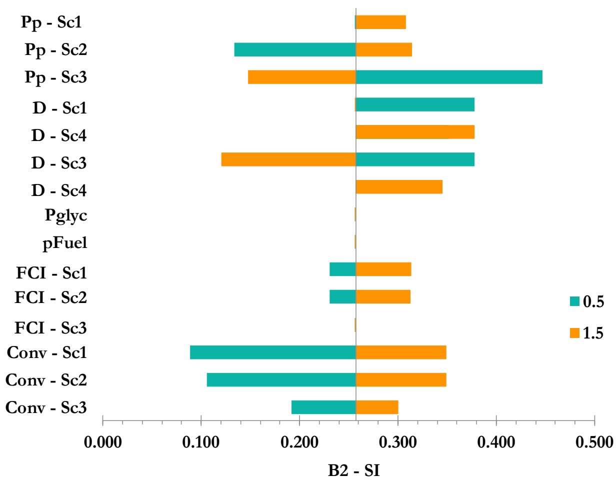


Figure E.2: Sensitivity analysis of the SI and corresponding SC structure to parameter variation, corresponding to B2 conditions.

B2

In Figure E.3 the optimal NPV obtained for the optimization problem resulting of each Monte Carlo sample is presented. Opposite to the previous sub-section where the model was free to choose the optimal flow of glycerol to convert in order to maximize the NPV, under B2 conditions the model is constrained to convert the total amount of glycerol available. Therefore, as consequence of the uncertainty on the product prices and demand, the NPV obtained with all scenarios is significantly lower than the deterministic B2 (with -5.21×10^3 MM$ as average value), making the project unfeasible over the entire range, as the maximum and the minimum NPV attained are negative (Figure E.3).

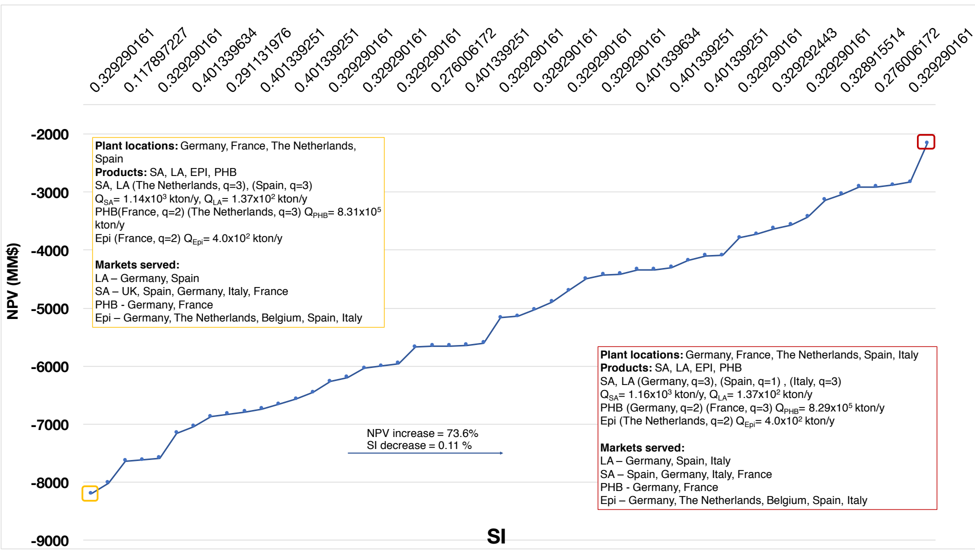


Figure E.3: NPV variation for all scenarios along with the highlight of some significant SC structures and their characteristics for B2.

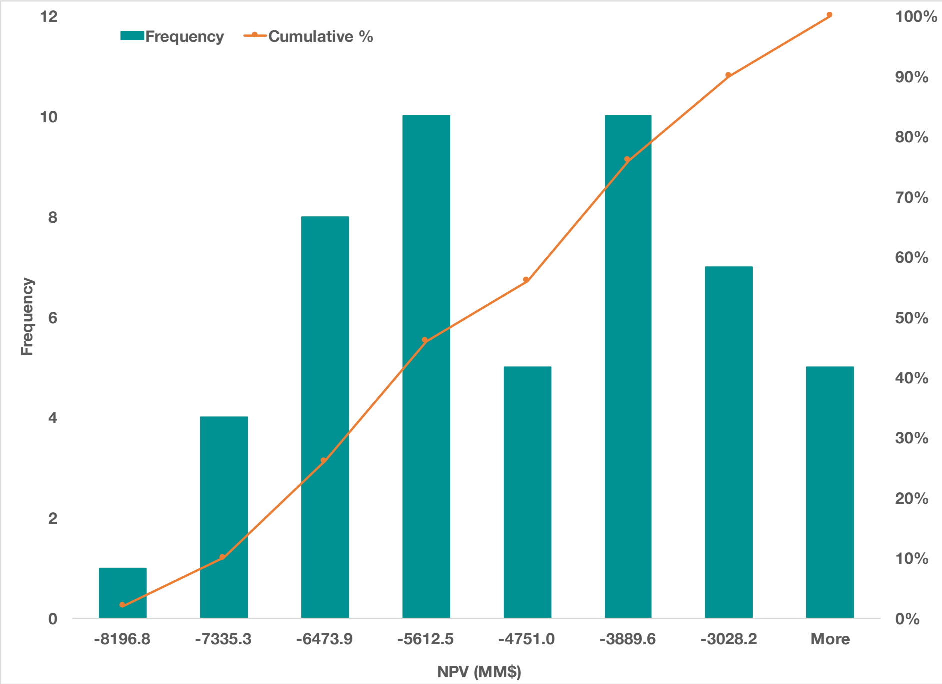


Figure E.4: Cumulative probability distribution of the NPV and frequency of selection of the corresponding SC structures for B2.

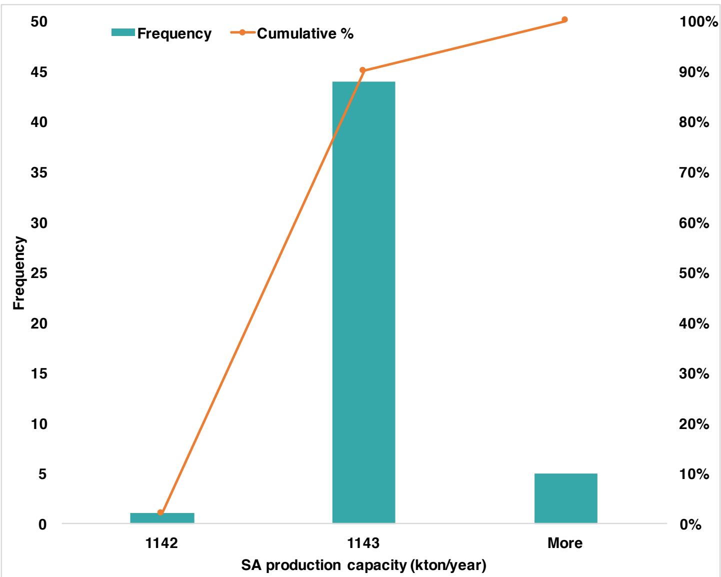
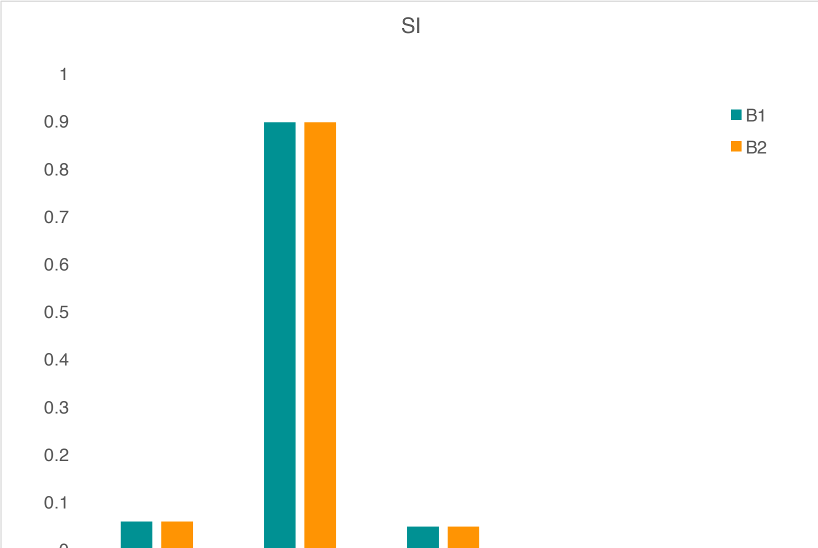


Figure E.5: Cumulative probability distribution of the SA production capacity and frequency of selection for B1.



	GHG	TA	POP	FE	HT
B1	0.057312906	0.895928824	0.046265578	0.000431414	6.12782E-05
B2	0.057319809	0.895939138	0.046262542	0.000375471	0.00010304

Figure E.6: Test SI: GHG and TA are the categories with more impact, and thus are selected to be included in the analysis of S2.

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