EX-ANTE ASSESSMENT
OF
NOVEL TECHNOLOGIES
FOR
BIO-BASED CHEMICALS PRODUCTION

JONATHAN MONCADA BOTERO

EX-ANTE ASSESSMENT OF NOVEL TECHNOLOGIES FOR BIO-BASED CHEMICALS PRODUCTION

Ex-ante assessment of novel technologies for bio-based chemicals production

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ISBN 978-90-8672-083-5

Cover Design Your Thesis | www.designyourthesis.com
Lay-out Nikki Vermeulen | Ridderprint BV
Printing Ridderprint BV | www.ridderprint.nl

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Ex-ante assessment of novel technologies for bio-based chemicals production

Ex-antebeoordeling van nieuwe technologieën voor
de productie van biobased chemicaliën
(met een samenvatting in het Nederlands)

Evaluación ex-ante de nuevas tecnologías para
la producción de bioquímicos
(Con un resumen en Español)

Proefschrift

ter verkrijging van de graad van doctor aan de Universiteit Utrecht
op gezag van de rector magnificus, prof.dr. H.R.B.M. Kummeling,
ingevolge het besluit van het college voor promoties
in het openbaar te verdedigen op
woensdag 11 juli 2018 des middags te 2.30 uur

door

Jonathan Moncada Botero
geboren op 12 februari 1988 te Manizales, Colombia

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UNITS AND ABBREVIATIONS

1G	First generation
2G	Second generation
3G	Third generation
ALOP	Agricultural land depletion potential
BBE	Bio-based economy
CAL	Caprolactam
CAPEX	Capital expenditures
CCP	Climate change potential
CCS	Carbon capture and storage
CED	Cumulative energy demand
CEPCI	Chemical engineering plant cost index
CHP	Combined heat and power
CO	Carbon monoxide
CO_2	Carbon dioxide
CSA	Need of complex separation alternatives
DST	Need of distillation
EASAC	European Academies Science Advisory Council
EC	Economic constraint
EHSI	Environmental-health-safety index
EI	Environmental impact of raw materials
EIRM	Energy related impact of raw materials
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
g	gram
GHG	greenhouse gas
GJ	Gigajoule (1 MJ=10^9 joule)
GTBE	Glycerol tert-butyl ether
GVL	γ-valerolactone
H_2	Hydrogen
H_2S	Hydrogen sulfide
HMF	Hydroxymethylfurfural
HP	High pressure
HTP	Human toxicity potential
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
IRR	Internal Return Rate
ISO	International Standardization Organization
IWF	Internal weighting factor
kg	kilogram
kJ	Kilojoule (1 MJ=10^3 joule)

km	Kilometer
ktonne	Kilotonne (1 ktonne = 10^3 tonne)
kWh	Kilowatt hour
L	Liter
LA	Levulinic acid
LCA	Life Cycle Assessment
LP	Low pressure
M€	Million EUR
m^3	Cubic meter
MJ	Megajoule (1 MJ=10^6 joule)
MLI	Mass loss index
MP	Mid pressure
MP	Methyl pentenoate
Mtonne	Megatonne (1 ktonne = 10^6 tonne)
NIST	National Institute of Standards and Technology
NMP	n-methyl-2-pyrrolidone
NPV	Net Present Value
NREU	Non-renewable energy use
NRTL	Nonrandom two-liquid
O_2	Oxygen
OPEX	Operating expenditures
P	Pressure
PA	Penteneamide
PAZ	Presence of azeotropes
PC	Process complexity
PCEI	Process costs and environmental impact
PN	Process nature
PS	Presence of solids
RA	Risk aspects
Ru	Ruthenium
SO_2	Sulfur dioxide
T	Temperature
TEA	Techno-economic analysis
TJ	Terajoule (1 TJ=10^{12} joule)
TM	Type of metabolite
tonne	metric tonne
TRL	Technology readiness level
USA	United States of America
WDP	Water depletion potential
wt%	Percentage by weight
ZrO2	Zirconium dioxide

CHAPTER 1

Introduction

1.1. BIO-BASED ECONOMY

Fossil resources dominate the world's primary energy use, with a contribution of about 81% [1]. These resources are consumed to meet society's demand for heat, power, transportation fuels and materials. Fossil resources are intensively ingrained in today's global economy. According to the Intergovernmental Panel on Climate Change (IPCC), they have contributed up to 78% of the increase of greenhouse gas (GHG) emissions since 1970 [2]. In addition, uncertainties about reserves and location concentration of fossil resources caused a growing concern on energy security. The IPCC advises that mitigation of GHG emissions requires important changes to the traditional energy system (*i.e.,* fossil-based). including substituting fossil resources by renewable resources, increasing energy efficiency and using CO_2 mitigation technologies [2]. Among the different opportunities to contribute to long-term GHG emission reduction targets, the use of biomass is expected to have an important role [2, 3]. For instance, biomass is projected to contribute to about half to the EU Renewable Energy target in 2020 [3].

In this context, the concept of the bio-based economy (BBE) is receiving increasing attention in both research and policy [3-6]. A bio-based economy can be defined as an economy in which all economic activities are generated by the transformation of renewable resources into energy, materials and chemicals [5, 6]. Many countries and regions (*e.g.,* USA, Brazil, China, EU) have set up policies for the production of first generation (1G) biofuels [7]. There are however concerns on the use of 1G biomass regarding food security and land use change, which could result in (indirect) increases in GHG emissions, increased pressure on ecosystems and negative socio-economic impacts [7-9]. The lessons learned from the use of 1G biofuels and other traditional uses of biomass, have led the BBE community to focus on new feedstock sources to cover a broader range of bio-based products including chemicals and materials [7, 8, 10].

1.2. BIOREFINERIES, THE ROLE OF THE CARBOHYDRATE PLATFORM AND BIO-BASED CHEMICALS

1.2.1. Biorefineries

The biorefinery concept has emerged as an analogy of oil refining, where instead of using oil, biomass is fractionated into a portfolio of products [11, 12]. A biorefinery is a processing facility where biomass is treated and converted in different steps to produce the final products. When compared to oil refineries, biorefineries are complex systems which can in principle produce a larger palette of products than those that current oil refineries produce [9, 13].

Cherubini et al.,[12] proposed a classification of biorefineries as part of the task 42 of the International Energy Agency (IEA) Bioenergy Task 42. It characterizes the complexity of biorefineries according to 4 main features: i) feedstocks, ii) processes, iii) platforms and, iv) products. Figure 1.1 provides an overall picture of this classification of biorefineries. A brief description of each is provided below.

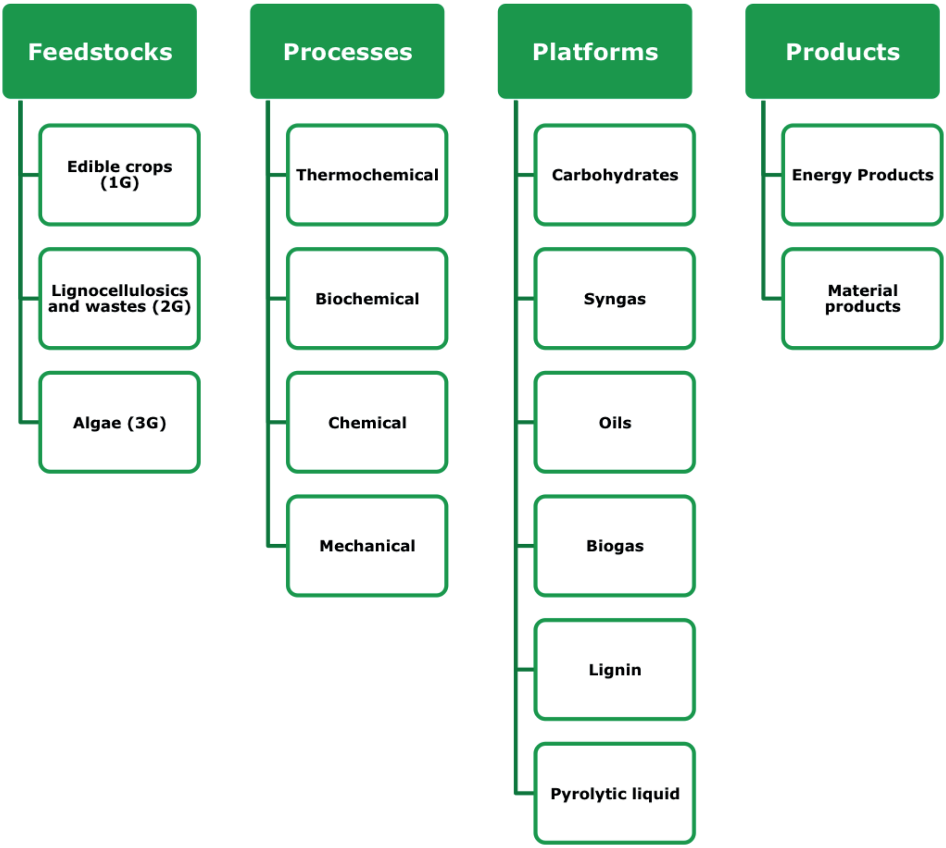


FIGURE 1.1. Classification of biorefineries according to Cherubini et al., [12].

Feedstocks: feedstocks refer to the biomass that is converted into products. Moncada et al., [9] have shown that biorefineries can be classified into first, second and third generation according to the feedstock source they use. First generation (1G) feedstocks mostly refer to crops that traditionally have been used for food [9, 14]. 1G feedstocks are mostly sucrose containing biomass [13, 14] (*e.g.,* sugar beet, sweet sorghum, sugarcane), starchy biomass [3, 13] (*e.g.,* wheat, corn), and triglyceride biomass derived from crops and animals[9, 13] (*e.g.,* vegetable oils, animal fats). Second generation (2G) feedstocks mostly refer to lignocellulosic biomass (*e.g.,* agricultural wastes, energy crops, wood and wood residues) [9, 14], and waste (*e.g.,* municipal solid wastes, waste cooking oil) [9]. Third generation (3G) feedstocks mostly refer to macroalgae and microalgae biomass[9]. The net benefits of 2G and 3G feedstocks in biorefining for the environment still need a deeper understanding.

Processes: processes denote the conversion routes of feedstocks and intermediates (platforms) into value-added products. These technologies are commonly classified as mechanical (*e.g.,* milling), chemical (*e.g.,* pulping), biochemical (*e.g.,* fermentation) and thermochemical (*e.g.,* pyrolysis) [12]. In general, biorefineries can combine the four groups of processes in a single plant, due to the growing interest in moving from standalone processes to multiproduct biorefineries, enabling diversification of feedstocks and products [15].

Platforms: platforms are intermediates that connect feedstocks with final products [12]. The most common platforms in biorefineries are syngas, carbohydrates, biogas, vegetable oils, juices extracted from plant materials (*e.g.,* organic solutions), lignin and pyrolysis oil [11, 12, 16-18]. As about approximately 75% of the world's biomass is carbohydrate in nature [13] (mainly as cellulose, starch, saccharose), the understanding and exploitation of the carbohydrate platform is relevant for the development of biorefinery systems. ***Therefore, this dissertation pays special attention to the carbohydrates platform.***

Products: can be classified in different ways. For instance, Cherubini et al.,[12] classify biorefinery products in two main groups: i) energy products and ii) material products. Moncada et al., [9] classify products into more segregated subgroups such as biofuels (related to liquid fuels), bioenergy (related to direct energy as electricity), biomaterials, biochemicals (including natural product extracts), food and feed and biofertilizers. ***This dissertation focuses on the assessment of biochemicals.***

1.2.2. The carbohydrates platform and chemicals from biomass

The carbohydrates platform includes carbohydrates containing five, six and twelve carbon atoms in the molecular structure (commonly known as C5 sugars, C6 sugar and disaccharides, respectively) [19]. These carbohydrates can be obtained from the primary conversion of 1G, 2G and even 3G feedstocks [16, 20, 21]. In the case of 1G feedstocks, a good example of a carbohydrate containing feedstock is sugarcane. Traditionally, carbohydrates are extracted by sugarcane milling [22], ending up in a sucrose (a C12 sugar) rich juice and a by-product containing the cane bagasse. Lignocellulosic biomass such as wood, wood residues and agricultural residues represent 2G feedstocks for producing the carbohydrate platform. The complex chemical structure of lignocellulosic biomass makes it in principle more difficult to convert into the monomeric carbohydrates compared to 1G feedstocks. Lignocellulosic biomass requires a pretreatment stage aiming to first simultaneously refine the biomass into its main components (*i.e.,* lignin, hemicellulose hydrolysate (hemicellulose fraction) and cellulose pulp), and second to enable the cellulose fraction to undergo effective saccharification [23, 24]. The hemicellulose hydrolysate is generally rich in C5 sugars (also depends on the type of lignocellulosic biomass) [24], while the cellulose hydrolysate (after hydrolysis is rich in C6 sugars [24].The lignin fraction is a by-product of the processing of lignocellulosic biomass which can be marketed [25], and later transformed into valuable products [26] (lignin being itself a platform, see Figure 1.1). Among the most common pretreatment technologies are dilute acid, soda pulping, steam explosion and organosolv [23, 24]. The hydrolysis of cellulose is generally carried out by the action of enzymes [24]. Macroalgae and microalgae also contain high amounts of polysaccharides, which can be converted into carbohydrates by means of enzymatic hydrolysis [20, 27].

The number of chemicals that can be produced from biomass, either chemically or biochemically is large. Among the different platforms, syngas and carbohydrates stand out as the most promising for producing chemicals. In the case of syngas (combination of CO and H_2), chemicals can be obtained via Fischer-Tropsch synthesis such as hydrocarbons [28] or via fermentation such as ethanol, 2,3-butanediol and hexanoic acid [29]. In the case of carbohydrates, some authors[21, 30-33] have identified potential conversion routes to obtain products such as alcohols, furans, hydrocarbons, diols and carboxylic acids (see Figure 1.2).

Figure 1.3 shows the technology readiness level (TRL) of different sugar based products according to Taylor et al. [19]. Although some technologies are already at commercial stage, there is still a significant gap between the number of technologies that are at pilot or lab scale compared to those that are already commercially available. Despite extensive research activities to explore carbohydrate conversion routes and develop new catalyst and strains (for fermentation), the commercialization of such technologies has been slow [32]. This reflects the need to understand and assess emerging technologies at early development stages to provide useful information to technology developers and decision makers to come to a commercialization of potentially successful technologies.

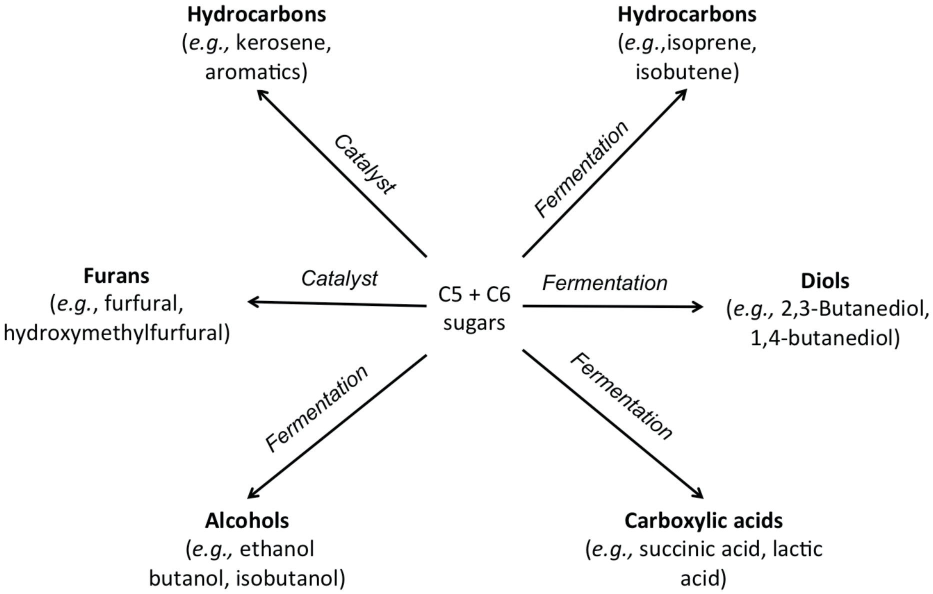
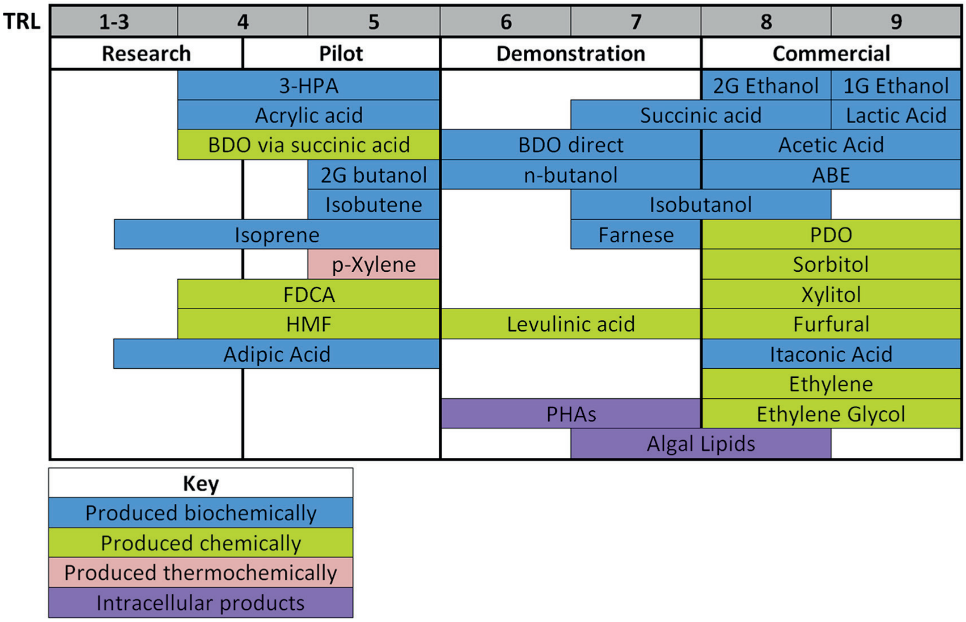


FIGURE 1.2. Potential conversion routes of carbohydrates into chemicals. Adapted from Sheldon [33].



TRL	**1-3**	**4**	**5**	**6**	**7**	**8**	**9**
	Research	**Pilot**		**Demonstration**		**Commercial**	
		🟦 3-HPA				🟦 2G Ethanol	🟦 1G Ethanol
		🟦 Acrylic acid			🟦 Succinic acid		🟦 Lactic Acid
		🟩 BDO via succinic acid		🟦 BDO direct		🟦 Acetic Acid	
			🟦 2G butanol	🟦 n-butanol		🟦 ABE	
			🟦 Isobutene		🟦 Isobutanol		
	🟦 Isoprene				🟦 Farnese	🟩 PDO	
			🟥 p-Xylene			🟩 Sorbitol	
		🟩 FDCA				🟩 Xylitol	
		🟩 HMF		🟩 Levulinic acid		🟩 Furfural	
	🟦 Adipic Acid					🟦 Itaconic Acid	
						🟩 Ethylene	
				🟪 PHAs		🟩 Ethylene Glycol	
					🟪 Algal Lipids		

Key
🟦 Produced biochemically
🟩 Produced chemically
🟥 Produced thermochemically
🟪 Intracellular products

FIGURE 1.3. Technology readiness level of technologies for producing derivatives from the carbohydrates platform. Adapted from Taylor et al., [19].

1.3. EX-ANTE ASSESSMENT OF BIOREFINERY SYSTEMS

Until this point the focus has been on individual processes and products, but biorefineries go beyond process configuration. The multiple combination of feedstocks, platforms, processes and products that can appear in any bio-based supply chain, makes biorefineries very complex systems. Due to this and the fact that most of the developments in technologies for biomass conversion are still in early development stages [34, 35], ex-ante assessments have become a powerful approach to understand which feedstocks, technologies and products are interesting to be further developed [35, 36]. Mistakenly, biorefineries have often been considered sustainable, solely due to the renewable characteristic of biomass [35, 37]. However, as discussed above for the case of 1G biofuels, the use of biomass does not necessarily means that a process and/or product is sustainable as aspects such as e.g. land use, ecosystems, costs, food security, can be impacted [9, 35]. The development of biorefineries should take into account all dimensions of sustainability [35]. In this context, ex-ante assessment of biorefineries at early development stages is becoming increasingly relevant to provide useful insights regarding their prospective performance from a sustainability perspective (covering technical, economic and environmental aspects and in some cases social aspects [9, 35, 36, 38, 39]), when knowledge and availability of data related to technologies, products, markets, feedstocks is limited [34].

There are several methods/approaches for the ex-ante assessment of biorefineries at early development stages reported in literature (*e.g.,* [9, 34, 39-50]). Depending on the level of detail, data requirements, resources needed and type of output needed, two main assessment types are identified: i) screening studies, and ii) detailed studies.

1.3.1. Screening studies

Screening studies are generally done when there is a large number of technologies or configurations to be assessed. This type of studies usually follows a multi-criteria approach (e.g. including technical, economic and environmental aspects) aiming to identify significant differences (e.g. an order of magnitude) between the options assessed, to identify potential winners. These studies are also applied when time and resources are limited. On one hand, screening studies can provide a quick picture on which products and processes to concentrate [51], and on the other hand, the level of uncertainty is high, although at the early stage screening level this is not necessarily a problem.

Early stage screening methods as those reported by Patel et al. [50], Posada et al. [46], Kokossis et al. [48], Kelloway and Daotidis [47], Sugiyama et al. [52], have been applied to assess biomass conversion routes. These methods rely heavily on the analysis of the reactions taking place in the process to build an input-output model, which roughly quantifies the amount of products and co-products that can be produced (under the assumption that those can be fully recovered in the downstream process). Details of upstream operations and downstream processing are not directly quantified (*i.e.* building detailed mass and energy balances of each process unit). Based on the overall mass balances of the simplified structure and additional data (*e.g.,* prices, GHG emissions of feedstocks) a series of indicators relating technical, economic and/or environmental aspects to the outputs are calculated and assessed. As illustration, Patel et al. [50] consider a five-indicator method that accounts for economics, environmental impacts of raw materials, extra costs and environmental impacts related to the complexity of the conversion route, an environment health and safety indicator and risks aspects. The above cited screening methods were only applied to chemical and thermochemical conversion processes, with no attention on biochemical conversion processes.

1.3.2. Detailed studies

Detailed studies are generally carried-out when the number of technologies, configurations or value chains to be assessed is reduced. This type of studies aims to assess the techno-economic competitiveness and environmental impacts of specific conversion routes. Depending on the stage of development of the technologies under study, uncertainty can be an issue. Detailed studies are demanding in time and resources. These types of studies are useful to identify hot spots and bottlenecks of specific conversion routes in comparison to a reference system (e.g., petrochemical counterparts). One of the characteristic aspects of the detailed early assessment of biorefineries is that these are generally carried out for standalone technologies. Until now, there is a lack of studies focusing on the early assessment of integrated biorefinery systems for bio-based chemicals production. Detailed early assessments of biorefinery systems are generally divided into two main categories: *i)* techno-economic analysis and *ii)* environmental assessment.

Techno-economic analysis

Techno-economic analysis [53-58] (TEA) has been applied to prospective biorefinery concepts to identify bottlenecks and hotspots related to technical aspects such as conversion efficiency, energy intensity, process capacity, processing yields, and economic aspects such as operating costs (*e.g.,* raw materials, utilities) capital investment needs, return on investment and product selling prices. TEAs generally follow a process engineering perspective where mass and energy balances of the technologies are estimated, usually by means of process design and process modeling (*e.g.*, [59, 60]). Mass and energy balances serve as a basis for estimating operating expenditures (OPEX) and sizing of equipment, which is the basis for estimating capital expenditures (CAPEX). OPEX and CAPEX are then used to derive economic metrics such as Net Present Value (NPV) or Internal Return Rate (IRR) that reflect on the competitiveness of a prospective biorefinery concept.

Environmental assessment

Environmental assessments have [61-68] been applied to prospective biorefinery systems to assess what the potential environmental impacts could be. Environmental assessments are usually performed to identify the advantages or disadvantages of a biomass conversion pathway in comparison to a traditional system (*e.g.,* petrochemical counterparts). Environmental assessments can also serve as a guideline to identify bottlenecks and hot spots related to aspects such as the production and use of energy inputs, the production and transportation of feedstocks, disposal of waste streams and end of life of products. Environmental assessments methods for bio-based chemicals production are generally based on the Life Cycle Assessment (LCA) methodology [69, 70]. LCA studies have the advantage to provide insights into different environmental impacts related to damage or resources. For the case of bio-based chemicals (non-energy application), the focus on climate change is very strong (damage), followed by energy (resources) and in fewer occurrences e.g. eutrophication, acidification, land and water use [34].

1.4. KNOWLEDGE GAPS

In order to gain knowledge on the techno-economic and environmental performances of novel technologies for bio-based chemicals production, three main research needs are identified:

- The need to develop early stage screening methods, including techno-economic and environmental criteria that are flexible to be applied to different conversion processes such as chemical and biochemical.
- The need to understand the advantages and disadvantages, from a techno-economic and environmental points of view, of the use 2G biomass in comparison to 1G biomass for bio-based chemicals production.
- The need to identify and assess the trade-offs, of the techno-economic and environmental performances, of integrated biorefinery systems in comparison to standalone conversion systems for producing chemicals.

1.4.1. Development of early stage screening methods

As stated above, many early stage screening methods reported in literature (*e.g.,* Patel et al. [50]) have focused their attention into catalytic and thermochemical conversion technologies for bio-based chemicals production while little attention has been paid to biochemical conversion technologies. Nevertheless, it is key to include biochemical conversion processes as part of early screening methods due to the growing role of technologies such as enzymatic conversions and fermentation in the production of chemicals from biomass [71] (see Figures 1.2 and 1.3). Developing early stage screening methods able to capture the features of thermochemical, chemical and biochemical conversion processes would provide a broader perspective to researchers, technology developers and decision makers to select the technologies, products and configurations they should focus at the research and development (R&D) stage. This thesis will address this gap by adapting and extending an existing early stage screening assessment method [50] to cover both chemical and biochemical conversion processes, and testing it to a broad number of conversion routes for chemicals production.

1.4.2. The use of 2G biomass for chemicals production

The attention on the use of 2G biomass for fuels and chemicals production has increased as a reaction to concerns faced by the use of 1G biomass. The use of 2G feedstocks aims to decrease the pressure on land use and to avoid competition with food [7, 9]. However, the complexity due to the nature of 2G feedstocks (*i.e.,* containing cellulose, hemicellulose and lignin) has been identified as a key barrier for 2G development as it leads to higher energy demand, and therefore higher processing costs when compared to 1G feedstocks [8]. An important barrier is related to the efficiency of the biomass pretreatment stage, which is key for further conversion of the released sugars into fuels and chemicals [19]. Therefore, assessing the techno-economic and environmental performances of biomass pretreatment technologies can allow identifying the main bottlenecks and challenges of the use 2G biomass for carbohydrates and chemicals production. Although, pretreatment technologies such as steam explosion and dilute acid are at demonstration or commercial stages, there are other pretreatment technologies that are just being investigated [19]. In this context, this thesis will contribute to the current state of knowledge by assessing the pretreatment of woody biomass using the organosolv technology to produce a carbohydrate platform and its conversion into chemicals. This thesis also compares the organosolv technology to conventional technology using 1G biomass for the production of carbohydrates.

1.4.3. Standalone vs. Integrated biorefinery systems

Up to date, one of the particularities of the early assessment of biorefinery systems is the strong focus on biofuels and/or standalone technologies for a single product. The European Commission [19] emphasizes that integrated biorefinery concepts (multiple input and output synergies) could play a vital role in the carbohydrate platform. Besides, a recent report by the European Academies Science Advisory Council (EASAC) advises that the use of woody biomass should focus on material products and biorefineries before ultimately using it for energy recovery, as higher mitigation potentials can be achieved [72]. In this context, integrated multiproduct biorefineries receive increasing attention to provide a better exploitation of biomass, and ultimately improve the competitiveness and reduce environmental impacts compared to standalone technologies [10]. Nevertheless, identifying the synergies and assessing the trade-offs of integrated biorefinery systems are not straightforward tasks as these are generally case specific. Besides, the early assessments of integrated biorefinery systems generally focus on one or two dimensions (*e.g.,* techno-economic), and rarely on the joint assessment of techno-economic and environmental performances. Carrying out assessments of integrated biorefinery systems including the techno-economic and environmental dimensions, can allow identifying and assessing key trade-offs to guide on synergies such as valorization of waste streams and co-production of utilities (*e.g.,* heat and power). This thesis will address this knowledge gap by assessing, from a techno-economic and environmental point of view, carbohydrate based multiproduct biorefinery concepts. This will help to assess whether or when to upgrade standalone technologies into integrated portfolios is feasible (*e.g.,* by accounting for valorization of waste streams).

1.5. OBJECTIVES AND OVERVIEW OF THE THESIS

In the context of the identified knowledge gaps, the main goal of the thesis is to generate in depth insights into the key factors that affect the techno-economic and environmental performances of novel technologies for bio-based chemicals production. This is done by assessing multiple case studies both at the screening and detailed level. In this thesis, the following objectives are formulated:

1. To develop screening methods that can address novel biochemical conversion routes of chemicals production and provide insights into their techno-economic and environmental performances.
2. To assess the importance and challenges of biomass pretreatment in the performance of carbohydrate based biorefineries.

3. To identify and evaluate the trade-offs of standalone vs. integrated configurations for the economic and environmental performance of biorefineries.

Table 1.1 provides an overview of the thesis chapters and the objectives they address.

TABLE 1.1. Overview of chapters two to six.

Chapter	Title	Objectives		
		1	2	3
2	Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals	x		
3	Comparative early sustainability assessment of multiproduct biorefinery systems: an application to the isobutanol platform	x	x	
4	Techno-economic and ex-ante environmental assessment of C6 sugars production from lignocellulosic biomass and corn. Comparison of organosolv and wet milling technologies.		x	x
5	1,3-Butadiene and ε-Caprolactam production from C6 sugars: techno-economic analysis			x
6	Integrated production of 1,3-Butadiene and ε-Caprolactam from C6 sugars : ex-ante environmental assessment		x	x

Chapter 2 addresses objective 1 by adapting and extending an existing early-stage screening assessment method to cover both catalytic and biochemical conversion processes in biorefineries. The method combines proxy indicators describing economic, environmental and operational aspects . The extended method is tested by assessing three case-studies: i) the catalytic conversion of bio-based syngas (derived from lignocellulosic biomass) into chemicals (16 systems assessed), ii) the biochemical conversion of carbohydrates (derived from lignocellulosic biomass) into chemicals (12 systems assessed), iii) the biochemical and catalytic conversion of glycerol into chemicals (8 systems assessed). All systems are compared to their petrochemical counterparts to provide a ranking of potential winners by classifying them as favorable, promising and unfavorable derivatives. Furthermore, scenario analyses were conducted to account for differences among three regions: EU, USA and China.

Chapter 3 addresses objectives 1 and 2 by applying the extended early screening method (developed in chapter 2) to the production of isobutanol from lignocellulosic biomass (including organosolv fractionation as intermediate step), and three multiproduct biorefinery concepts from the conversion of isobutanol. The configurations includes products such as isobutyl acetate, glycerol tert-butyl ether (GTBE), ketones and alkanes. The analysis considers carrying out the screening based only on environmental aspects or based on economic performance is assessed. Also, the effect of varying inputs such as prices is also part of the analysis.

Chapter 4 addresses objectives 2 and 3 by conducting techno-economic and environmental assessments of the production of C6 sugars from softwood (spruce) and corn. This chapter compares organosolv of spruce (2G) with corn wet milling (1G) for producing C6 sugars. Process models are developed to generate mass and energy balances to assess the technical performance and derive inputs for the economic and cradle-to-gate life cycle assessments. This chapter identifies and assesses the bottlenecks and hotspots of the organosolv technology related to energy intensity, process yields, co-product recovery, capital investment needs, operating costs and cradle-to-gate environmental impacts in comparison to the wet milling technology. This chapter also provides an integration approach to valorize waste streams in the organosolv technology, and identifies and assesses the trade-offs of process intensification from economic and environmental points of view.

Chapter 5 addresses objective 3 by presenting a techno-economic analysis of the integrated production of 1,3-butadiene and ε-caprolactam from C6 sugars. Process models of the two production processes are developed to generate mass and energy balances to assess the technical performance, and derive inputs for the economic analysis that uses the Net Present Value (NPV) and production costs as indicators. This chapter presents an integrated biorefinery approach not only by using C6 sugar feedstock for the two processes, but also by using waste stream as inputs for a common utility production system (*i.e.,* heat and power). Trade-offs related to processing capacities, variation in price inputs, and the valorization of waste streams are identified and assessed.

Chapter 6 addresses objectives 2 and 3 by performing a cradle-to-gate life cycle assessment of the integrated production 1,3-butadiene and ε-caprolactam from C6 sugars. Technical outputs (mass and energy balances) from Chapter 5 are used as inputs for carrying out the environmental analysis. This chapter provides insights into the challenges of multifunctionality when carrying out environmental assessments of multiproduct biorefineries by considering different allocation approaches. This chapter also generates insights into the effect of using C6 sugars derived from corn or from spruce, the valorization of waste streams to produce heat and power.

Chapter 7 summarizes the objectives and the previous chapters, provides answers to the objectives and discusses recommendations.

CHAPTER 2

Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals

Published: Moncada J., Posada J.A., Ramírez A. Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals. 2015. Biofuels, Bioproducts & Biorefining 9 (6), 722-748.

ABSTRACT

This study aims to identify potential bio-based derivatives from the conversion of platform chemicals at early design phases. To do this, an existing early-stage sustainability assessment method was extended, to cover both catalytic and biochemical conversion processes in biorefinery systems. The method combines proxy indicators describing economic, environmental and operational aspects. Conversion routes are analyzed by using 3 case-studies: catalytic conversion of bio-based syngas to derivatives with petrochemical counterpart (16 systems), biochemical conversion of carbohydrates to derivatives with petrochemical counterpart (12 systems), and biochemical and catalytic conversion of glycerol to derivatives with petrochemical counterpart (8 systems). The indicators were combined into a single score, and then compared to a petrochemical counterpart. Sensitivity analysis was carried-out to analyze the influence of conversion yields and prices on the index ratio. Furthermore, scenario analyses were conducted to account for three different regions (EU, USA and China). Results confirmed the successful application of the method to processes that considered catalytic and/or biochemical conversion processes. The method showed to be an effective tool for the selection of bio-based derivatives with favorable potential sustainability performances in comparison to their petrochemical counterparts. The results show 2 systems from syngas, 5 systems from carbohydrates and 7 systems from glycerol as favorable. The results serve as a primary database to draw recommendations on *e.g.,* future configurations of integrated biorefineries.

2.1. INTRODUCTION

Biomass is an interesting renewable feedstock to obtain fuels, chemicals and materials. Efforts to use biomass to substitute oil derivatives occurred first in the production of biofuels [21], and then for bio-based materials and chemicals [16, 17, 21]. This has resulted in efforts and advances on novel processes to obtain biomass based products, leading to the development of the biorefinery concept. This concept is analogous to that of oil refineries, where multiple products are made from petroleum [11]. Biorefineries have been classified according to feedstocks, processes, platforms and products [12]. Feedstocks refer to the raw material and can include crops, residues and algae among other materials. Processes denote the conversion routes of feedstocks, platforms and building blocks into products and are commonly classified as chemical, biochemical, thermochemical and mechanical. Platforms chemicals are intermediates from which new products are derived, thus linking feedstocks and final products [12, 18].

The most common chemical platforms for biorefineries are syngas, carbohydrates (C5, C6 sugars), biogas, vegetable oils, organic solutions (e.g. juices), lignin and pyrolysis oil [11, 12, 16-18]. Syngas is produced by the thermochemical conversion of biomass (*i.e.* gasification), and is generally used to produce heat, power, and derivatives (e.g. hydrogen, alcohols, and olefins) [18, 73, 74]. Syngas can also be fermented to methanol and ethanol [18, 75]. Within the carbohydrate platform C6 sugars (hexoses) can be obtained from sucrose, cellulose or starch [11, 21], and can be converted into derivatives such as carboxylic acids, alcohols, acetone, sorbitol and hydroxymethylfurfural [76]. C5 sugars (pentoses) are obtained by hydrolysis of hemicellulose, and can be used to obtain chemicals such as xylitol, furfural and ethanol [76]. C5-C6 sugars mixtures are considered as a platform to produce chemicals such as ethanol [18]. Biogas is generally produced by anaerobic digestion of biomass and is mainly used for energy applications [18]. Oils are extracted from plant seeds and algae, and have applications in sectors like food, biofuels, chemicals, fatty alcohols, lubricants and care products [18]. Organic solutions refer to the extract/product (e.g., juice) obtained after wet milling and/or pressing of wet biomass such as grass. This juice is generally rich in proteins, amino acids, enzymes and carbohydrates and its composition depends on the raw material used to obtain the juice [77]. Lignin is obtained after hydrolysis of hemicellulose and cellulose fractions of lignocellulosic materials. Lignin can directly be converted into syngas and chemicals like benzene, toluene, xylenes, ethyl benzene, vanillin, phenol and styrene [18, 78]. Pyrolysis oil is obtained by thermochemical conversion of biomass and it may be further fractionated and upgraded into a range of products similar as those produced by the petrochemical industry [79].

Many of the derivatives from platform chemicals can function as chemical building blocks offering a wide range of possibilities for future substitution of petrochemical derivatives. However, the large number of technological alternatives, added to the many possible combinations of feedstocks, platforms and building blocks, imply that biorefinery systems can be designed and assessed in many ways. The design, screening and assessment of biorefinery systems have traditionally been addressed by bottom-up approaches based on process engineering principles with subsequent or integrated economic and environmental assessments. Many authors have used superstructure optimization models to design, screen and assess biorefineries [80, 81]. Other authors have followed a knowledge-based approach for biorefinery design such as flowsheeting in Aspen Plus with subsequent economic and environmental assessment of biorefinery alternatives [82, 83]. These types of approaches allow screening and assessing possible biorefinery process lineups and thus prospective products. Nevertheless, the requirements on data inputs are very large and are generally related to reactions, downstream processing, capital investment, utilities and life cycle inventory. The quality and accuracy of these approaches highly rely on the availability of data, which is generally an issue for products and processes at early design phases [46]. Consequently, there is a need for an approach that systematically assesses and screens biorefinery products and identifies those with the best potential from a sustainability perspective at early design phases. Sugiyama et al., [84] proposed a multi-objective decision framework which allows quickly screening processes based on available information at early design phases including proxy indicators which combine environmental, economic and technical aspects. This framework was modified by Patel et al., [85] by including features such as need of biomass pretreatment, distribution of environmental burdens, number of co-products, risks aspects and process comparison to a petrochemical counterpart. This method was later applied by Posada et al., [46] screening and categorizing derivatives obtained from the catalytic conversion of bioethanol. Hence, the method is able to assess, at an early stage, whether a bio-based derivative is attractive from a sustainability perspective when looking for options to substitute petrochemical counterparts. However, this comparison was only possible for catalytic conversion. Although catalytic conversion routes are highly relevant for the development of future biorefinery portfolios, it is also very important to include/assess other conversion processes (*e.g.* biochemical, thermochemical) at early design phases. Therefore, there is a need to extend the method to include both catalytic and biochemical conversion processes allowing a comprehensive screening and assessment of broader bio-based alternatives.

Summarizing, two main aspects have been identified: *i)* the need to screen and to assess potential biorefinery products from platform chemicals and chemical building blocks at early design stages (prior a more detailed analysis), and *ii)* the need to extend the current early stage sustainability assessment method, to include a broader range of conversion options (*i.e.* catalytic, biochemical, thermochemical). By addressing these aspects, it would be possible to identify, at an early stage, bio-based derivatives with potentially attractive sustainability performances, and therefore identify which bio-based routes are good candidates for further analysis (detailed analysis). In this context, this study aims to extend the early-stage sustainability assessment method to cover both catalytic and biochemical conversion processes, and to identify bio-based derivatives with potential benefits over petrochemical counterparts, from the conversion of platform chemicals and chemical building blocks. The method is tested in three case studies: *i)* comparison of derivatives obtained via catalytic conversion, *ii)* comparison of derivatives obtained via biochemical conversion, and *iii)* comparison of derivatives obtained by both catalytic and biochemical conversion. In all cases the derivatives are compared against their petrochemical counterparts.

2.2. METHODOLOGY

The method considers 6 steps as shown in Figure 2.1.

2.2.1. Revision of early stage sustainability assessment method

The early stage sustainability assessment method [85] was revised to identify key strengths and weaknesses, and its suitability to deal with both catalytic and biochemical conversions. This method considers five sustainability indicators: economic constraint (EC), environmental impact of raw materials (EI), process costs and environmental impact (PCEI), environmental-health-safety index (EHSI) and risk aspects (RA). These indicators are combined into a single score index by means of weighting factors, allowing a quick comparison and screening of process alternatives. EC relates the cost of raw materials to that of marketable products, presenting a simple approach to evaluate the economic feasibility of a chemical process. EI relates the environmental impacts of raw materials per unit of product represented by greenhouse gas emissions (GHG) and cumulative energy demand (CED). PCEI indicates the possible costs and impacts generated by the conversion of raw materials and subsequent downstream processing, thus representing potential challenges from a technical point of view. EHSI is a proxy for hazards related to a chemical process. RA relies on external economic and technical aspects that can play a crucial role in the practical implementation of a chemical process. This method was applied by Posada et al. [46] to screen derivatives from bioethanol. One conclusion of the study was that by only considering the EC, EI and PCEI indicators, the final results did not change significantly and that the time required for the analysis was reduced by more than 50%. Therefore, the EHSI and RA indicators are not further considered in this chapter. Furthermore, the study identified the need for modifying the indicator PCEI to take into account additional technological alternatives (*e.g.* biochemical conversion). The description of the three indicators used in this study and the reasoning behind the changes made are presented in the following section.

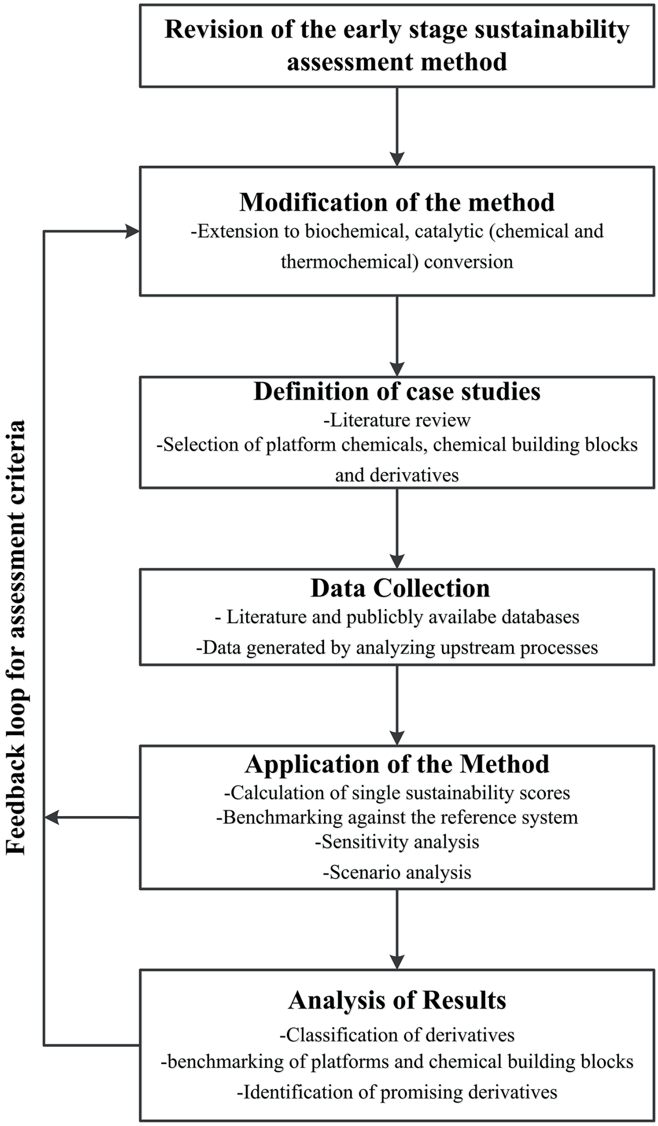


FIGURE 2.1. General description of the methodological approach for the comparative early sustainability assessment of bio-based platform chemicals and chemical building blocks

TABLE 2.1. Equations of indicators and weighting factors

Indicator	Equations and Values	Eq. No.	Internal weighting factor	Global weighting factor *
Economic Constraint	$EC = \sum_{i=1}^{r} m =_{i}^{RM} C=_{i}^{RM} / \sum_{j=1}^{P} m_{j}^{P} C_{j}^{P}$	(1.1)	1.0	0.40
Allocation factor	$AF_{n} = m_{n}^{P} C_{n}^{P} / \sum_{j=1}^{P} m_{j}^{P} C_{j}^{P}$	(1.1.1)	NA	NA
Energy related impact of raw materials	$EIRM = CED_{n} + GHG_{n}$ (after normalization)	(1.2)	1.0	0.3
Cumulative energy demand	$CED_{n} = AF_{n} (1/m_{n}^{P}) \sum_{i=1}^{r} m_{i}^{RM} CED_{i}^{RM}$	(1.2.1)	0.5	
Greenhouse gas emissions	$GHG_{n} = AF_{n} (1/m_{n}^{P}) \sum_{i=1}^{r} m_{i}^{RM} GHG_{i}^{RM} + FC_{n}^{P}$	(1. 2.2)	0.5	
Process Complexity	$PC = \sum_{i=1}^{PC} IWF_{i} \cdot PC_{i}$	(1.3)	1.0	0.3
Downstream processing	$PC_{1} = PN + TM + PS + DST + PAZ + CSA$	(1.3.1)	1/6	
Process Nature	$PN =$ 0 if catalytic processes 0.1 if biochemical processes	(1.3.1.1)	NA	
Type of metabolite	$TM =$ 0 if catalytic processes 0 if extracellular metabolites 0.1 if intracellular metabolites	(1.3.1.2)	NA	
Presence of solids	$PS =$ 0 if non-solids involved 0.1 if presence of solids	(1.3.1.3)	NA	
Need of distillation	$DST =$ 0 if no distillation requirement 0.2 if distillation requirement	(1.3.1.4)	NA	
Presence of azeotropes	$PAZ =$ 0 if non-presence of azeotropes 0.2 if presence of azeotropes	(1.3.1.5)	NA	
Complex separation alternative	$CSA =$ 0 if no complex separation alternatives are needed 0.3 if complex separation alternatives are needed	(1.3.1.6)	NA	
Concentration of main product	$PC_{2.cat} =$ 0 if conc. is above 0.25 (mol/mol) 1 if conc. is below 0.01 (mol/mol) $1-(1/2)\log_{5}(100 \cdot conc.)$ for values between 0.25 and 0.01 (mol/mol) or $PC_{2.biotech} =$ 0 if conc. is above 80 (g/L) 1 if conc. is below 10 (g/L) $-0.48\ln(conc.)$ for values between 80 and 10 (g/L)	(1.3.2)	1/6	

TABLE 2.1. Equations of indicators and weighting factors *(Continued)*

Indicator	Equations and Values		Eq. No.	Internal weighting factor	Global weighting factor *
Inherent mass loss	$PC_3 =$	0 if MLI is below 0.1 1 if MLI is above 5 $0.5\log_{10}(MLI) + 1$ for values of MLI between 0.1 and 5	(1.3.3)	1/6	
Reaction enthalpy	$PC_4 =$	$\left(\lvert\Delta H^{O}_{Rxn}\rvert \text{-}100\right)/200 \text{ if: } \Delta H^{O}_{Rxn} \geq 0 \text{ or } \Delta H^{O}_{Rxn} < 0 \textit{ and } T_{Rxn} < 200°C$ $\left(100 - \lvert\Delta H^{O}_{Rxn}\rvert\right)/200 \text{ if: } \Delta H^{O}_{Rxn} < 0 \textit{ and } T_{Rxn} < 200°C$	(1.3.4)	1/6	
Number of co-products	$PC_5 =$	0 if N_{cp} are below 1 1 if N_{cp} are above 6 $-0.0167N_{cp}^{2} + 0.3167N_{cp} - 0.3$ for values between 1 and 6	(1.3.5)	1/6	
Reaction pressure	$PC_6 =$	0 if P_{rxn} is below 12.5 bar 1 if P_{rxn} is above 125 bar $0.4343\ln(P_{Rxn}) - 1.0986$ for values between 12.5 and 125 bar	(1.3.6)	1/6	

* Global weighting factors based-on [85]. AF: allocation factor, C: commercial price or cost (€/kg), conc.: concentration of main product (mol/mol or g/L), CED: cumulative energy demand (MJ/kg), CSA: complex separation alternative, DST: need for distillation, EC: economic constraint, EIRM: energy related impact of raw materials, GHG: greenhouse gas (kg CO_{2eq}/kg), IWF: Internal weighting factor, m: mass (kg), MLI: mass loss index, calculated as the ratio of the total mass of all components in the reactor outlet except for the main product and co-products, to the mass of main product and co-products in the reaction. N_{cp}: Number of co-products, PAZ: presence of azeotropes, PC: process complexity, PN: process nature, P_{Rxn}: reaction pressure, PS: presence of solids, TM: type of metabolite, T_{Rxn}: reaction temperature (°C). *Sub-indexes:*i,j,n: counter for species i, j, and main product, cat: refers to catalytic process, biotech: refers to biotechnological process. ΔH^{o}_{rxn}: standard reaction enthalpy. *Super-Indexes:* P: refers to product stream, RM: refers to raw materials stream, p: number of products, r: number of reactants.

2.2.2. Modification of early stage sustainability assessment method

In the modified method, the new indicators have been named as follows: economic constraint (EC), energy related impact of raw materials (EIRM) (formerly EI), and process complexity (PC) (formerly PCEI).

Economic constraint

Economic constraint (EC) represents the ratio of raw material costs to the value of marketable products and co-products as shown by Eq. (1.1) in Table 2.1. This index is a simplified approach to evaluate the economic potential of a process alternative. A ratio lower than "1" indicates a potential economic benefit. The index takes into account reaction performance (*e.g.*, yields and conversion) by including the mass of products and co-products.

Energy related impacts of raw materials

Energy related impacts of raw materials (EIRM) were determined based on cumulative energy demand (CED) and greenhouse gas (GHG) emissions of raw materials (Eq. (1.2.1) and Eq. (1.2.2) in Table 2.1). CED represents the total energy requirements (i.e. renewable and non-renewable) from cradle to factory gate covering total fossil and renewable energy inputs for feedstocks production. GHG emissions are used as an indicator of non-renewable resource use and climate change. GHG emissions includes the fossil carbon embedded in the product following a cradle-to-grave approach [85]. In case of multiproduct processes, it is necessary to allocate the environmental burdens (CED and GHG emissions) between products and co-products. In this chapter, allocation factors are calculated using the prices and mass flows of the products (economic allocation) (Eq. (1.1.1) in Table 2.1). The EIRM indicator is calculated using Eq. (1.2) in Table 2.1. Note that equal weighting factors are used (internal weighting factors, Table 2.1) for CED and GHG after a normalization procedure as explained later in the text.

Process Complexity

The process complexity (PC) indicator aims to provide insights into the possible costs and environmental impacts from a technical point of view, thus considering operational aspects. The PC indicator was modified to cover both catalytic and biochemical conversion processes. It considers 6 categories: i) downstream processing; ii) concentration of main product; iii) inherent reaction mass loss; iv) reaction enthalpy; v) number of co-products; and vi) reaction pressure. A category named *"pre-treatment of feedstocks"* in [85], was left out from in this list because the analysis starts from a platform chemical or the chemical building block where pre-treatment is already considered as part of the upstream processes. A brief explanation on the each category is provided next.

Downstream processing

This category *downstream processing* (Eq. (1.3.1) in Table 2.1) takes into account the presence of water, the energy requirement to separate it from a mixture, its tendency to form azeotropic mixtures, and the difference of boiling points between the main product and other co-products. In this study, the boiling point difference is used as decision criteria to determine whether a separation based on the co-existence of valor-liquid phases is applicable, since gas-liquid or liquid-liquid separations are also possible. Furthermore, a solid phase may also be present in the conversion system making it more complex.

This category is based on classical conceptual design approaches that use heuristics as guideline to select basic separation alternatives [86, 87]. It is based on a qualitative analysis of the products leaving the reaction step. The category is scored between 0 (no downstream required) to 1 (for a very complex downstream processing). A checklist is provided here to guide the scoring of the category by using the following 6 subcategories (see Eq. (1.3.1)): process nature (PN) (*i.e.,* catalytic or biochemical), the type of metabolite is considered (TM) (*i.e.,* intracellular, extracellular), presence of solids (PS), need of distillation (DST), presence of azeotropes (PAZ), and need of complex separation alternatives (CSA) (e.g., liquid-liquid extraction, adsorption, absorption). These subcategories are presented in Eqs. (1.3.1.1) to (1.3.1.6) in Table 2.1. PN and TM provide higher scores for biochemical processes rather than catalytic processes due to their higher complexity in terms of process stability, sensitivity to contamination of the reaction medium, and difficulty to extract the main product from cell biomass in case of intracellular metabolites. As shown in Table 2.1, the subcategories have different scores. For instance, PN, TM and PS accounts for a maximum of 10% each of the total score of the category while need of distillation accounts for a 20%. These differences aim to represent the difficulty of each downstream alternative, e.g., distillation is in general a more complex separation alternative than that of a solid from a mixture.

Concentration of main product

This category accounts for the energy requirements needed to recover the main product from the reaction mixture. For catalytic conversion, the original definition considers molar concentrations based on typical values (see Eq. (1.3.2) in Table 2.1, $PC_{2,cat}$) [85]. A similar reasoning is now followed for biochemical processes and takes into account typical values of fermentative processes to account for high and low concentration of metabolites. The category is scored 0 (high concentration) or 1 (low concentration), respectively (see Eq. (1.3.2) in Table 2.1, $PC_{2,\text{ biotech}}$) [88, 89].

Inherent mass loss, Reaction enthalpy, number of co-products

These three categories were not modified from Patel et al., [85] (see Eqs. (1.3.3) to (1.3.6)). The category *inherent mass loss* accounts for the unconverted reactants in the conversion step and the formation of waste. *Reaction enthalpy* accounts for the energy required to carry out the reaction step (including the energy that can be recovered in exothermal reactions at high temperature). *Number of co-products* takes into account the increasing number of downstream processes related to the number of co-products.

Reaction pressure

In the case of catalytic processes, pressure plays an important role on the performance of the reaction system [90]. To correlate the effect of pressure and give a score between 0 and 1, three levels of pressure were selected according to the definition presented in Meerman et al. [73].A system is at low pressure at values below 12.5 bar (score is 0), while a system is at high pressure at values above 125 bar (score 1). A score of 0.5 was set to 40 bar [73]. This category is presented in Eq. (1.3.6) in Table 2.1.

2.2.3. Case studies

A number of case studies have been conducted to test the screening methodology. Two main criteria were considered in the selection procedure namely: *i)* availability of experimental data (either from research papers and patents) to calculate the reaction mass balances, and *ii)* availability of data related to the conventional route for comparison purposes. This resulted in the identification of three platforms: syngas, carbohydrates and glycerol.

Syngas is selected as a platform that represents the catalytic conversion of biomass to obtain derivatives that are identical in function to their petrochemical counterparts. Figure 2.2a show the eleven selected in this study. For each derivative, there were many possible literature studies to be considered, however, only those showing higher conversions and also higher selectivities to the desired products were selected. It was checked that selectivities and conversions led to completion of mass balances. Reactions, conversions and selectivities used to calculate the mass balances for syngas derivatives are listed in Appendix A (see Table 2.6) and for their respective petrochemical counterpart in Appendix C.

In the case of carbohydrates, five derivatives were selected as shown in Figure 2.2b. The carbohydrates platform is one of the most important sources to obtain derivatives via biochemical conversion. Similarly to syngas, literature studies presenting higher yields and conversions were considered. Also, it was checked whether the mass balances led to logical results. Yields and conditions of the carbohydrate platform are presented in Appendix A (see Table 2.7), while the petrochemical counterparts are shown in Appendix C.

Finally glycerol was selected because it offers a wide range of derivatives to be obtained both via catalytic and biochemical conversion. In total, seven derivatives from glycerol were selected as shown in Figure 2.2 c,d. Reactions, conversions, selectivities and yields are presented in Table 2.8 and Table 2.9 in appendix A.

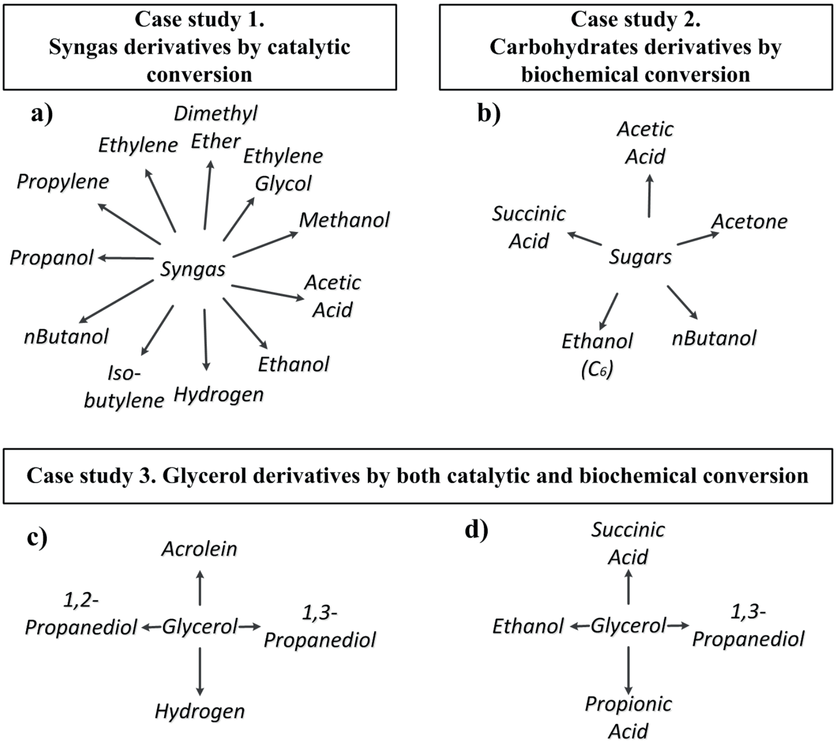


FIGURE 2.2. Derivatives from platform chemicals: a) derivatives from syngas by catalytic conversion, b) derivatives from carbohydrates by biochemical conversion, c) derivatives from glycerol by catalytic conversion, d) derivatives from glycerol by biochemical conversion.

2.2.4. Data inputs

The method requires data to describe mass balances of the reaction system, standard enthalpy of formation of the compounds involved to calculate heat of reaction, prices of raw materials and products, and CED and GHG of raw materials. The information is obtained from literature or generated from the analysis of upstream processes and databases.

Data from literature and databases

Data on the reaction systems was obtained from research papers and patents (see Appendix A). Data on the standard heat of formation and other physical-chemical properties (*e.g.* boiling points) were gathered from Aspen Properties databases available in Aspen Plus V8.4 (Aspentech, USA). This database was used because it compiles a large set of thermodynamic properties allowing easier data collection. Prices of raw materials and products were collected from different sources such as Platts McGraw Hill financial, ICIS pricing, research papers and the Alibaba group. The prices used, together with references, are presented in Table 2.10 of appendix B. Finally, available data of CED and GHG of raw materials were gathered from Ecoinvent databases [91].

Data generated by the analysis of upstream processes

Platforms are usually produced in the same facility that produces the end product. One of the reasons for centralizing production is to avoid transportation costs and be able to integrate processing steps. Commercial prices, CED and GHG data of carbohydrates and syngas derived from lignocellulosic biomass were not available in literature databases. Due to the lack of data, it was necessary to study the first stages of the production chain and start from the lignocellulosic material. To analyze derivatives using EU conditions, wheat straw was selected as lignocellulosic material. This residue was selected due to the large production of wheat in France and Germany (around 60 million tonnes in 2012 according to FAO statistics). CED and GHG were available for wheat crop at farm gate [91]. Based on mass grain/crop and residue/crop ratios (*i.e.* kg of residue per kg of crop and kg of grain per kg of crop), and prices for both grains and lignocellulosic residue (average 72 €/tonne for wheat straw grain) economic allocation factors were used to calculate CED and GHG emissions related to the lignocellulosic material [92]. Economic allocation was used instead of mass allocation or energy allocation since the economic value of grains is currently much higher than the economic value of agricultural residues (Details in Table 2.12 in Appendix B). On the other hand, the use of different prices of feedstocks as well as crop to grain ratio may affect the values of CED and GHG allocated to the residues. Nevertheless, the effect of these aspects was not covered in this study. It was also necessary to calculate production costs, CED, and GHG emissions related to the production of syngas and carbohydrates from the conversion of the lignocellulosic feedstock (wheat straw). For this, flowsheeting in Aspen Plus was used as a tool to generate the mass and energy balances and based on this data, production costs, CED and GHG emissions were calculated.

The conversion of wheat straw to sugars (C5, C6 and lignin) was modeled by using both dilute acid pretreatment and hydrolysis of the hemicellulose and cellulose fractions, respectively (based on the model described by Moncada et al. [93]). Three main product streams were obtained: i) one stream rich in C5 sugars (from pre-treatment), ii) one stream rich in C6 sugars (from cellulose hydrolysis), and iii) a stream rich in lignin and unconverted hemicellulose and cellulose. Based on data from gate to gate energy balances (generated from process modeling), CED and GHG emissions of the processing stages were calculated and added up to the CED and GHG emissions of the lignocellulosic biomass. Similarly, based on mass and energy balances, the production costs were calculated. At this point, costs and impacts are calculated for the entire process, however, it is necessary to distribute them among the products by using allocation factors. To calculate individual production costs and CED and GHG emissions of each stream (*i.e.,* C5, C6, lignin) two approaches were considered: i) mass allocation based on processing yields (allocation factors calculated by the share of the total mass of products), ii) economic allocation by assuming a price ratio of 3:2:1 for C6:C5:lignin (Allocation factors calculated by the share of total sales of products). In both cases, it was assumed that lignin would have a share on the total costs and energy related impacts due to its prospective use and market for future biorefineries. Price ratios were chosen assuming that C6 sugars are most likely to be the main product in current lignocellulosic-based biorefineries because of their high potential for chemical and biochemical conversion, followed by an increasing interest on the conversion of C5 sugars into chemicals such as xylitol and ethanol [76], and an emerging interest on derivatives based on lignin. The assumption on price ratios is based on the fact that there are no relevant commercial data for the prices of lignin and C5 sugars. The data is presented in Table 2.13 and Table 2.14 for mass and economic allocation, respectively.

Mass and energy balances of the conversion of wheat straw (mainly CO/H_2 mixtures) were obtained by adapting the process model presented by Meerman et al. [73] focusing only on the sections of biomass gasification and gas cleaning and optimizing. This last step is relevant in order to remove impurities and adjust the H_2:CO ratio to the desired value [73]. Depending on the derivative to be obtained (see Figure 1a), different H_2:CO ratios are required (See Appendix A). Therefore, production cost, CED and GHG emissions were calculated for the syngas required for each derivative or group of derivatives (See

Table 2.15). In this case, allocation was not necessary because the main product stream was syngas.

Glycerol prices were available in literature [94]. It was assumed glycerol is derived from biodiesel produced from rape oil (conditions in the European Union). However, the CED and GHG values of glycerol found in databases [91], do not represent the current situation given its lower commercial price. Therefore, CED and GHG were estimated by updating allocation factors from the impacts of glycerol derived from rape previously presented by Jungbluth et al.[91]. This data are presented in Table 2.11(see Appendix B).

2.2.5. Application

The application of the method started with the generation of mass balances for each conversion alternative. After this, each sustainability indicator was calculated by using the set of equations and values shown in Table 2.1. Internal weighting factors were used to integrate individual scores of subcategories for each indicator. After calculating the indicators, each one was normalized by the maximum (*i.e.,* the worst) score of the two processes under comparison (*e.g.,* bio-based vs. petrochemical). The maximum possible value for each indicator after normalizing is 1, which is obtained for the processing option with a higher index score (less attractive) while the alternative process receives a lower normalized value (more attractive). The normalized score of each indicator was then multiplied by the weighting factors (see Table 2.1) before their aggregation into a single score. Note that weighting factors were modified accordingly to the work presented by Posada et al. [46]. This was done by normalizing the weighting factors for EC, EIRM and PCEI. Selection of these weighting factors were based on expert elicitations [85] and supported by the reasoning that economic feasibility is the first requirement to implement a process on a commercial scale and long term sustainability should be complemented by minimization of environmental impacts. 40% of the total score accounts for economic constraint, 30% accounts for energy related impacts of raw materials, and 30% accounts for process complexity (see Table 2.1). The ranking of the weighting factors did not change and the highest contribution was maintained for the EC. Consequently, each processing alternative has a total score. The index ratio is defined as the ratio of the single score of the bio-based process over the single score of the reference system offering a final direct comparison. An index ratio <1 indicates that the bio-based alternative shows a better performance in terms of sustainability than its alternate counterpart, however, an index ratio >1 indicates that there are not clear benefits of the bio-based route in comparison to the petrochemical one. An example on the calculation of the aggregated single scores and the index ratio is presented in Appendix D.

Finally, sensitivity and scenario analyses were carried out in order to account for variations of relevant input data such as yields and prices. Yields were varied by a reduction of 20%, and the maximum achievable yield (theoretical), while prices were varied in a range of ±30%. In the case of carbohydrates derivatives, it is also analyzed the effect of mass and economic allocation of the upstream process, over the index ratio of the selected systems. Additionally, as part of sensitivity analysis, ethanol produced from both the fermentation of C6 sugars, and a mixture of C5-C6 sugars were considered as cases. For the syngas platform, methanol was obtained by direct synthesis and via mixed alcohols. Besides, the mixed alcohols route (mixed production of methanol, ethanol, propanol and butanol, see Table 2.6) produces a gas stream that contains valuable gases such as methane, propane and butane. Two cases were considered, one including the sale of this gaseous co-products and other without recovering them. As the method considers economic allocation the environmental burdens are allocated among all marketable products. These cases are also considered as part of the sensitivity analysis of the syngas platform.

Scenario analysis considered three different countries/regions: EU, USA and China by using specific data for CED, GHG emission and cost/prices of raw materials. As previously mentioned, it was considered glycerol from rape for EU, while for USA and China it is considered glycerol derived from soybean and palm, respectively. In the case of carbohydrates, wheat straw was used as feedstock for EU. For USA and China it was considered corn stover and rice husk, respectively. These residues were selected based on the high quantity produced according to the feedstocks from where they come (FAOSTAT).

2.2.6. Categorization

Depending on the index ratio obtained, the derivatives are categorized in three groups namely: favorable (Group I), promising (Group II) and unfavorable (Group III). Group I considers those derivatives with high sustainability potential for the bio-based alternative, and it is considered for index ratios lower than 0.9 [46]. Group II considers those derivatives for which advantages are not substantial, but where technological and economic improvements could lead to better performance of the bio-based alternatives. Index ratios of group II range from 0.9 to 1.2. Group III relates those derivatives with low sustainability potential for bio-based derivatives (index ratios higher than 1.2).

2.3. RESULTS AND DISCUSSION

2.3.1. Derivatives from the catalytic conversion of bio-based syngas

The index ratio together with sensitivity analysis on yields and prices are presented in Figure 2.3 for the derivatives from the catalytic conversion of syngas. In total 16 systems were analyzed (accounting for 11 derivatives) 3 were found as favorable (Group I), 8 as promising (Group II), and 5 as unfavorable (Group III). For each system, the aggregated scores for both the bio-based and the fossil-based processes are displayed in Figure 2.8 and Figure 2.9 in Appendix E. The derivatives with the highest potential were dimethyl ether and ethylene glycol. In both cases, the major contribution is due to the scores of the EC and EIRM indicators (see Figure 2.8). This can be explained by the fact that bio-based syngas has lower price, GHG emissions and CED than methanol and ethylene oxide which are the raw materials used to produce dimethyl ether and ethylene glycol, respectively. In the case of dimethyl ether, for low CO_2 emission plants based on torrefied biomass, production costs varied from 120 to 400 €/tonne (depending on feedstock price and technology) [95]. These costs are lower than the selling prices displayed in Table 2.10 (see Appendix B), therefore confirming the score of EC for dimethyl ether screened by using the early stage sustainability assessment method.

Group II (promising) contains 8 cases, which are ranked according to index ratios in the following order: butanol[1*], ethanol[*], hydrogen, butanol, propanol[*] and ethanol. The two first products have similar performance (index ratios between 0.9 and 1). In both cases, the EC and EIRM scores were lower for the bio-based alternative, while, the PC score was always higher which is due mainly to the number of co-products. Butanol* and ethanol* were hardly affected by sensitivity on yields due mostly to the number of usable co-products (see Appendix A). Sensitivity on prices showed to have strong effect on butanol* due to the updating of allocation factors, thus affecting the score of EIRM indicator. The index ratio for Hydrogen was close to 1, where the EC was higher for the bio-based alternative, but EIRM and PC were always lower. Sensitivity on product prices barely showed any significant variation for hydrogen, since EC was almost constant and allocation factors slightly changed. Sensitivity on yields scarcely affected the index ratio for hydrogen, as only the water gas shift reaction was considered and no co-products were obtained. Butanol, propanol*, and ethanol showed index ratios close to 1.2. In the production of mixed alcohols (*i.e.,* methanol, ethanol, propanol and butanol), the inclusion of the gaseous marketable co-products improved their index ratios. The benefits are reflected in the EC by including more value-added products, and in the EIRM by distributing the environmental burdens in a larger number of products. This explains why butanol*, ethanol* and propanol* show better performances than

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[1] [*] Products including *"asterisk"* are for cases where the gaseous co-products are assumed to be sold

butanol, ethanol and propanol, respectively (see Figure 2.3). Additionally, previous studies reported that in the mixed alcohols route, special attention should be paid to the valorization of co-products to be competitive from an economic point of view [96, 97].

Group III (unfavorable) contains 8 cases: propylene, acetic acid, ethylene, propanol, methanol (produced via direct synthesis), methanol* and methanol (both produced via mixed alcohols). Propylene, acetic acid ethylene, propanol and isobutylene showed similar index ratios. In all cases, the score of the EC indicator was higher for the bio-based alternative, notoriously affecting the index ratios. In the case of propylene and ethylene (produced together), despite of the differences of bio-based syngas and naphtha on prices, CED and GHG (see Appendix B and C), the steam cracking of naphtha derived a higher number of marketable products in comparison to those derived from the catalytic conversion of syngas. An improvement on the selectivity of ethylene and propylene can lead to better performances. However, these two products are still categorized as unfavorable since both propylene and ethylene are likely to be produced together, and an improvement on the selectivity of one derivative can result on a decrease on the selectivity of the other. Methanol can be obtained from syngas via either "direct synthesis" or "mixed alcohols". In both cases, the scores of all indicators were higher for the bio-based alternative. In the case of methanol produced via "direct synthesis", the difference with the coal-based alternative is the H_2/CO ratio used (see Appendix A). In the case of methanol via "mixed alcohols", its selectivity is much lower than the direct synthesis route, but it should be considered that it is a co-product from the production of butanol, ethanol and propanol which are products with a better sustainability performance.

Table 2.2 shows the categorization of the derivatives from bio-based syngas for the three locations considered in this study *i.e.,* the EU, USA and China. In the case of USA, ethanol* also belongs to the list of favorable derivatives due to the lower production cost of syngas in USA compared to the EU. China also included butanol* and ethanol* in Group I due to the lower production cost of syngas (see Appendix B). Similar to Group I, USA and China added derivatives to Group II that were previously classified in Group III in the EU. USA accounted for three additional derivatives in Group II (*i.e.* ethylene, acetic acid, propylene), while China accounted for five additional derivatives (i.e. ethylene, acetic acid, propylene, propanol, isobutylene). This is mainly due to the lower costs, CED and GHG obtained for syngas from corn stover (USA) and rice husk (China) (see Table 2.15). The latter is a consequence of both prices and energy related impacts of the lignocellulosic materials used to produce syngas. Compared to the EU, USA and China showed lower index ratios ranging from 3-18%, and from 6-22%, respectively.

TABLE 2.2. Categorization of syngas derivatives by catalytic conversion

Country/ Region	Dimethyl Ether	Ethylene Glycol	Butanol*	Ethanol*	Hydrogen	Butanol	Propanol*	Ethanol	Ethylene	Acetic Acid	Propylene	Propanol	Isobutylene	Methanol	Methanol* (MA)	Methanol (MA)
EU	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-II	G-III	G-III	G-III	G-III	G-III	G-III	G-III	G-III
USA	G-I	G-I	G-II	G-I	G-II	G-II	G-II	G-II	G-II	G-II	G-II	G-III	G-III	G-III	G-III	G-III
China	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-II	G-II	G-II	G-II	G-III	G-III	G-III

G-I: Group I, most favourable compounds to be produced from syngas
G-II: Group II, promising derivatives.
G-III: unfavourable derivatives from syngas.
* Including sale of gaseous co-products (Methane, Butane, Propane).

TABLE 2.3. Categorization of sugars (C6 sugars, C5-C6 Mixtures in some cases) derivatives by biochemical conversion

Country/ Region	Succinic Acid **	Succinic Acid	Ethanol ** (C5-C6)	Ethanol (C6) **	Ethanol (C5,C6)	Butanol **	Acetic Acid **	Ethanol (C6)	Acetone **	Butanol	Acetic Acid	Acetone
EU	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-III	G-III	G-III
USA	G-I	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-III
China	G-I	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-III

G-I: Group I, most favourable compounds to be produced from sugars from lignocellulosic biomass
G-II: Group II, promising derivatives.
G-III: unfavourable derivatives from sugars from lignocellulosic biomass
** Denotes that costs and energy related impact of raw materials were obtained from mass allocation of impacts of lignocellulosic biomass and its further treatment to obtain C5, C6 sugar streams, and lignin.
For derivatives without **, the costs and energy related impacts were obtained via economic allocation assuming a price ratio for C6:C5:lignin of 3:2:1.
C6: denotes fermentation of C6 rich stream. C5, C6: denotes fermentation of C5,C6 mixtures.

China shows a high potential to produce bulk chemicals derived from the catalytic conversion of bio-based syngas. This is interesting in view of the growing chemical industry in China and also that many chemicals are produced based on methanol, such as acetic acid and dimethyl ether [98]. In general, the syngas platform has a wide application in future development of biorefineries with applications in both materials and energy sectors. However, the method showed an efficient way to screen and to identify derivatives from the catalytic conversion of bio-based syngas.

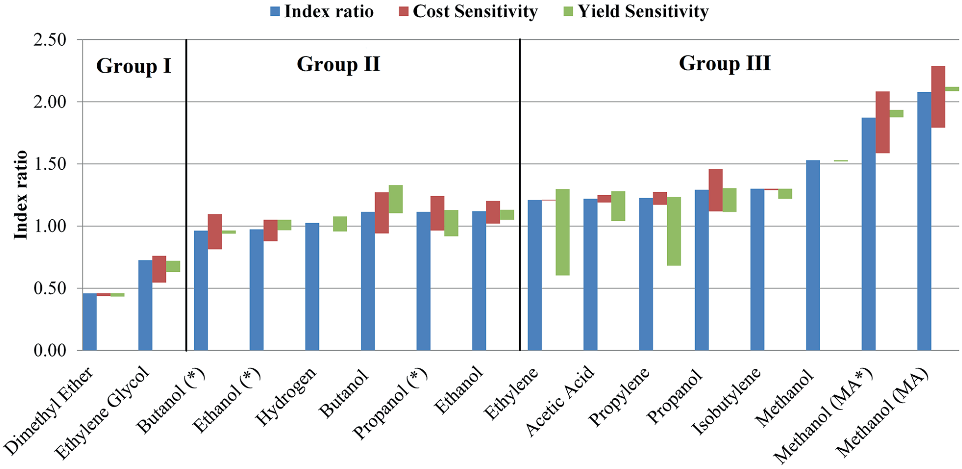

FIGURE 2.3. Index ratio and sensitivity analyses on yields and prices for derivatives from syngas by catalytic conversion (EU). * Includes sale of gaseous co-products (Methane, Butane, Propane). MA: denotes via Mixed-Alcohols. Group I: favorable, Group II: promising, Group III: unfavorable.

2.3.2. Derivatives from the biochemical conversion of carbohydrates

Index ratios and sensitivity analyses on prices and yields are presented in Figure 2.4 for derivatives from the biochemical conversion of sugars from lignocellulosics in the EU. In total 12 cases were evaluated (representing 5 derivatives) of which 5 were categorized in Group I, 4 in Group II and 3 in Group III. From the 12 cases analyzed, 6 were calculated using data from mass allocation (marked with [2]** e.g., succinic acid **) and the remaining 6 using data from economic allocation. The cases categorized in Group I included succinic acid and ethanol obtained both from C6 and C5-C6 fermentation. Succinic acid (considering either mass or economic allocation) had the lowest index ratios, with the EC and EIRM scores as the major contributors. These low index ratios are achieved due to the high price, CED and GHG of 1,4-Butanediol (the petrochemical raw material for succinic acid production, see Appendix C), compared to those obtained for C6 sugars

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[2] ** denotes the calculation of sustainability indicators using data from mass allocation

derived from lignocellulosic biomass. The index ratio of succinic is only slightly affected by either variations on price or yields due to the differences of C6 sugars compared to 1-4,Butanediol. The latter is confirmed in the work presented by Pinazo et al., [99] where succinic acid produced via biochemical conversion of sugars was compared against its petrochemical production. This also confirms the interest on producing succinic acid from carbohydrates and the importance it may have as a chemical building block [100]. Ethanol, from the two routes (C6 sugars and C5-C6 mix sugars), is the second derivative appearing in Group I. Ethanol** derived from C5-C6 fermentation showed a slightly better performance than ethanol** from C6 fermentation. This difference is influenced by the fact that C5-C6 fermentation leads to higher yields than standalone C6 fermentation. Ethanol from C5-C6 mixtures shows a similar behavior (but higher index ratio) to ethanol** from C5-C6 fermentation. For all ethanol cases, variation on prices hardly affected the trend of index ratio. However, ethanol** from C6 sugars is more sensitive to an improvement of yield due to better EC and EIRM scores.

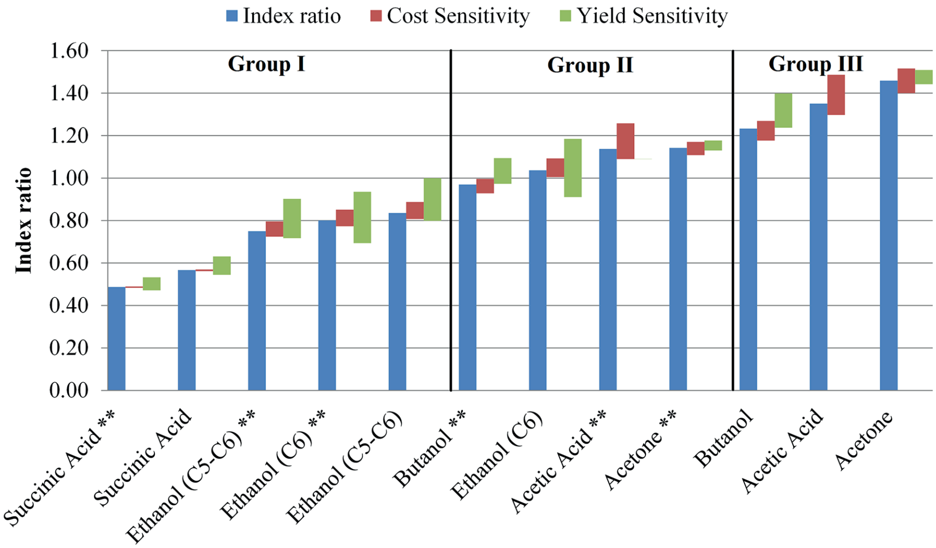

FIGURE 2.4. Index ratio and sensitivity analyses on yields and prices for derivatives from lignocellulosic sugars by biochemical conversion (EU). For derivatives without **, the costs and energy related impacts were obtained via economic allocation assuming a price ratio for C6:C5:lignin of 3:2:1. ** Denotes that costs and energy related impacts of raw materials were obtained from mass allocation of impacts of lignocellulosic biomass and its further treatment to obtain C5-C6 sugar streams, and lignin. C6: denotes fermentation of C6 rich stream. C5-C6: denotes fermentation of C5-C6 mixtures.

Group II contains butanol**, ethanol (C6), acetic acid** and acetone**. The index ratios for butanol** and ethanol (C6) are close to 1. In the case of butanol**, despite of the differences on prices among C6 sugars and propylene (raw materials), the score of EC indexes were not very different mainly because yields were much higher and selective to butanol in the petrochemical route. For the petrochemical counterpart, EIRM was highly affected by GHG embedded in the product. Butanol* is not highly affected by changes in prices, however, it is significantly affected by unfavorable yield conditions (reduction of 20%) and therefore increasing the score of EC indicator. In fact, the work presented by Uyttebroek et al., [101] discusses that fossil-based butanol shows a better sustainability performance than bio-based butanol, however, it is argued that bio-based can be competitive if its production yield is improved. Acetic acid** and acetone** showed similar index ratios (approx. 1.15). In both cases, EC was lower for the petrochemical counterpart due to the large number of marketable products (acetic acid**) and higher yield (acetone**). However, the score of EIRM index was lower for the bio-based alternative due to the differences on raw materials (among the petrochemical and bio-based routes) in terms of CED and GHG (see Appendix B and Appendix C).

Group III includes butanol, acetic acid and acetone, due to the effect of price ratios (3:2:1 for C6:C5:lignin). Thus, the costs and energy related impacts allocated to C6 sugars were much higher than those from mass allocation (see Appendix B, Table 2.13 and Table 2.14). Only ethanol from C5-C6 sugars considered C5 sugars as substrate, the remaining derivatives are produced from C6 sugars. Consequently, all cases that were assessed using data inputs from economic allocation showed higher index ratios than their equivalent derivatives using data inputs from mass allocation. Economic allocation factors are dependent on prices and mass ratios of the products. Mass ratios may vary significantly depending on the pretreatment and hydrolysis technologies, and also depending on the inherent characteristics of the raw material (i.e. cellulose, hemicellulose and lignin content). Many combinations of pretreatment and hydrolysis technologies may appear resulting in different costs and energy related impacts of raw materials. Furthermore, it should be considered the fact that biomass availability and biomass trade may bring additional discussion issues such as facility location, impacts and costs associated to transportation among others.

The analysis presented so far considered the EU as regional context. Similarly to the case of syngas, USA and China showed better performances than the EU by including butanol** in Group I and only acetone in Group III (see **Table 2.3**). Index ratios for China are lower by 1 to 11%, while index ratios for USA are lower by 6 to 16% compared to the EU. This can be explained by the fact that the considered GHG and costs were always lower for USA compared to both EU and China (see Table 2.13 and Table 2.14). This effect is also caused by the higher processing yields of the sugars obtained after the treatment, which are related to the characteristics of the raw materials and technologies. In contrast to the case of syngas, USA showed better performances for derivatives from carbohydrates taking advantage of the higher yields of C5 and C6 sugars than that one that can be obtained from corn stover in comparison to wheat straw and rice husk.

2.3.3. Derivatives from glycerol

Catalytic conversion of glycerol

In total 4 cases were analyzed, and their index ratios and sensitivity analysis on yields and prices are shown in Figure 2.5. Group I includes 3 of the cases ranked in the following order: 1,2-propanediol, 1,3-propanediol and acrolein. For both, 1,2- and 1,3-propanediol the bio-based alternative showed lower scores for the EC and EIRM indicators. This can be attributed by the differences of raw materials in terms of cost, CED and GHG in comparison to those of the petrochemical counterparts. As a consequence, 1,2- and 1,3-propanediol were scarcely affected by changes on prices and yields under favorable and unfavorable conditions. The sustainability of 1,2-propanediol production from glycerol was discussed by Marinas et al. [102], ratifying that the bio-based route has a better sustainability performance than its petrochemical counterpart. Additionally, based on the results presented by Posada et al. [82], it is confirmed that glycerol based 1,2- and 1,3-propanediol are derivatives with the highest sale price to cost ratio. Acrolein derived from glycerol also showed a similar behavior of that of 1,2 and 1,3-propanediol, with lower EC and EIRM scores for the bio-based alternative. In contrast to the case of 1,2-propanediol, where propylene is also used as raw material, the differences of the bio-based acrolein in terms of EC and EIRM are not large due to the fact that the petrochemical route also produces 1,3-propanediol as co-product. Therefore, the differences between the petrochemical route and the bio-based alternative are not only related to raw materials but also to the selectivities of the reaction system and the value-added of co-products. For the catalytic conversion of glycerol, no derivatives were categorized in Group II and only hydrogen was categorized in Group III. The high index ratio of glycerol-based hydrogen was mainly caused by the contribution of EC and EIRM indexes. Therefore, variations on prices and yields did not affect the index ratio. In the work presented by Posada et al. [82], hydrogen was the less attractive glycerol based product, with a selling price to production cost ratio of about 1. In the case of USA and China the categorization of the derivatives stayed equal to the one presented for EU (See Table 2.4). However, USA showed lower index ratios (by 10-20%) while the values obtained for China (around 5%) were comparable to those for the EU. The reason of the potentiality of USA depends on the lower impacts of glycerol derived from biodiesel from soy (see Table 2.11).

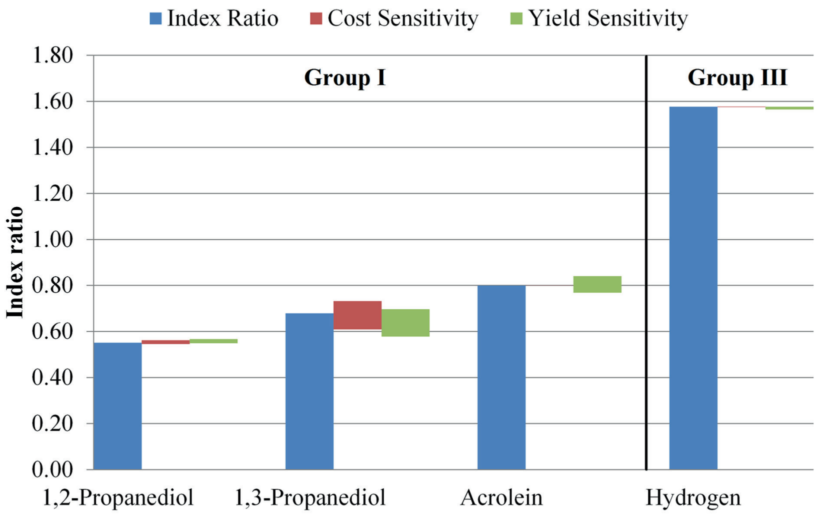

FIGURE 2.5. Index ratio and sensitivity analyses on yields and prices for derivatives from glycerol by catalytic conversion (EU).

TABLE 2.4. Categorization of glycerol derivatives by catalytic conversion

Country/Region	1,2-Propanediol	1,3-Propanediol	Acrolein	Hydrogen
EU	G-I	G-I	G-I	G-III
USA	G-I	G-I	G-I	G-III
China	G-I	G-I	G-I	G-III

G-I: Group I, most favourable compounds to be produced from glycerol
G-II: Group II, promising candidates.
G-III, unfavourable derivatives from glycerol.

Biochemical conversion of glycerol

For the biochemical conversion of glycerol, 4 cases were analyzed. Their index ratios and sensitivity analysis on yields and prices are presented in Figure 2.6. All derivatives were categorized in Group I (favorable). In all cases, the score of EC and EIRM indicators were lower for the bio-based alternative in comparison to the petrochemical counterparts. Succinic acid showed the best performance, and similarly to the case of succinic acid from sugars, the cost and CED and GHG impacts of 1,4-butanediol are much higher than those from glycerol (see appendix B and appendix C). In the remaining cases, the index ratios are highly influenced by the differences of raw materials, i.e., glycerol and those used for the petrochemical counterparts. On the other hand, USA and China also categorized all derivatives as favorable (Group I) as presented in Table 2.5. In comparison to EU, China presents lower index ratios ranging from 3 to 8%, while USA ranging from 7 to 14%. Again, USA showed a higher potentiality due to the lower impacts of glycerol derived from soy biodiesel. For the three country/regions (i.e. EU, USA, China), it is clear that glycerol is a promising platform chemical in comparison to petrochemical counterparts.

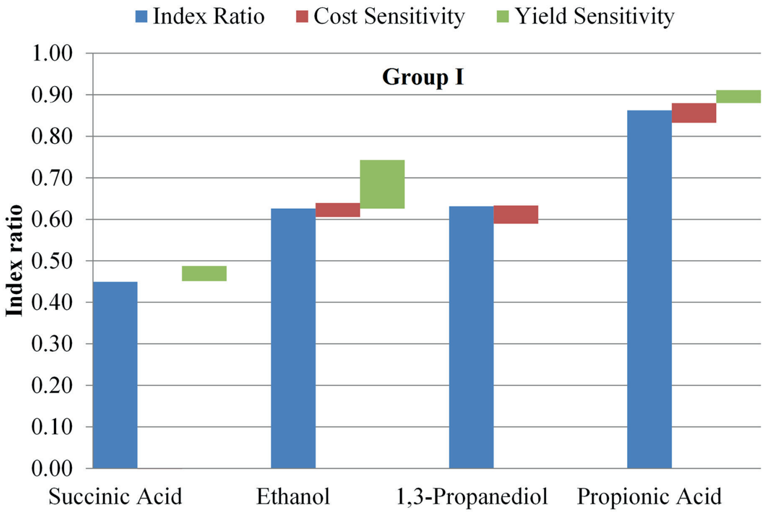

FIGURE 2.6. Index ratio and sensitivity analyses on yields and prices for derivatives from glycerol by biotechnological conversion (EU).

TABLE 2.5. Categorization of glycerol derivatives by its biochemical conversion

Country/Region	Succinic Acid	Ethanol	1,3-Propanediol	Propionic Acid
EU	G-I	G-I	G-I	G-I
USA	G-I	G-I	G-I	G-I
China	G-I	G-I	G-I	G-I

G-I: Group I, most favourable compounds to be produced from glycerol
G-II: Group II, promising candidates.
G-III, unfavourable derivatives from glycerol.

2.3.4. Comparison between platforms

Our findings indicate that the extended version of the method, is an effective tool to assess and screen derivatives from both catalytic and biochemical conversions of platforms and building blocks in comparison to their petrochemical counterparts. Nevertheless, after analyzing and categorizing the different cases, it was identified that there are common derivatives between the different platforms. Thus, the methodology may also be used as a tool to screen, at a second level, derivatives from different platforms. For instance, the case of ethanol, which was assessed in the syngas platform and also appears in the carbohydrate platform (produced by two technologies) and the glycerol platform (see Figure 2.2). Ethanol from syngas shows the highest index ratio among the three routes, which in its best case appeared categorized in Group II (promising). Ethanol from glycerol and carbohydrates (best case) were categorized in Group I (favorable). Consequently, ethanol from syngas is discarded for further discussion between platforms. The main differences between ethanol derived from glycerol and sugars, is that in the case of glycerol all indicators were lower than the petrochemical counterpart. The case of succinic acid is very interesting considering that there is not clear difference between glycerol and sugars as possible platforms. In the case of butanol, by comparing the worst cases, butanol from carbohydrates shows a higher index ratio thus representing a lower sustainability potential than that produce from syngas. However, by comparing the best cases (lower index ratio, see Figures 3 and 4) the difference is not significant. Thus, both routes offer a very similar behavior independently of the remarkable differences among the two platforms. Acetic acid from both syngas and carbohydrates also show very similar index ratios.

For succinic acid, butanol and acetic acid, detailed techno-economic and environmental assessment is needed to select the most promising platform. Additionally, the availability of raw materials and infrastructure capacity to produce a platform will also be relevant to select the routes. In contrast, the case of hydrogen from syngas noticeably shows benefits over hydrogen from glycerol. The high differences are associated to the efficiency and selectivities of each conversion alternative. The case of 1,3-propanediol is interesting since it can be obtained from both catalytic and biochemical conversion of glycerol. However, the difference between both index ratios is not significant, and at an early-stage it is difficult to select the most promising route. This is an important result taking into account that in some cases the benchmarking of screened routes should be done by means of a more detailed analysis (*i.e.* bottom-up approaches). Thus, it can be further analyzed the effect of features such as utilities, equipment size and cost and efficiency of the downstream process.

2.4. CONCLUSIONS

The model applied in this chapter provides good insights on the sustainability of bio-based processes compared to their petrochemical counterparts. A database including the categorization of derivatives was built. The results seem to be reasonable and fairly in line with results published by different authors. When comparing common systems from different platforms (*e.g.,* 1,3-propanediol, succinic acid), a selection of the most promising platform was not always possible. To successfully complete this, detailed techno-economic and environmental assessment would be needed to evaluate further details for features such as downstream processing, utilities and equipment.

The method requires data related to yields, prices, life-cycle data and physico-chemical properties. For the screening of bio-based derivatives from platform chemicals, some of the data was difficult to collect. The methodological approach showed that it is possible to link upstream processes (producing bio-based platform chemicals) to the early stage sustainability assessment of derivatives from those platforms. For processes at early stage the method offers a good alternative to assessments based on detailed process design. In general, the results from this study show a quick approach for screening and selecting bio-based products, and where the efforts should be concentrated in future development of integrated biorefineries.

Based on the results from the case studies, the derivatives from bio-based syngas with a favorable sustainability performance were dimethyl ether and ethylene glycol. In the case of carbohydrates, the derivatives with favorable sustainability performances were succinic acid and ethanol. The derivatives with favorable sustainability performance from the conversion of glycerol were 1,2-propanediol, 1,3-propanediol, acrolein, succinic acid, ethanol and propionic acid. According to the scenario analysis, China and USA showed a higher potential to promote the production of bulk chemicals rather than EU. The latter is mainly due to lower feedstock prices in USA and China. In the future it can be worthwhile to carry out a more in-depth analysis regarding biomass availability to evaluate their effect on the sustainability performance of the screened routes.

Acknowledgements

The financial support from the Netherlands Organisation for Scientific Research (NWO, Nederlandse Organisatie voor Wetenschappelijk Onderzoek) in the context of the China-Netherlands Joint Scientific Thematic Research Programme (JSTP Project 700.10.703, Biorefineries for China and Europe? The Road to Sustainability is gratefully acknowledged.

APPENDIX

Appendix A

This section presents the reactions and conditions used to calculate the mass and energy balances of the conversion routes, which is the primary data used to calculate the sustainability indicators. Tables 2.6 and Table 2.8 show the reactions involved, conversion per pass, selectivities and conditions (i.e. temperature and pressure) of the catalytic conversion of syngas and glycerol, respectively. Table 2.7 and Table 2.9 show the conditions and yields of the biotechnological conversion of carbohydrates and glycerol.

TABLE 2.6. Reactions and conditions of derivatives from the catalytic conversion of syngas.

Product	Reactions	CO Conversion (per pass)	H_2/CO ratio	Cond. (T, P)	Selectivities	Ref.
Acetic Acid	1) $CO + 3H_2 \rightarrow CH_4 + H_2O$ 2) $2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$ 3) $3CO + 7H_2 \rightarrow C_3H_8 + 3H_2O$ 4) $4CO + 9H_2 \rightarrow C_4H_{10} + 4H_2O$ 5) $2CO + 3H_2 \rightarrow C_4H_4O + H_2O$ 6) $2CO + 2H_2 \rightarrow C_4H_4O_2 + H_2O$	1.12%	1.00	250 °C 10 bar	Methane: 19.55% Ethane: 7.52% Propane: 5.47% Butane: 8.83% Acetaldehyde: 3.41% Acetic Acid: 55.22%	103
Dimethyl Ether	1) $CO + 2H_2 \rightarrow CH_3OH$ 2) $CO + H_2O \rightarrow CO_2 + H_2O$ 3) $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ 4) $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ 5) $4H_2 + CO_2 \rightarrow CH_4 + H_2O$	49.00%	0.93	250 °C 40 bar	Carbon Dioxide: 33.70% Methane: 0.30% Methanol: 7.80% Dimethyl Ether: 58.20%	104
Ethylene, Propylene, iso-Butylene	1) $CO + H_2O \rightarrow CO_2 + H_2$ 2) $CO + 3H_2 \rightarrow CH_4 + H_2O$ 3) $2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$ 4) $3CO + 7H_2 \rightarrow C_3H_8 + 3H_2O$ 5) $4CO + 9H_2 \rightarrow C_4H_{10} + 4H_2O$ 6) $2CO + 4H_2 \rightarrow C_2H_4 + 2H_2O$ 7) $3CO + 6H_2 \rightarrow C_3H_6 + 3H_2O$ 8) $4CO + 8H_2 \rightarrow C_4H_8 + 4H_2O$	88.60%	2.00	347 °C 20 bar	Carbon Dioxide: 5% Hydrocarbons: 95% Sel. Dist. HC: Methane: 27.45% Ethane: 21.08% Propane: 3.42% Butane: 2.52% Ethylene: 22.60% Propylene: 4.67% isobutylene: 18.25%	105
Methanol	1) $CO + 2H_2 \rightarrow CH_3OH$ 2) $CO + H_2O \rightarrow CO_2 + H_2$ 3) $CO_2 + H_2O \rightarrow CH_3OH + H_2O$	36.81%	0.75	250 °C 52 bar	Methanol: 97% Water: 3%	104
Hydrogen	1) $CO + H_2O \rightarrow CO_2 + H_2$	83.00%	1.00	400 °C 40 bar	Hydrogen: 100%	106
Ethylene Glycol	1) $CO + H_2O \rightarrow CO_2 + H_2$ 2) $CO + 2H_2 \rightarrow CH_3OH$ 3) $2CO + 4H_2 \rightarrow C_2H_5OH + H_2O$ 4) $3CO + 6H_2 \rightarrow C_3H_7OH + 2H_2O$ 5) $2CO + 3H_2 \rightarrow C_2H_6O_2$	65.00%	0.62	220 °C 548 bar	Methanol: 30.90% Ethanol: 43.20% Propanol: 11.86% Ethylene Glycol: 14.04%	107
Methanol Ethanol Propanol nButanol	1) $CO + H_2O \rightarrow CO_2 + H_2$ 2) $CO + 2H_2 \rightarrow CH_3OH$ 3) $2CO + 4H_2 \rightarrow C_2H_5OH + H_2O$ 4) $3CO + 6H_2 \rightarrow C_3H_7OH + 2H_2O$ 5) $4CO + 6H_2 \rightarrow C_4H_9OH + 3H_2O$ 6) $CO + 3H_2 \rightarrow C_4 + H_2O$ 7) $2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$ 8) $3CO + 7H_2 \rightarrow C_3H_8 + 3H_2O$ 9) $4CO + 9H_2 \rightarrow C_4H_{10} + 4H_2O$	73.05%	1.00	300 °C 80 bar	Carbon Dioxide: 50.89% Alcohols: 23.39 % Hydrocarbons: 25.72% Sel. Alcohols: Methanol: 16.82% Ethanol: 37.58% Propanol: 22.07% nButanol: 23.54%	108

TABLE 2.7. Conditions and yields of derivatives from the biochemical conversion of carbohydrates

Product	Substrate	Yields [a] (g/g carbohydrate)		Microorganism	Carbohydrate Conversion	Cond. (T, 1) [b]	Ref.
Acetic Acid	glucose	Biomass: Ethanol: Gluconic acid: Acetic Acid:	0.0119 0.0265 0.0522 0.6225	Mixed culture *Z. mobilis* *A. aceti*	100.00%	31 °C 113.1 g/L	109
Succinic Acid	glucose	Biomass: Succinic Acid: Acetic acid: Formic Acid:	0.1400 0.7967 0.1363 0.0143	*A. succinogenes*	96.69%	32 °C 132.8 g/L	110
Acetone nButanol	glucose	Biomass: Acetone: nButanol: Ethanol: Butyric Acid:	0.0242 0.0773 0.3172 0.0129 0.0032	*C. beijerinckii*	93.00%	31.5 °C 62.1 g/L	111
Ethanol	glucose	Biomass: Ethanol:	0.0619 0.4310	*S. cerevisiae*	100.00%	31 °C 210 g/L	112
Ethanol	glucose-xylose mixtures	Biomass: Ethanol:	0.0619 0.4781	*Z. mobilis*	100.00%	31 °C 65 g/L 65 g/L	113

[a] Mass balances completed including gases (O_2, CO_2, H_2). Biomass general formula $CH_{1.9}O_{0.5}N_{0.2}$

[b] S_o refers to initial concentration of substrate

TABLE 2.8. Reactions and conditions of derivatives from the catalytic conversion of glycerol

Product	Reactions	Glycerol Conversion	Cond. (T, P)	Selectivities	Ref.
Hydrogen	1) $C_3H_8O_3 + H_2O \rightarrow 7H_2 + 3CO_2$ 2) $C_3H_8O_3 \rightarrow 4H_2 + 3CO$ 3) $CO + H_2O \rightarrow CO_2 + H_2$ 4) $CO + 3H_2 \rightarrow CH_4 + H_2O$	100 %	550 °C 1bar	Methane: 0.58% Carbon Monoxide: 5.25% Carbon Dioxide: 39.98% Hydrogen: 54.18%	114
1,3-Propanediol	1) $C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$ 2) $C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$ 3) $C_3H_8O_3 + 2H_2 \rightarrow C_3H_7OH + 2H_2O$	81.88%	170 °C 80 bar	Propanol: 42.83% 1,2-Propanediol: 19.47% 1,3-Propanediol: 37.69%	115
1,2-Propanediol	1) $C_3H_8O_3 + H_2 \rightarrow C_3H_8O_2 + H_2O$ 2) $C_3H_8O_3 + H_2 \rightarrow C_2H_6O_2 + CO + H_2$	72.00%	550 °C 1 bar	1,2-Propanediol: 97.6% Ethylene Glycol: 2.4%	116
Acrolein	1) $C_3H_8O_3 \rightarrow C_3H_4O + 2H_2O$ 2) $C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O$ 3) $C_3H_8O_3 \rightarrow C_2H_4O + CO_2 + 2H_2$ 4) $C_3H_8O_3 \rightarrow C_2H_4O_2 + CO + 2H_2$	100.00%	325 °C 1 bar	Acrolein: 84.47% Hydroxyacetone: 8.11% Acetaldehyde: 5.82% Acetic Acid: 1.60%	117

TABLE 2.9. Reactions and conditions of derivatives from the biochemical conversion of glycerol

Product	Substrate	Yields [a] (g/g glycerol)		Microorganism	Glycerol Conversion	Cond. (T, S_o) [b]	Ref.
1,3-Propanediol	glycerol	Biomass: 1,3-Propanediol: Butyric Acid: Acetic Acid: Lactic Acid:	0.0171 0.5300 0.0600 0.0300 0.0900	*C. butyricum*	100.00 %	37 ºC 70 g/L	118
Ethanol	glycerol	Biomass: Ethanol: Formic Acid:	0.0230 0.4848 0.4179	*E. coli*	95.00%	37 ºC 20 g/L	119
Propionic Acid	glycerol	Biomass: Propionic Acid: Acetic Acid: Succinic Acid:	0.1113 0.5400 0.0240 0.0650	*P. acidipropionici*	100.00%	32 ºC 40 g/L	120
Succinic Acid	glycerol	Biomass: Succinic Acid: Acetic Acid: Formic Acid:	0.0900 1.2300 0.0615 0.0861	*A. succinogenes*	100.00%	32 ºC 19.8 g/L	110

[a] Mass balances completed including gases (O_2, CO_2, H_2). Biomass general formula $CH_{1.9}O_{0.5}N_{0.2}$

[b] S_o refers to initial concentration of substrate

APPENDIX B

This section presents relevant data inputs such as production costs, CED, GHG emissions and prices. Table 2.10 shows the prices used in the analysis. Table 2.11 shows CED and GHG emissions of glycerol from biodiesel from rape oil, soybean oil and palm oil, which were updated from Jungbluth et al. (2007)[91] by using economic allocation.. Table 2.12 presents CED and GHG emissions of grains and lignocellulosic residues from wheat, corn, and rice by using economic allocation. The data of CED and GHG emissions of the lignocellulosic residues were used in the calculation of CED and GHG emissions of carbohydrates and syngas. Table 2.13 and Table 2.14 show CED, GHG emissions and production cost of pentose, hexose and lignin derived from lignocellulosic biomass by using mass and economic allocation, respectively. Table 2.15 shows CED, GHG emissions and production cost of syngas at different H2:CO ratios.

TABLE 2.10. Prices used to calculate the sustainability indicators

Chemical	Price (€/tonne)		
	EU	USA	China
Acetic Acid [a]	382	443	414
Ethanol [b]	780	598	698
Hydrogen [c]	1700	1700	1700
IsoButylene [c]	524	524	524
nButanol [d]	684	684	684
Propanol [d]	1044	1044	1044
Propylene [e]	1040	1040	1040
Ethylene [e]	1320	1320	1320
Dimethyl Ether [a]	792	864	540
Ethylene Glycol [d]	648	648	648
Methanol [f]	450	632	590
Succinic Acid [d]	1629	1629	1629
Acetone [d]	792	792	792
Acrolein [d]	1296	1296	1296
1,2-Propanediol [d]	828	828	828
1,3-Propanediol [d]	1152	1152	1152
Propionic Acid [d]	1415	1415	1415

[a] Price calculated as an average of the prices provided by suppliers in different regions from Alibaba group [121]

[b] Average price calculated from reports in energy agencies, Indexmundi and Platts McGraw Hill Financial [92, 122]

[c] Average price calculated from reports and white literature.

[d] Prices calculated as the average of the prices provided by suppliers from Alibaba group [121].

[e] Prices calculated as the average of data shown in price index from Platts McGraw Hill Financial [122].

[f] Prices obtained from Methanex corporation [123].

TABLE 2.11. Key data inputs for calculation of early stage sustainability indicators using glycerol as raw material.

Category	**Original Impacts**[a]		**Original A. Factor**[a]	**Global impacts**[b]		**Mass yields**	**Economic data**[c]		**Updated A. Factor**[d]	**Updated impacts**[e]	
Country/Region	CED* (MJ/kg)	GHG* (kg CO_{2eq}/kg)	Glycerol (%)	CED* (MJ/kg)	GHG* (kg CO_{2eq}/kg)	Glycerol/ biodiesel (kg/kg)	Biodiesel price (€/tonne)	Glycerol price (€/tonne)	Glycerol (%)	CED* (MJ/kg)	GHG* (kg CO_{2eq}/kg)
EU (Rape)	100.00	3.56	12.90	775.19	27.60	1:10	710.64	186.48	2.94	22.81	0.81
USA (Soybean)	38.70	0.85	8.00	483.75	10.59	1:10	795.00	176.40	2.50	12.09	0.26
Asia (Palm)	99.70	2.23	12.90	772.87	17.29	1:10	723.60	172.08	2.67	20.67	0.46

*CED: represented in MJ/kg of glycerol

*GHG: represented in kg CO_{2eq}/kg of glycerol

[a] Original data from Jungbluth et al. (2007)[91]. Impacts allocated to glycerol

[b] Global impacts calculated based on original allocation factors provided by Jungbluth et al. (2007)[91].

[c] Economic data adapted from literature [94] and energy agencies (US department of energy).

[d] Updated allocation factor based on economic data and mass yields.

[e] Updated impacts based on global impacts and new allocation factors.

TABLE 2.12. CED and GHG emissions of grains and lignocellulosic residues

Category [a]	CED [b] (MJ/kg)	GHG [c] (kg CO_{2eq}/kg)	Mass Yield (kg/kg Crop)	Price (€/tonne) [d]	A. Factor (%)
Wheat (Crop)	20.56	0.65	-	-	-
Corn (Crop)	20.20	0.43	-	-	-
Rice (Crop)	29.90	1.77	-	-	-
Wheat grain	29.21	0.92	0.55	212.00	78.37
Wheat Straw	9.92	0.31	0.45	72.00	21.63
Corn grain	28.67	0.61	0.50	146.00	70.96
Corn stover	11.73	0.25	0.50	59.76	29.04
Rice grain	36.61	2.17	0.78	324.00	95.51
Rice Husk	6.10	0.36	0.22	54.00	4.49

[a] Wheat represents EU, Corn represents USA and Rice represents China

[b] CED: represented in MJ/kg of the corresponding feature. For instance CED for wheat grain is expressed in MJ/kg of wheat grain.

[c] GHG: represented in kg CO_{2eq}/kg

[d] Prices from Indexmundi [92]

TABLE 2.13. CED, GHG emissions and production cost of pentose, hexose and lignin rich streams from the pretreatment and hydrolysis of lignocellulosic raw materials using mass allocation.

Stream [a]	Country/ Region [b]	Mass yields kg/kg residue	A. Factor [c] (%)	CED (MJ/kg)[d]	GHG (kg CO_{2eq}/kg)[e]	Production Cost (€/tonne)
Pentose	EU	0.16	19.58	17.64	0.77	270.57
	USA	0.16	17.86	17.48	0.61	224.21
	China	0.14	17.08	12.44	0.80	239.65
Hexose	EU	0.42	51.86	17.64	0.77	270.57
	USA	0.54	59.39	17.48	0.61	224.21
	China	0.28	33.46	12.44	0.80	239.65
Lignin	EU	0.23	28.56	17.64	0.77	270.57
	USA	0.21	22.75	17.48	0.61	224.21
	China	0.41	49.46	12.44	0.80	239.65

[a] Pentose and Hexose rich streams were assumed to have a 25 wt. % of water.

[b] EU: represented by wheat straw, USA: represented by corn stover, China: represented by rice husk

[c] mass allocation factor calculated based on mass yields.

[d,e] Values expressed per kg of the corresponding stream. For instance, for pentose it is expressed in MJ/kg of pentose. For the processing stage CED and GHG were calculated using natural gas for heating and process water for cooling [91]

Table 2.14. CED, GHG emissions and production cost of pentose, hexose and lignin rich streams from the pretreatment and hydrolysis of lignocellulosic raw materials using economic allocation.

Stream [a]	Country/ Region [b]	Mass yields kg/kg residue	A. Factor [c] (%)	CED (MJ/kg)[d]	GHG (kg CO_{2eq}/kg)[e]	Production Cost (€/tonne)
Pentose	EU	0.16	17.54	14.26	0.64	242.34
	USA	0.16	15.09	16.53	0.55	189.49
	China	0.14	18.56	13.52	0.87	260.50
Hexose	EU	0.42	69.67	23.70	1.45	363.50
	USA	0.54	75.29	22.16	1.45	284.23
	China	0.28	54.55	20.28	1.11	390.75
Lignin	EU	0.23	12.79	7.90	0.34	121.17
	USA	0.21	9.61	7.39	0.26	94.74
	China	0.41	26.88	6.76	0.44	130.25

[a] Pentose and Hexose rich streams were assumed to have a 25 wt. % of water.

[b] EU: represented by wheat straw, USA: represented by corn stover, China: represented by rice husk

[c] economic allocation factor calculated based on mass yield and price ratios of 3:2:1 for hexose: pentose: lignin

[d,e] Values expressed per kg of the corresponding stream. For instance, for pentose it is expressed in MJ/kg of pentose. For the processing stage CED and GHG were calculated using natural gas for heating and process water for cooling [91]

TABLE 2.15. CED, GHG emissions and production cost of syngas derived from lignocellulosic raw materials.

H_2/CO ratio	Country/ Region [a]	CED [b] (MJ/kg)	GHG [b] (kg CO_{2eq}/kg)	Production Cost [b] (€/tonne)
0.62	EU	10.78	0.34	123.84
	USA	11.45	0.25	99.83
	China	6.38	0.38	101.20
0.75	EU	10.74	0.34	123.34
	USA	11.41	0.24	99.42
	China	6.35	0.38	100.79
0.93	EU	9.13	0.29	104.87
	USA	9.70	0.21	84.53
	China	5.40	0.32	85.70
1.00	EU	10.54	0.33	121.07
	USA	11.98	0.26	104.46
	China	6.24	0.37	98.94
2.00	EU	18.22	0.57	209.18
	USA	22.76	0.49	198.37
	China	11.28	0.67	179.02

[a] EU: represented by wheat straw, USA: represented by corn stover, China: represented by rice husk.

[b] Values represented per kg of syngas at its corresponding H_2/CO ratio. For the processing stage CED and GHG were calculated using natural gas for heating and process water for cooling [91]

APPENDIX C

This appendix presents routes and relevant data associated to petrochemical counterparts of each of the derivatives analyzed. The data showed is related to EU.

TABLE 2.16. Conventional routes used as petrochemical counterparts in the early stage sustainability assessment of derivatives from syngas, carbohydrates and glycerol.

Product	Conventional (petrochemical) Route	Raw Material	CED [a] (MJ/kg)	GHG [a] (kg CO_{2eq}/kg)	Price (€/tonne)
Dimethyl Ether	Dehydration of methanol	Methanol	40.40	1.17	450 [b]
Ethylene Glycol	Hydration of ethylene oxide	Ethylene Oxide	59.30	1.81	1170 [c]
Methanol	Direct Synthesis from syngas	Coal-based syngas	6.37	0.38	109 [d]
Acetic Acid	Methanol carbonylation	Methanol	40.40	1.17	450 [b]
Ethanol	Ethylene Hydration	Ethylene	60.40	0.71	1320 [b]
Hydrogen	Steam cracking of methane	Methane	58.27	0.52	143 [e]
nButanol	Ethylene Hydroformylation	Propylene	65.80	1.31	1040 [b]
Propanol	Propylene Hydroformylation	Ethylene	60.40	0.71	1320 [b]
Ethylene	Steam cracking of naphtha	Naphtha	50.10	0.37	668 [f]
Propylene	Steam cracking of naphtha	Naphtha	50.10	0.37	668 [f]
Isobutylene	Steam cracking of naphtha	Naphtha	50.10	0.37	668 [f]
Acetone	Via cumene process	Cumene	79.50	2.31	976 [c]
Succinic Acid	Oxidation of 1,4-Butanediol	1,4-Butanediol	97.00	4.35	1476 [g]
1,2-Propanediol	Hydration of propylene oxide	Acrolein	65.80	1.31	1296 [b]
1,3-Propanediol	Hydration of acrolein	Propylene oxide	93.50	3.32	1260 [g]
Acrolein	Oxidation of propylene	Propylene	65.80	1.31	1040 [b]
Propionic Acid	Hydrocarboxylation of ethylene	Ethylene	60.40	0.71	1320 [b]

[a] Values referred to raw materials
[b] Sources presented in Table 2.10 (Appendix B)
[c] Prices obtained from ICIS pricing [124]
[d] Cost obtained using the same approach to calculate bio-based syngas
[e] Price estimated as natural gas, Indexmundi [92]
[f] Average price calculated from reports and white literature
[g] Prices calculated as the average provided by suppliers from Alibaba group [121]

APPENDIX D

This appendix shows the procedure to calculate the aggregated single score of the bio-based process and the fossil-based process for the production of succinic acid. The indicators were calculated according to the model presented in Table 2.1. These results are shown in Table 2.17 for the different scenarios (EU, USA, China). Secondly, the indicators were normalized according to the procedure explained above. These results are presented in Table 2.18. Finally, the normalized indicators were multiplied by the weighting factors and aggregated into a single score as shown in Table 2.19. Based on the aggregated single scores, the index ratio is then calculated. The contribution of each indicator on the single score for the bio-based process and the fossil-based process is shown in Figure 2.7. The aforementioned procedure was repeated for each system from each case study (36 systems in total), as well as for the values considered in the sensitivity and scenario analyses.

TABLE 2.17. Early stage sustainability indicators for succinic acid

Indicators	Scenario 1: EU		Scenario 2: USA		Scenario 3: China	
	Bio-based	Fossil-based	Bio-based	Fossil-based	Bio-based	Fossil-based
Economic constraint	0.19	0.69	0.16	0.69	0.17	0.69
CED (MJ/Kg prod) (allocated)	20.48	76.40	20.12	76.40	14.40	76.40
GHG (Kg CO2-eq/Kg prod) (allocated)	0.89	4.92	0.70	4.92	0.93	4.92
Process Complexity	2.60	2.27	2.60	2.27	2.60	2.27

TABLE 2.18. Normalized early stage sustainability indicators for succinic acid.

Normalized Indicators	Scenario 1: EU		Scenario 2: USA		Scenario 3: China	
	Bio-based	Fossil-based	Bio-based	Fossil-based	Bio-based	Fossil-based
Economic constraint	0.28	1.00	0.23	1.00	0.25	1.00
CED	0.27	1.00	0.26	1.00	0.19	1.00
GHG	0.18	1.00	0.14	1.00	0.19	1.00
Process Complexity	1.00	0.87	1.00	0.87	1.00	0.87

TABLE 2.19. Normalized and weighted early stage sustainability indicators, single score and index ratio for succinic acid.

Normalized and Weighted indicators	Scenario 1: EU		Scenario 2: USA		Scenario 3: China	
	Bio-based	Fossil-based	Bio-based	Fossil-based	Bio-based	Fossil-based
Economic constraint	0.11	0.40	0.09	0.40	0.10	0.40
CED	0.04	0.15	0.04	0.15	0.03	0.15
GHG	0.03	0.15	0.02	0.15	0.03	0.15
Process Complexity	0.30	0.26	0.30	0.26	0.30	0.26
Aggregated single score	**0.48**	**0.96**	**0.45**	**0.96**	**0.46**	**0.96**
Index Ratio (Bio-based/Fossil-based)	**0.50**		**0.47**		**0.47**	

Weighting factors EC=0.40, CED=0.15, GHG=0.15, PC=0.30

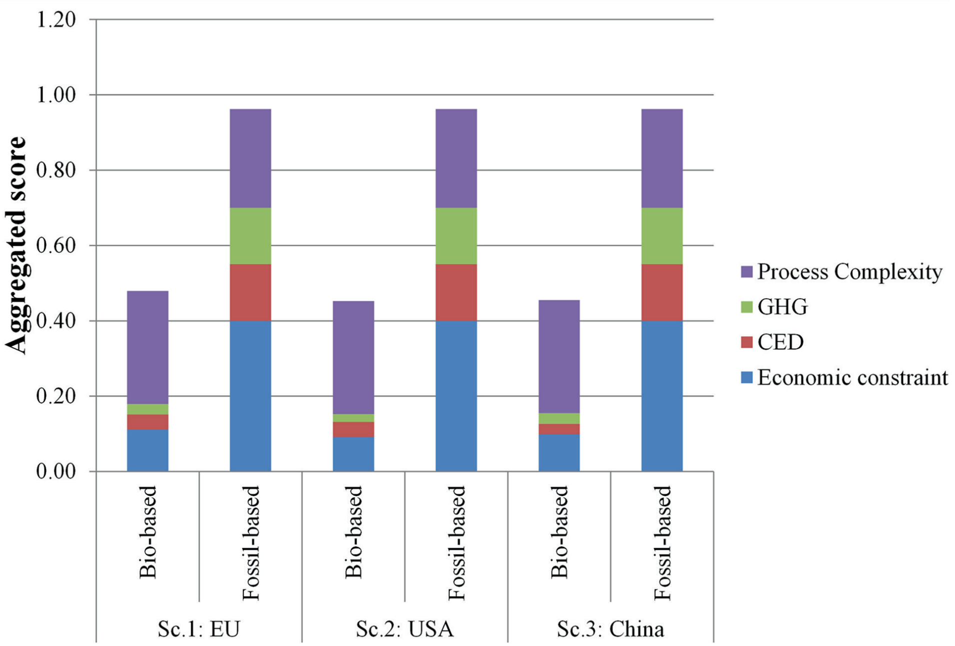

FIGURE 2.7. Aggregated single score for succinic acid from carbohydrates. Comparison of bio-based and fossil-based routes in EU, USA and China.

APPENDIX E

This appendix shows the aggregated single score and the contribution of each indicator of each system for the bio-based and the fossil-based processes, which were later used to calculate the index ratios (Figure 2.3 to Figure 2.6). The aggregated scores presented in this appendix correspond to the values in Europe. Figure 2.8 and Figure 2.9 show the aggregated single score for the systems from the syngas platform. Figure 2.10 and Figure 2.11 show the aggregated single score for the systems from the carbohydrates platform. Figure 2.12 and Figure 2.13 show the aggregated single score for the systems from the glycerol platform.

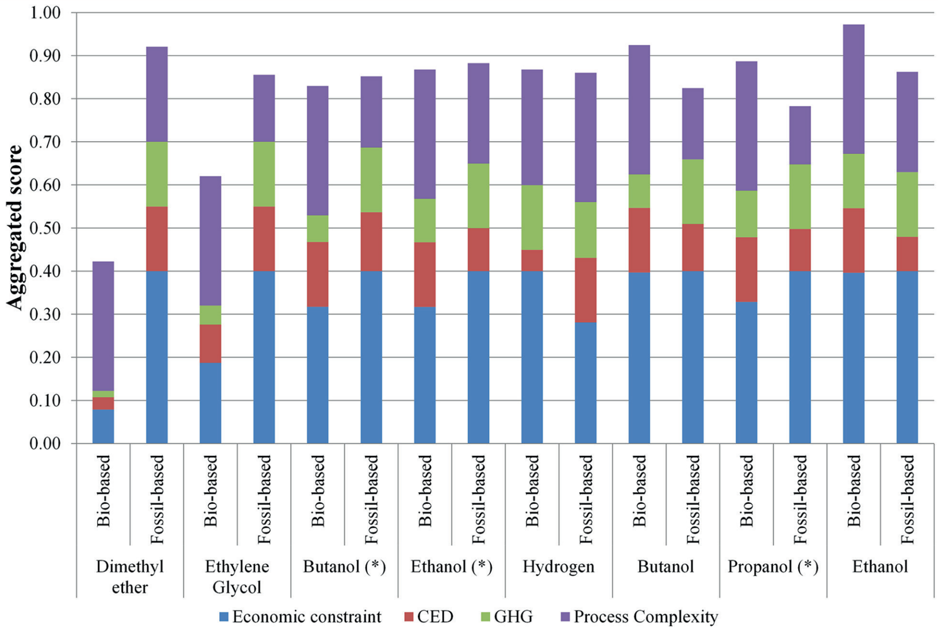

FIGURE 2.8. Aggregated single scores for the systems from the catalytic conversion of syngas in EU (Part 1).

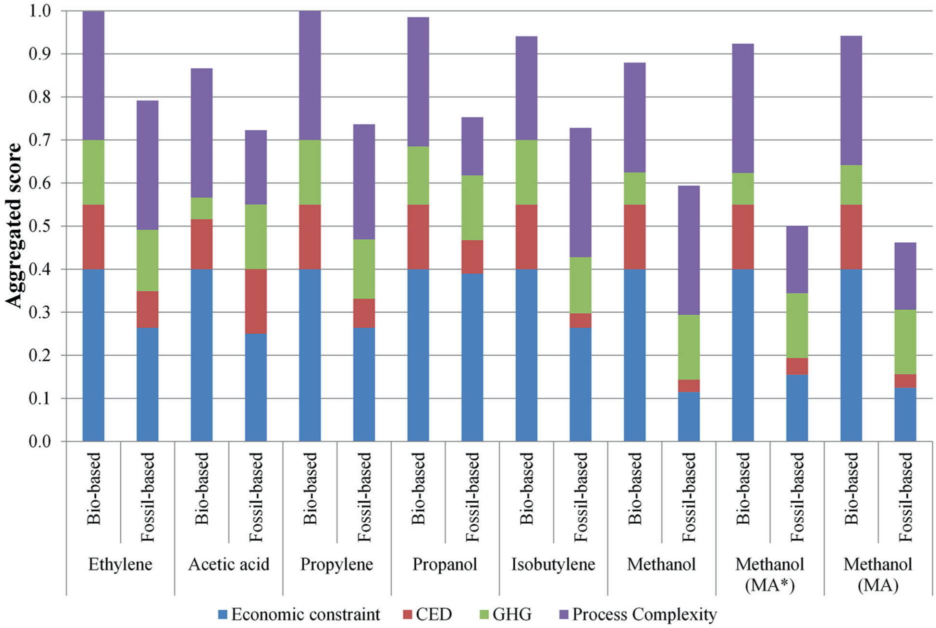

FIGURE 2.9. Aggregated single scores for the systems from the catalytic conversion of syngas in EU (Part 2).

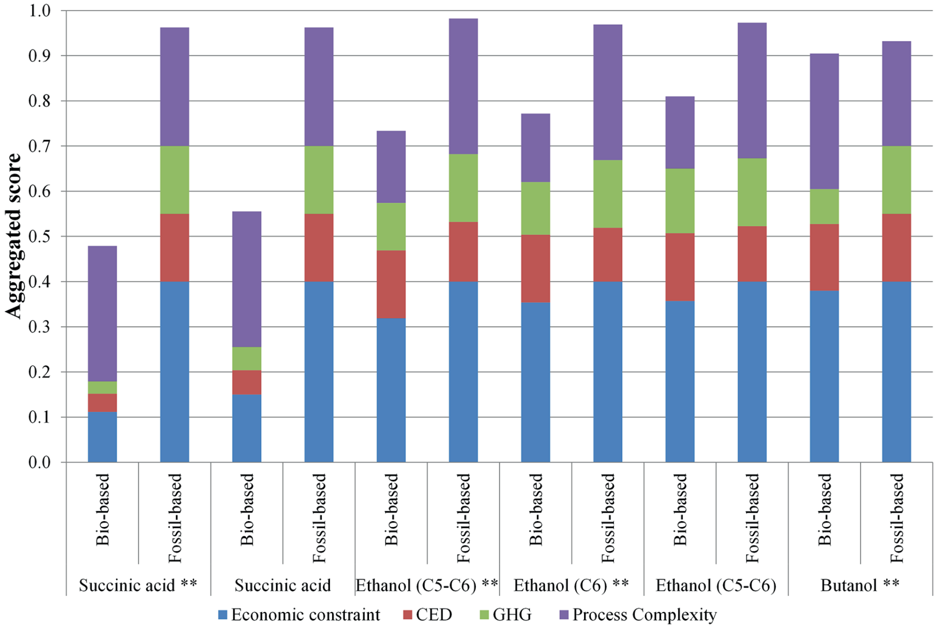

FIGURE 2.10. Aggregated single scores for the systems from the biochemical conversion of carbohydrates in EU (Part 1).

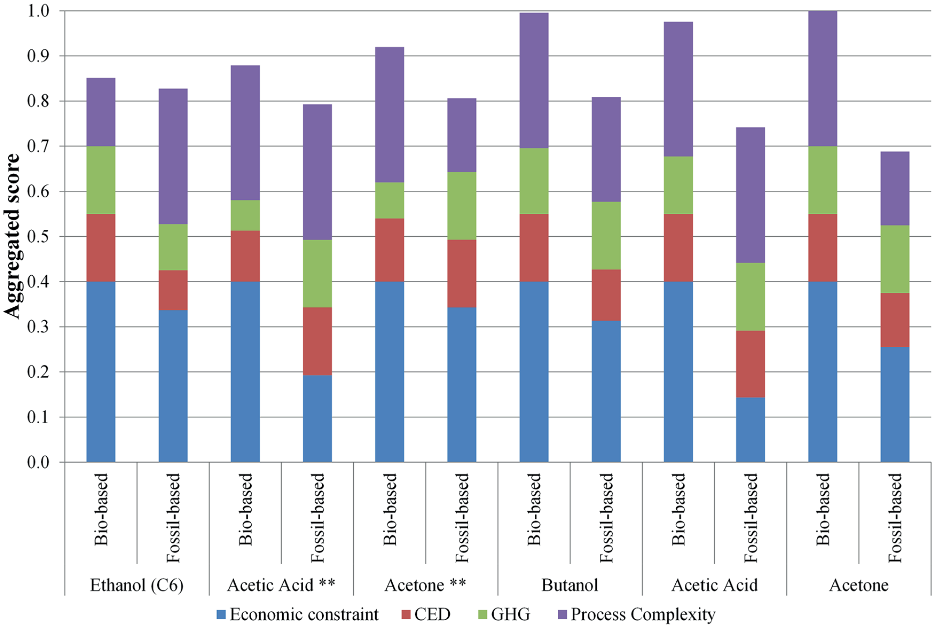

FIGURE 2.11. Aggregated single scores for the systems from the biochemical conversion of carbohydrates in EU (Part 2).

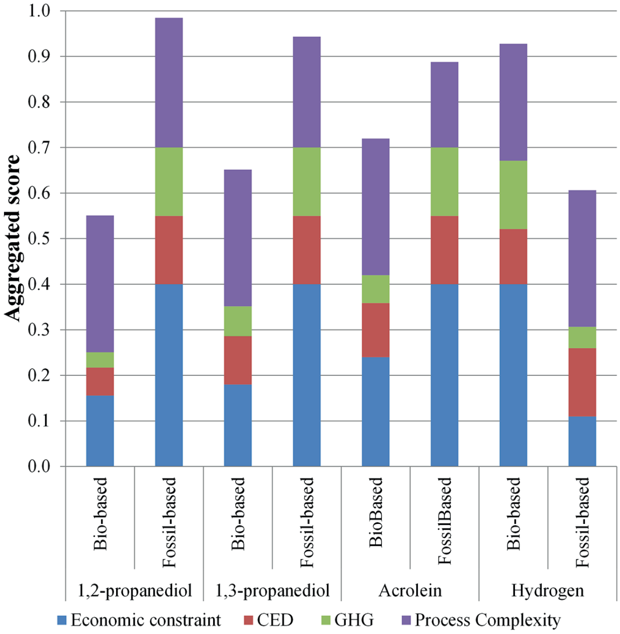

FIGURE 2.12. Aggregated single scores for the systems from the catalytic conversion of glycerol in EU.

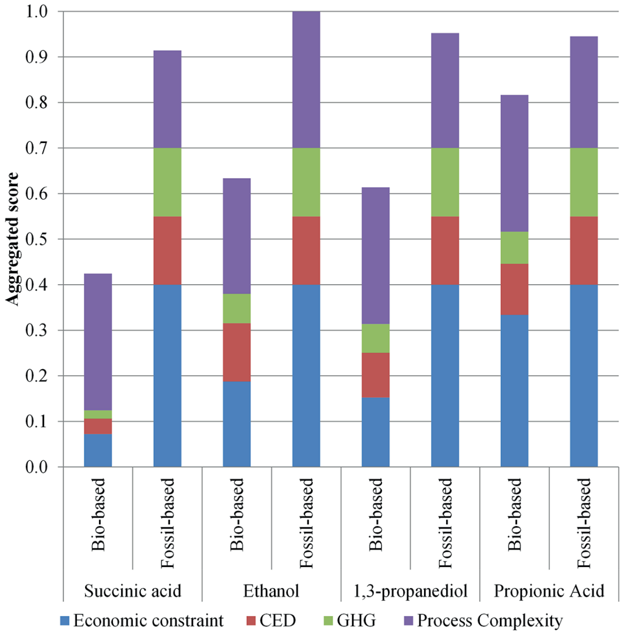

FIGURE 2.13. Aggregated single scores for the systems from the biochemical conversion of glycerol in EU.

CHAPTER 3

Comparative early stage assessment of multiproduct biorefinery systems: an application to the isobutanol platform

Published: Moncada J., Posada J.A., Ramírez A.
Comparative early stage assessment of multiproduct biorefinery
systems: an application to the isobutanol platform. 2017.
Bioresource Technology 241, 44-53.

ABSTRACT

An early stage assessment method is applied to the production of isobutanol from lignocellulosic biomass, and to three multiproduct portfolios from the conversion of isobutanol: Case 1: production of isobutyl acetate and glycerol tert-butyl ether (GTBE), Case 2: production of isobutyl acetate and ketones, and Case 3: production of isobutyl acetate alkanes. The method screens and compares each route with its equivalent petrochemical counterpart. The method is composed by different indicators involving economic and environmental aspects. Sensitivity analyses were carried out to account for variation in prices, weighting factors and distribution of isobutanol to isobutyl acetate (in multiproduct portfolios). Results show that bio-based isobutanol has advantages over fossil-based isobutanol. In multiproduct systems, case 1 performs better, followed by cases 2 and 3. Screening using economic or environmental aspects show to have a significant effect on the results, where bio-based systems tend to perform better when environmental aspects are included.

3.1. INTRODUCTION

Isobutanol is an important building block with broad applications in markets such as solvents, coatings, paints, fuels and as precursor for the production of commodity chemicals [125]. Traditionally, isobutanol has been produced from the hydroformylation of propylene (oxo process) [126]. In recent years, there has been great interest in producing isobutanol from sugars [127]. Gevo Inc. and Butamax Advance Biofuels-LCC are two companies producing bio-based isobutanol, and recently confirmed a global cross-license and settlement agreements to open clear paths on the development of markets for bio-based isobutanol [128].

There are several pathways to obtain fuels and chemicals from isobutanol. Isobutanol can be dehydrated into isobutylene, which is a feedstock for products such as tertiary butyl ethers for fuel additives (*e.g.,* glycerol tertiary butyl ether (GTBE))[129], p-xylene [130], isooctane [131] and polymers [132]. Other application of isobutanol is its cross condensation with acetone to produce ketones (C7-C11), which can further be converted into alkanes/alkenes, amines as fuel and fuel additives [133, 134]. Isobutanol is also used in estherification and transestherification reactions for producing isobutyl acetate which has broad applications in inks, coatings and adhesives, among others [135].

Given the several options for isobutanol applications, there appear many alternatives to develop process schemes. An important element on designing new processes is the integrated assessment of technical, economic and environmental aspects. The classical approach for assessing and selecting the most promising routes involves the full process design followed by economic analysis and ex-ante environmental assessment. Nevertheless, depending on the stage of development, availability of data (*e.g.,* downstream processing configuration, utilities consumption, equipment sizing) can be limited to perform a comprehensive analysis. Alternatively, early stage assessment methods (*i.e.,* including technical, economic and environmental aspects) have been used in previous works for screening bio-based derivatives [50, 136]. On top of this, most of literature on bio-based isobutanol production focuses on experimental work (*e.g.,* [127, 137]) and literature is scarce on isobutanol production from a systems analysis perspective. The major contribution is from Tao et al., [138], who carried out a detailed techno-economic and life cycle assessments on isobutanol production, and its comparison to ethanol and butanol. Nevertheless, conversion of isobutanol into prospective products was not covered. Literature is also scarce on early techno-economic and environmental assessment of multiproduct biorefinery systems using isobutanol as feedstock. In this study, the early assessment is applied for both the production of isobutanol from lignocellulosic biomass, and the conversion of isobutanol into isobutyl acetate, Glycerol tert-butyl ether and C7- C11-ketones and alkanes following a multiproduct biorefinery approach. Both isobutanol production and its conversion of value-added products are novel processes. The goal of this study is threefold: *i)* to assess the early performance of bio-based isobutanol in comparison to its petrochemical counterpart; *ii)* to screen and compare integrated multiproduct biorefinery systems for the conversion of isobutanol; and iii) to assess to which extent the early assessment method can be applied to integrated portfolios and how the screening based on solely economic or environmental aspects affect the comparisons.

3.2. MATERIALS AND METHODS

A first level of analysis corresponds to the comparison (early stage) of standalone bio-based isobutanol against standalone fossil-based isobutanol, while a second level focuses on the comparison of multiproduct systems from the conversion of isobutanol (both bio-based and fossil based). For both levels, the approach consisted of 3 main steps: i) basis of design ii) process modeling and iii) early assessment. Each step is explained below.

3.2.1. Basis of Design

This section focuses on the data, process steps and assumptions to calculate the mass and energy balances of the reaction system(s) of both standalone isobutanol (bio-based and petrochemical) and integrated multiproduct schemes.
Isobutanol production

Bio-based route

The system for producing bio-based isobutanol from lignocellulosic biomass is composed of two sections: i) biomass pretreatment and ii) hydrolysis and fermentation (see Figure 3.1a). There are different technologies to pretreat lignocellulosic biomass. In this work, organosolv was selected as pretreatment technology due to the interest on producing high quality lignin and the possibility to obtain relatively high purity pulp to further convert it into C6 sugars [139]. The resulting C6 sugars are subsequently converted into isobutanol by action of yeasts.

Spruce wood was used as feedstock and acetone as solvent. The organosolv reactor was modeled at 150 ºC, acetone concentration 60 wt% in water, sulfuric acid as catalyst with a dosage of 60 mM, a solvent to biomass ratio of 5 L per kg and an operating pressure of 15 bar. Conditions were gathered based organosolv of spruce [140]. A pulp yield of 45% (based on initial biomass loading) and a lignin yield of 75% were obtained experimentally (based on initial lignin content). The reactions describing organosolv fractionation were set to match the pulp and lignin yields. After the pretreatment stage, the solvent is recovered and recycled (see Appendix C) .The cellulose rich pulp is enzymatically hydrolyzed to produce a C6 sugars rich stream assuming a conversion rate of 95% [141]. Next, the hydrolyzed liquor (rich in C6 sugars) is used as substrate to produce isobutanol assuming 93% of the theoretical yield to account for cell growth and product formation. C6 sugars derived from organosolv fractionation (hemicellulose fraction rich in mannan which are hydrolyzed into C6 sugars, see Table 3.5 and Table 3.6 in Appendix) are also used to feed the fermentation step.

Fossil-based route

The fossil-based route also comprises two main steps (see Figure 3.1b): i) steam reforming of methane and ii) hydroformylation of propylene into butyraldehydes and butanols. Steam reforming of methane produces syngas (H_2: CO ratio 3:1), which later reacts with propylene to produce butyraldehyde, isobutanol and n-butanol. The excess of hydrogen is assumed as a co-product of the system. Reactions and conversions were calculated based on the work presented by Sutter [142].

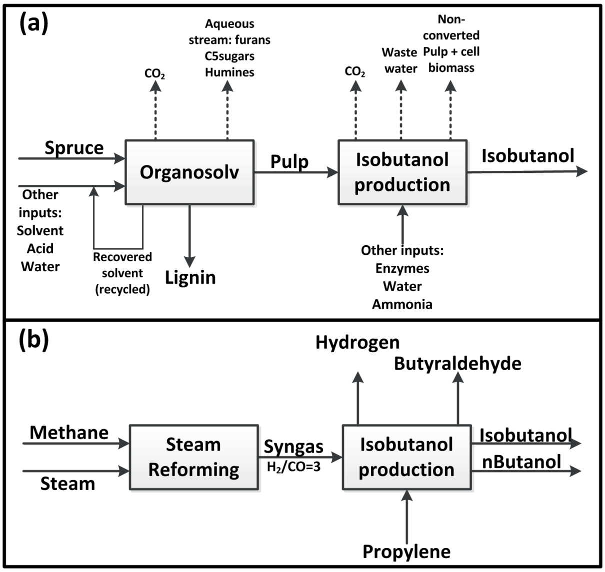

FIGURE 3.1. Simplified flow diagram of the different steps of isobutanol production: a) bio-based isobutanol, b) fossil-based isobutanol. Dotted streams represent waste streams

Integrated multiproduct biorefinery cases

The downstream conversion of isobutanol considers four end possible products: i) Glycerol Tert-butyl Ether (GTBE), ii) Acetone-isobutanol condensation products, iii) hydrogenated acetone-isobutanol condensation products, and iv) isobutyl acetate. In this chapter, three configurations of multiproduct systems are considered. The three multiproduct systems aim to include two processing lines for obtaining one product with material application (*i.e.,* isobutyl acetate), and one product with fuel or fuel additive application (*e.g.,* GTBE, ketones or alkanes). A multiproduct integrated biorefinery approach was adopted to model the three systems, as this has shown to be beneficial for the overall performance of the integrated concept over standalone decentralize production lines as previously discussed in literature [143, 144]. As isobutanol is the initial feedstock for the two processing lines in each case, it needs to be distributed between each one. Explanation of each case is provided below.

Case 1

This case considers the joint production of isobutyl acetate and GTBE as final products from the conversion of isobutanol, which is assumed to be distributed (either bio-based or fossil-based) in a 50:50 ratio (see Figure 3.2a). The production of isobutyl acetate corresponds to the estherification of acetic acid and isobutanol. This reaction was modeled at equilibrium (Gibbs free energy minimization) at 60 ^{o}C and 1 bar, and acetic acid: isobutanol feed ratio of 2:1 (mol basis). Non-converted acetic acid and isobutanol are recycled back to the reaction stage.

In the case of GTBE production, two conversion steps are needed. The first one is the dehydration of isobutanol into isobutylene at 290 ^{o}C and 51.5 bar according to Lin et al., [130]. The second conversion step involves the production of GTBE from glycerol and isobutylene considering an isobutylene to glycerol feed ratio of 2 (mol basis), 90 ^{o}C and 15 bar [145]. GTBE is considered a mixture of di- and tri-GTBE, thus mono-GTBE is recycled to the reactor to further be converted into di and tri-GTBE. Butenes obtained in both isobutylene and GTBE stages are considered as co-products. Note that in this chapter the integrated production of GTBE and isobutyl acetate is assessed for both bio-based and fossil-based isobutanol.

Case 2

This case considers the production of isobutyl acetate and isobutanol-acetone condensation ketones as final products, also assuming a distribution ratio of 50:50 for isobutanol (see Figure 3.2b). The production of isobutyl acetate is analogue to that explained in Case 1. The production of isobutanol-acetone condensation products (C7 &

C11 ketones) is carried-out at 330 ºC, 5 bar and acetone to alcohol feed ratio of 2:1 (mol basis) according to Breitkreuz et al., [134]. Both, non-converted isobutanol and acetone are recycled back to the reactor.

Case 3

This case considers the production of isobutyl acetate and hydrogenated isobutanol-acetone condensation products (C11 Alkanes), assuming an isobutanol distribution in a 50:50 ratio (see Figure 3.2c). The production of isobutyl acetate is analogue to that explained in Cases 1 and 2. The production of condensation products (C7 & C11 ketones) is analogous to that explained in Case 2. However, non-converted isobutanol and acetone, and C7 ketones are recycled to shift the reaction to C11-ketones. After this, the C11-ketones are hydrogenated into C11-Alkanes. Reactions for the three cases can be found in Appendix C.

3.2.2. Process Modeling

Given the early stage of development, block diagrams displayed in Figure 3.1 and Figure 3.2 were modeled in Aspen Plus v8.4 (Aspen Technology, Inc., USA) to generate their overall mass balances, which are the basis for the early assessment. Each conversion step (process) considers the ideal separation of solvents, products, co-products and non-converted reactants, which are recycled back to complete conversion. This assumption is in accordance to the level of detail of the early assessment method [50, 136]. The plant capacity was set to 1000 ktonne/year of spruce wood chips (dry basis) for the bio-based routes (water content assumed as 10 wt%). This capacity is fixed in order to obtain high volume of products (benefiting from the economies of scale) for a biorefinery located in Rotterdam, the Netherlands. The chemical composition of spruce wood used to model spruce in Aspen Plus was gathered from the work of Constant et al., [140]. The size of the petrochemical route was set to match the isobutanol capacity produced in the bio-based route.

Physicochemical properties for lignin and hemicellulose were manually introduced into Aspen Plus v8.4 property databases and obtained from Wooley & Putsche., [146]. In other cases, if the molecular structure is known and can be drawn in the compound wizard of Aspen Plus v8.4, it was exported into the properties module which uses experimental data reported by the National Institute of Standards and Technology (NIST). The nonrandom two-liquid (NRTL) thermodynamic model was used to calculate the activity coefficients of the liquid phase and the Hayden O'Connell equation of state was used to describe the vapor phase.

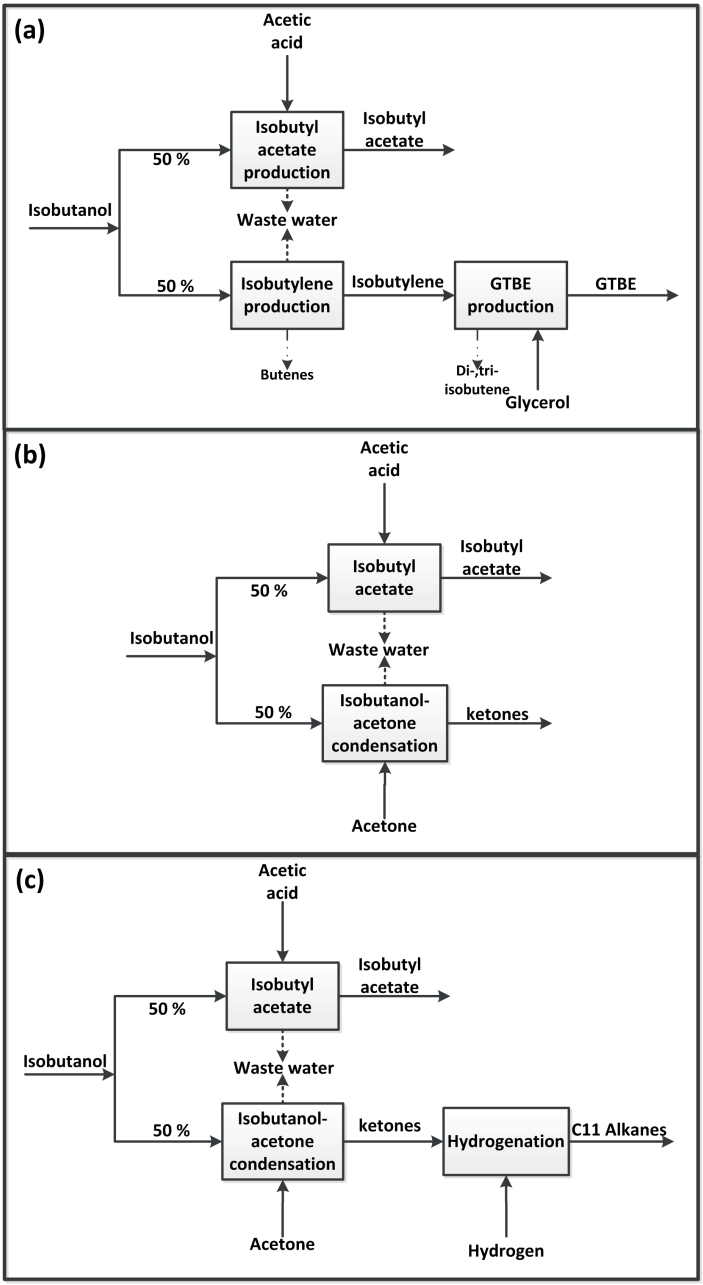

FIGURE 3.2. Simplified block diagrams of isobutanol conversion into isobutyl acetate, glycerol tert-butyl ether (GTBE), ketones and alkanes: a) integrated production of isobutyl acetate and GTBE, b) integrated production isobutyl acetate and ketones (acetone-isobutanol condensation products), c) integrated production of isobutyl acetate and C11-alkanes.

3.2.3. Early stage assessment

Three early assessment indicators compose the method: economic constraint (EC), energy related impacts of raw materials (EIRM) and process complexity (PC) [136]. The indicator economic constraint (EC) represents the ratio of raw material costs to the value of marketable products and co-products, which is a simplified approach to evaluate the economic potential of a process alternative (nevertheless incomplete since it only accounts the raw material contribution in the cost section [136, 147]). A ratio lower than "1" indicates a potential economic benefit [136, 147].

The indicator energy related impacts of raw materials (EIRM) is composed by the cradle-to-gate cumulative energy demand (CED, MJ per functional unit) and greenhouse gas emissions (GHG, kg of CO_2-eq per functional unit). For both standalone isobutanol production (see Figure 3.1), and multiproduct systems (see Figure 3.2) the functional unit is 1 kg of isobutanol. This relies on the fact that isobutanol is not only the main product from the conversion of biomass, but also the intermediate for the multiproduct systems. All systems are multiproduct portfolios (*i.e.,* several products are produced), which implies multi-functionality. There are multiple approaches to address multi-functionality [148]. In this case the upstream section of isobutanol production (*i.e.,* standalone isobutanol systems and upstream section of multiproduct systems) was subdivided from the downstream conversion of isobutanol (*i.e.,* multiproduct systems described above). System expansion is also not possible since many of the co-products do not have identical fossil counterparts (*e.g.,* lignin), therefore, including additional functions of the co-products within the system boundaries can be a very difficult task. Allocation of both GHG and CED of the raw materials is therefore necessary among all co-products. Therefore, allocation is applied for the isobutanol production step (*i.e.,* standalone systems and upstream section of multiproduct systems).

According to the ISO guidelines [148], when allocation cannot be avoided, the environmental burdens of a system need to be first partitioned between the functions reflecting the physical relationships between them. In case where physical relationships cannot be established, other approaches for partitioning can be adopted (such as allocation based on the economic value of the functions) [148]. Following this reasoning, mass allocation is preferred over economic and energy allocation, since mass flowrates represent a physical relationship between the functions of the system and exclusively depend on the technology performance. Energy allocation may also be used as it also depends on physical relationships of the functions, however, it is avoided since the products obtained in each system have material functionality rather than energy functionality. Economic allocation is avoided, first following the ISO guidelines [148], and second due to high uncertainty on prices assigned to each product (for instance high uncertainty in lignin price). In the case of downstream conversion of isobutanol allocation is avoided by the selection of the functional unit.

Process complexity provides an indication of the possible extra costs and environmental impacts of processing stage related to one conversion step, by considering 6 categories: i) downstream processing; ii) concentration of main product; iii) inherent reaction mass loss; iv) reaction enthalpy; v) number of co-products; and vi) reaction pressure [136].

The three early assessment indicators were applied to both the bio-based and fossil-based routes. Each indicator was normalized by the maximum (*i.e.,* the worst) score of the two processes that are being compared (bio-based vs. fossil-based). The three indicators were aggregated into a single score by using the following weighting factors: 40% for EC, 30% for EIRM (15% CED, 15% GHG) and 30% PC [136] (overview of weighting factors can be found in Appendix A, Figure 3.7). These weighting factors are based on expert elicitations [136, 147]. These indicators can be grouped into economic and environmental aspects. The indicator PC aims to mimic both costs and environmental impacts of the processing stage, thus 50% of its weighting can be split into economic aspects while the remaining 50% into environmental aspects. By grouping the indicators, the weighting factor would be 55% and 45% for economic and environmental aspects, respectively. The weighting factors reflect economic feasibility as the first requirement to implement a process on a commercial scale and long term sustainability should be complemented by reduction of environmental impacts [136].

The single scores of the bio-based and fossil-based routes are related through an index ratio, defined as the score of the bio-based route over the score of the fossil-based route. Index ratios lower than 1 indicates a better performance of the bio-based system in comparison to the petrochemical system. Index ratios higher than 1 indicates better performance of the petrochemical system in comparison to the bio-based system.

For multiproduct systems and following the multiproduct biorefinery approach, all indicators are calculated for the integrated cases rather than the standalone processing lines. Thus, the EC and EIRM indicator reflect the influence of each processing line and the distribution of isobutanol on the multiproduct system. The calculation of EC and EIRM indicators are based on information supplied in Appendix D. For instance, the EC indicator of case 1, is calculated using revenues of products and raw material costs from the isobutyl acetate, GTBE processes, and the upstream section (*e.g.,* lignin revenues in the case of bio-based isobutanol). In consequence, in case that the distribution of isobutanol changes, and accounting for the difference in prices between GTBE and isobutyl acetate, the EC indicator can also change. Same reasoning is followed for the EIRM indicator where all raw materials of all processes contribute to this indicator. For instance, glycerol used in GTBE production and acetic acid used in the isobutyl acetate process contribute to the EIRM indicator, together with the upstream EIRM of isobutanol production. In consequence, in case that the isobutanol distribution changes, the contribution of glycerol or acetic acid on the overall EIRM can also change and a different proxy can be obtained. However, since the fossil route and the bio-based route consider identical downstream conversion processes, and because the index ratio is used as proxy to relate both the fossil and bio-based routes, the difference in EIRM can only be reflected in the difference in feedstock to produce isobutanol (*i.e.,* lignocellulosic biomass, or propylene and methane). The PC indicator can be used for processes with more than one conversion step by adding the PC indicator of each conversion step into one global PC indicator for each multiproduct biorefinery structure. For the multiproduct systems, aggregation of the indicators followed the same approach as described above (Individual PC indicator is shown in Appendix E).

3.2.4. Prices and energy related impacts of raw materials

Two types of data inputs are used in the current study. The first one corresponds to data on the process level (process modeling). The second type of inputs corresponds to prices, and energy related impacts of the raw materials, which are required to calculate the assessment indicators. Table 3.1 displays the cumulative energy demand (CED) and greenhouse emissions (GHG) of the raw materials involved in each scheme. Table 3.2 shows the input prices for both raw materials and products.

TABLE 3.1. CED and GHG data of raw materials. Input data for calculation of early stage assessment indicators.

Raw Material	CED MJ/kg	GHG kgCO_2eq/kg	Remark	Source
Biomass	0.72	0.03	Spruce chips at mill	[149]
Sulfuric Acid	2.12	0.12	At plant in Europe	[149]
Enzyme	2.10	0.12	Assumed as protein	[149]
Ammonia	39.90	1.91	At plant in Europe	[149]
Propylene	68.50	1.43	At plant in Europe	[149]
Natural Gas	42.80	0.33	At pipeline in The Netherlands	[149]
Steam [a]	3.19	0.18	At plant in Europe, fuel: Natural gas	[149]
Hydrogen	72.50	1.70	At plant in Europe: from steam reforming of methane	[149]
Acetic Acid	53.40	1.54	At plant in Europe	[149]
Glycerol	22.81	0.81	At biodiesel plant in Europe	Updated from [136]
Acetone	67.40	2.23	At plant in Europe	[149]

[a] Latent heat: 2.80 MJ/kg

TABLE 3.2. Summary of input prices used to calculate the economic constraint calculator.

Feature	Value	Unit	Source
Biomass	100	€/tonne (dry)	Based on [150]
Sulfuric Acid	220	€/tonne	Average from [151]
Cellulase Enzyme cocktail	2000	€/tonne	[152]
Ammonia	308	€/tonne	Average from [151]
Lignin	630	€/tonne	[152]
Propylene	600	€/tonne	Estimated production costs, from refinery
Natural Gas	11	€/GJ	[153]
Steam [a]	44	€/tonne	Based on [154] and updated to 2014 price
Isobutanol	1200	€/tonne	Average from [151]
n-Butanol	680	€/tonne	[136]
Butyraldehyde	3000	€/tonne	Assumed based on [155]
Hydrogen	1700	€/tonne	[136]
Acetic Acid	540	€/tonne	Average from [151]
Glycerol	200	€/tonne	Updated from [136]
Acetone	780	€/tonne	[136]
Isobutyl acetate	1400	€/tonne	Average from [151]
GTBE	900	€/tonne	Assumed, based on fuel prices
C7/C11 ketone	1000	€/tonne	Assumed, based on fuel prices
Alkanes	1000	€/tonne	Assumed, based on fuel prices

[a] Latent heat: 2.80 MJ/kg

3.2.5. Sensitivity Analysis

The early assessment of the routes is highly affected by input parameters. To assess this influence, several sensitivity analyses are taken into account. The first accounts for sensitivity on prices due to possible volatility and uncertainty considering changes up to 100% below and above the reference values (see Table 3.2). Afterwards we assessed the influence of isobutanol distribution varying it from 0 to 100% going to isobutyl acetate. This will allow accounting the effect on the index ratio for a distribution of isobutanol that leads to standalone GTBE and condensation products (0% isobutanol distributed to isobutyl acetate), and also accounting for a distribution of isobutanol leading to standalone isobutyl acetate production (100% isobutanol distributed to isobutyl acetate). Finally, the potential impact of weighting of economic and environmental aspects was assessed. One could argue that the comparison of two processes can be carried out by means of economic aspects excluding environmental aspects, or by means of environmental aspect excluding the economic aspects. The sensitivity analysis considers the effect on the index ratio up to 100% contribution of economic aspects is considered, and in the case of up to100% contribution of environmental aspects. The latter implies sensitivity analysis of the weighting factor used for aggregating each indicator in a single score.

3.3. RESULTS AND DISCUSSION

3.3.1. Mass balances

Standalone systems

The early indicators build on the overall mass balances of each system. In the case of standalone bio-based isobutanol production, the main products are isobutanol and lignin with yields of 0.23 and 0.20 kg per kg of dry biomass processed, respectively. These yields are used to calculate mass allocation factors which later are used in the calculation of both CED and GHG indicators (46% for isobutanol). Regarding input streams, acetone is required at a rate of 2.87 kg per kg of dry biomass, however, it is 100% recovered within the system boundaries. Additional inputs account for water for dilution (3.12 kg/kg dry biomass), sulfuric acid (0.03 kg/kg dry biomass), enzyme (0.10 kg/kg dry biomass), and ammonia (0.02 kg/kg dry biomass). Additional outputs (assumed as waste) consists of CO_2 (0.24 kg/kg dry biomass), waste water containing humins, furans and C5 sugars (0.73 kg/kg dry biomass), waste water (2.81 kg/kg dry biomass) and non-converted pulp (0.09 kg/kg dry biomass). The high rate of solvent and water for dilution suggest that prospective separation stages could be difficult and required significant amounts of energy, and thus high process complexity indicator may be expected.

In the case of fossil-based production isobutanol, n-butanol, butyraldehyde and hydrogen are obtained as products with yields of 0.11, 1.39, 0.25 and 0.06 kg per kg of propylene feed. The mass allocation factor for isobutanol corresponds to 6%. Additional inputs are natural gas and steam at rates of 0.38 and 0.43 kg per kg of propylene feed. This system does not show waste streams (at the level of detail assumed for the early assessment), which suggest that the process complexity indicator may be lower than that of the bio-based system. Other important factor is the difference in allocation factors where the contribution of isobutanol in the bio-based process is factor 7 higher than that of the fossil-based process. For both the bio and fossil processes, the overall capacity of isobutanol production is equivalent to 197 ktonne/y.

Multiproduct portfolios

The downstream conversion of isobutanol is analogous for both the bio-based and fossil-based routes. For case 1, isobutyl acetate is produced at a rate of 1.57 kg per kg of isobutanol. At the base case distribution (50% of isobutanol going to this process, 98 ktonne/y), 154 ktonne of isobutyl acetate are produced yearly. Waste water is also obtained in this process (0.27 kg/kg isobutanol). Acetic acid is consumed at a rate of 0.84 kg/kg isobutanol. In the GTBE process (including the isobutylene production step), GTBE is obtained as main product (86 wt% di-GTBE, 14 wt% tri-GTBE) at a rate of 1.28 kg per kg of isobutanol (98 ktonne/y of isobutanol feed to GTBE process), which yields a yearly production of 126 ktonne. Other butylene isomers (0.02 kg/kg isobutanol) and Di-,Tri-isobutylene (0.01 kg/kg isobutanol) are obtained as co-products. Waste water is obtained as additional output (0.24 kg/kg isobutanol) and glycerol an additional input, consumed at a rate of 0.56 kg/kg isobutanol.

For case 2, yields of the isobutyl acetate process are analogous to those explained for case 1. For the condensation products process, C7 and C11 ketones is the main product (31 wt% C7, 69 wt% C11) obtained at a rate of 1.25 kg/kg isobutanol (isobutanol feed flowrate of 98 ktonne/y), yielding 123 ktonne per year. Waste water is obtained as additional output (0.26 kg/kg isobutanol). Acetone is consumed at a rate of 0.5 kg per kg of isobutanol used in the condensation process.

In case 3, yields of the isobutyl acetate process is also analogous to those of cases 1 and 2. However, the condensation process involves an additional hydrogenation step to produce C11-alkanes as main product at a yield of 1.05 kg per kg of isobutanol (98 ktonne/y of isobutanol feed, base case). The annual production of C11-alkanes is equivalent to 104 ktonne. In this process, waste water is produced at a higher rate (0.38 kg/kg isobutanol) than that shown for case 2. Acetone is consumed at a rate of 0.4 kg/kg isobutanol, and hydrogen at a rate of 0.03 kg/kg of isobutanol. Inputs such as hydrogen and acetone are traditionally produced from fossil-sources, thus, higher GHG and CED of raw materials can be expected for the ketone/alkane systems (cases 2 and 3) than those of GTBE where glycerol is the additional input (case 1).

3.3.2. Early assessment

Isobutanol production

Table 3.3 shows the results for the early assessment indicators. For both bio and fossil routes the EC indicators is below 1, which reflects that the income by revenues is higher than the costs of raw materials. However, the EC of the bio-based route is lower (better) than that of the fossil route by 17%. Note however that the bio-based route highly relies on the income by isobutanol sales with a share of 62% (62% isobutanol, 38% lignin) while in the case of the fossil route isobutanol sales accounts for 7% of the total revenues (7% isobutanol, 49% n-butanol, 5% hydrogen, 39% butyraldehyde). This reflects the big difference in the two systems in terms of co-product distribution. In the case of EIRM, both CED and GHG emissions of the raw materials are lower (better) for the bio-based route than those of the fossil route. In the case of CED, the bio-based is 90% lower than the petrochemical counterpart. The main difference is due to the high contribution of propylene on the total CED of the fossil route (76%). In the case of GHG emissions, the bio-based route is 73% lower than the petrochemical counterpart. By comparing the PC indicator, the bio-based route has a score 44% higher (worse) than the petrochemical counterpart. The main difference is due to higher complexity of the bio-based route to convert lignocellulosic biomass into fermentable sugars, which requires the use of a solvent and high dilution rates as described in the mass balances.

TABLE 3.3. Early stage assessment indicators for standalone isobutanol. Normalized scores in brackets. Weighting factors: EC=0.4, CED=0.15, GHG=0.15, PC=0.3. Allocation to isobutanol based on mass.

Indicators	Bio-based	Fossil-based
Economic constraint	0.35 (0.83)	0.42 (1.00)
CED (MJ/kg iBuOH) (allocated)	4.93 (0.10)	49.89 (1.00)
GHG (kg CO2-eq/kg iBuOH) (allocated)	0.25 (0.27)	0.92 (1.00)
Process Complexity	5.44 (1.00)	3.05 (0.56)
Single aggregated score (after normalization)	**0.69**	**0.87**
Index ratio	**0.79**	

The aggregated score of the bio-based route is lower (better) than that of the petrochemical route by 21%. This difference drives to an index ratio (bio-based score/ fossil-based score) of 0.79. A derivative can be classified as favorable if its index ratio is below 0.9, promising if its index ratio is between 0.9 and 1.2, and unfavorable if its index ratio is above 1.2 [136]. According to this classification, bio-based isobutanol falls within the group of favorable derivatives, which reflects the advantages of the bio-based route in comparison to the fossil counterpart at base case conditions.

Figure 3.3a shows the results on sensitivity analysis on prices, showing that propylene price affects the index ratio the most. A decrease of its price over 30%, leads to index ratios above 0.9 (isobutanol classified as promising). The index ratio starts to be above 1.2 with a decrease of propylene price by 90%. Nevertheless, this is unlikely to happen since the price of propylene used in the base case (600 €/tonne) is relatively close to the price reported by Platts in January 2015 (786 USD/tonne, approx. 690 €/tonne) [156]. On the other hand, an increase of 100% of propylene price leads to an index ratio of 0.63, which would be the case if propylene price rises as high as values reported for 2014 [156]. Isobutanol price is the second price parameter that affects the index ratio the most. A decrease on isobutanol price over 40% of the reference value, results in index ratios above

0.9. An increase on isobutanol price has a similar effect than the case of propylene price, leading the index ratio to 0.66. If lignin is considered a non-valuable product (0 €/tonne) the system has an index ratio above 0.9 (approx. 1). The latter confirms the importance of lignin valorization on the overall performance of lignocellulosic based biorefineries [157]. Biomass price should also be considered as a key aspect on the performance of the bio-based route in contrast to the fossil-based alternative. Increases on its price above 40% of the reference, leads to index ratios above 0.9. Contrary, if biomass price is decreased the lowest index ratios can be reached. Even at drastic changes, the system is likely to be in between the favorable and promising groups. The latter suggest that in general, the system is robust to change in prices when comparing the bio-based route against the petrochemical counterpart.

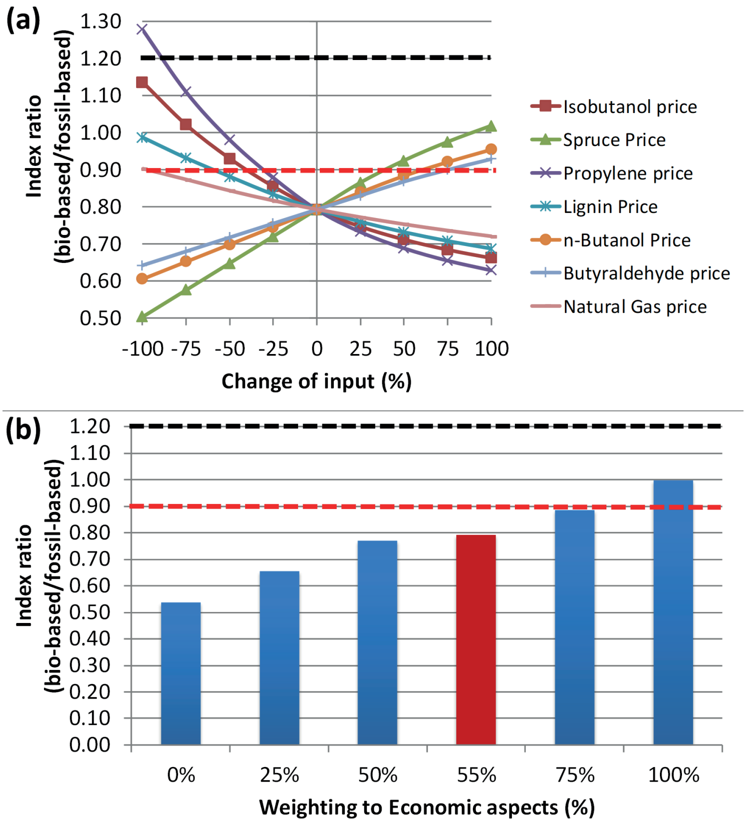

FIGURE 3.3. a) Sensitivity analysis of price inputs of isobutanol case: bio-based vs. fossil-based. Index ratio=0.79 (change of input 0%). For index ratios below 0.9 the bio-based system is favorable (red dotted line). For index ratios between 0.9 and 1.2, the bio-based system is promising. For index ratios above 1.2 the bio-based system is unfavorable (black dotted line). b) Sensitivity analysis of weighting factors of isobutanol production Red bar: base case. Blue bars: sensitivity cases.

The outcome of the early assessment highly depends on the distribution of economic and environmental aspects (base case 55% to economic aspects). In the case in which economic aspects are accounted as 100% (thus leaving out the effect of environmental aspects), the index ratio increases from 0.79 (base case) to 1 (see Figure 3.3b). In contrast, for 100% contribution of environmental aspects, the index ratio decreases from 0.79 to 0.54. In the first case (screening based on economic aspects) the index ratio shifted from being favorable to being promising. In the case of screening using environmental aspects, the index ratio fall within the limit value of 0.9 classifying it as favorable. Overall, changes in weighting factors remain isobutanol within the favorable and promising region, suggesting robustness. Nevertheless, this may not always be the case and will exclusively be dependent on the case studied and the conditions related to each. Imagine the case in which lignin price drops to 100 €/tonne (leaving other parameters fixed at base case values), the index ratio at base case weighting (55% to economic aspects) is 0.95 which classifies bio-based isobutanol as promising. However, when only economic aspects are considered the index ratio increases up to 1.34, which classifies bio-based isobutanol as unfavorable. On the other hand, when only environmental aspects are considered (100 %), the index ratio is 0.54, which classifies isobutanol as favorable. The latter reflects how conflictive would be deciding whether bio-based isobutanol offer advantages over fossil-based isobutanol when lignin is sold at 100 €/tonne. From an economic perspective the system is still classified as unfavorable, which would imply special attention on developing lignin markets which may hold the system competitive in contrast to the conventional technology. In terms of environmental aspects, the advantages are clearer for the bio-based route in contrast to the fossil based route.

When comparing bio-based isobutanol with other derivatives from lignocellulosic biomass (assessed using the same method, and derived from sugars from lignocellulosic biomass [136]), isobutanol stands behind succinic acid in the ranking of derivatives, and before ethanol (see Figure 3.4). This highlights the potential of bio-based isobutanol production and its potential capacity to replace a fraction of the current petrochemical counterpart.

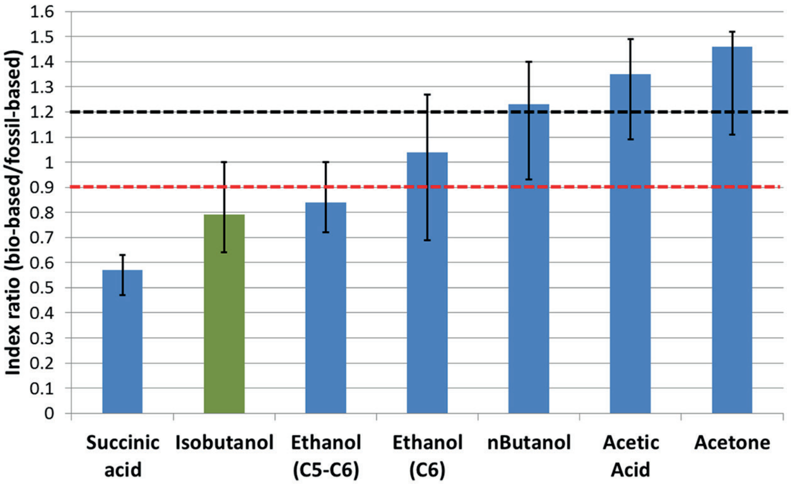

FIGURE 3.4. Ranking of isobutanol in comparison to other bio-based derivatives. For index ratios below 0.9 the bio-based system is favorable (red dotted line). For index ratios between 0.9 and 1.2, the bio-based system is promising. For index ratios above 1.2 the bio-based system is unfavorable (black dotted line)

Multiproduct systems

Table 3.4 shows the results of the early assessment indicators for the multiproduct systems. By comparing the EC indicator, in the three cases, the values are below 1 indicating potential economic benefits for all bio-based and fossil routes in cases 1,2 and 3. For all cases the EC indicator is similar, however, only in case 1 it is lower (better) by 6% for the bio-based route in comparison to the fossil route. In cases 2 and 3, the fossil route shows lower (better) EC indicators than the bio-based route by 4 and 9%, respectively. By comparing the CED indicator, in all cases, the bio-based routes are lower (better) than the fossil routes by 56, 49 and 49%, respectively. The GHG indicator shows a similar trend than the CED indicator, where in all cases the bio-based routes are lower (better) than the fossil routes by 37, 31 and 31%, respectively. The main difference between the fossil routes and bio-based routes in the CED and GHG indicators, is related to the difference in upstream impacts of the initial raw materials (*i.e.,* biomass and propylene). When aggregating the PC indicator of the different conversion steps, in all cases, the fossil routes show lower values (better) than the bio-based routes by 27, 28 and 26%, respectively. The main difference is reflected in the upstream section before the isobutanol conversion step as explained for standalone isobutanol.

TABLE 3.4. Early stage assessment indicators of the multiproduct cases. Normalized scores in brackets. Weighting factors: EC=0.4, CED=0.15, GHG=0.15, PC=0.3.

Indicators	Case 1		Case 2		Case 3	
	Bio-based	Fossil-based	Bio-based	Fossil-based	Bio-based	Fossil-based
Economic constraint	0.40 (0.94)	0.42 (1.00)	0.45 (1.00)	0.43 (0.96)	0.47 (1.00)	0.43 (0.91)
CED (MJ/kg iBuOH) (allocated)	33.44 (0.44)	76.32 (1.00)	44.06 (0.51)	86.95 (1.00)	44.51 (0.51)	87.01 (1.00)
GHG (kg CO2-eq/ kg iBuOH) (allocated)	1.11 (0.63)	1.77 (1.00)	1.45 (0.69)	2.11 (1.00)	1.46 (0.69)	2.11 (1.00)
Process Complexity	7.71 (1.00)	5.61 (0.73)	7.51 (1.00)	5.41 (0.72)	7.92 (1.00)	5.82 (0.74)
Single aggregated score (after normalization)	**0.84**	**0.92**	**0.88**	**0.90**	**0.88**	**0.89**
Index ratio	**0.91**		**0.98**		**0.99**	

When comparing the aggregated scores, in all cases the bio-based routes show lower (better) values than the fossil routes. When combining the single scores through the index ratio, case 1 shows the lower value (0.91), followed by case 2 (0.98) and case 3 (0.99). In the three cases, the differences of the bio-based routes and fossil routes are not that significant as in the case of standalone isobutanol production. The three cases show index ratios above 0.9 but below 1.2, which classify them as promising schemes. In the three cases, the isobutyl acetate process is analogue, however, case 1 converts isobutanol into GTBE, case 2 into ketones and case 3 into alkanes. The differences in index ratios thus suggests that the most promising option is the combination of isobutyl acetate and GTBE (case 1), followed by isobutyl acetate and ketones (case 2) and lastly isobutyl acetate and alkanes (case 3). This highlights the advantage of GTBE over ketones and alkanes systems due to the fact that glycerol (auxiliary raw material) shows lower price, CED and GHG indicators than acetone and hydrogen which are the auxiliary raw materials for ketones and alkanes production.

Figure 3.5 shows the sensitivity analysis results for cases 1 to 3, considering possible variations on prices. For case 1 (see Figure 3.5a), propylene price affects the index ratio the most, and decreases above 75% will lead the index ratio to be in the unfavorable region. Nevertheless, this is unlikely to happen since the base case price of propylene (600 €/tonne) is at its low end in comparison to historical prices reported by [156]. In contrast, increases of propylene prices above the base case value will lead the index ratio to be in the favorable classification region. Since the index ratio is on the threshold value of 0.9 for classifying the system as favorable or promising, any increase on prices of isobutyl acetate, lignin, natural gas and GTBE, and decreases in prices of spruce, butanol, butyraldehyde and acetic acid lead the system to be in the favorable region.

However, an opposite behavior of these parameters lead the system to be in the promising region. The latter reflects that even at drastic changes in prices, case 1 is still able to be classified between the favorable and promising regions. For case 2, the index is highly affected by propylene price, followed by isobutyl acetate, lignin, butanol and spruce prices. However, for case two changes need to be more drastic to be able to move the index ratio to the favorable region (see Figure 3.5b) and to most changes, the index ratio is robust in the promising group. Case 3 shows a similar behavior than case 2 in which drastic changes in prices are needed to allocate the index ratio as favorable, and for most changes the systems is robust as promising.

Figure 3.6a shows the results on sensitivity analysis of the distribution of isobutanol to isobutyl acetate. When the distribution of isobutanol is equal to each processing line (*i.e.,* isobutanol going to isobutyl acetate production, and isobutanol going to other products), the index ratio for the three cases is classified as promising. However, in case 1, when the distribution of isobutanol starts to be lower for isobutyl acetate (but higher for GTBE), the index ratio tends to be lower (better). For distributions below 20% to isobutyl acetate the system can be classified as favorable. This result suggests that at higher GTBE production rates, the system shows better performance. The index ratio was broken down to understand better which indicator is contributing to this tendency the most. Although revenues and raw material costs changed, the EC indicator remained mostly unchanged. The PC indicator is slightly affected showing higher values when the production of GTBE was increased (considering lower distribution of isobutanol to isobutyl acetate production), since the GTBE process shows higher PC scores than the isobutyl acetate process. The major impact is reflected in both GHG and CED indicators, where the lower values are obtained at lower distributions to isobutyl acetate. The latter is due to lower GHG and CED emissions of glycerol in comparison to those of acetic acid, which are auxiliary raw materials to GTBE and isobutyl acetate, respectively. This results also highlights the importance of the EIRM indicator on the overall behavior of each system, and how it can influence the index ratio. In cases 2 and 3, the behavior of the index ratio is opposite to that described for case 1. In these cases, when the distribution to isobutyl acetate is higher, the index ratios tend to be lower (better). In both cases 2 and 3, the index ratios remain in the promising region, with the highest values when both standalone ketones (case 2) and alkanes (case 3) are considered (0% distribution to isobutyl acetate). When breaking down the index ratios, the EC is significantly affected since at higher distribution to isobutyl acetate revenues are also higher leading to higher values. In contrast to case 1, the EIRM indicator is hardly affected since both CED and GHG impacts related to auxiliary raw materials is similar for cases 2 and 3. The PC indicator starts to be higher (worse) at lower distributions to isobutyl acetate since the

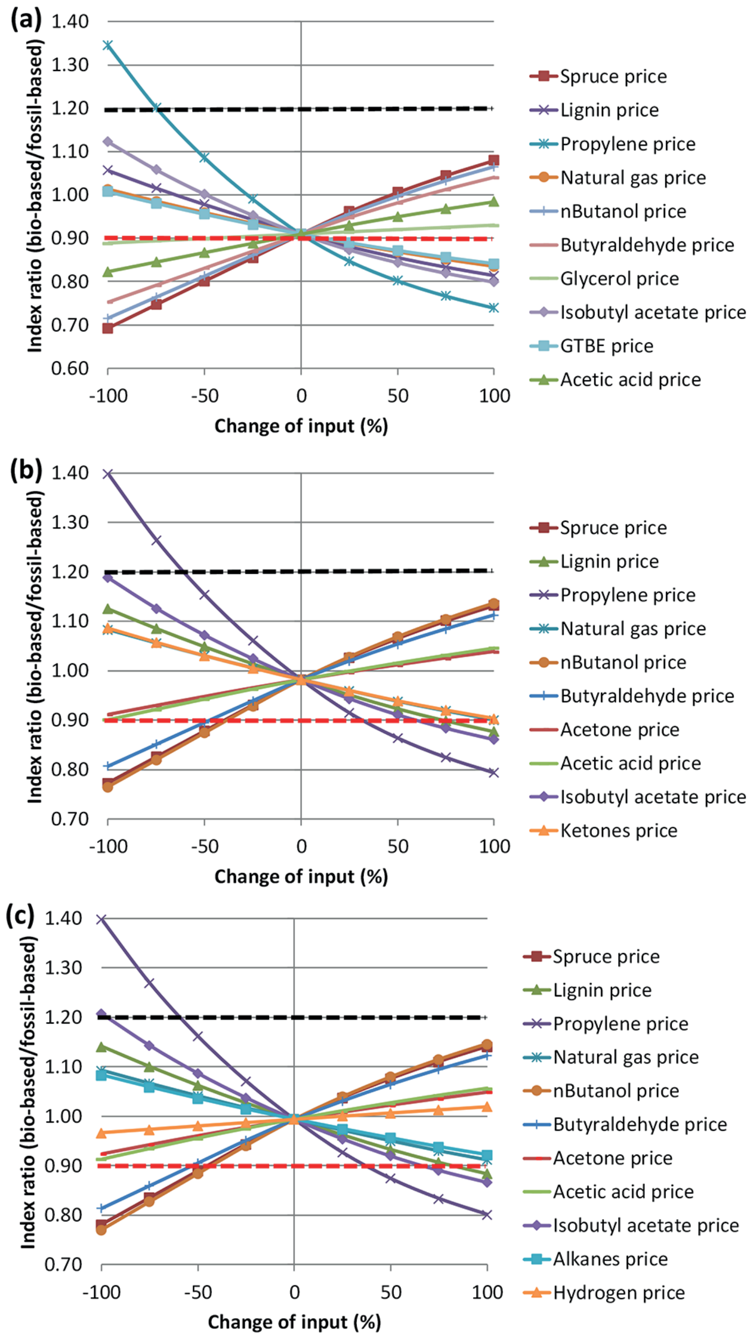

FIGURE 3.5. Results of sensitivity analysis on prices of multiproduct cases, a) case 1, b) case 2, c) case 3. Dotted lines represent thresholds for group classification.

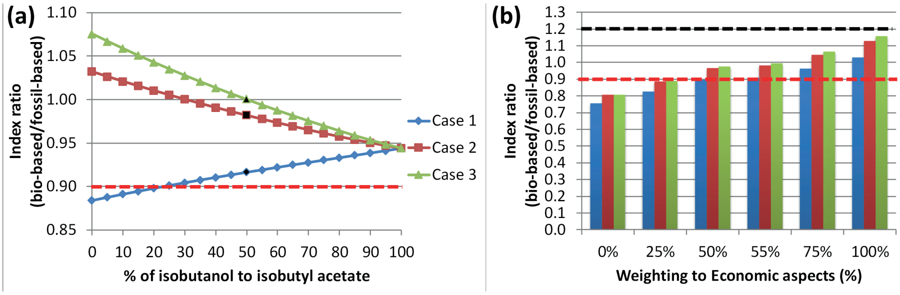

FIGURE 3.6. Results of sensitivity analysis of multiproduct systems, a) distribution of isobutanol to isobutyl acetate, base case values in black, b) weighting to economic aspects

individual scores of the acetone condensation step and hydrogenation are higher than that of isobutyl acetate. In contrast to case 1, in cases 2 and 3, when considering different distributions to isobutyl acetate the EC has a large effect. When considering standalone conversion of isobutanol (low and high ends in Figure 3.6a), the ranking (based on index ration) of the conversion alternatives from lower (better) to higher (worse) is GTBE production, isobutyl acetate production, ketones production and alkanes production.

Figure 3.6b shows the results of sensitivity analysis when weighting to economic aspects is changed. At base case conditions (55% to economic aspects), all cases are classified as promising. Nevertheless, when the weighting is more oriented to environmental aspects the systems can shift and classify as favorable (for values higher than 75% to environmental aspects). This highlights the importance of including environmental aspects in the screening of prospective technologies for the conversion of biomass. This will also allow identifying weaknesses and strengths of the screened technologies. When the weighting is only considered to economic aspects (100% in Figure 3.6b), the index ratios are the highest and all above 1, which suggest better economic performance of the petrochemical counterparts than the bio-based systems. However, the index ratios remain in the promising region at base case prices, but as discussed for standalone isobutanol production, it may change if different price scenarios are included such as the case of low lignin price. On one hand, an interesting feature when considering 100% weighting to economic aspects is that the difference in index ratios between the three cases is larger, with cases 2 and 3, 9 and 12% higher than case 1. On the other hand, when 100% weighting is considered to environmental aspects, the difference in index ratios is shorter, where cases 2 and 3 are both 6% higher than case 1. Overall, the influence of weighting is large when deciding whether a route is attractive for further analysis. It should be taken into account that weightings can always be modified and for further analysis the stakeholders can easily adapt them depending on their interests.

One of the limitations of the applied method is the assumption of ideal separation of the mixtures leaving each reactor system. In some cases, the recovery of products is not always 100% possible due to thermodynamic and equipment limitations. Although the complexity of each process is mimic by conducting scoring based on heuristics, many details that can influence the overall performance of each technology can be missing. For example, the contribution of utilities in both economics and environmental aspects is expected to be high in any chemical/biochemical process. The use of the CED as an indicator of the environmental impacts of raw materials needs to be carefully revised, since it reports both renewable and non-renewable energy use. Therefore, it can provide a misleading picture depending on the perception of the user. For instance, on one hand, in the case where renewable energy is dominant in the CED indicator, the user can misunderstand the results assuming that all energy is provided from non-renewable sources. On the other hand, the CED can also be very informative on energy resource use independently of its nature. The method is adaptable and it is possible, for instance, to only use the non-renewable energy use component of the CED indicator. Other limitation of the method can be reflected in lack of data of investment costs and additional cots categories, which could be a determining driver to understand the economic feasibility of each system. All in all, this limitations bring with themselves high uncertainty, for instance in the incompleteness of the EC indicator. Nevertheless, it should be taken into account that all options either for the bio-based and fossil-based routes were compared and analyzed at the same level in order to derive a fair assessment. The method also shows that it is possible to be applied in multiproduct portfolios and that it can be useful for applying it for emerging technologies were relevant detailed data is not yet available. The method can be useful to support companies and research institutes interested in screening and selecting novel technology pathways in biorefineries. Something to remark is that we focused our analysis to the scope of a chemical process, specifically oriented to the chemical industry of the bio-based economy and the stakeholders related to it. In this case we considered technical, economic and environmental aspects. However, it should be taken into account that for instance social aspects are not embedded in the current analysis. On one hand, this is an additional limitation of the method, but on the other hand, the level of analysis is still at an early stage, which is considered due to limitations on data availability regarding different aspects of a prospective technology (*e.g.,* social). Following this reasoning, a more comprehensive analysis would always require higher resolution and quality of data inputs, which generally is an issue for systems that are not currently operating at large scales. In this case, the aggregation of economic, technical and environmental aspects helps to visualize, at an early stage, possible hotspots for scaling up the level of analysis of a system. For instance, information provided in this work, may be used to pre-screen technology configurations and later apply a more detailed techno-economic and environmental assessment on the screened options.

3.4. CONCLUSIONS

This study shows that at an early stage, bio-based isobutanol has advantages over petrochemical isobutanol production. All multiproduct cases, show to be promising, with the one combining isobutyl acetate and GTBE having the best performance, followed by the combination of isobutyl acetate and ketones, and combination of isobutyl acetate and alkanes. This study also shows that the screening of possible products is highly affected when considering solely economic and environmental aspects, suggesting that when environmental aspects are included, the systems tend to perform better than the petrochemical counterparts. This highlights the importance of environmental aspects in the assessment of technologies.

Acknowledgements

The financial support by the European Development Fund of the European Union, through the project Isobutanol Platform Rotterdam (IBPR) is greatly acknowledged.

APPENDIX

Appendix A. Distribution of weighting factors

Figure 3.7 shows an overview of the weighting and aggregation of the indicators into a single score.

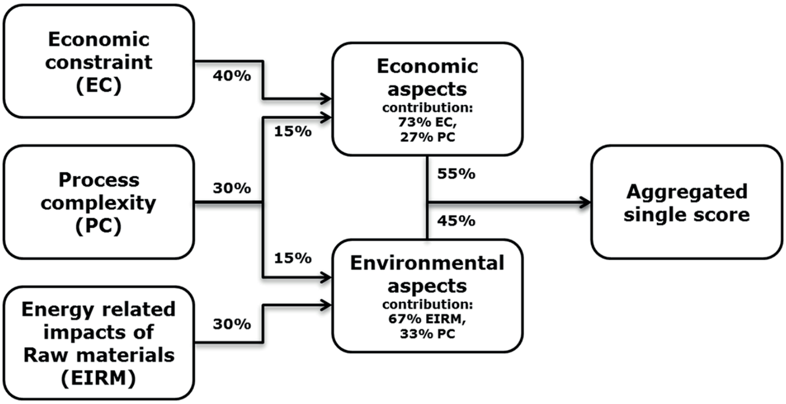

Figure 3.7. Overview of weighting and aggregation of indicators into a single sore. Contribution of Economic and Environmental aspects on the aggregated score

Appendix B. Chemical composition of spruce

Table 3.5 shows the chemical composition used to model spruce in Aspen Plus.

TABLE 3.5. Average spruce composition used to model spruce wood chips in Aspen Plus [158]. Composition expressed in dry basis.

Compound groups	wt. %
Extractives, water [a]	6.40%
Extractives, ethanol [b]	0.90%
Glucan	41.60%
Xylan	3.60%
Galactan	1.20%
Arabinan	0.20%
Mannan	10.40%
Lignin, acid insoluble	27.30%
Lignin, acid soluble	0.30%
Ash	0.30%
Other, unknown [c]	7.80%
Total	**100.00%**

[a] Extractives modeled as Gallic Acid.

[b] Extractives modeled as Oleic Acid.

[c] Others modeled as inert to close mass balances.

Appendix C. Set of reactions modeled in Aspen Plus

This section shows the reactions and conversions used to model the mass balances of both isobutanol production and integrated multiproduct portfolios. Table 3.6 shows the set of reactions of Organosolv conversion modeled in Aspen Plus. Table 3.7 accounts for hydrolysis and fermentation steps of bio-based isobutanol production. Table 3.8 shows the set of reactions for petrochemical isobutanol production. Table 3.9 displays the estherification reaction between isobutanol and acetic acid to produce isobutyl acetate. Table 3.10 shows the set of reactions of isobutanol dehydration to isobutylene. Table 3.11 shows the set of reactions used to model GTBE production. Table 3.12 displays the set of reactions used to model the production of isobutanol-acetone derived ketones, and Table 3.13 displays the reaction to model the hydrogenation of C11-ketones into C11-Alkanes.

TABLE 3.6. Reactions modeled in organosolv pretreatment. Cipsd: compound modeled as solid with particle size distribution. Mixed: compound modeled as soluble. Gallic Acid and oleic acid were used as model compounds to account for extractives contained in the biomass.

Reaction	Conversion
Lignin(Cipsd) → Lignin(Mixed)	75%
Glucan(Cipsd) → Glucan(Mixed)	10%
Xylan(Cipsd) → Xylan(Mixed)	100%
Galactan(Cipsd) → Galactan(Mixed)	100%
Arabinan(Cipsd) → Arabinan(Mixed)	100%
Mannan(Cipsd) → Mannan(Mixed)	90%
Extractives, water(Cipsd) → Extractives, water(Mixed)	99%
Extractives, ethanol(Cipsd) → Extractives, ethanol(Mixed)	99%
Glucan(Mixed) + Water(Mixed) → Glucose(Mixed)	100%
Xylan(Mixed) + Water(Mixed) → Xylose(Mixed)	100%
Galactan(Mixed) + Water(Mixed) → Galactose(Mixed)	100%
Arabinan(Mixed) + Water(Mixed) → Arabinose(Mixed)	100%
Mannan(Mixed) + Water(Mixed) → Mannose(Mixed)	100%
Glucose(Mixed) → 3 Water(Mixed) + Hydroxymethylfurfural(Mixed)	28%
Galactose(Mixed) → 3 Water(Mixed) + Hydroxymethylfurfural(Mixed)	28%
Mannose(Mixed) → 3 Water(Mixed) + Hydroxymethylfurfural(Mixed)	28%
Xylose(Mixed) → 3 Water(Mixed) + Furfural(Mixed)	52%
Arabinose(Mixed) → Furfural(Mixed) + 3 Water(Mixed)	52%
27 Xylose(Mixed) → 10 Humins(Mixed) + 95 Water(Mixed) + 15 CO_2(Mixed)	5%
27 Arabinose(Mixed) → 10 Humins(Mixed) + 95 Water(Mixed) + 15 CO_2(Mixed)	5%
9 Glucose(Mixed) → 4 Humins(Mixed) + 38 Water(Mixed) + 6 CO_2(Mixed)	5%
9 Galactose(Mixed) → 4 Humins(Mixed) + 38 Water(Mixed) + 6 CO_2(Mixed)	5%
9 Mannose(Mixed) → 4 Humins(Mixed) + 38 Water(Mixed) + 6 CO_2(Mixed)	5%

TABLE 3.7. Reactions modeled in Hydrolysis and fermentation steps. Cipsd: compound modeled as solid with particle size distribution. Mixed: compound modeled as soluble. Cell biomass formula: $CH_{1.8}O_{0.5}N_{0.2.}$ [a] 0.381 g iBuOH/g glucose, 93% of maximum theoretical yield.

Reactions	Conversion
Hydrolysis Cellulose(Mixed) + Water(Mixed) --> Glucose(Mixed)	95%
Fermentation Glucose(Mixed) + 0.084 NH_4OH(Mixed) --> 0.42 Cells (Cipsd) + 0.926 Isobutanol(Mixed) + 1.874 CO_2(Mixed) + 1.199 Water(Mixed)	100% [a]

TABLE 3.8. Reactions modeled in fossil-based isobutanol case. Conversion calculated based on [142].

Reactions	Conversion
Steam reforming Methane + Water --> CO + $3H_2$	1.000
Hydroformylation Propylene + $2H_2$ + CO --> nButanol	0.7891
Propylene + $2H_2$ + CO --> Isobutanol	0.0625
Propylene + H_2 + CO --> Butyraldehyde	0.1484

TABLE 3.9. Estherification reaction modeled in isobutyl acetate production. Reaction modeled using the Gibb free energy minimization method. CIPSD: compound modeled as solid with particle size distribution. MIXED: compound modeled as soluble.

Reactions
Isobutanol + Acetic Acid --> Isobutyl Acetate + Water

TABLE 3.10. Reactions considered to model isobutanol dehydration to isobutylene [159]. CIPSD: compound modeled as solid with particle size distribution. MIXED: compound modeled as soluble.

Reactions	Conversion
Isobutanol --> Isobutylene + Water	0.9496
Isobutanol --> 1-butylene + Water	0.0152
Isobutanol --> 2-butylene + Water	0.0152

TABLE 3.11. Reactions considered to model GTBE production. Reactions modeled in series [160]. [a] Conversion calculated after first three reactions, conversion based on isobutylene. [b] Conversion calculated after third reaction, conversion based on di-Isobutylene.

Reactions	Conversion
Glycerol + Isobutylene --> Mono-GTBE	0.9127
Mono-GTBE + Isobutylene --> di-GTBE	0.5393
di-GTBE + Isobutylene --> tri-GTBE	0.1110
2 Isobutylene --> di-Isobutylene	0.3946 [a]
Di-Isobutylene + Isobutylene --> tri-Isobutylene	0.3774 [b]

TABLE 3.12. Reactions modeled in isobutanol-acetone condensation [161]. C7-ketone modeled as 5-methyl-2-hexanone. C11-ketone modeled as 2,8-dimethyl-5-nonanone.

Reactions	Conversion
Isobutanol + Acetone --> C7-Ketone + Water	0.90
Isobutanol + C7-Ketone --> C11-Ketone + Water	0.60

TABLE 3.13. Reactions modeled in hydrogenation of ketones. C11-ketone modeled as 2,8-dimethyl-5-nonanone. C11-alkane modeled as 2,8-dimethylnonane.

Reactions	Conversion
C11-Ketone + 2 H_2 --> C11-Alkane + Water	1.00

Appendix D. Mass balances of isobutanol production and integrated biorefinery cases

This section shows the overall mass balances of isobutanol production and integrated biorefinery cases for both the bio-based and fossil-based system. Table 3.14 shows the overall mass balance of isobutanol production. The overall mass balance of the integrated biorefinery case 1 is displayed in Table 3.15. Table 3.16 displays the overall mass balance of integrated biorefinery case 2, while Table 3.17 displays the overall mass balance of integrated biorefinery case 3.

TABLE 3.14. Overall mass balance of isobutanol production of both bio-based and fossil-based routes.

Stream	Bio-based – ktonne/year			Fossil-Based – ktonne/year		
	Raw materials	Products	Waste	Raw Materials	Products	Waste
Biomass [a]	1111	-	-	-	-	-
Sulfuric Acid	33	-	-	-	-	-
Enzyme	10	-	-	-	-	-
Ammonia	16	-	-	-	-	-
Water	3122	-	-	-	-	-
Acetone (solvent)	2868	-	-	-	-	-
Propylene	-	-	-	1788	-	-
Natural Gas	-	-	-	682	-	-
Steam	-	-	-	765	-	-
Recovered Solvent	-	2868	-	-	-	-
Lignin [b]	-	231	-	-	-	-
Isobutanol	-	197	-	-	197	-
n-Butanol	-	-	-	-	2485	-
Butyraldehyde	-	-	-	-	455	-
Hydrogen	-	-	-	-	98	-
CO_2	-	-	237	-	-	-
Waste water	-	-	2808	-	-	-
Non-converted pulp + cells	-	-	91	-	-	-
Waste water [c]	-	-	729	-	-	-
Total	7161	3296	3865	3234	3234	-

[a,b] Water content 10 wt%. [c] Waste water containing furans, humins and C5 sugars.

TABLE 3.15. Overall mass balance of integrated biorefinery case 1.

Stream	Bio-based – ktonne/year			Fossil-Based – ktonne/year		
	Raw materials	Products	Waste	Raw Materials	Products	Waste
Biomass [a]	1111	-	-	-	-	-
Sulfuric Acid	33	-	-	-	-	-
Enzyme	10	-	-	-	-	-
Ammonia	16	-	-	-	-	-
Water	3122	-	-	-	-	-
Acetone (solvent)	2868	-	-	-	-	-
Propylene	-	-	-	1788	-	-
Natural Gas	-	-	-	682	-	-
Steam	-	-	-	765	-	-
Recovered Solvent	-	2868	-	-	-	-
Lignin [b]	-	231	-	-	-	-
n-Butanol	-	-	-	-	2485	-
Butyraldehyde	-	-	-	-	455	-
Hydrogen	-	-	-	-	98	-
CO_2	-	-	237	-	-	-
Waste water	-	-	2858	-	-	50
Non-converted pulp + cells	-	-	91	-	-	-
Waste water [c]	-	-	729	-	-	-
Acetic Acid	82	-	-	82	-	-
Glycerol	55	-	-	55	-	-
Acetone	-	-	-	-	-	-
Isobutyl acetate	-	154	-	-	154	-
GTBE	-	126	-	-	126	-
1-, 2-Butylene	-	2	-	-	2	-
Di-, Tri-Isobutylene	-	1	-	-	1	-
C7/C11 ketones	-	-	-	-	-	-
Alkanes	-	-	-	-	-	-
Total	**7298**	**3383**	**3915**	**3372**	**3321**	**50**

[a,b] Water content 10 wt%. [c] Waste water containing furans, humins and C5 sugars

TABLE 3.16. Overall mass balance of integrated biorefinery case 2.

Stream	Bio-based – ktonne/year			Fossil-Based – ktonne/year		
	Raw materials	Products	Waste	Raw Materials	Products	Waste
Biomass [a]	1111	-	-	-	-	-
Sulfuric Acid	33	-	-	-	-	-
Enzyme	10	-	-	-	-	-
Ammonia	16	-	-	-	-	-
Water	3122	-	-	-	-	-
Acetone (solvent)	2868	-	-	-	-	-
Propylene	-	-	-	1788	-	-
Natural Gas	-	-	-	682	-	-
Steam	-	-	-	765	-	-
Recovered Solvent	-	2868	-	-	-	-
Lignin [b]	-	231	-	-	-	-
n-Butanol	-	-	-	-	2485	-
Butyraldehyde	-	-	-	-	455	-
Hydrogen	-	-	-	-	98	-
CO_2	-	-	237	-	-	-
Waste water	-	-	2860	-	-	52
Non-converted pulp + cells	-	-	91	-	-	-
Waste water [c]	-	-	729	-	-	-
Acetic Acid	82	-	-	82	-	-
Glycerol	-	-	-	-	-	-
Acetone	50	-	-	50	-	-
Isobutyl acetate	-	154	-	-	154	-
GTBE	-	-	-	-	-	-
1-, 2-Butylene	-	-	-	-	-	-
Di-, Tri-Isobutylene	-	-	-	-	-	-
C7/C11 ketones	-	123	-	-	123	-
Alkanes	-	-	-	-	-	-
Total	**7293**	**3376**	**3917**	**3366**	**3315**	**52**

[a,b] Water content 10 wt%. [c] Waste water containing furans, humins and C5 sugars.

TABLE 3.17. Overall mass balance of integrated biorefinery case 3.

Stream	Bio-based – ktonne/year			Fossil-Based – ktonne/year		
	Raw materials	Products	Waste	Raw Materials	Products	Waste
Biomass [a]	1111	-	-	-	-	-
Sulfuric Acid	33	-	-	-	-	-
Enzyme	10	-	-	-	-	-
Ammonia	16	-	-	-	-	-
Water	3122	-	-	-	-	-
Acetone (solvent)	2868	-	-	-	-	-
Propylene	-	-	-	1788	-	-
Natural Gas	-	-	-	682	-	-
Steam	-	-	-	765	-	-
Recovered Solvent	-	2868	-	-	-	-
Lignin [b]	-	231	-	-	-	-
n-Butanol	-	-	-	-	2485	-
Butyraldehyde	-	-	-	-	455	-
Hydrogen	3	-	-	3	98	-
CO_2	-	-	237	-	-	-
Waste water	-	-	2872	-	-	63
Non-converted pulp + cells	-	-	91	-	-	-
Waste water [c]	-	-	729	-	-	-
Acetic Acid	82	-	-	82	-	-
Glycerol	-	-	-	-	-	-
Acetone	40	-	-	40	-	-
Isobutyl acetate	-	154	-	-	154	-
GTBE	-	-	-	-	-	-
1-, 2-Butylene	-	-	-	-	-	-
Di-, Tri-Isobutylene	-	-	-	-	-	-
C7/C11 ketones	-	-	-	-	-	-
Alkanes	-	104	-	-	104	-
Total	**7286**	**3357**	**3928**	**3359**	**3296**	**63**

[a,b] Water content 10 wt%. [c] Waste water containing furans, humins and C5 sugars.

Appendix E. Process complexity indicator

Table 3.18 shows the process complexity indicator estimated for each individual conversion step.

TABLE 3.18. Individual PC scores of each process options. Values used to aggregate the overall PC indicator

Process section	PC indicator
Isobutanol - biobased	5.14
Isobutanol - fossil	3.05
Isobutyl Acetate	1.62
Isobutylene	1.51
GTBE	2.00
Ketones	1.60
Alkanes	0.83

CHAPTER 4

Techno-economic and ex-ante environmental assessment of C6 sugars production from spruce and corn. Comparison of organosolv and wet milling technologies

Published: Moncada J., Vural Gursel I., Huijgen W.J.J., Dijkstra J.W.,
Ramírez A. 2018. Journal of Cleaner Production 170, 610-624.

ABSTRACT

This study assesses the techno-economic and environmental performance of C6 sugars production from softwood (spruce) and corn. Two technologies were considered in the assessment: organosolv of spruce woodchips (2nd generation) and corn wet milling (1st generation). Process models were developed to generate relevant data to assess the technical performance and derive inputs for the economic and environmental assessments. The economic assessment was carried out using Net Present Value (NPV) as indicator, while the environmental assessment followed a prospective cradle-to-gate life cycle assessment (LCA) for 5 impact categories. The results indicate that when organosolv is integrated with an anaerobic digestion unit, the net energy requirements are lower than those of the wet milling process to produce an equivalent flowrate of C6 sugars. Assuming equivalent C6 sugar prices for the two technologies (300 €/t), the corn based technology shows positive NPV (178 M€) and lowest fixed capital investment requirements (55 M€). The organosolv technology (coupled to anaerobic digestion) also shows positive NPV (238 M€) at base case lignin prices (630 €/tonne), but higher fixed capital investment needs (236 M€). The economics of the organosolv process were found to be highly sensitive to sugar and lignin yields and prices as well as biomass feedstock costs. From an environmental perspective, the organosolv based routes show relatively better performance than corn wet milling, with 3 categories including climate change and non-renewable energy use showing lower impacts and 2 showing potentially higher impacts. Overall, the organosolv process (2nd generation) shows better performance from an environmental point of view in addition to a positive NPV. However, the inherent risks of new technologies and high investments associated with the 2nd generation technologies assessed in this work, mean that significant additional development, coupled with appropriate government support, are likely necessary before full-scale implementation.

4.1. INTRODUCTION

Biomass is a plentiful renewable raw material that can contribute to reach global warming targets by decarbonizing products that are conventionally produced from fossil sources. The biorefinery concept has been widely defined as an analogy to oil refineries where a large portfolio of products can be obtained [162]. Biorefineries are classified according to feedstocks, processes, platforms and products [163]. Similar to the oil industry, the platforms link the feedstocks with final products by a number of processing steps [18, 163].

In biorefineries, the most common platform chemicals are syngas, biogas, vegetable oils, organic solutions (nutrient rich juice extracted from fresh wet biomass such as grass), lignin, pyrolysis oil and carbohydrates [18, 163]. The carbohydrates platform offers a wide variety of options to produce valuable products such as alcohols, organic acids, polyols among other [164, 165].

The carbohydrates platform can be obtained from crops such as corn, sugarcane and sugar beets, and from lignocellulosic biomass such as wood and wood residues, grasses and agricultural residues. There are many technologies to convert biomass into the carbohydrates platform (*i.e.,* disaccharides, C5 and C6 sugars) either from food crops or lignocellulosic feedstocks. In the case of food crops feedstocks, the most common are corn wet milling [166], sugarcane milling [22] and sugar beets milling [167]. In the case of lignocellulosic biomass, biomass pretreatment is generally applied first to enable effective enzymatic saccharification. Among the most common pretreatment methods are dilute acid, soda pulping, steam explosion and organosolv [23, 24]. In the pretreatment stage, the lignocellulosic biomass is may be simultaneously refined into its main components and three main streams are obtained, namely: lignin, hemicellulose hydrolysate (hemicellulose fraction) and cellulose pulp. Lignin can be considered a by-product which can be marketed [25]. The hemicellulose hydrolysate can be used for fermentation (*e.g.,* to produce ethanol) [24], to obtain other products such as furfural [168], or as feed for anaerobic digestion [169]. The pulp stream (rich in cellulose) is generally used as substrate for its further enzymatic hydrolysis into C6 sugars [24].

Currently, there is a debate on the use of food related feedstocks for biorefinery systems (*e.g.,* crops for 1st generation (1G) technologies) due to sustainability concerns such as environmental impacts related to land use change and food security [170, 171]. Consequently, increasing attention has been paid on producing energy carriers and materials from lignocellulosic biomass (as feedstock for 2nd generation (2G) technologies) due to its abundancy, potential lower costs than crops, potential reductions on land use change and non-competition with food [170-172]. In this context, techno-economic and environmental assessments of biorefinery systems based on lignocellulosic feedstocks are needed in order to be able to early identify potential bottlenecks and adopt lessons learned from the processing of crop related feedstocks. Many of the studies carrying out techno-economic and/or environmental assessments comparing food related and lignocellulosic feedstocks, generally focus on a final product such as bioethanol [173-175] and little attention has been paid to the comparison of C6 sugars production which can be used for fuels production (*e.g.,* ethanol, butanol) and/or chemicals production (*e.g.,* lactic acid, succinic acid).

In this study, techno-economic and ex-ante environmental assessments of C6 sugars production are carried out for one 2G technology for lignocellulosic biomass conversion and one 1G technology for food crops processing. Corn is used as representative food crop feedstock for the production of C6 sugar. The wet milling technology was selected due to the relatively high maturity of this technology in the USA [166], and the role that corn may play as a source of C6 sugars in Europe [176]. In the case of lignocellulosic biomass, various biomass sources were considered as candidates for the production of C6 sugars such as agricultural residues (e.g., wheat straw, cane bagasse, rice straw, corn stover) and, wood and wood residues (e.g., softwood, hardwood). Although agricultural residues have large potential due to their availability, their supply at large scale is complicated by issues in collection, handling, and transport as well as the relatively fragmented supply chain in some countries [177]. Instead, as representative of lignocellulosic biomass, softwood (spruce in this case) was selected as feedstock relying on the advantage and maturity related to logistics, large biomass supply and general infrastructure of the existing pulp and paper industry [178]. Organosolv technology was selected as pretreatment technology as it allows obtaining good pulp quality for further conversion into C6 sugars, as well as a lignin by-product, which can be used for further conversion into high value-added chemicals [169, 179, 180].

In summary, three main questions will be addressed in the article: i) What is the technical performance of the organosolv process for producing C6 sugars[1] from spruce in comparison to the wet milling process for producing C6 sugar from corn?; ii) What is the economic performance of the organosolv process to produce C6 sugars from spruce in comparison to the wet milling process for producing C6 sugars from corn?; and iii) What is the ex-ante environmental performance (in key impact categories) of the organosolv process for producing C6 sugars from spruce in comparison to the wet milling of corn for producing C6 sugars?

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[1] In this work, C6 sugars refer to hexoses (mainly glucose) derived from the cellulose fraction of spruce. In the case of corn, C6 sugars refer to hexoses (mainly glucose and fructose).

4.2. METHODOLOGY

This study has three levels of analysis. The first level compares the production of C6 sugars from lignocellulosic biomass and corn from a technical perspective on the processing level (*e.g.,* mass flows, energy consumption, processing yields). The second level focuses on the economic analysis a (*e.g.,* production costs, net present value). The third level focuses on the Life Cycle Assessment of the production of C6 sugars for each option. The three levels of analysis are linked to each other (Figure 4.1). In the first step, the pretreatment technology, feedstock (*i.e.,* lignocellulosic biomass), plant capacity and location were defined. Simultaneously, a benchmark technology, feedstock (*i.e.,* corn) and plant capacity were also selected. In the second step, data such as feedstock composition, conversion steps, product distribution and energy consumption of each technology option were collected and used as input for the process modeling, economic and environmental assessments. The third step is the development of process models for both technologies (*i.e.,* second generation and first generation) aiming to generate mass and energy balances. The fourth step is the economic and environmental assessments. Final results have been obtained after feedback and fine-tuning of the data after several runs.

4.2.1. Plant capacities

A plant capacity of 1000 ktonne of dry wood (feedstock) per year was defined, considering that large scale of biomass processing is needed to economically compete with conventional fossil refineries [181]. Organosolv processes also showed benefits from economies of scale as reported in previous studies [182]. The plant capacity of corn processing was set to match the capacity of C6 sugars produced with the organosolv technology. To be able to compare both feedstocks and technologies under the same basis, the port of Rotterdam was assumed as location for both lignocellulosic and corn based C6 sugars production.

4.2.2. Process Modeling

Process models were developed in Aspen Plus v8.4 (Aspen Technology, Inc., USA). As several of the compounds involved in the modeling were not available in the databases of Aspen Properties, a property database of the National Renewable Energy Laboratory was used, which is based on the work of Wooley and Putsche [183]. Furthermore, the nonrandom two-liquid (NRTL) thermodynamic model was used to calculate the activity coefficients of the liquid phase and the Hayden O’Connell equation of state was used to describe the vapor phase. All processes are assumed in continuous mode and whole year operation (*i.e.,* 8000 h/y). In all cases energy integration was considered by using excess heat of available streams, nevertheless, optimization using pinch analysis was not considered. Integration of water stream and water recycling was not considered in the scope of this study.

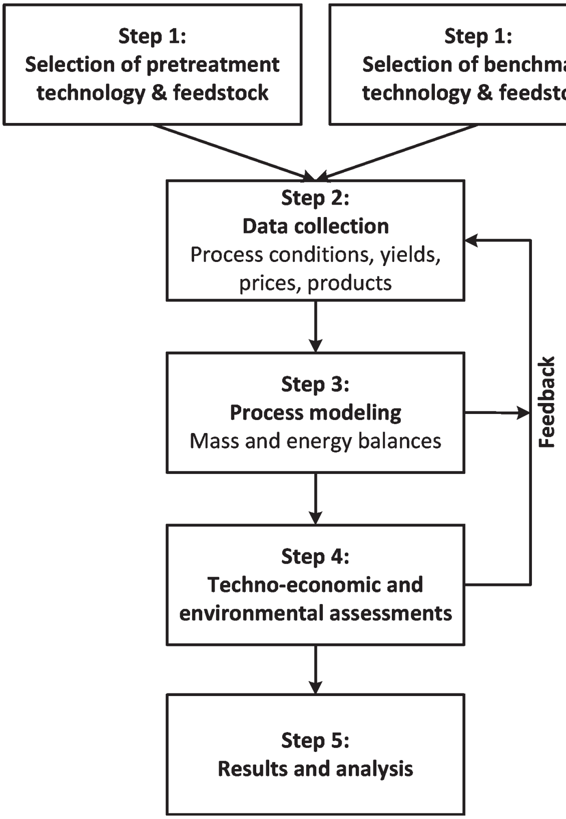

FIGURE 4.1. General description of the methodological approach for the comparative assessment of C6 sugars production from lignocellulosic biomass and corn.

4.2.3. Process description

This section provides a brief description of the processes and main assumptions used for model them.

Organosolv process

The organosolv processes (see Figure 4.2) is composed of four main sections: i) spruce wood chips conditioning and organosolv fractionation; ii) lignin precipitation and recovery; iii) solvent recovery and recycling, and iv) pulp stripping and enzymatic hydrolysis. The main outputs of this process are the C6 sugar stream (crystallized), organosolv lignin (dried), furfural (concentrated, 97 wt%), non-converted solids (from enzymatic hydrolysis, diluted stream) and hemicellulose derived sugars (including extractives, diluted stream). It should be mentioned that since organosolv fractionation is a technology under development, not all unit operations as depicted in Figure 4.2 have been technically proven (for example, lignin precipitator (column 12) and pulp stripper (column 5)).

The main data inputs are the composition of spruce wood, process conditions and set of reactions describing the organosolv fractionation. The chemical composition of spruce wood was gathered from the work of [185], and assuming a water content of 10 wt%. The organosolv reactor operates at 190 ºC and 15 bar, using sulfuric acid as catalyst (dosage 10 mM), and a solid to liquid ratio of 5 L per kg of dry biomass using ethanol as solvent at 60 wt% in water. Conditions used for the organosolv fractionation were taken from [185]. Delignification and hemicellulose hydrolysis reactions during the organosolv fractionation step were proposed based on lignin and pulp recovering yields reported by [185]. The chemical composition of spruce, organosolv description and set of reactions can be found in Table 4.7 in Appendix A, as well as the assumptions on process parameters used in solvent recovery steps and enzymatic hydrolysis of pulp.

Anaerobic digestion

The hemicellulose sugar stream from the organosolv process and non-converted solid stream from the enzymatic hydrolysis contain significant amounts of organics such as C6 sugars, C5 sugars, humins, furans, extractives, lignin and hemicellulose[2]. An option for utilizing these streams is to develop by-product recovery and separation systems and extract e.g. the useful sugars as additional products. However, since these are complex streams which are diluted in water, product separation is probably energy-intensive and costly [169, 186]. Therefore, this study considers the use hemicellulosic sugars and non-converted solids streams, as feedstock to produce biogas and later heat and power to fully (or partially) cover the demand of the organosolv process. The biogas unit was modeled using biogas yields according to the description provided by [169], and the combined cycle system for producing steam and electricity was modeled according to descriptions provided in [187, 188].

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[2] C6 sugars, furans and humins are the major compounds in the hemicellulose rich stream derived from the organosolv process. Lignin and hemicellulose are the major compounds of the non-converted solids resulted from the enzymatic hydrolysis step.

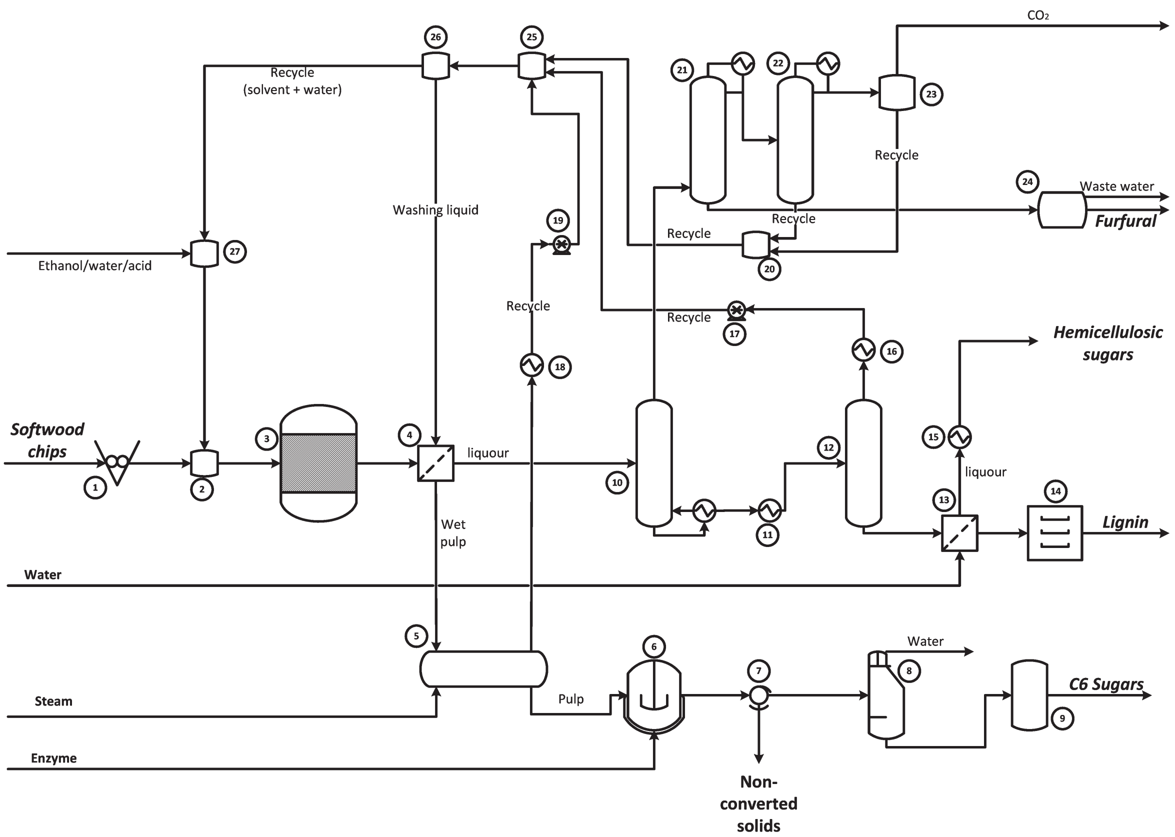


FIGURE 4.2. Simplified flowsheet diagram of organosolv fractionation of spruce wood chips to produce C6 sugars and lignin. Equipment list: 1. Milling, 2. Mixer, 3. Organosolv reactor, 4. Filter/Washer, 5. Pulp stripping, 6. Enzymatic hydrolysis reactor, 7. Filter/Washer, 8. Evaporation train, 9. Crystallizer, 10. Column 1, 11. Heat Exchanger, 12. Column 2 (Precipitator), 13. Filter, 14. Dryer, 15. Heat Exchanger, 16. Heat Exchanger, 17. Pump, 20. Mixer, 21. Column 4, 22. Column 5, 23. Knockout drum, 24. Decanter, 25. Mixer, 26. Mixer, 27. Mixer. Process modeled based on descriptions from [169, 184].

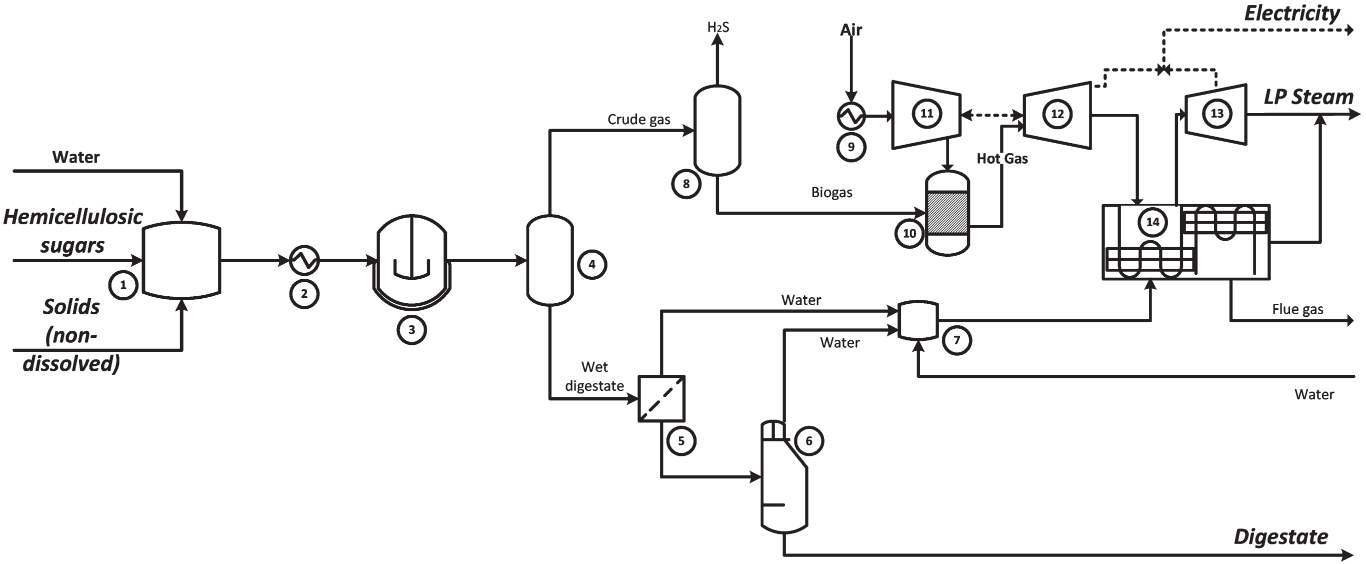


FIGURE 4.3. Simplified flowsheet diagram of anaerobic digestion integrated to a combined heat and power unit. Equipment list: 1. Mixer tank, 2. Heat exchanger, 3. Digester, 4. Gas separation, 5. Dewatering, 6. Evaporation and drying, 7. Mixer, 8. Gas Cleaning, 9. Heat Exchanger, 10. Combustion Chamber, 11. Compressor, 12. Gas Turbine, 13. Steam Turbine, 14. Heat Recovery Steam Generator (HRSG).

Figure 4.3 shows the simplified flowsheet diagram of the biogas plant coupled to a combined heat and power unit. The detailed explanation of input data and assumptions used to model the anaerobic digestion process can be found in Appendix A.

Corn wet milling

This system (see Figure 4.4) is comprised of four main sections: i) handling and steeping; ii) germ and fiber separation; iii) gluten separation, and iv) starch separation and hydrolysis. Input data (*e.g.,* process yields, utilities consumption, consumables) to calculate the mass and energy balances for was gathered from [166]. Additional steps on the hydrolysis stage (conversion of starch into glucose) were incorporated using calculations in Aspen Plus. The main outputs of this technology are the C6 sugars stream, corn germ, corn gluten meal and corn gluten feed. Detailed information on input data and assumptions used to model the corn wet milling process is provided in Appendix A.

4.2.4. Process Systems

Three systems were considered for the technical, economic and environmental assessments. These systems allow us to compare organosolv with and without anaerobic digestion with corn wet milling, and assess the effect of the integration of anaerobic digestion to the organosolv system. System I consists of standalone organosolv (including hydrolysis) to produce C6 sugars, lignin and furfural. The hemicellulose sugar stream and the non-converted solid from the enzymatic hydrolysis are assumed as waste streams, implying that the hemicellulose fraction is not valorized. System II consist of organosolv plus anaerobic digestion to account for the use of the hemicellulose hydrolysate stream and non-converted solids. The system will assess whether their further processing improves the overall performance of the organosolv system. In this system, the products are C6 sugars, lignin furfural, digestate (can be considered as biofertilizer) and electricity. System III is the corn wet milling process (benchmark).

4.2.5. Economic Assessment

The economic assessment provides an overview of the capital and operating costs, which were estimated using information (equipment list, mass and energy flows) generated in the process modeling. In the case of the organosolv and anaerobic digestion processes, the capital investment is based on adding up equipment costs (estimated using Aspen Economic Analyzer v8.4) and using typical factors for capital investment according to [189]. The factors used in this study can be found in Appendix B. In the case of the wet milling process, the capital investment was estimated using the capital costs data reported by [166]. Since the capital costs only covers until the starch recovery step, the equipment costs of the hydrolysis step were estimated using Aspen Economic Analyzer v8.4. All costs were updated to 2014 prices using the Chemical Engineering Plant Cost Index (CEPCI) and are expressed in Euros. When necessary an average 2014 exchange rate of 0.784 €/USD was applied.

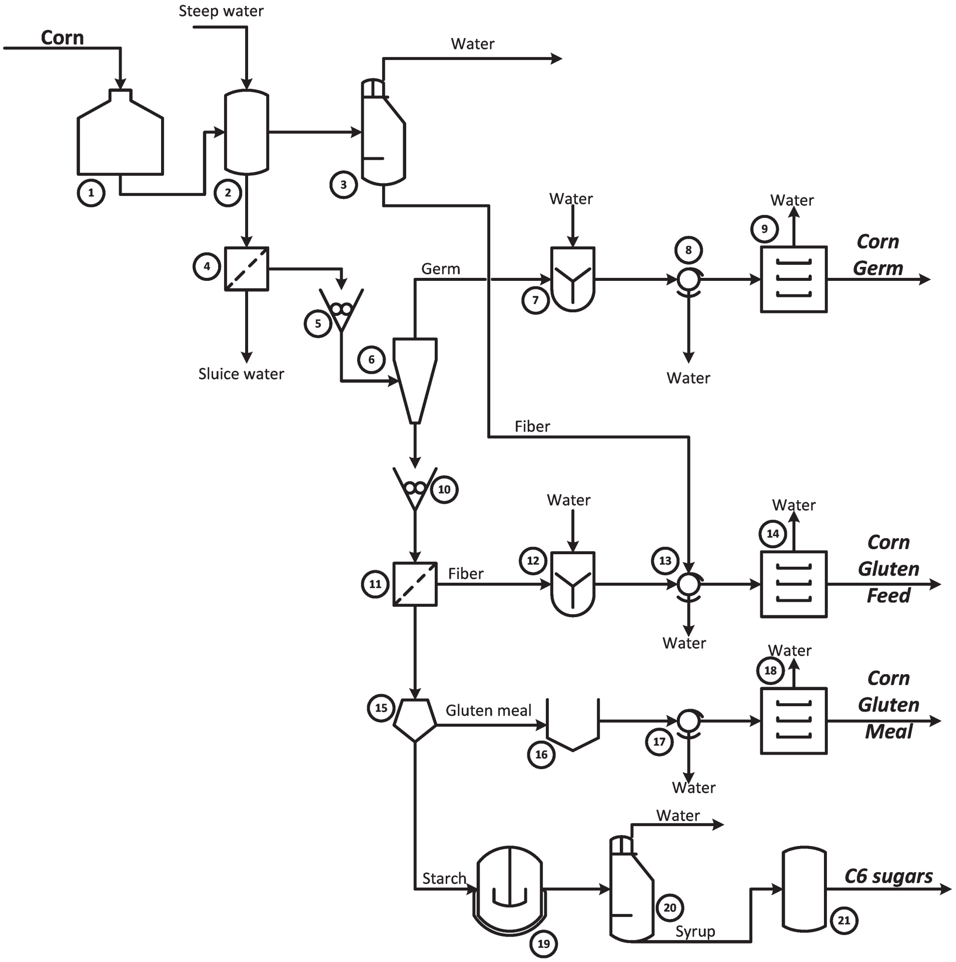


FIGURE 4.4. Simplified flow diagram of the corn wet milling process. Equipment list: 1. Corn Storage, 2. Corn Steeping, 3. Steep water evaporator, 4. Screen, 5. Mill, 6. Germ Separator, 7. Washer, 8. Dewatering, 9. Dryer, 10. Mill, 11. Screen, 12. Washer, 13. Dewatering, 14. Dryer, 15. Centrifuge, 16. Thickener, 17. Dewatering, 18. Dryer, 19. Starch Hydrolysis, 20. Evaporator, 21. Crystallizer

Annualized costs include raw materials, utilities, maintenance, labor, fixed & general, overheads and capital depreciation. Raw materials costs were based on the mass balances, and prices. Utilities costs were estimated using energy balances and prices calculated as additional process modules based on the equations reported by [190] and updated to 2014 prices (using 2014 CEPCI). Labor costs consisted of operating labor cost (3 shifts of 8 h each, 10 operators per shift for organosolv and 5 for wet milling), operating supervision cost and laboratory charges cost [189]. The yearly wage was assumed at 50,000 € per person. Additional cost categories such as maintenance, fixed & general, and plant overhead were included in the analysis. Estimation of these categories was carried out using typical factors [189] as shown in Appendix B. Green premiums, CO_2 credits and subsidies were not taken into account in the analysis. Capital depreciation was estimated using the straight line method for a depreciation time of 10 years based on suggestions by [189].

To assess the profitability of each system, the Net Present Value (NPV) was used as indicator. The NPV was estimated for 20 years using information on capital investment, operating costs and revenues from products by calculating discounted cash flows. The discount rate was set to 10% and income tax of 25% for the Netherlands (NPV calculations after taxes). Each step considered in NPV calculations were based on those reported by [189]. Details on NPV calculations are provided in Appendix E. Prices and main economic input parameters used in the assessment are displayed in Table 4.1.

Sensitivity analyses were considered at two different levels. The first one corresponds to changes in NPV results when conversions from lignin and glucan in the organosolv fractionation step were increased or decreased, and also when pulp digestibility is increased or decreased in the enzymatic hydrolysis step (in the organosolv process). The set of conversions considered in the sensitivity analysis are listed in Appendix B. The second level, corresponds to changes in NPV results when input prices change up to 50% above and below the reference values shown in Table 4.1. These sensitivity analyses allow identifying key parameters affecting the economic analysis accounting for both uncertainties in the performance of the technology and uncertainty in economic parameters such as volatility in prices.

4.2.6. Life Cycle Assessment

The life cycle assessment was carried out following the steps suggested by the International Standardization Organization (ISO) in their ISO 14040 series [198].

Goal definition and system boundaries

The analyses use three systems considered in the techno-economic assessment (see section 2.4). Each system is divided into three main process modules (stages of the life cycle): feedstock production (i.e., spruce woodchips and corn), feedstock transportation (*i.e.,* transportation to the processing facility) and biorefinery (*i.e.,* feedstock processing). Utilities production, auxiliary raw materials production (*e.g.,* enzymes, solvents, sulfuric acid) and waste treatment/disposal are considered within the LCA. The system boundaries correspond to the aggregation of all process modules, and is a cradle-to-gate analysis. System boundaries are depicted in Appendix C.

TABLE 4.1. Price inputs used in economic assessment of organosolv, anaerobic digestion and corn wet milling processes.

Feature	Value	Unit	Reference
Spruce woodchips	100	€/tonne (dry)	Based on [191]
Sulfuric Acid [a]	220	€/tonne	Average from [151]
Cellulase Enzyme cocktail [a]	2000	€/tonne	[169]
Ethanol [a]	620	€/tonne	[192], Price assumed to be applicable for 2014
Lignin [a,b]	630	€/tonne	[169]
C6 sugars [a]	300	€/tonne	Price assumed based on ranges reported by [193] and by [186].
Furfural [a]	900	€/tonne	Average from [151]
Natural Gas Price [a]	11	€/GJ	[194], Price assumed to be applicable for 2014
Electricity [a]	0.10	€/kWh	[194], Price assumed to be applicable for 2014
Digestate	10	€/tonne	Price assumed based on [195] and updated to 2014
Corn [a]	160	€/tonne	Price based on [196]
Sulfur [a]	10	€/tonne	Average from [151]
Gluten feed [a]	158	€/tonne	Price based on [197]
Germ [a]	270	€/tonne	Price based on [197]
Gluten meal [a]	632	€/tonne	Price based on [197]
α-Amylase, gluco-amylase enzyme cocktail [a]	700	€/tonne	Average from [151]
Cooling Water [c]	0.12	€/m^3	Based on [190] and updated to 2014 price
Low-pressure Steam [c]	40	€/tonne	Based on [190] and updated to 2014 price
Mid-pressure Steam [c]	46	€/tonne	Based on [190] and updated to 2014 price
Wastewater treatment [c]	0.08	€/m^3	Based on [190] and updated to 2014 price
Process water [c]	0.10	€/m^3	Based on [190] and updated to 2014 price
Demineralized water [c]	6.53	€/m^3	Based on [190] and updated to 2014 price
Solid disposal [c]	23	€/tonne	Based on [190] and updated to 2014 price

[a] Prices assumed to be representative for 2014.
[b] Price of lignin considered for high value added applications. Assumed as market price for organosolv lignin.
[c] Prices calculated using the equations proposed by [190], updated to 2014 prices using the CEPCI, and using natural gas as fuel source in the Netherlands (11 €/GJ, [194]).

The functional unit is 1 kg of C6 (dry) sugars since the objective of the analysis is to compare the environmental performance of C6 sugars from lignocellulosic biomass and corn. The three systems are multiproduct biorefineries, which implies multi-functionality.

As a consequence, the environmental impacts need to be allocated among the different products.

In this study, two main approaches were considered:

1) All environmental impacts were allocated to the C6 sugars stream, leaving all co-products burden free. From the point of view of C6 sugars production, this is the most conservative case.
2) Distributing the impacts between the main product and co-products using mass allocation. For all systems allocation factors were calculated using equation 1.

$$AF_i = \frac{m_i}{\sum_{j=1}^{n} m_j} \tag{4.1}$$

Where *AF* are the allocation factors, the product flowrates, and *i,j* counters for the products.

In the case of the electricity produced in system II, mass allocation is not possible to be applied. However, a fraction of the biogas produced can be associated to the production of electricity. This mass was then used to calculate the electricity mass allocation factor. Justification of the allocation approaches and detailed justification of the approach for calculating the allocation factor for electricity can be found in Appendix C.

The LCA was carried out for 4 impact categories using the ReCiPe impact characterization method [199]: Climate change potential (CCP), water depletion potential (WDP), agricultural land depletion potential (ALOP), and human toxicity potential (HTP). Non-renewable energy use (NREU) was considered as additional impact category, using the non-renewable section of the cumulative energy demand characterization method [200].

Life cycle inventory and data

Detailed explanation of the assumptions and data inputs of the feedstock production and transportation steps can be found in the Appendix D. Data related to impacts of corn and woodchips was gathered from the Ecoinvent v2.2 databases [149]. Data related to drying efficiency of woodchips and transport efficiencies (rail and maritime) was gathered from [201]. Additional data on rail transport efficiencies was collected from [202]. Sea distances were retrieved from [203]. Additional data related to fuel inputs such as diesel and heavy fuel oil was gathered from the Ecoinvent v2.2 database [149].

4.3. RESULTS AND DISCUSSION

This section focuses on results and discussion of process modeling (*i.e.,* mass and energy balances), economic analysis and environmental assessment.

4.3.1. Process modeling

Table 4.2 shows the mass balances of organosolv (System I), organosolv with anaerobic digestion (System II) and corn wet milling (System III). All mass balances are expressed on wet basis and provide an indication on the consumption of raw materials and the efficiency of the technologies. As shown in Table 4.2, the mass balances of Systems I and II, the input streams are identical (since the organosolv section is equal in both systems) with exception of the air stream in System II, which is used for combusting biogas. The flowrates of furfural and lignin are also identical, however, additional products such as digestate, steam (although used internally) and recovered water are obtained in System II. In terms of waste streams, System I shows 17% higher flowrates than System II. This highlights the importance of anaerobic digestion for recovering the carbon fraction of the non-converted solids and crude sugars stream and obtain additional products, which can be integrated within the organosolv process (*i.e.,* steam and electricity). Material inputs significantly differ among the systems. In terms of feedstock (i.e., woodchips and corn), the corn wet milling (System III) requires 52% less than organosolv (on a dry basis) for producing the same amount of C6 sugars. The latter is due differences in polysaccharide content of each raw material to produce the C6 sugar stream, and the efficiency of each technology to recover the sugars. In the case of corn, starch represents 67% of the corn mass (dry basis), while in the case of spruce only the cellulose fraction was used for producing the C6 sugar stream, which represents approx. 42% of the biomass. It should be noted that if C6 sugars can be recovered from the hemicellulose stream (not considered in this study), higher C6 sugars yields from spruce could be expected. When translating this into processing yields (total feed to C6 sugars basis), values of 0.36 kg C6 sugars per kg of woodchips (Systems I and II), and 0.74 kg C6 sugars per kg of corn (System III) are obtained on a dry basis. The C6 sugars yield based on corn is 107% higher than that from woodchips. In terms of waste streams, System I and II produce 3.0 and 2.5 times higher flowrates than those of System III, respectively. The higher contribution to waste streams is wastewater with 62%, 73% and 100% for Systems I, II and III, respectively. These high flowrates are a consequence of high water input requirements for dilution, in steps such as organosolv fractionation in Systems I and II, steeping in System III and hydrolysis steps in the three systems. It should be noted that integration of water stream was not considered in the scope of this study and thus further improvement is possible if the reader would extent the current analysis. The only integration of water considered in this study, was using part of the clean water after anaerobic digestion as feed for producing LP and MP steam. This is why water inputs are not increased in System II in comparison to System I. Table 4.2 also shows that the recovery of the organic solvent is high. However, it should be taken into account that possible ethoxylation reactions of lignin and carbohydrates were not considered. In consequence, it may be possible that a higher ethanol make-up is required after recycling.

The yield of hemicellulosic sugars plus non-converted solids (dry basis) is 0.52 kg per kg of woodchips, which reflects that 52% of the initial mass of dry biomass is contained within these two streams. In System II, the conversion of hemicellulosic sugars and non-converted solids leads to a biogas flowrate of 148 ktonne per year, which is equivalent to 0.15 kg per kg of woodchips (dry). The yields of corn wet milling are in agreement with results reported in literature [166, 176].

Table 4.3 displays the energy inputs, outputs and net requirements for the three systems. In System I, heating utilities (*i.e.,* LP and MP steam) contribute to 58% of the net energy requirements, followed by cooling water (42%) and electricity (1%). When comparing the total energy requirement with literature (including all utilities types), [169] reported a consumption of 2.5 MJ per kg of dry biomass processed (value calculated only using the pretreatment and hydrolysis sections in [169]), while this study reports a consumption of 2.4 MJ per kg of dry biomass processed (approx. 13% of the LHV of dry woodchips). In System II, the energy inputs are equal to those of System I, however, electricity and steam are produced. In the case of LP and MP steam, the cogeneration system is able to cover 96 and 100%, respectively. The latter implies a reduction of net requirements on heating utilities of about 97% in System II (in comparison to system I). In the case of electricity, the requirements are 100% covered by the cogeneration unit with surplus electricity (*i.e.,* electricity for revenues) of 99% of the total produced (1% of total electricity produced used for biorefinery consumption). This shows the importance of valorizing the hemicellulose and non-converted solids streams, which in this case were used for energy production. Based on the lower heating value of biogas, the efficiency of the cogeneration system corresponds to 49% to heat, 41% to electricity and 10% energy loses. Although heating utilities are not 100% covered by the cogeneration unit, the requirement of outsourced steam significantly decreased and its contribution to net requirements decreased from 58% in System I to 4% in System II. The remaining fraction of net energy requirements of System II is satisfied with cooling water (96% contribution). Net energy requirements of System II are 56% lower than net requirements of System I when electricity surplus is not accounted for, and 100% when electricity surplus is accounted for. In the case of System III, the contribution of heating

TABLE 4.2. Mass balances accounting for key material inputs and outputs of each system, expressed in ktonne/y.

Systems	**Organosolv, No valorization of hemicellulose fraction (System I)**		**Organosolv & Anaerobic Digestion, Valorization of hemicellulose fraction (System II)**		**Corn wet milling (System III)**	
Stream	**Inputs**	**Outputs**	**Inputs**	**Outputs**	**Inputs**	**Outputs**
Raw materials						
Woodchips [a]	1111	-	1111	-	-	-
Corn [b]	-	-	-	-	563	-
Sulfuric Acid	6	-	6	-	-	-
Sulfur	-	-	-	-	1	-
Solvent [c]	0.01	-	0.01	-	-	-
Water	4231	-	4321	-	1581	-
Enzyme	10	-	10	-	3	-
Air	-	-	937	-	-	-
Products						
C6 sugars [d]	-	359	-	359	-	359
Furfural [e]	-	12	-	12	-	-
Lignin [f]	-	191	-	191	-	-
Digestate	-	-	-	352	-	-
MP steam [g]	-	-	-	195	-	-
LP Steam [g]	-	-	-	462	-	-
Treated water [h]	-	-	-	655	-	-
Gluten Feed [i]	-	-	-	-	-	104
Germ [i]	-	-	-	-	-	38
Gluten Meal [i]	-	-	-	-	-	33
Waste streams						
CO_2 [j]	-	1	-	1	-	-
Hemicellulosic sugars [k, l]	-	950	-	-	-	-
Non-converted solids [k, l]	-	857	-	-	-	-
Waste water	-	2989	-	2989	-	1613
H_2S	-	-	-	2	-	-
Flue gas [m]	-	-	-	1077	-	-
Total	**5358**	**5358**	**6295**	**6295**	**2148**	**2148**

[a] Woodchips water content 10 wt%.

[b] Corn water content 14 wt%.

[c] Fresh ethanol required at 96 wt%. The required solvent is recycled within the battery limits.

[d] Stream free of water, C6 sugars purity 100%.

[e] Furfural purity 98 wt%.

[f] Lignin water content 10 wt%.

[g] LP steam pressure: 3 bar, MP steam pressure: 10 bar. Products integrated within the organosolv process in the energy balance.

[h] Water recovered after anaerobic digestion.

[i] Water content: gluten feed 10 wt%, germ 3 wt%, gluten meal 10 wt%.

[j] CO_2 produced during organosolv fractionation.

[k] Water content: hemicellulosic sugars 70 wt%, non-converted solids 74 wt%

[l] Residues composition (dry basis): hemicellulosic sugars: sugars 53 wt%, furans 14 wt%, humins 1 wt%, others 33 wt%. Non-converted solids: Cellulose and hemicellulose 15 wt%, lignin 50 wt%, other 35 wt%.

[m] Flue gas composition: water 11 wt%, CO_2 21 wt%, O_2 1 wt%, N_2 67 wt%.

utilities to net requirements is 82% (i.e., LP steam and natural gas) and contribution by electricity is 18%. System III consumes less energy than Systems I by 60%, however, System II consumes 100% less energy than System III. Thus, it is expected higher costs in utilities in Systems I in comparison to System III, and higher utilities costs in System III in comparison to System II. The energy consumption levels are in alignment with the data reported by [166]. The economic performance of each system is explained in more detailed in the following section.

TABLE 4.3. Energy requirements and energy produced in each system, expressed by utility type in TJ/y.

Systems	**Organosolv, No valorization of hemicellulose fraction (System I)**			**Organosolv & Anaerobic Digestion, Valorization of hemicellulose fraction (System II)**			**Corn wet milling (System III)**		
Utility type	**Input**	**Output**	**Net [a]**	**Input**	**Output**	**Net [a]**	**Input**	**Output**	**Net [a]**
Cooling water [b]	998	0	998	998	0	998	0	0	0
LP Steam [c]	1025	0	1025	1025	980	45	219	0	219
MP Steam [c]	350	0	350	350	350	0	0	0	0
Natural gas [d]	0	0	0	0	0	0	556	0	556
Electricity	13	0	13	13	1059	-1046	175	0	175
Total	**2386**	**0**	**2386**	**2386**	**2389**	**-3**	**950**	**0**	**950**

[a] Negative values indicate surplus for sales.
[b] Cooling water heat capacity: 50 kJ/kg
[c] Latent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg
[d] Natural gas lower heating value (LHV): 47.1 MJ/kg

4.3.2. Economic Assessment

The economic analysis focuses on the net present value (NPV), which include aspects such as annualized operating costs and capital investment. Table 4.4 shows the summary of capital investment for each system. For System I, capital costs are split among organosolv and hydrolysis sections with a contribution of 82% and 18%, respectively. In the case of System II, the contributions of organosolv, hydrolysis and anaerobic digestion (including cogeneration unit) are 75%, 17% and 8%, respectively. Total investment costs (Fixed capital investment + working capital) in System II are 12% higher than those of System I as anaerobic digestion was included as an additional process. It can be predicted higher operating costs in System II, that depend on fixed capital investment (*e.g.,* maintenance, depreciation), in comparison to System I. In the case of corn wet milling (System III), the contribution of starch production (including germ, gluten meal and gluten feed production) and starch hydrolysis to total capital investment is 85% and 15% respectively.

TABLE 4.4. Summary of capital investment costs for each system

Capital investment	Organosolv (System I)	Organosolv & A. Digestion (System II)	Corn wet milling (System III)
Fixed Capital Investment – M€	210	236	55
Working capital – M€	48	52	10

The capital costs of the corn wet milling are relatively known due to its maturity for producing corn derived products and ethanol [166, 204]. However, this is not the case for the organosolv technology which is still at early development stages, thus bringing uncertainties on capital costs at large scales. From literature, it becomes difficult to make a direct comparison of capital investment of the organosolv section since many of the studies focuses on C6 sugars derived products such as ethanol. Consequently, data for certain process sections are difficult to split due to differences in scope (*e.g.,* battery limits, production capacities). Nevertheless, there are few studies which provide a more detailed breakdown of capital costs of the organosolv section (excluding hydrolysis section). Table 4.5 shows the fixed capital investment of the organosolv section to obtain pulp, in comparison to other studies available in literature (The comparison excludes the enzymatic hydrolysis and C6 sugars recovery sections due to differences in scope among the referenced literature). All studies were at different biomass processing capacities (see Table 4.5), thus, the six-tenth rule of thumb was used to scale up the fixed capital investment of each study to the feedstock capacity of this work. At 1 Mtonne/y capacity, the low end is for the work reported by [169], while the high end for the work reported by [186]. Table 4.5 shows a range of 126 M€, which reflects the uncertainty on capital cost estimation for the organosolv technology and the importance to include it as part of the sensitivity analysis.

TABLE 4.5. Fixed capital investment of organosolv pretreatment section. Investment cost comparison only considers the organosolv pretreatment section for obtaining pulp.

Parameters	Source			
	Michels, [186]	van der Linden et al., [205]	Nitzsche et al., [169]	This Study
Base Capacity - ktonne/y dry biomass	150	150	400	1000
Fixed Capital Investment (at base capacity) - M€	80	75	71	172
Fixed Capital Investment at 1 Mtonne/y dry biomass - M€ [a, b]	250	234	124	172

[a] Capital investment scaled to 1000 ktonne/y of biomass supply (capacity used in this study).

[b] The comparison excludes the enzymatic hydrolysis and C6 sugars recovery sections due to differences in scope among all studies compared. Cogeneration investment costs are also excluded.

Table 4.6 shows the annualized operating costs (year zero), capital investment and revenues for each system (inputs used for calculating NPV). In the three systems, the aspects that contribute the most to operating costs are raw materials and utilities. Due to savings on external energy use after the integration of anaerobic digestion with organosolv, System II shows a reduction of utilities costs by approx. 90%, in comparison to System I. System I shows the highest operating costs, being 16% and 66% higher than those for Systems II and III, respectively. System III shows the best performance for producing C6 sugars in terms of operating costs. In Systems I and II, C6 sugars has the highest contribution to revenues, followed by lignin. This shows the high correlation between the valorization of lignin with the feasibility of the system. In the case of corn wet milling, revenues are highly dominated by C6 sugars income. In terms of product revenues, System II shows the highest income being 16% and 63% higher than Systems I and III, respectively. This highlights the importance of the valorization of the hemicellulosic sugar stream for producing biogas and subsequently, electricity and steam.

TABLE 4.6. Annualized production costs, revenues and Net Present Value of all Systems.

Feature	Organosolv (System I)		Organosolv & A. Digestion (System II)		Corn wet milling (System III)	
	M€/y	**Share (%)**	**M€/y**	**Share (%)**	**M€/y**	**Share (%)**
Operating costs						
Raw materials	121.7	62%	121.7	72%	92.6	78%
Utilities	36.0	18%	3.5	2%	15.3	13%
Maintenance	14.5	7%	16.5	10%	3.5	3%
Labor	2.0	1%	2.0	1%	1.0	1%
Fixed & general	13.4	7%	15.2	9%	3.3	3%
Overhead	8.6	4%	9.6	6%	2.3	2%
Total	**196.1**	**100%**	**168.4**	**100%**	**118.0**	**100%**
Revenues						
C6 sugars	107.6	49%	107.6	42%	107.6	69%
Lignin	100.5	46%	100.5	39%	-	-
Furfural	10.6	5%	10.6	4%	-	-
Digestate	-	-	3.7	1%	-	-
Electricity	-	-	32.3	13%	-	-
Gluten feed	-	-	-	-	16.5	11%
Germ	-	-	-	-	10.4	7%
Gluten meal	-	-	-	-	21.1	14%
Total	**235.8**	**100%**	**261.1**	**100%**	**181.9**	**100%**
Fixed capital investment						
M€	**210**		**236**		**55**	
Net present value after taxes [a]						
M€	**-119**		**238**		**168**	

[a] NPV at the end of project lifetime

The NPV results (see Table 4.6) show a negative value for System I, which implies economic unfeasibility. To reach break-even (assuming all other parameters fixed, such as C6 sugars and furfural prices), the price of lignin needs to be increased from 630 €/t (base case lignin price in Table 4.1) to 751 €/tonne. Similarly, in case that lignin price is to remain fixed at 630 €/tonne, to reach break-even (assuming all other parameters fixed), the price of C6 sugars needs to be increased from 300 €/tonne to 354 €/tonne. The NPV for System II is above break-even indicating economic feasibility of the organosolv system when anaerobic digestion is included (valorization of hemicellulosic sugars). The NPV of this system is also above break even due to the fact that lignin price was set to 630 €/tonne. On one hand, the minimum lignin price to keep system II working above break-even (leaving all other parameters fixed) corresponds to 388 €/tonne. When comparing the price of lignin reported in literature (for organosolv systems) with the value used in this study (630 €/tonne), our findings fall within the ranges reported: van der Linden et al., [205] reports a lignin price of 750 €/tonne, while Michels [186] reports a base lignin price of 622 €/tonne, and low and high ends of 400 to 800 €/tonne, respectively. However, it is important to highlight that the base capacities (dry biomass processing) of the cited studies are lower than that of this study, implying that for small scale systems higher product prices (*e.g.,* lignin price) will be required. The common aspect of this study and literature on organosolv fractionation systems is the high price dependency of lignin to allow the system to work above break-even. System's III NPV is positive indicating the economic feasibility of corn wet milling. Figure 4.5 shows the cumulative NPV for each System. System I shows that the payback period is outside the project's lifetime, while System II shows a payback period of 8 years. In the case System III, the investment is recovered in year 4 (payback period). However, in economic terms, System II shows higher NPV value at the end of projects lifetime. This behavior can be explained by the fact that although higher capital investment is required for System II in comparison to System III, higher revenues guarantee higher NPV at the end of projects lifetime. It is also important to highlight that system II shows positive economic outcome if markets of organosolv lignin can be developed. Nevertheless, this study shows that in the case that lignin price drops (up to 388 €/tonne), when anaerobic digestion is included, organosolv can still be feasible.

Sensitivity Analysis

The results of sensitivity analysis focus on the NPV. Figure 4.6 shows the results in sensitivity analysis when main prices are varied. The reader should note that all prices discussed in this section were considered independent of each other (*i.e.,* varying one price at a time and leaving all other parameters fixed). The results for System I (see Figure 4.6a) suggest that the parameters that influence NPV the most are C6 sugars price, lignin price, biomass price and capital investment. In the case of lignin price an increase of 20% will lead the system to reach break-even. However, price decreases will lead to more unfeasible scenarios. Similarly, the price of C6 sugars needs to be 18% higher than the reference value shown in Table 4.1 to reach break-even, while a decrease of its price leads to a very unfeasible case. One of the options to decrease the dependency on lignin revenues is to increase the price of C6 sugars. However, this aspect depends on market prices and uncertainties on C6 sugars prices would have an impact on lignin minimum selling price. The base case price of C6 sugars (300 €/tonne in Table 4.1) seems low in comparison to 400 €/tonne reported by [186]. If the price of C6 sugars is increased to 400 €/tonne, the minimum selling price of lignin (to reach NPV=0, leaving all other parameters fixed) in System I is reduced by 17% (from 630 €/tonne to 526 €/tonne), while in System II it decreases from 630 €/tonne to 163 €/tonne. Nevertheless, on one hand, a lower C6 sugar price is more attractive for downstream processes such as the conversion of C6 sugars into fuels and chemicals. On the other hand, low prices in lignin are also attractive for downstream processes using organosolv lignin as feedstock. This clearly shows that a good balance need to be found and/or that both markets (cellulose and lignin) need to be well-developed to allow taking-off of both products at sufficient prices. It should also be taken into account that both lignin and C6 sugar yields are dependent on the fractionation degree. Finally, changes in feedstock can imply different composition and fractionation degree and therefore different techno-economic performances.

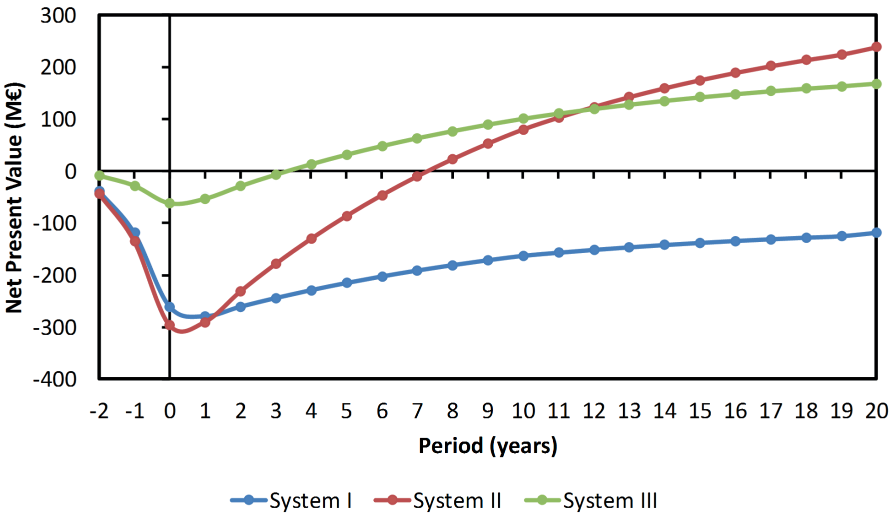


FIGURE 4.5. Cumulative Net Present Value of all Systems for a project life-time of 20 years. Lignin price of 630 €/tonne for Systems I and II

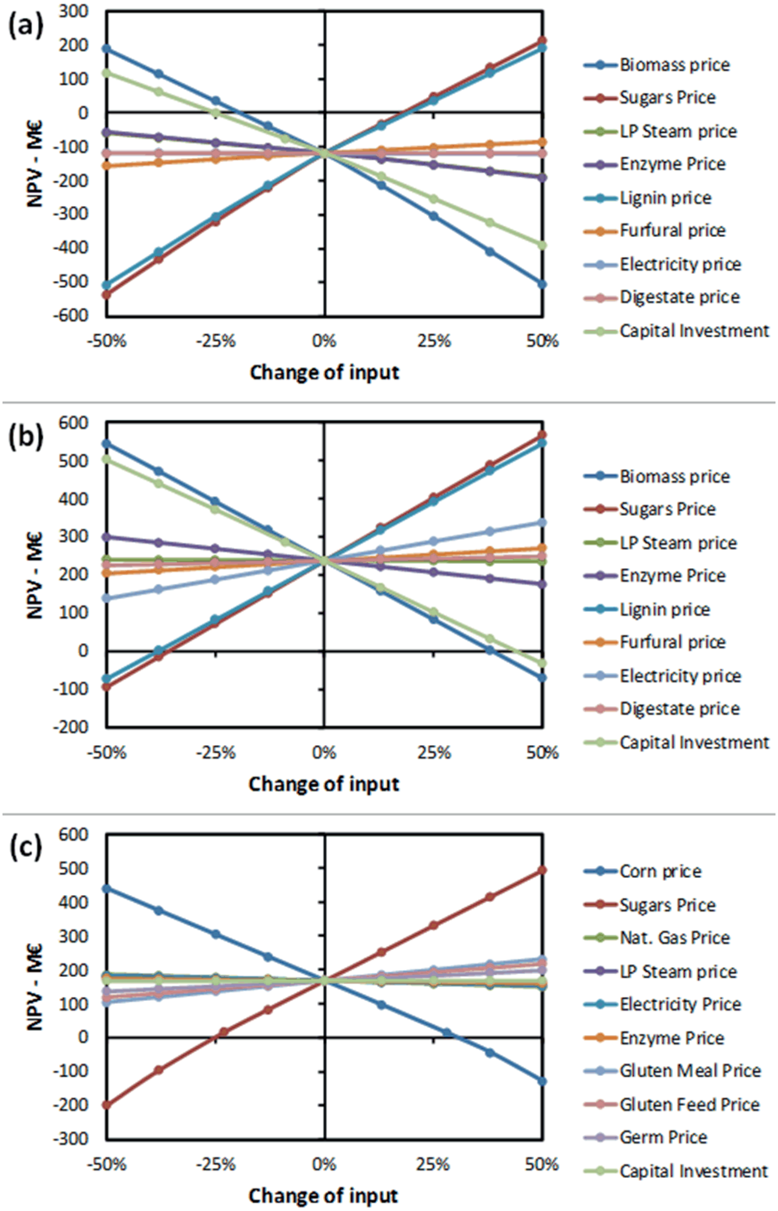


FIGURE 4.6. Results of sensitivity analysis on economic parameters of all Systems: a) System I, b) System II, c) System III

Biomass price should also be considered as a key aspect on the performance of the systems, slight price fluctuations of biomass significantly affect the performances. For instance, decreases above 20% allows System I to reach break-even, while increases on woodchips prices will make the system even more unfeasible. This highlights the importance on developing a biomass supply structure that guarantees low fluctuations on feedstock prices. The influence of capital investment is also important since decreases above 25% of the capital costs may lead System I to work in NPV values above its break-even point (NPV > 0). In contrast, increases on capital investment negatively affect the overall performance of the system. The effect of LP steam and enzyme price on the NPV is similar, though significant, it is not at the level of the previously mentioned parameters. In the case of enzyme consumption, this is relevant to mention that we assumed the highest enzyme dosage reported in literature among techno-economic studies for biomass conversion (see Appendix A). In consequence, if enzymes dosages and prices can be decreased it is expected to have a positive contribution on the overall economic performance of organosolv fractionation systems. The effect of furfural and electricity price is low in comparison to the previously mentioned parameters.

The parameters that affect the NPV of System II (see Figure 4.6b) the most are C6 sugars, lignin price, biomass price and capital investment. Small fluctuations of the four parameters (*i.e.,* lignin price, C6 sugar price, biomass price and capital investment) may drastically impact the economic performance of the system. However, the threshold to keep the system working above break-even is larger in comparison to that of System I. If biomass price is increased above 40% of the reference price, the system starts to be unfeasible. The effect of capital investment is similar and increases above 44% lead the system to be unfeasible. In terms of C6 sugars price, decreases above 36% lead the system to be unfeasible. Similarly, in the case that lignin price drops by 39% of the reference price, the system starts to be unfeasible. The effect of the remaining parameters is not that strong, and even by varying those (independently) up to ± 50%, the system is still able to operate under feasible conditions. All in all, System II seems robust given the possibility to remain in the feasibility zone if parameters such as lignin and C6 sugars price vary. Overall, Systems I is very sensitive to changes in most economic parameters, thus, suggesting higher risks to implementing this technology. Although system II seems more robust, fluctuations in some parameters highly affect positively and negatively the NPV. Thus, this analysis allows identifying hotspots for further developing the technology, which in this case is to ensure a stable biomass supply system to avoid high fluctuations on prices and reach a proper balance between the markets of sugars and lignin. The latter can be overcome for instance by increasing C6 sugars prices which include premiums for favoring 2G technologies.

The results of sensitivity analysis for System III (see Figure 4.6c) show strong influence of the prices of biomass and C6 sugars on NPV. An increase of corn prices above 30%, leads the system to work under unfeasible conditions. The effect of varying C6 sugar prices is similar, though with opposite direction than that of corn price. A decrease of C6 sugars price of approx. 25% will lead the system to work under unfeasible conditions. The strong influence of corn and C6 sugars prices is not surprising since both raw materials costs and revenues of C6 sugars are the features with the highest contribution to annualized production costs and product revenues, respectively. The effect of co-product prices (*i.e.,* corn germ, gluten meal and gluten feed) follow the previous parameters that affect the NPV the most. As expected, the recovery and sales of gluten meal, gluten feed and germ have a significant effect on the NPV. However, at the considered range these do not lead to unfeasible scenarios. Finally, parameters such as natural gas, electricity and enzyme prices and capital investment can negatively affect the system if those are increased. Nevertheless, due to the maturity of the technology, it is unlikely to have high fluctuation on those costs. Overall, the corn wet milling (System III) seems to show lower risks than System I. However, System II seems to have less risk in comparison to System III since only changes in corn and C6 sugars prices can lead the system to work under unfeasible conditions. In the case of System II, it is important to highlight the high dependency of lignin valorization, and the sensitiveness to capital investment changes. In general, it should be taken into account that 2G technologies are in principle more expensive than 1G technologies and that a transition to 2G should be accompanied by incentives for its development.

Figure 4.7, shows the effect of varying conversions (see Table 4.8 and Table 4.9 in Appendix A) on lignin, glucan and pulp. In the case of System I (Figure 4.7a), lignin and pulp conversions show to have an important influence on the techno-economic performance. By increasing lignin conversion by 20% (conversion from 57.8% to 69.4%, see Table 4.12), and therefore increasing the lignin yield to 0.17 kg/kg of woodchips (dry), the NPV of the system becomes positive (7 M€). In the case that C6 sugars yield increases (up to 0.40 kg/kg woodchips dry), by the action of increasing pulp conversion during enzymatic hydrolysis, the NPV is still negative (-44 M€), but closer to breakeven. Additionally, in the case where glucan solubilization could be decreased during organosolv fractionation, higher C6 sugar yields could be obtained (0.39 kg/kg woodchips dry, leaving all other parameters fixed). This yields a higher NPV, though still negative for System I (-62 M€). These results suggest that both by increasing C6 sugars and lignin yields, the system can perform economically better. In the case of System II (see Figure 4.7b), although changes in the three conversion can significantly affect the system those do not lead to unfeasible scenarios. However, the NPV of the system is clearly benefited by increases in lignin yield.

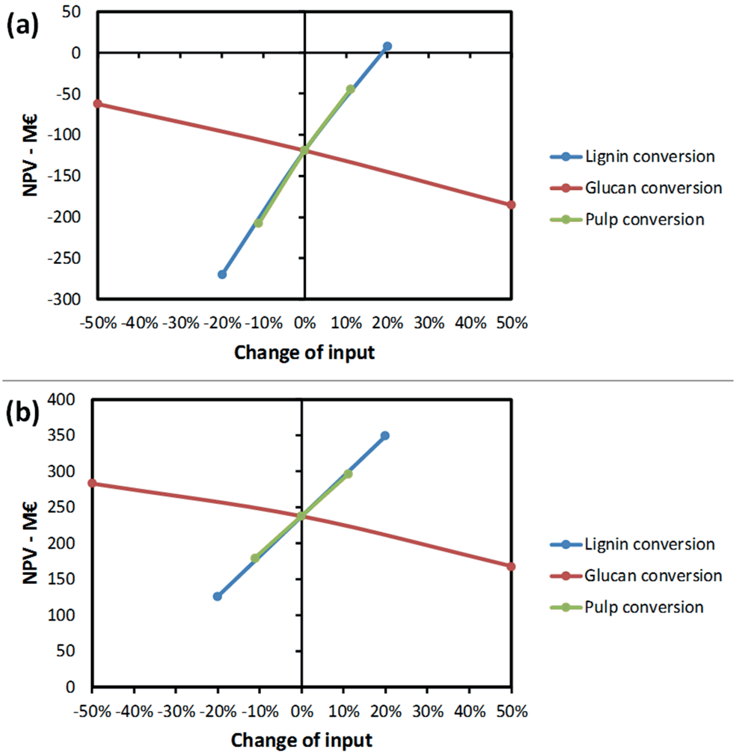


FIGURE 4.7. Results of sensitivity analysis on lignin, glucan and pulp conversions: a) System I, b) System II.

4.3.3. Life cycle assessment

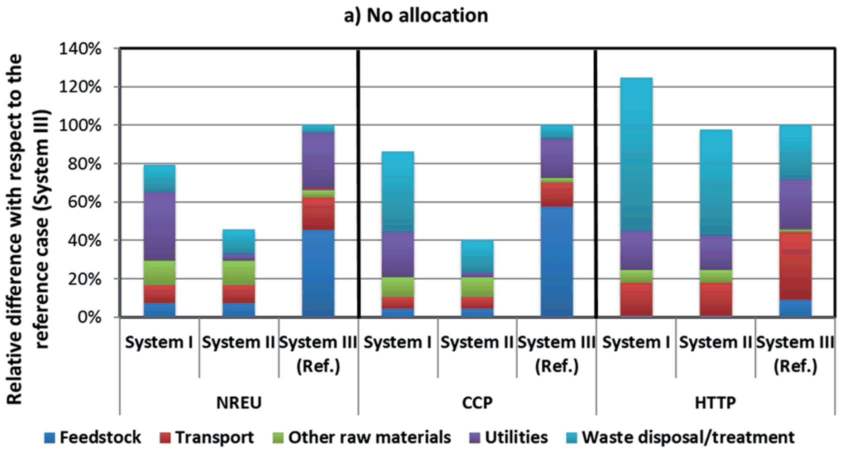
Technical data obtained from process modeling regarding mass and energy balances (see Table 4.2 and Table 4.3) were used to complete the life cycle inventory of the biorefinery section (see Appendix C). Figure 4.8 and Figure 4.9 show the results of the life cycle environmental impacts, including the two allocation approaches (*i.e.,* no allocation, mass allocation) of the three systems relative to the reference case (corn wet milling, System III). The results also present the process contribution analysis for each system split into features such as feedstock, transportation, other raw material inputs, utilities (*e.g.,* steam, cooling water, electricity) and waste treatment/disposal. The absolute values of the life cycle environmental impacts expressed per functional unit (kg of C6 sugars) are shown in Appendix F.

Figure 4.8 shows the results for the categories CCP, NREU and HTP. When no allocation among co-products is used (Allocation approach 1, see Figure 4.8a), NREU is 21 and 54% lower in Systems I and II than for System III (reference system). When comparing Systems

I and II, the NREU is 42% lower for System II than for System I. The reduction on NREU in System II is due to energy savings from the production of steam and electricity from biogas. This emphasizes the importance of valorizing the hemicellulosic sugar stream and non-converted solid stream to improve the overall performance of the organosolv process. In the case of CCP using allocation approach 1, the potential environmental impact of Systems I and II are 14 and 60% lower than that of System III. Analogous to NREU, System II shows lower CCP by 54% in comparison to System I. Overall, the main difference in NREU and CCP for organosolv (Systems I and II) and corn wet milling (System III) processes, is on the feedstock production step with higher impacts for corn (See Figure 4.8a). In the case HTP, when using allocation approach 1, the impacts for System I are higher than that of System III (25%), while the impact for System II are lower than that of System III (2%). The difference between System I and II is due to reduction of impacts related to waste disposal/treatment and utilities due to the use of electricity and steam produced after the anaerobic digestion of the hemicellulosic sugars stream. For the three impact categories discussed so far, System II shows to be highly benefitted by the valorization of the hemicellulose sugar stream in comparison to System I.

When using mass allocation among the C6 sugar stream and co-products (Allocation approach 2, see Figure 4.8b), for NREU and CCP categories, the direction of the impacts is not affected (*e.g.,* lower values for Systems I and II in comparison to System III, and lower impacts of System II in comparison to System I), however, the relative difference to the reference system is affected by decreasing further the NREU and CCP of the woodchips based processes (Systems II mainly) in comparison to the corn wet milling (Reference system). In the case of HTP, the direction of results does not change (*i.e.,* higher for System I and lower for System II compared to System III), however, the relative difference in comparison to the reference system is increased (see Figure 4.8b). By comparing System II with System I when using allocation approach 2, the difference of NREU, CCP and HTP is larger in favor of System II (lower by 68%, 75% and 57% respectively). This is due to the difference in allocation factors (based on mass, see Methodology section, equation 1) among the processes (Allocation factors shown Table 4.20 in Appendix F). The use of allocation is controversial since it is affected by the products that are included in the distribution of environmental impacts. For instance, in System II, 39% of the total impacts are allocated to dry digestate from anaerobic digestion, however, this stream only contributes to less than 1% of total revenues. Instead, if economic allocation is used (assumed as % of total revenues in Table 4.6), the allocation factor for C6 sugars would be 49% for Systems I, which would bring lower impacts to those using mass allocation (allocation factor based on mass, 68%, see Table 4.20 in Appendix F). In contrast, in the case of System II, mass allocation and economic allocation factors

(37 and 42%, respectively) seem relatively close. In System III, if economic allocation is used, the allocation factor to C6 sugars for corn wet milling would be 69%, which is relatively robust when compared to the allocation factor based on mass (67%). Due to the multiple possible approaches for distributing the environmental impacts among the multiple products and the possible deviations that this may bring to the objectivity of the comparison of the systems, the approach of allocating all impacts to the C6 sugars stream (allocation approach 1, see methodology section) allows a better understanding of the total performance of each system.


a) No allocation

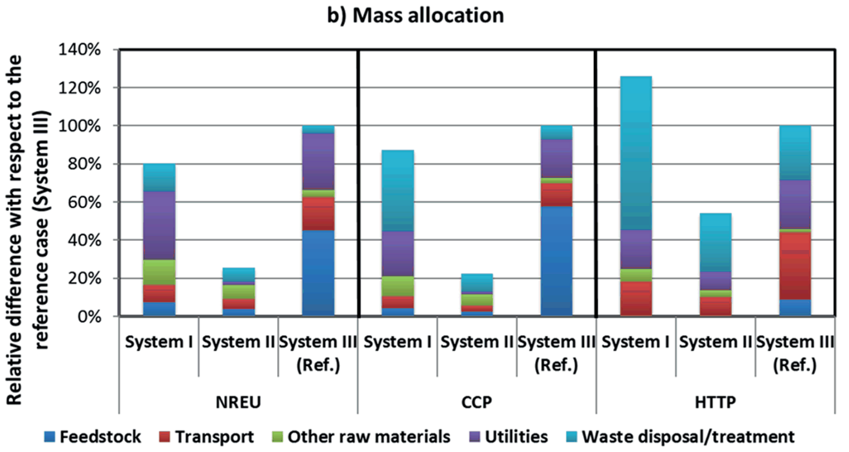

b) Mass allocation

FIGURE 4.8. Environmental impacts for non-renewable energy use (NREU) climate change potential (CCP) and human toxicity potential (HTP) relative to the reference system (System III, corn wet milling). Each system is divided into contributions from feedstock production, feedstock transportation, consumption of auxiliary raw materials, utilities and waste treatment/disposal. a) Results when no allocation is applied (100% of environmental impacts allocated to C6 sugars), b) mass allocation applied to C6 sugars streams and co-products.

To further understand the results, a comparison is made with results published in literature. NREU and CCP are the most reported impact categories for bio-based systems. Nevertheless, in the case of production of C6 sugars from lignocellulosic biomass using the organosolv technology, little is reported and direct comparison was not possible (due to differences in scope). In the case of C6 sugars production from corn, [176] reported the cradle-to-gate NREU and CCP discussing the differences when using different allocation approaches. Our findings show a NREU of 9.01 MJ/kg of C6 sugars (using mass allocation, see Table 4.19 in Appendix F), which falls within the range of 6.8 to 9.3 MJ/kg of C6sugars reported by [176]. In the case of CCP, our findings show a value of 0.79 kg CO_{2eq}/kg of C6sugars which also falls within the range of 0.7 to 1.1 kg CO_{2eq}/kg of C6sugars reported by [176].

Figure 4.9 shows the results of ALOP and WDP categories, where Systems I and II have higher values than the reference System (System III). When using allocation approach 1 (See Figure 4.9a), the results for ALOP show that the impact of both Systems I and II are a factor 4.5 higher than those of System III. ALOP impacts are driven by the feedstock production step (>99.5%), thus suggesting an advantage of corn over woodchips in agricultural land occupation. This is due to difference in feedstock flowrates for producing the same volume of C6 sugars, with woodchips (dry basis) requiring 2.1 times more than corn for producing 1 kg of sugars (see Table 4.2). It should be taken into account that the current analysis highly rely on the characterization factors of the ReCiPe method, which may be questionable when comparing forestry feedstocks (woodchips in this case) to agricultural feedstocks such as corn. In the case of WDP, the impact of both Systems I and II are approx. factor 3.6 higher than that of System III. The main difference can be attributed to higher cooling water consumption in the organosolv process in comparison to the corn wet milling (utilities consumption calculated based on data reported in Table 4.3). The inclusion of anaerobic digestion does not improve the performance of System II compared to System I, since their relative difference (compared to System III) is almost identical in the two impact categories. It is important to highlight that in the case of the organosolv systems, optimization on the use of cooling utilities (integrated with water effluents from the system) was not considered. In consequence, there is room for improvement in WDP of the organosolv systems in case that cooling utilities can be decreased by further integration of streams. It is also important to note that in the case of corn wet milling (System III), no cooling utilities were reported (see Table 4.3). When using allocation approach 2 (*i.e.,* mass allocation, See Figure 4.9b), the direction of the impacts of ALOP, WDP do not change (*i.e.,* impacts higher than reference system, System III) when comparing with allocation approach 1. Nevertheless, the relative difference of the impacts of both System I and II compared to those of System III decreases in the two categories. Additionally, when comparing System I and II, System II seems to have lower impacts than those of System I. This can be explained by the difference in allocation factors to C6 sugars in all three Systems as discussed previously for NREU, CCP and HTP.

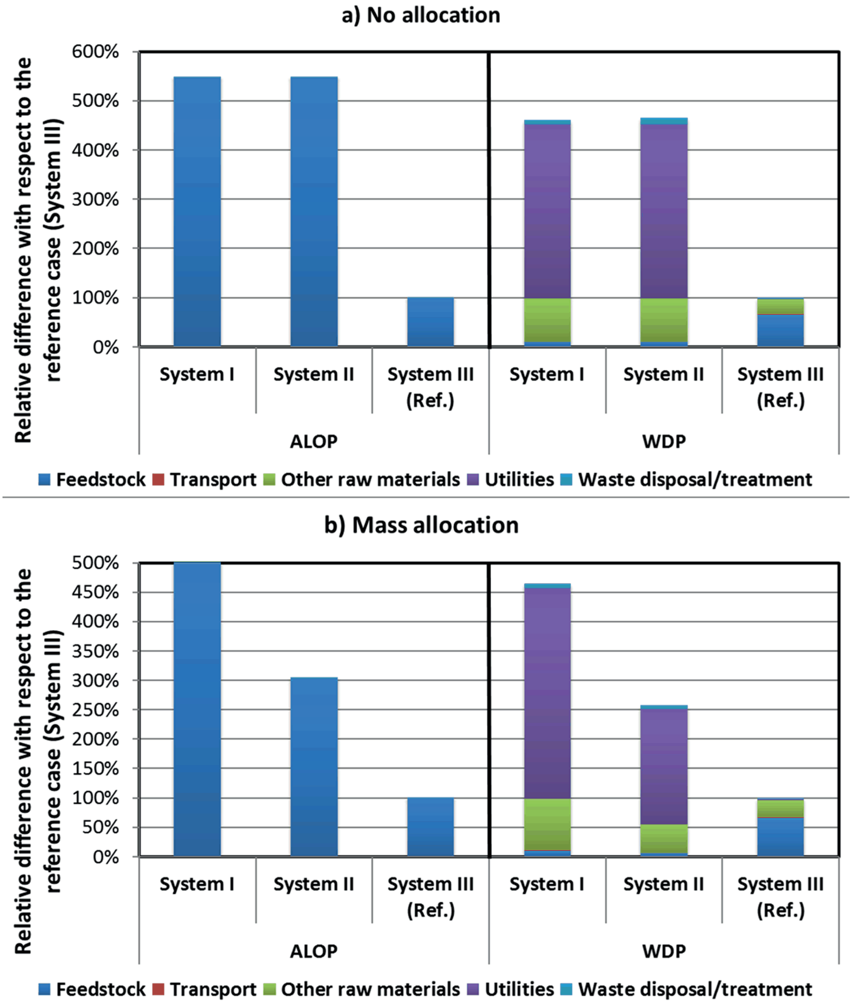


FIGURE 4.9. Environmental impacts for agricultural land occupation potential (ALOP) and water depletion potential (WDP) categories relative to the reference system (System III, corn wet milling). Each system is divided into contributions from feedstock production, feedstock transportation, consumption of auxiliary raw materials, utilities and waste treatment/disposal. a) Results when no allocation is applied (100% of environmental impacts allocated to C6 sugars), b) mass allocation applied to C6 sugars streams and co-products.

Independent of the allocation approach used, 2 (NREU and CCP) out of the 5 categories assessed, showed lower impacts for the organosolv based Systems (Systems I and II) compared to the corn wet milling System (reference, System III). However, 2 (ALOP and WDP) out of the 5 impact categories showed higher impacts for the organosolv (with and without anaerobic digestion) compared to corn wet milling. Finally, 1 (HTP) out of the 5 impact categories showed to have higher values for System I and lower for System II in comparison to System III. When comparing Systems I and II, 3 (NREU, CCP and HTP) out of the 5 impact categories showed lower impacts for System II, suggesting clear benefits for including anaerobic digestion to the organosolv process as an option for valorizing the hemicellulosic sugar stream. Finally, 2 (ALOP and WDP) out of the 5 impact categories showed little difference in System II in comparison to System I.

4.4. CONCLUSIONS

The results presented in this study provide insights into the technical, economic and environmental performance of organosolv (2G) and corn wet milling technologies (1G) for producing C6 sugars. When integrated with anaerobic digestion of organic residues (in this case essential for valorizing the hemicellulose sugar stream), the organosolv technology (System II) shows lower net energy consumption than corn wet milling (System III). However, in terms of processing yields to C6 sugars (total feed to C6 sugars basis), the corn wet milling technology shows higher values due to higher polysaccharide availability for producing the C6 sugar stream. From an economic point of view, organosolv coupled to anaerobic digestion (System II) shows the highest NPV (feasible scenario at base case lignin price of 630 €/t), but it also requires the highest fixed capital investment. The corn wet milling (System III) also showed positive NPV (feasible scenario)with the lowest fixed capital investment costs. The economic performance of the wet milling technology (System III) is sensitive to variation of C6 sugars and corn prices. However, the organosolv technology (Systems I and II) is very sensitive to changes in lignin, C6 sugars and woodchips prices, as well as changes in capital investment. The latter suggests higher robustness of the corn based technology relative to changes in economic input parameters (*e.g.,* prices). The feasibility of the organosolv technology (System I and II) highly relies on whether lignin and C6 sugars can be sold at good prices. The latter, highlights that 2G technologies can perform well for producing C6 sugars in the long term if markets for lignin have been developed. Nevertheless, 2G technologies also require large initials investments compared to 1G technologies. In the case of organosolv, integration of an anaerobic digestion unit as an option for valorizing the hemicellulosic sugars, has an important effect on improving the performance of the technology by decreasing energy requirements (*i.e.,* steam and electricity) and consequently utilities costs. Extra revenues by surplus power generated also have a positive effect on the economic performance of the organosolv technology.

From an environmental point of view, 3 out of the 5 assessed impact categories showed lower impacts for the organosolv based systems in comparison to the corn wet milling route (i.e., climate change, non-renewable energy use and human toxicity). This is mainly due to the high contribution of corn production in the total aggregation of the impacts in the corn wet milling process, in comparison to the low contribution of woodchips production in the organosolv based processes. In 2 of the 5 assessed categories (agricultural land occupation and water depletion), the organosolv based systems showed higher impacts than corn wet milling. Overall, the results indicate that the organosolv technology shows a better environmental performance than corn wet milling. The latter also highlights the possible environmental benefits of using 2G technologies over 1G technologies. However, special attention needs to be paid to prioritize impact categories with a higher long term impact on policy making for implementing 2G technologies. For instance, care needs to be taken into account when assessing agricultural land occupation for feedstocks such as spruce. The environmental assessment also showed the large influence that allocation brings into the results.

Summarizing, the 2G systems described herein have better environmental performance on most impact categories than the baseline (1G) case. However, both 2G scenarios (Systems I and II) have far higher capital costs than the 1G case (System III). The non-energy-recovery 2G process (System I) was not able to achieve positive NPV for this reason, but the addition of anaerobic digestion to System II revealed that a 2G case could ultimately outperform the 1G case on an NPV basis (at a lignin price of 630 €/tonne). However, the inherent risks of new technologies and high investments associated with the 2nd generation technologies assessed in this work, mean that significant additional development, coupled with appropriate government support, are likely necessary before full-scale implementation of 2G systems.

Acknowledgements

This research has been performed within the framework of the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science. Project number 053.70.381.

APPENDIX

Appendix A. Process description and data inputs used in process modeling

Organosolv

The chemical composition of spruce wood used to model spruce chips in Aspen Plus (see Table 4.7) was gathered from the work of Constant et al., [185]. The water content of biomass was assumed as 10 wt%.

TABLE 4.7. Average spruce composition used to model spruce wood chips in Aspen Plus [185]. Composition expressed in dry basis.

Compound groups	Content, wt %
Extractives, water [a]	6.4
Extractives, ethanol [b]	0.9
Glucan	41.6
Xylan	3.6
Galactan	1.2
Arabinan	0.2
Mannan	10.4
Lignin, acid insoluble	27.3
Lignin, acid soluble	0.3
Ash	0.3
Other, unknown [c]	7.8
Total	**100.0**

[a] Extractives modeled as gallic acid.
[b] Extractives modeled as oleic acid.
[c] Others modeled as inert to close mass balances.

The process starts with the reception and particle size reduction of spruce woodchips. Next, the reduced size feedstock is mixed with the solvent/catalyst solution (solvent: 60 wt% aqueous ethanol, catalyst: sulfuric acid) at a ratio of 5 L of solvent per kg of dry biomass. The acid dosage was set to 10 mM as suggested by [185]. Subsequently, the biomass/solvent/catalyst mixture is fed to the reactor operating at 190 ºC and 15 bar [185]. Conditions of the organosolv section are also within the range of conditions reported in other studies [169, 186, 206]. The set of reactions of the organosolv fractionation section are listed in Table 4.8 and account for delignification, hemicellulose conversion and humins formations, which are typical steps of organosolv fractionation processes [207-209]. Delignification and hemicellulose hydrolysis reactions were based on lignin and pulp recovering yields reported by [185]. Additional reactions were formulated based on streams for softwood organosolv processing reported by [207].

TABLE 4.8. Reactions modeled in Aspen Plus (as reaction in series) in organosolv pretreatment. Cipsd: compound modeled as solid with particle size distribution. Mixed: compound modeled as soluble. Gallic acid, and oleic acid were used as model compounds to account for extractives contained in the biomass.

Reaction	Conversion
Lignin(Cipsd) → Lignin(Mixed)	58%
Glucan(Cipsd) → Glucan(Mixed)	15%
Xylan(Cipsd) → Xylan(Mixed)	91%
Galactan(Cipsd) → Galactan(Mixed)	100%
Arabinan(Cipsd) → Arabinan(Mixed)	100%
Mannan(Cipsd) → Mannan(Mixed)	96%
Extractives, water(Cipsd) → Extractives, water(Mixed)	99%
Extractives, ethanol(Cipsd) → Extractives, ethanol(Mixed)	99%
Glucan(Mixed) + Water(Mixed) → Glucose(Mixed)	100%
Xylan(Mixed) + Water(Mixed) → Xylose(Mixed)	100%
Galactan(Mixed) + Water(Mixed) → Galactose(Mixed)	100%
Arabinan(Mixed) + Water(Mixed) → Arabinose(Mixed)	100%
Mannan(Mixed) + Water(Mixed) → Mannose(Mixed)	100%
Glucose(Mixed) → 3 Water(Mixed) + Hydroxymethylfurfural(Mixed)	28%
Galactose(Mixed) → 3 Water(Mixed) + Hydroxymethylfurfural(Mixed)	28%
Mannose(Mixed) → 3 Water(Mixed) + Hydroxymethylfurfural(Mixed)	28%
Xylose(Mixed) → 3 Water(Mixed) + Furfural(Mixed)	52%
Arabinose(Mixed) → Furfural(Mixed) + 3 Water(Mixed)	52%
27 Xylose(Mixed) → 10 Humins(Mixed) + 95 Water(Mixed) + 15 CO_2(Mixed)	5%
27 Arabinose(Mixed) → 10 Humins(Mixed) + 95 Water(Mixed) + 15 CO_2(Mixed)	5%
9 Glucose(Mixed) → 4 Humins(Mixed) + 38 Water(Mixed) + 6 CO_2(Mixed)	5%
9 Galactose(Mixed) → 4 Humins(Mixed) + 38 Water(Mixed) + 6 CO_2(Mixed)	5%
9 Mannose(Mixed) → 4 Humins(Mixed) + 38 Water(Mixed) + 6 CO_2(Mixed)	5%

The mixture at the reactor outlet is composed by a solid fraction and a liquid fraction. The solid fraction is mostly composed of cellulose as well as undissolved lignin and hemicelluloses. The liquid fraction is mainly composed of dissolved lignin, hemicelluloses derived sugars and furans (*e.g.,* hydroxymethylfurfural and furfural). The solid fraction is separated from the liquid fraction in a filter/washer unit (block number 4 in Figure 4.2, see article). The washed pulp is stripped (block number 5 in Figure 4.2) with steam to remove remaining solvent and sent to the enzymatic hydrolysis section. The liquid stream from the reaction is sent to a distillation column (block 10 in Figure 4.2) which is set to decrease the concentration of ethanol from 60 to 35 wt% in the bottom stream to allow lignin precipitation in a subsequent step (for lignin precipitation, the ethanol content needs to be below 20 wt% according to [169]). In this column fractions of ethanol, water, furfural and CO_2 are recovered as top product and a stream rich in dissolved lignin and hemicelluloses derivatives as bottom product. The top stream is directed to a stripping section (blocks 21 and 22 in Figure 4.2) in which first furfural is separated from the mixture as bottom product in block 21 and finally separated from water by decantation (block 24, Figure 4.2). Later CO_2 is stripped as top product in block 22. The solvent is recovered and recycled to the process. The bottom product (from block 10, rich in dissolved lignin and hemicelluloses derivatives) is sent to a second column (block 12 in Figure 4.2) in which lignin is precipitated and ethanol is recovered (>99%) in the top and recycled to the organosolv reactor. The precipitated lignin is washed with water, filtered (block 13 Figure 4.2) and later dried to a water content of 10 wt% in a drum dryer [169]. The liquor from the washing step contains hemicellulose derived sugars, hydroxymethylfurfural (HMF), furfural and small traces humins. This stream (called hemicellulosic sugars in Figure 4.2, is used as input for the anaerobic digestion step).

The washed pulp from the pretreatment is enzymatically converted into C6 sugars by the action of enzymes using a cocktail of cellulase and beta-glucosidase in a mass ratio of 1:10 according to [169, 210]. In literature related to techno-economic studies of the conversion of cellulosic materials into fermentable sugars (or ethanol), the enzyme dosage is expressed between 2-10 g/kg of dry biomass [169, 211, 212]. In this study, we follow a conservative approach by considering the high end of the previously mentioned range (enzyme dosage 10 g/kg dry biomass) according to [212].

The enzymatic conversion step results in two main streams: an unconverted solid fraction and a C6 sugar rich fraction. For the enzymatic reaction (see Table 4.9) 95% a conversion of the cellulosic fraction of the pulp has been assumed based on typical values reported in literature [179, 207]. The latter implies that the unconverted solid is mainly composed of non-dissolved lignin and hemicellulose. The solid fraction is separated from the liquor in a filter/washer unit. The C6 sugar liquor is sent to an evaporator to reduce the water content and later to a crystallizer to recover the sugars as a pure stream. 100% water removal was assumed in this stage.

TABLE 4.9. Reactions modeled in enzymatic hydrolysis of pulp. Cipsd: compound modeled as solid with particle size distribution. Mixed: compound modeled as soluble.

Reactions	Conversion
Cellulose (Cipsd) + Water (Mixed) --> Glucose (Mixed)	90%

Anaerobic digestion

The biogas unit operates at 40 ºC and 1 bar. The yield of biogas was assumed as 344 Nm^3 per t of organic matter in the substrate, according to [169]. The biogas composition was assumed as 64 vol% for CH_4, and 36 vol% for CO_2 which is a typical biogas composition. The substrate contains traces of sulfur which are also converted into H_2S in the digester assuming 100% sulfur conversion. To close the mass balances in the digester, the remaining fraction constitutes the digestate product. The conversion of organic matter in the digester can be summarized using the following yields: 0.71 kg of digestate/kg of organic matter and 0.29 kg of biogas/kg of organic matter. The product from the digester is separated into a crude gas stream and a wet stream containing the digestate. The wet digestate is filtered and later dewatered (blocks 6 and 7 in Figure 4.3) for commercialization. Water is recovered in this step and recycled to the process. The crude gas stream is cleaned to separate the H_2S from the biogas. Next, the biogas is sent to a combustion chamber coupled to a gas turbine (blocks 11 and 13 in Figure 4.3). The combustion chamber is operated at 30 bar and the gases decompressed to 1.05 bar in the gas turbine. A fraction of electric power is produced in this stage. The hot gases are used to produce steam in a heat steam generation unit (block 15, Figure 4.3) producing high pressure (HP), mid pressure steam (MP) and low pressure (LP) steam. The high pressure steam is depressurized to low pressure steam levels in a steam turbine where additional power is produced (block 14, Figure 4.3). The combined cycle system for producing steam and electricity was modeled according to descriptions provided in [187, 188]. The electricity produced aims to cover the demand of the organosolv process itself and if possible a surplus will be sold to the grid. The steam produced aims to cover the demand of LP steam and MP steam of the organosolv process.

Corn wet milling

The process starts with reception, storage and cleaning of impurities of the corn grains (represented in block 1, Figure 4.4). Next, the clean corn is sent to the steeping step where it gets soaked with a steep acid solution (diluted SO_2 [3]) in order to break down the protein matrix to release the starch granules by softening the kernel [166]. An important amount of soluble solids are carried in the steepwater, thus, it is concentrated up to 50 wt% in an evaporator unit (block 3, Figure 4.4). The corn kernels are sent to the germ separation stage where after grinding and washing the oil-rich corn germ is separated from the starchy slurry. The germ is washed, dewatered and dried (blocks 7,8 and 9 in Figure 4.4) to a water content of 3 wt% [166].

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[3] It is assumed that he SO_2 required for the steeping stage is produced by oxidizing elemental sulfur.

The corn slurry (degermed) from the germ separation is screened to separate starch and gluten from the fiber. The fiber is washed and mixed with the concentrated steepwater from the steeping stage. This mixture is later dewatered in a press and dried to water content of 10 wt%. The mixture is considered a marketable product named corn gluten feed [166]. After the fiber separation stage, the starch and gluten rich solid is sent to the gluten separation stage where starch is separated from the gluten in a centrifuge train (block 15, Figure 4.4). The gluten is thickened, dewatered and dried to reduce the water content to 10 wt% [166]. This stream is marketed as corn gluten meal. After the gluten meal separation, the starch is washed and dewatered to a water content of 60 wt%. On a dry basis, the yields (expressed as % of dry corn fed) used to calculate the mass balances were 7.7% for dry germ, 19.4% for gluten feed, 6.2% for gluten meal and 66.7% for starch [166]. These yields are in line with the yields reported by [176]. The starch rich stream is subjected to enzymatic hydrolysis assuming that starch is fully converted into glucose. This assumption is in alignment with classical wet milling factories where high conversion of starch is obtained [176]. The aqueous C6 sugar solution is concentrated in evaporators and later the glucose is crystallized. This last step is in agreement with the assumption of recovering high purity C6 sugars from the organosolv process, thus, a direct comparison of C6 sugars production can be carried out.

APPENDIX B. ECONOMIC ASSESSMENT ADDITIONAL DATA INPUTS AND FACTORS

Table 4.10 displays the factors used for the estimation of capital investment. Table 4.11 shows the factors used for the estimation of operating costs. Table 4.12 displays the conversions considered in the sensitivity analysis on lignin, glucan and pulp digestibility in the organosolv process.

TABLE 4.10. Factors used for the estimation of capital investment according to Peters et al., [189].

Purchased equipment	Percentage of purchased equipment [a]
Direct Costs	
Purchased equipment installation	39%
Instrumentation and Controls (installed)	26%
Piping (installed)	31%
Electrical systems (installed)	10%
Buildings (including services)	29%
Yard improvements	12%
Service facilities (installed)	55%
Total Direct	***202%***
Indirect Costs	
Engineering and supervision	32%
Construction expenses	34%
Legal expenses	4%
Contractor's fee	19%
Contingency	37%
Total Indirect	***126%***
Working capital	75%

[a] Purchased equipment including delivery costs (10%)

TABLE 4.11. Factors used for the estimation of additional features of operating costs [189].

Category	Feature	Factor
Labor costs	Operating supervision	15% of operating labor
	Laboratory charges	15% of operating labor
Maintenance costs	Maintenance	6% of fix capital investment
	Operating supplies	15% of maintenance
Fixed & general costs	Taxes	2% of fix capital investment
	General costs	20% of labor, supervision and maintenance
Plant overhead	Plant overhead	60% of labor, supervision and maintenance

TABLE 4.12. Conversions considered in the sensitivity analysis on lignin, glucan and pulp digestibility in the organosolv process.

Parameter	Base case	Low conversion	High conversion
Delignification [a]	58%	46%	69%
Glucan hydrolysis [b]	15%	7%	22%
Enzymatic glucan digestibility [c]	90%	80%	100%

[a] Reaction 1 listed in Table 4.8.
[b] Reaction 2 listed in Table 4.9.
[c] Reaction listed in Table 4.9.

APPENDIX C. LIFE CYCLE ASSESSMENT SCOPE AND SYSTEM BOUNDARIES

Figure 4.10, Figure 4.11, and Figure 4.12 show the system boundaries of the systems considered in the life cycle assessment. Table 4.13 shows the impact categories considered in this study, their units and abbreviations.

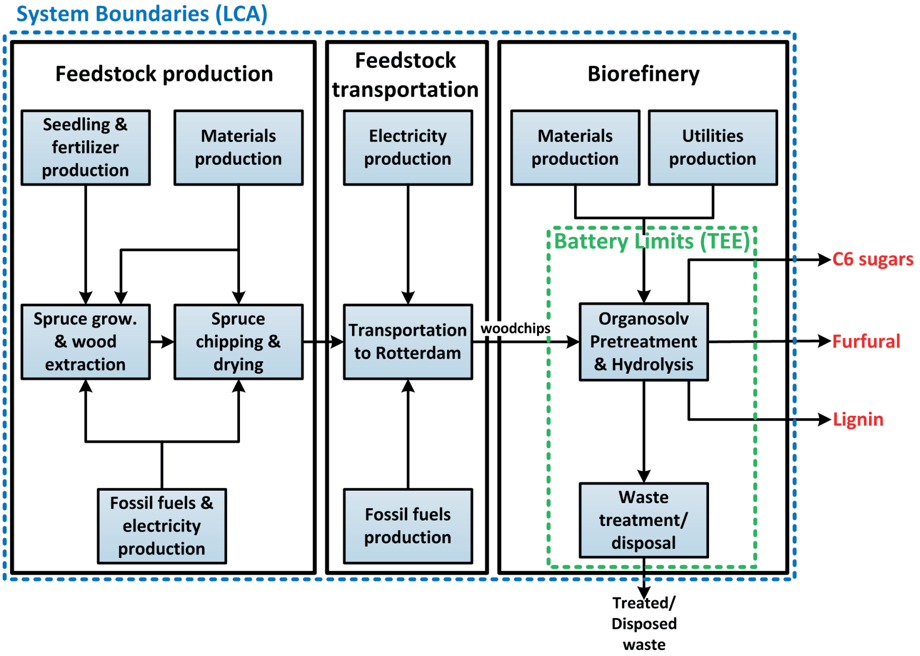

FIGURE 4.10. Main process steps involved in the production of C6 sugars production from Spruce woodchips (System I). Each box (solid black boxes) represents a process module. The system boundaries for the LCA correspond to the aggregation of all process modules (blue dotted lines). The battery limits of the techno-economic evaluation (TEE) only considers the biorefinery module (green dotted lines).

There are multiple approaches to address multi-functionality. For the systems assessed in this study, a subdivision approach is not possible since many of the processes are integrated by sharing streams for heat and mass recovery and detailed data is required for each process step of the biorefinery. System expansion is also not possible since many of the co-products do not have identical fossil counterparts (*e.g.,* lignin), therefore, including additional functions of the co-products within the system boundaries can be a very difficult task. Allocation is therefore necessary among all co-products. There are many ways to allocate the environmental impacts. The most used approaches involve mass allocation, economic allocation and energy allocation [198].

Mass allocation is preferred over economic and energy allocation, since the mass flowrates of the products will exclusively depend on the technical performance of each technology. Economic allocation is avoided due to high uncertainty on prices assigned to each product, which may over- or under-assign environmental burdens among co-products. Energy allocation is avoided since the products obtained in each systems have material functionality rather than energy use (in exception of electricity in organosolv + anaerobic digestion).

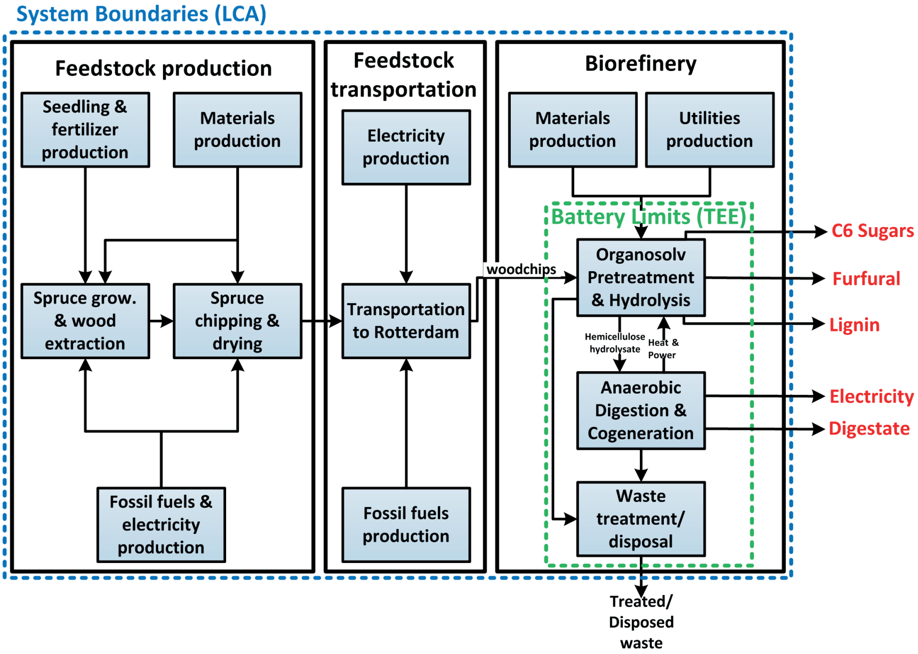

FIGURE 4.11. Main process steps involved in the production of C6 sugars production from spruce woodchips (System II). Each box (solid black boxes) represents a process module. The system boundaries for the LCA correspond to the aggregation of all process modules (blue dotted lines). The battery limits of the techno-economic evaluation (TEE) only considers the biorefinery module (green dotted lines).

In the case of the organosolv and anaerobic digestion system, electricity is also produced as co-product and it is not possible to estimate an allocation factor using mass allocation. However, electricity is produced from biogas which can be accounted as a material in a prior conversion step with a fraction of the energy of the biogas used to produce electricity. consequently, the mass of biogas also needs to be split to allocate which fraction is used to electricity production. The electric efficiency factor of the cogeneration unit was used to allocate the mass flowrate of biogas related to electricity production according to equation S1. Next, the allocated mass flowrate of biogas used to produce electricity was used to calculate the allocation factor of electricity production (See equation 4.1).

$$Mbiogas_e = Mbiogas_{total} \bullet n2 \tag{4.2}$$

Where, $Mbiogas_e$ is the mass of biogas allocated to the production of electricity, is the total mass of biogas produced in the anaerobic digestion unit, and is the electric efficiency of the cogeneration unit.

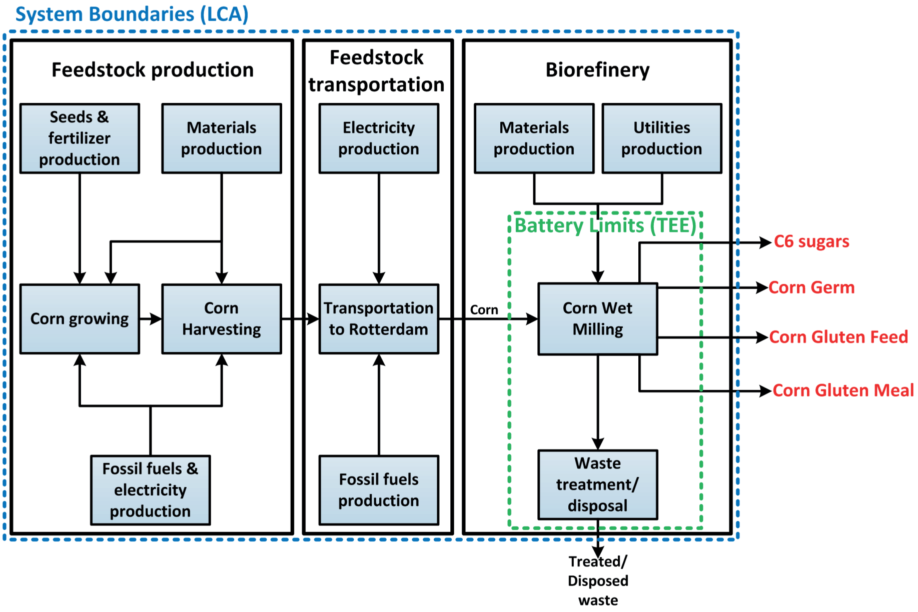

FIGURE 4.12. Main process steps involved in the production of C6 sugars production from Corn (System III). Each box (solid black boxes) represents a process module. The system boundaries for the LCA correspond to the aggregation of all process modules (blue dotted lines). The battery limits of the techno-economic evaluation (TEE) only considers the biorefinery module (green dotted lines).

TABLE 4.13. Data inputs description for LCI gathered from Ecoinvent databases [149].

Impact Category	Abbreviation	Unit
Non-renewable energy use	NREU	MJ_{eq}
Climate change potential	CCP	kg CO_{2eq}
Human toxicity potential	HTP	kg 1,4-DB_{eq}
Agricultural land occupation potential	ALOP	$m^2 \bullet a$
Water depletion potential	WDP	m^3

APPENDIX D. LIFE CYCLE INVENTORY DATA AND ASSUMPTIONS

Feedstock production

Data related to the impacts of woodchips from Scandinavian softwood was gathered from the Ecoinvent v2.2 databases [149] which involves the growing and felling of trees and later their chipping. The water content of the chips is indicated as 40 wt%. In this work, it was assumed that spruce wood need to be delivered to Rotterdam in the form of chips with a moisture content of 10 wt% (based on input conditions of organosolv process). Consequently, the environmental impacts related to chipping and drying operations need to be accounted for. The efficiencies for the drying processes were gathered from Giuntoli et al., [201]. The most important assumptions in this step are natural drying of woodchips (reduction in moisture content from 40 wt% to 10 wt%) and 5 wt% loss of the dry mass of the chips during the drying process.

Data related to the impacts of corn from USA was gathered from the Ecoinvent v2.2 databases [149]. The water content of corn is indicated as 14 wt%, which is assumed as same moisture content of corn kernels delivered to Rotterdam for its processing.

Feedstock transportation

Feedstock transportation (*i.e.,* woodchips and corn) to the biorefinery facility is divided in three steps. First, the biomass is transported from the feedstock collection sites (i.e., either wood mills or farms) to the shipping ports. In the case of woodchips, the port of Gothenburg is the closest Swedish port to the port of Rotterdam. An average transport distance of 200 km from the mills to the port of Gothenburg was assumed using freight rail. The efficiency of freight rail transportation was assumed to be that of Europe, in which 40% is covered by diesel, while the remaining 60% is covered by electricity [202]. Energy consumptions of 79 kJ/(tonne•km) for diesel and 118 kJ/(tonne•km) for electricity were used [202]. The electricity mix used correspond to Swedish conditions [149]. In the case of corn, an average transport distance of 300 km from the farms to the port of Norfolk (north-east of USA) was assumed using freight rail. The efficiency of freight rail transport in USA was taken from [201], corresponding to 252 kJ/(tonne•km) using diesel.

The second step involves the transportation from the ports to Rotterdam. In the case of woodchips, this is covered by maritime transportation using a handysize bulk carrier [201], with 241 kJ of heavy fuel oil per tonne•km [201]. The distance between the port of Gothenburg and the port of Rotterdam is 928 km [203]. In the case of corn, transportation is also covered by maritime transport but using a Supramax bulk carrier with a fuel consumption of 152 kJ of heavy fuel oil per tonne•km [201]. The distance between the port of Norfolk and the port of Rotterdam is 6569 km [203].

The third step is the transport of feedstocks from the port of Rotterdam to the biorefinery facility. For both woodchips and corn, it was assumed a distance of 20 km transported in trucks of 20 t [149]. Additional data related to fuel inputs such as diesel and heavy fuel oil was gathered from the Ecoinvent v2.2 database [149].

Biorefinery (biomass conversion)

Outputs of the technical assessment (*i.e.,* mass and energy flows) and data from the Ecoinvent v2.2 database [149] were used for completing the life cycle inventory which include inputs of auxiliary raw materials and energy carriers such as steam, natural gas (for fired heat) and waste disposal/treatment impacts. Table 4.14 shows the description of inputs gathered from the Ecoinvent v2.2 database [149]

TABLE 4.14. Data inputs description for LCI gathered from Ecoinvent database [149]

Input	Ecoinvent description	Unit
Woodchips	Chips, Scandinavian softwood (plant-debarked), u=70%, at plant/NORDEL S	1 m^3
Corn	Corn, at farm/US S	1 kg
Diesel	Diesel, at regional storage/RER S	1 kg
Electricity, in Sweden	Electricity, medium voltage, production SE, at grid/SE S	1 kWh
Heavy fuel oil	Heavy fuel oil, burned in industrial furnace 1MW, non-modulating/RER S	1 MJ
Truck >20 tonne	Transport, truck >20t, EURO5, 80%LF, empty return/GLO Energy	1 kg•km
Sulfuric acid	Sulfuric acid, liquid, at plant/RER S	1 kg
Ethanol	Ethanol, 99.7% in H_2O, from biomass, production RER, at service station/CH S	1 kg
Water	Tap water, at user/RER S	1 kg
Enzyme, corn processing	Enzyme, alpha-amylase, Novozyme Liquozyme/RER S	1 kg
Enzyme, corn processing	Enzyme, glucoamylase, Novozyme Spirizyme/RER S	1 kg
Enzyme, woodchips processing	Enzyme, cellulase, Novozyme Celluclast/RER S	1 kg
Sulfur	Sulfur, from crude oil, consumption mix, at refinery, elemental sulphur EU-15 S	1 kg
Waste water treatment	Treatment, sewage whey digestion, to wastewater treatment, class 4/CH S'	1 m^3
Waste disposal	Disposal, biowaste, to anaerobic digestion/CH S	1 kg
Steam, in Netherlands	Process steam from natural gas, heat plant, consumption mix, at plant, NL S	1 kg
Electricity, in Netherlands	Electricity, medium voltage, production NL, at grid/NL S	1 kWh
Natural, for heat supply	Natural gas, burned in industrial furnace >100kW/RER S	1 MJ

APPENDIX E. ECONOMIC SUPPLEMENTARY RESULTS

Table 4.15, Table 4.16 and Table 4.17 show details on calculations of base case NPV for all Systems.

TABLE 4.15. Details on NPV calculations for System I.

	-2	-1	0	1	2	3	4	5	6	7	8	9	10
Fixed Capital Investment, M€	31.47	73.44	104.91	-	-	-	-	-	-	-	-	-	-
Working capital, M€			37.03	-	-	-	-	-	-	-	-	-	-
Total Capital Investment, M€	31.47	73.44	141.94	-	-	-	-	-	-	-	-	-	-
Start-up cost, M€	-	-	-	20.98	-	-	-	-	-	-	-	-	-
Operating rate, fraction of capacity	-	-	-	0.5	1	1	1	1	1	1	1	1	1
Annual sales, M€	-	-	-	109.36	218.72	218.72	218.72	218.72	218.72	218.72	218.72	218.72	218.72
Annual Total Product Cost, depreciation not included, M€	-	-	-	109.01	196.08	196.08	196.08	196.08	196.08	196.08	196.08	196.08	196.08
Annual depreciation, M€	-	-	-	20.98	20.98	20.98	20.98	20.98	20.98	20.98	20.98	20.98	20.98
Annual Gross Profit, M€	-	-	-	-41.62	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65
Annual Net Profit, M€	-	-	-	-41.62	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24
Annual operating cash flow, M€	-	-	-	-20.64	22.22	22.22	22.22	22.22	22.22	22.22	22.22	22.22	22.22
Total annual cash flow, M€	-31.47	-73.44	-141.94	-20.64	22.22	22.22	22.22	22.22	22.22	22.22	22.22	22.22	22.22
Cumulative cash position, M€	-31.47	-104.91	-246.85	-267.49	-245.27	-223.04	-200.82	-178.60	-156.37	-134.15	-111.93	-89.70	-67.48
Present worth factor	1.21	1.10	1.00	0.91	0.83	0.75	0.68	0.62	0.56	0.51	0.47	0.42	0.39
Present worth of annual cash flows, M€	-38.08	-80.78	-141.94	-18.76	18.37	16.70	15.18	13.80	12.54	11.40	10.37	9.42	8.57
Cumulative NPV, M€	-38.08	-118.87	-260.81	-279.57	-261.20	-244.50	-229.32	-215.53	-202.98	-191.58	-181.21	-171.78	-163.22

TABLE 4.15. Continued

	11	12	13	14	15	16	17	18	19	20	Total
Fixed Capital Investment, M€	-	-	-	-	-	-	-	-	-	-	
Working capital, M€	-	-	-	-	-	-	-	-	-		
Total Capital Investment, M€	-	-	-	-	-	-	-	-	-	-	
Start-up cost, M€	-	-	-	-	-	-	-	-	-	-	
Operating rate, fraction of capacity	1	1	1	1	1	1	1	1	1	1	
Annual sales, M€	218.72	218.72	218.72	218.72	218.72	218.72	218.72	218.72	218.72	218.72	4265.04
Annual Total Product Cost, depreciation not included, M€	196.08	196.08	196.08	196.08	196.08	196.08	196.08	196.08	196.08	196.08	3834.59
Annual	-	-	-	-	-	-	-	-	-	-	209.83
Annual Gross Profit, M€	22.64	22.64	22.64	22.64	22.64	22.64	22.64	22.64	22.64	22.64	236.67
Annual Net Profit, M€	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	167.10
Annual operating cash flow, M€	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	376.92
Total annual cash flow, M€	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	16.98	130.07
Cumulative cash position, M€	-50.50	-33.52	-16.55	0.43	17.41	34.39	51.37	68.34	85.32	130.07	
Present worth factor	0.35	0.32	0.29	0.26	0.24	0.22	0.20	0.18	0.16	0.15	
Present worth of annual cash flows, M€	5.95	5.41	4.92	4.47	4.06	3.69	3.36	3.05	2.78	6.65	-118.87
Cumulative NPV, M€	-157.27	-151.86	-146.94	-142.47	-138.40	-134.71	-131.35	-128.30	-125.52	-118.87	

TABLE 4.16. Details on NPV calculations for System II.

Year	-2	-1	0	1	2	3	4	5	6	7	8	9	10
Fixed Capital Investment, M€	35.84	83.63	119.48	-	-	-	-	-	-	-	-	-	-
Working capital, M€			42.17	-	-	-	-	-	-	-	-	-	-
Total Capital Investment, M€	35.84	83.63	161.65	-	-	-	-	-	-	-	-	-	-
Start-up cost, M€	-	-	-	23.90	-	-	-	-	-	-	-	-	-
Operating rate, fraction of capacity	-	-	-	0.5	1	1	1	1	1	1	1	1	1
Annual sales, M€	-	-	-	127.38	254.75	254.75	254.75	254.75	254.75	254.75	254.75	254.75	254.75
Annual Total Product Cost, depreciation not included, M€	-	-	-	96.60	168.40	168.40	168.40	168.40	168.40	168.40	168.40	168.40	168.40
Annual depreciation, M€	-	-	-	23.90	23.90	23.90	23.90	23.90	23.90	23.90	23.90	23.90	23.90
Annual Gross Profit, M€	-	-	-	-17.01	62.46	62.46	62.46	62.46	62.46	62.46	62.46	62.46	62.46
Annual Net Profit, M€	-	-	-	-17.01	46.84	46.84	46.84	46.84	46.84	46.84	46.84	46.84	46.84
Annual operating cash flow, M€	-	-	-	6.88	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74
Total annual cash flow, M€	-35.84	-83.63	-161.65	6.88	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74
Cumulative cash position, M€	-35.84	-119.48	-281.12	-274.24	-203.50	-132.76	-62.02	8.72	79.46	150.20	220.94	291.68	362.42
Present worth factor	1.21	1.10	1.00	0.91	0.83	0.75	0.68	0.62	0.56	0.51	0.47	0.42	0.39
Present worth of annual cash flows, M€	-43.37	-92.00	-161.65	6.26	58.46	53.15	48.32	43.92	39.93	36.30	33.00	30.00	27.27
Cumulative NPV, M€	-43.37	-135.37	-297.01	-290.76	-232.29	-179.15	-130.83	-86.90	-46.97	-10.67	22.33	52.33	79.60

TABLE 4.16. Continued

Year	-2	-1	0	1	2	3	4	5	6	7	8	9	10
Fixed Capital Investment, M€	35.84	83.63	119.48	-	-	-	-	-	-	-	-	-	-
Working capital, M€			42.17	-	-	-	-	-	-	-	-	-	-
Total Capital Investment, M€	35.84	83.63	161.65	-	-	-	-	-	-	-	-	-	-
Start-up cost, M€	-	-	-	23.90	-	-	-	-	-	-	-	-	-
Operating rate, fraction of capacity	-	-	-	0.5	1	1	1	1	1	1	1	1	1
Annual sales, M€	-	-	-	127.38	254.75	254.75	254.75	254.75	254.75	254.75	254.75	254.75	254.75
Annual Total Product Cost, depreciation not included, M€	-	-	-	96.60	168.40	168.40	168.40	168.40	168.40	168.40	168.40	168.40	168.40
Annual depreciation, M€	-	-	-	23.90	23.90	23.90	23.90	23.90	23.90	23.90	23.90	23.90	23.90
Annual Gross Profit, M€	-	-	-	-17.01	62.46	62.46	62.46	62.46	62.46	62.46	62.46	62.46	62.46
Annual Net Profit, M€	-	-	-	-17.01	46.84	46.84	46.84	46.84	46.84	46.84	46.84	46.84	46.84
Annual operating cash flow, M€	-	-	-	6.88	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74
Total annual cash flow, M€	-35.84	-83.63	-161.65	6.88	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74	70.74
Cumulative cash position, M€	-35.84	-119.48	-281.12	-274.24	-203.50	-132.76	-62.02	8.72	79.46	150.20	220.94	291.68	362.42
Present worth factor	1.21	1.10	1.00	0.91	0.83	0.75	0.68	0.62	0.56	0.51	0.47	0.42	0.39
Present worth of annual cash flows, M€	-43.37	-92.00	-161.65	6.26	58.46	53.15	48.32	43.92	39.93	36.30	33.00	30.00	27.27
Cumulative NPV, M€	-43.37	-135.37	-297.01	-290.76	-232.29	-179.15	-130.83	-86.90	-46.97	-10.67	22.33	52.33	79.60

TABLE 4.17. Details on NPV calculations for System III.

Year	-2	-1	0	1	2	3	4	5	6	7	8	9	10
Fixed Capital Investment, M€	7.54	17.60	25.14	-	-	-	-	-	-	-	-	-	-
Working capital, M€			8.87	-	-	-	-	-	-	-	-	-	-
Total Capital Investment, M€	7.54	17.60	34.01	-	-	-	-	-	-	-	-	-	-
Start-up cost, M€	-	-	-	5.03	-	-	-	-	-	-	-	-	-
Operating rate, fraction of capacity	-	-	-	0.5	1	1	1	1	1	1	1	1	1
Annual sales, M€	-	-	-	77.75	155.51	155.51	155.51	155.51	155.51	155.51	155.51	155.51	155.51
Annual Total Product Cost, depreciation not included, M€	-	-	-	61.79	117.95	117.95	117.95	117.95	117.95	117.95	117.95	117.95	117.95
Annual depreciation, M€	-	-	-	5.03	5.03	5.03	5.03	5.03	5.03	5.03	5.03	5.03	5.03
Annual Gross Profit, M€	-	-	-	5.91	32.52	32.52	32.52	32.52	32.52	32.52	32.52	32.52	32.52
Annual Net Profit, M€	-	-	-	4.43	24.39	24.39	24.39	24.39	24.39	24.39	24.39	24.39	24.39
Annual operating cash flow, M€	-	-	-	9.46	29.42	29.42	29.42	29.42	29.42	29.42	29.42	29.42	29.42
Total annual cash flow, M€	-7.54	-17.60	-34.01	9.46	29.42	29.42	29.42	29.42	29.42	29.42	29.42	29.42	29.42
Cumulative cash position, M€	-7.54	-25.14	-59.16	-49.69	-20.27	9.15	38.57	67.99	97.41	126.83	156.25	185.67	215.09
Present worth factor	1.21	1.10	1.00	0.91	0.83	0.75	0.68	0.62	0.56	0.51	0.47	0.42	0.39
Present worth of annual cash flows, M€	-9.13	-19.36	-34.01	8.60	24.31	22.10	20.09	18.27	16.61	15.10	13.72	12.48	11.34
Cumulative NPV, M€	-9.13	-28.48	-62.50	-53.90	-29.58	-7.48	12.62	30.88	47.49	62.59	76.31	88.79	100.13

TABLE 4.17. Continued.

Year	11	12	13	14	15	16	17	18	19	20	Total
Fixed Capital Investment, M€	-	-	-	-	-	-	-	-	-	-	50.28
Working capital, M€	-	-	-	-	-	-	-	-	-	-8.87	
Total Capital Investment, M€	-	-	-	-	-	-	-	-	-	-	59.16
Start-up cost, M€	-	-	-	-	-	-	-	-	-	-	5.03
Operating rate, fraction of capacity	1	1	1	1	1	1	1	1	1	1	
Annual sales, M€	155.51	155.51	155.51	155.51	155.51	155.51	155.51	155.51	155.51	155.51	3032.35
Annual Total Product Cost, depreciation not included, M€	117.95	117.95	117.95	117.95	117.95	17.95	117.95	117.95	117.95	117.95	2302.91
Annual depreciation, M€	-	-	-	-	-	-	-	-	-	-	50.28
Annual Gross Profit, M€	37.55	37.55	37.55	37.55	37.55	37.55	37.55	37.55	37.55	46.42	683.01
Annual Net Profit, M€	28.16	28.16	28.16	28.16	28.16	28.16	28.16	28.16	28.16	34.82	512.26
Annual operating cash flow, M€	28.16	28.16	28.16	28.16	28.16	28.16	28.16	28.16	28.16	34.82	562.54
Total annual cash flow, M€	28.16	28.16	28.16	28.16	28.16	28.16	28.16	28.16	28.16	34.82	503.38
Cumulative cash position, M€	243.25	271.42	299.58	327.75	355.91	384.07	412.24	440.40	468.56	503.38	
Present worth factor	0.35	0.32	0.29	0.26	0.24	0.22	0.20	0.18	0.16	0.15	
Present worth of annual cash flows, M€	9.87	8.97	8.16	7.42	6.74	6.13	5.57	5.07	4.60	5.18	167.84
Cumulative NPV, M€	110.00	118.98	127.14	134.55	141.29	147.42	153.00	158.06	162.67	167.84	

APPENDIX F. LIFE CYCLE ASSESSMENT SUPPLEMENTARY RESULTS

Table 4.18 and Table 4.19 display the absolute values of the life cycle environmental impacts expressed per functional unit (kg of C6 sugars) for no allocation and mass allocation approaches, respectively. Table 4.20 displays the allocation factors considered in the analysis.

TABLE 4.18. Environmental impacts of all categories expressed per kg of C6 sugars (functional unit) when no allocation is considered (conservative approach assuming all impacts are allocated to the C6 sugars stream).

Impact Category	Unit	Organosolv (System I)	Organosolv & A. Digestion (System II)	Corn wet milling (System III)
NREU	MJ_{eq}	10.66	6.13	13.43
CCP	kg CO_{2eq}	1.02	0.47	1.18
HTP	kg 1,4-DB_{eq}	$8.97 \cdot 10^{-2}$	$7.01 \cdot 10^{-2}$	$7.19 \cdot 10^{-2}$
ALOP	m^2a	6.18	6.18	1.13
WDP	m^3	$8.16 \cdot 10^{-2}$	$8.24 \cdot 10^{-2}$	$1.77 \cdot 10^{-2}$

TABLE 4.19. Environmental impacts of all categories expressed per kg of C6 sugars (functional unit) when mass allocation is considered.

Impact Category	Unit	Organosolv (System I)	Organosolv & A. Digestion (System II)	Corn wet milling (System III)
NREU	MJ_{eq}	7.22	2.29	9.01
CCP	kg CO_{2eq}	0.69	0.18	0.79
HTP	kg 1,4-DB_{eq}	$6.07 \cdot 10^{-2}$	$2.61 \cdot 10^{-2}$	$4.82 \cdot 10^{-2}$
ALOP	m^2a	4.18	2.30	0.76
WDP	m^3	$6.07 \cdot 10^{-2}$	$2.61 \cdot 10^{-2}$	$4.82 \cdot 10^{-2}$

TABLE 4.20. Allocation factors used in each approach, %

Allocation factors	Approach 1: No allocation			Approach 2: Mass allocation		
	Organosolv (System I)	Organosolv & A. Digestion (System II)	Corn wet milling (System III)	Organosolv (System I)	Organosolv & A. Digestion (System II)	Corn wet milling (System III)
C6 Sugars	**100**	**100**	**100**	**68**	**37**	**67**
Furfural	0	0	0	2	1	0
Lignin	0	0	0	30	17	0
Digestate	0	0	0	0	39	0
Biogas (Electricity)	0	0	0	0	6	0
Gluten feed	0	0	0	0	0	20
Germ	0	0	0	0	0	7
Gluten meal	0	0	0	0	0	6

CHAPTER 5

Production of 1,3-Butadiene and ε-Caprolactam from C6 sugars: Techno-economic analysis

Published: Moncada J., Vural Gursel I., Worrell E., Ramírez A. 2018.
Biofuels, Bioproducts & Biorefining. In press.
https://doi.org/10.1002/bbb.1876.

ABSTRACT

This study assesses the techno-economic performance of the production lines of 1,3-butadiene and ε-caprolactam from C6 sugars. Process models were developed to assess the technical performance and derive inputs for the economic analysis. The economic assessment was carried out using Net Present Value (NPV) and production costs as indicators. Sensitivity analyses were carried out to account for variations in inputs such as processing capacity, valorization of humins, and prices on the economic outputs. Results indicate that both production lines perform similarly from an energy intensity point of view (34-50 MJ/kg of main product). However, in terms of yield (kg of product per kg C6 sugar), caprolactam shows higher values by a factor 1.6-3.6 in comparison to that of butadiene. The butadiene production line is not economically attractive, showing negative NPV (-647 to -642 M€) and production costs 3-5 times higher in comparison to the reference market price (Case I 4369 €/tonne, Case II 3406 €/tonne). The production line of caprolactam seems to be unfeasible with negative NPV (-229 M€) and production costs 30% higher than the reference price (Case III 2595 €/tonne, Case IV 1875 €/tonne). However, if the production yield is increased, the caprolactam production line becomes economically attractive with production costs 6% lower than its reference market price. Production costs of caprolactam can be further decreased if the process capacity is increased, reflecting benefits of the economies of scale, as well as including heat and power produced from humins. Overall, the caprolactam production line shows higher economic potential.

5.1. INTRODUCTION

The biorefinery concept has emerged as an analogy to oil refineries, where instead of using oil, biomass is used as feedstock and refined into multiple streams with broad applications in industry [213, 214]. Multiple feedstocks types are used in biorefineries, varying from crops, lignocellulosic biomass, macroalgae and microalgae [214, 215]. These feedstocks have been used as potential precursors to obtain platforms (*e.g.,* carbohydrates, vegetable oil, biogas, lignin) which are later converted into fuels, chemicals and/or materials [18, 216].

The carbohydrates platform stands out due to its unique versatility as precursor for multiple valuable products with many applications [217-219]. The carbohydrates platform, which is generally composed by hexoses (e.g., C6 sugars), pentoses (e.g., C5 sugars) or disaccharides, has traditionally been produced from sugary crops such as corn, sugarcane and sugar beets, and recently attention is increased to produce it from lignocellulosic biomass such as agricultural residues (*e.g.,* corn stover, wheat straw), grasses (*e.g.,* switchgrass), wood (*e.g.,* softwood) among others. Independent of the source of the carbohydrates, many of the derivatives from the conversion can be used as chemical building blocks and can be produced via chemical catalysis, via bio-catalysis (*e.g.,* fermentation) or by both pathways [217]. Bozell & Petersen, (2010) [218] highlighted a top-10 list of possible derivatives from carbohydrates with high relevance for biorefineries. Among that list, ethanol appeared as one of the most representative ones not only due to its application as fuel but also due to its use as a building block. Ethanol is a potential raw material for chemicals such as *e.g.,* ethylene, propylene diethyl ether, 1,3-butadiene [220]. Bozell & Petersen [218] also pointed out levulinic acid as an important carbohydrate derivative due to its possible use as raw material for producing pyrrolidones, lactones and levulinate esters. Bio-based levulinic acid may be directly produced from C6 sugars using the biofine process [221, 222].

Among the different potential carbohydrate derivatives, 1,3-butadiene and ε-caprolactam appear to be of great interest as possible bio-based materials. Butadiene is an important chemical for the production of synthetic rubbers. About 70% of the worldwide butadiene production is used for tires manufacturing. Butadiene has traditionally been produced in oil refineries as a by-product from steam cracking of naphtha, liquefied petroleum gas (LPG), ethane, propane or butane to produce ethylene and other olefins [223, 224]. Alternatively, 1,3-butadiene can be produced from the catalytic conversion of ethanol [220, 223-225]. Caprolactam is the feedstock for producing nylon-6, a well-known polymer and one of the most widely used nylons [226]. Caprolactam is traditionally produced from benzene in a four step process in which first benzene is converted into cyclohexane, and subsequently converted into cyclohexanone [226, 227]. The third step consists of the conversion of cyclohexanone into cyclohexanone oxime, which is finally converted into ε-Caprolactam [226, 227]. As an alternative, the production of Caprolactam can start from γ-valerolactone (GVL) which can be produced from bio-based levulinic acid (LA) [226].

Many authors have studied the reaction mechanisms, process conditions, yield and selectivity for producing butadiene from ethanol [228-230], however, literature is scarce on techno-economic assessments of butadiene production from carbohydrates. Early stage assessments (combining techno-economic and environmental indicators) of butadiene production from ethanol were carried out, concluding that it has benefits over naphtha-based butadiene [220, 231]. Nevertheless, the scope of these analyses did not include aspects such as capital investment and some operating costs as the case of utilities. Cespi et al., (2016) [232] made a multi-criteria assessment (including techno-economic and environmental indicators) of different processes of butadiene production from ethanol, concluding that one-step conversion performs better than a two-step method. The economic assessment in this study included operational costs such as raw materials and utilities, but excluded aspects such as capital investment. Recently, Farzad et al., (2017) [233] carried out a more detailed techno-economic and environmental assessment of butadiene production from sugarcane bagasse (with ethanol as intermediate and co-product), concluding that there is a need for higher butadiene selling prices to make bio-based production economically attractive.

Similar to butadiene, many authors have studied reaction mechanisms, conditions, yields and selectivities of the steps to produce caprolactam from carbohydrates including all intermediate routes. For instance, Girisuta & Heeres [234] reported a summary of yields, process conditions of several routes, as well as kinetic studies to produce levulinic acid. Other authors have reported yields and conditions of γ-valerolactone from levulinic acid [235, 236], as well as the production of caprolactam from γ-valerolactone [226]. Literature is scarce on the techno-economic assessment of bio-based caprolactam production. Han, (2017) [237] carried out a techno-economic assessment of caprolactam production starting from lignocellulosic biomass.

One common aspect of the studies on detailed techno-economic assessment of butadiene [233] and caprolactam [237], is that the scope of the analysis starts directly from lignocellulosic biomass. However, given the importance of the carbohydrate platform for the bio-based economy, it would be interesting to carry out the assessment starting from C6 sugars. This is important for countries where availability of biomass is limited and where C6 sugars trade may play a crucial role, for instance by importing glucose syrup derived from corn for biorefineries. Considering the background discussed above, the scarcity of literature on systems analysis perspective of both butadiene and caprolactam production lines and their potential on the bio-based chemical market to possibly substitute chemicals that have traditionally been produced from oil sources, the aim of this study is to investigate the production lines of both butadiene and caprolactam using C6 sugars as feedstock from a techno-economic perspective, to identify bottle necks in each production line and to determine which is the most economically attractive. The analysis will follow an integrated biorefinery approach and will report on the effect of various process improvements, valorization of residues, processing scales and economic parameters such as prices on the overall performance.

5.2. MATERIALS AND METHODS

In this study a techno-economic analysis of the production of 1,3-butadiene and ε-caprolactam was conducted. The sequence of steps followed is summarized in Figure 5.1. Details on methods used, data and assumptions are provided below.

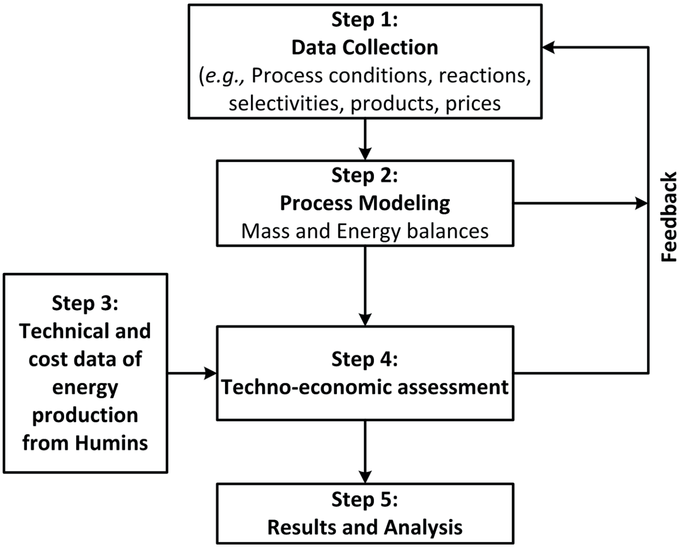

FIGURE 5.1. General description of the methodological approach for assessment of butadiene and caprolactam from C6 sugars.

5.2.1. Process Modeling

To assess the technical performance, process models were developed in Aspen Plus v8.4 (Aspen Technology, Inc., USA). As several of the compounds involved in the modeling were not available in the databases of Aspen Properties, a property database of the National Renewable Energy Laboratory was used, which is based on the work of Wooley and Putsche, (1996) [238]. Furthermore, the nonrandom two-liquid (NRTL) thermodynamic model was used to calculate the activity coefficients of the liquid phase and the Hayden O'Connell equation of state was used to describe the vapor phase. All processes are assumed to operate in continuous mode and whole year operation (*i.e.,* 8000 h/year). In all cases energy integration was considered by using excess heat of available streams internally. Nevertheless, optimization using pinch analysis was not considered, also integration of water stream and water recycling was not included.

5.2.2. Basis of design

This section focuses on the assumptions and data used to build the process models for both the butadiene and caprolactam processes. The processes were designed based on similar processes reported in literature and in some cases following heuristics of typical chemical engineering conceptual design.

For both butadiene and caprolactam processes, C6 sugars is the main feedstock. In this study, the capacity of C6 sugars is set to 400 ktonne per year. This capacity was estimated roughly, based on the conversion of 1000 ktonne/y of dry lignocellulosic biomass, which is representative for large commercial operation of biorefineries [239]. In the base case, this flowrate was equally distributed to feed the production processes of butadiene and caprolactam (200 ktonne/year of C6 sugars feeding each process). The impact of this assumption is considered as part of sensitivity analysis. The C6 sugars price (independently of whether it was produced from crops or lignocellulosic biomass) is fixed as an input for the economic analysis of both butadiene and caprolactam production (300 €/tonne [239], typical range of 200-400 €/tonne).

Figure 5.2 shows a simplified block diagram of the sequences considered in this study. Each block represents a production process which are explained in more detailed below. The doted block represents a combined heat and power unit in case humins are valorized. It is assumed that both heat and power produced in this step are distributed equally to both the butadiene and caprolactam lines. Surplus electricity (if any) is considered as additional product.

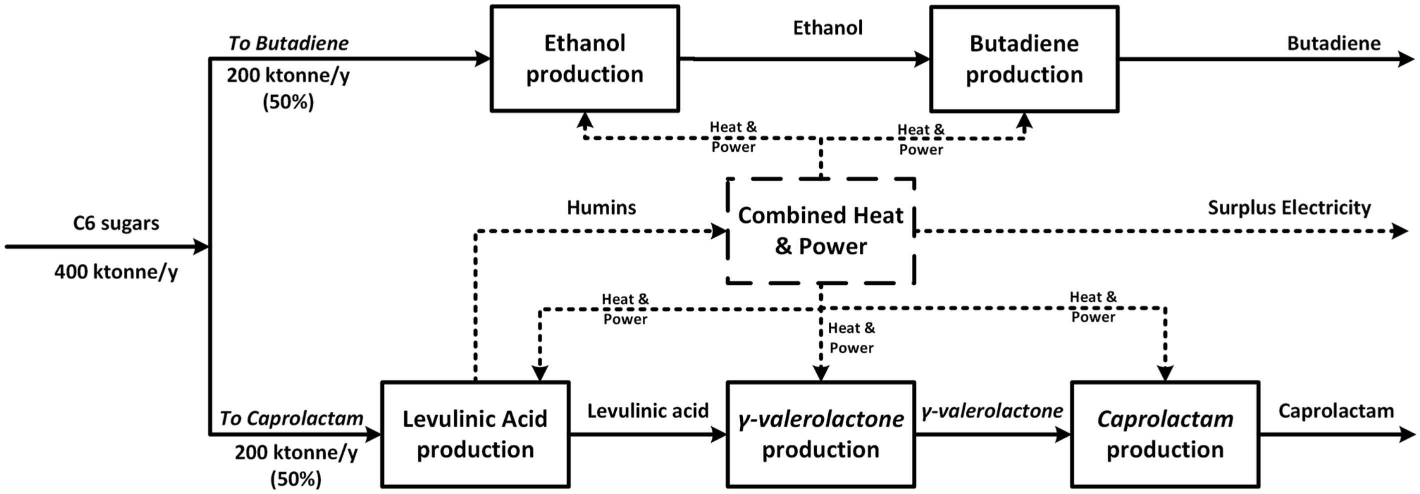

FIGURE 5.2. Simplified block diagram of butadiene and caprolactam production from C6 sugars.

Butadiene production process

This process comprises two main sections: i) ethanol production; ii) butadiene production and recovery. Figure 5.3 shows the simplified flowsheet of the ethanol production step, comprised of three main steps: fermentation, distillation, and dehydration. The ethanol section was modeled based on the description provided by Quintero et al., (2008) [240]. It starts with the reception and conditioning of the C6 sugars stream by diluting and mixing it with the fermentation media. The fermentation step was modeled assuming 85% of the theoretical yield (Ethanol yield: 0.43 kg/kg C6 sugars, theoretical: 0.51 kg/kg C6 sugar) using *S. cerevisiae* as fermenting yeast. CO_2 is produced at a rate of 1.1 kg per kg of ethanol, and yeast at a rate of 0.23 kg per kg of ethanol [112]. The fermentation unit works at 31ºC, which is the recommended temperature to avoid yield loss [112]. Next, the fermentation broth is sent to a distillation column in which ethanol is concentrated from 8wt% to 50 wt% in the top stream. The bottom stream contains impurities and it is assumed as wastewater. The concentrated ethanol stream is further concentrated in a second distillation column up to 96 wt% (azeotropic concentration). Finally, ethanol is dehydrated in a sequence of molecular sieves until its concentration reaches 99.7 wt%. Figure 5.4 shows a simplified flowsheet of the conversion of ethanol into butadiene. The dehydrated ethanol stream is directed to the butadiene process where ethanol is converted into butadiene and co-products. The base case (Case I) conditions and reactions of the conversion of ethanol into butadiene were gathered by direct communication with experts in butadiene production from Delft University of Technology[1]. The reactor operates at 425 ºC and 1 bar. Reactions and ethanol conversion rates used in this study are listed in Table 5.9 in appendix A. The reactor effluent contains a large number of compounds, leading to the design of a complex downstream process to recover the butadiene rich stream. The downstream processing was designed based on an analogy of the traditional petrochemical production of butadiene [241, 242]. The downstream processing selected, is in principle similar to that proposed by Shylesh et al., (2016) [243] for bio-based butadiene. The first assumption of the downstream processing was that hydrogen produced in the reaction is separated as top product (block 4, Figure 5.4). This assumption is in agreement with the model discussed by Shylesh et al., (2016) [243]. The remaining stream is then separated into light and heavy fractions in a flash column (block 4, Figure 5.4). The heavy fraction contains mainly water, unconverted ethanol, butanols and octanol. This fraction (from block 4 in Figure 5.4) is sent to a distillation train (blocks 14 and 15, Figure 5.4), where ethanol and water are recovered at the top of the first column and later recycled to the ethanol dehydration step shown in Figure 5.3.

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[1] Personal communication with Constantino Garcia Maldonado, M.Sc Chemical Engineering Department, Delft University of Technology on reactions for ethanol to butadiene, conversion, selectivities and conditions (*i.e.,* temperature, pressure and ethanol concentration in feed).

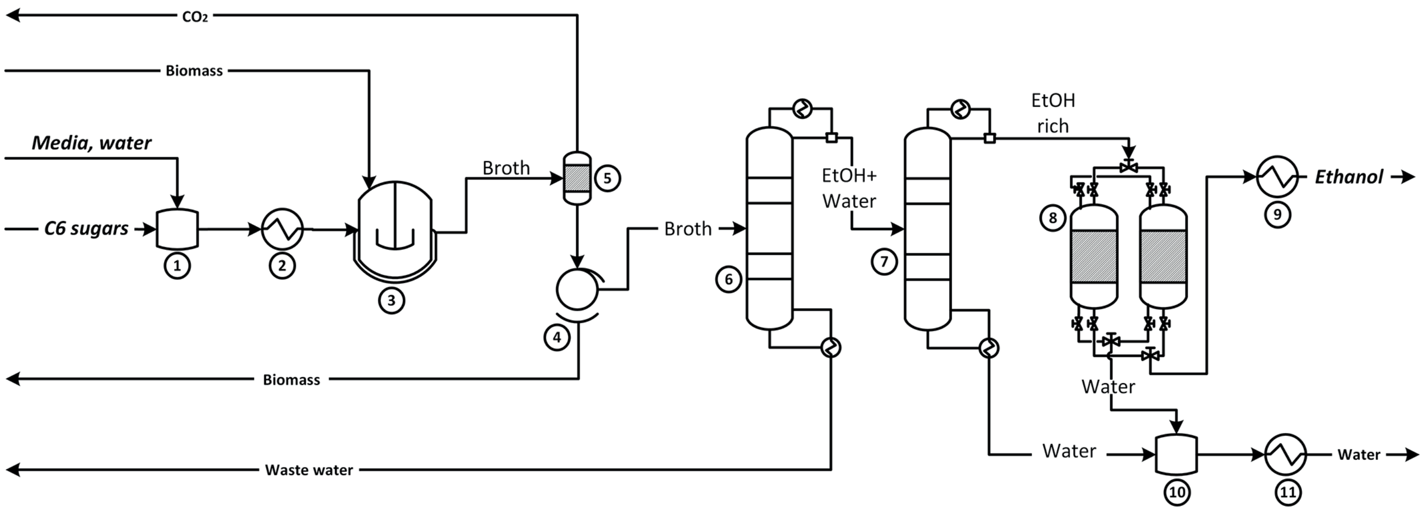


FIGURE 5.3. Simplified flowsheet diagram of ethanol production from C6 sugars. Equipment list: 1. Mixer, 2. Heat exchanger, 3. Fermenter, 4. Filter, 5. Knockout drum, 6. Column 1, 7. Column 2, 8. Molecular sieves, 9. Heat exchanger, 10. Mixer, 11. Heat exchanger.

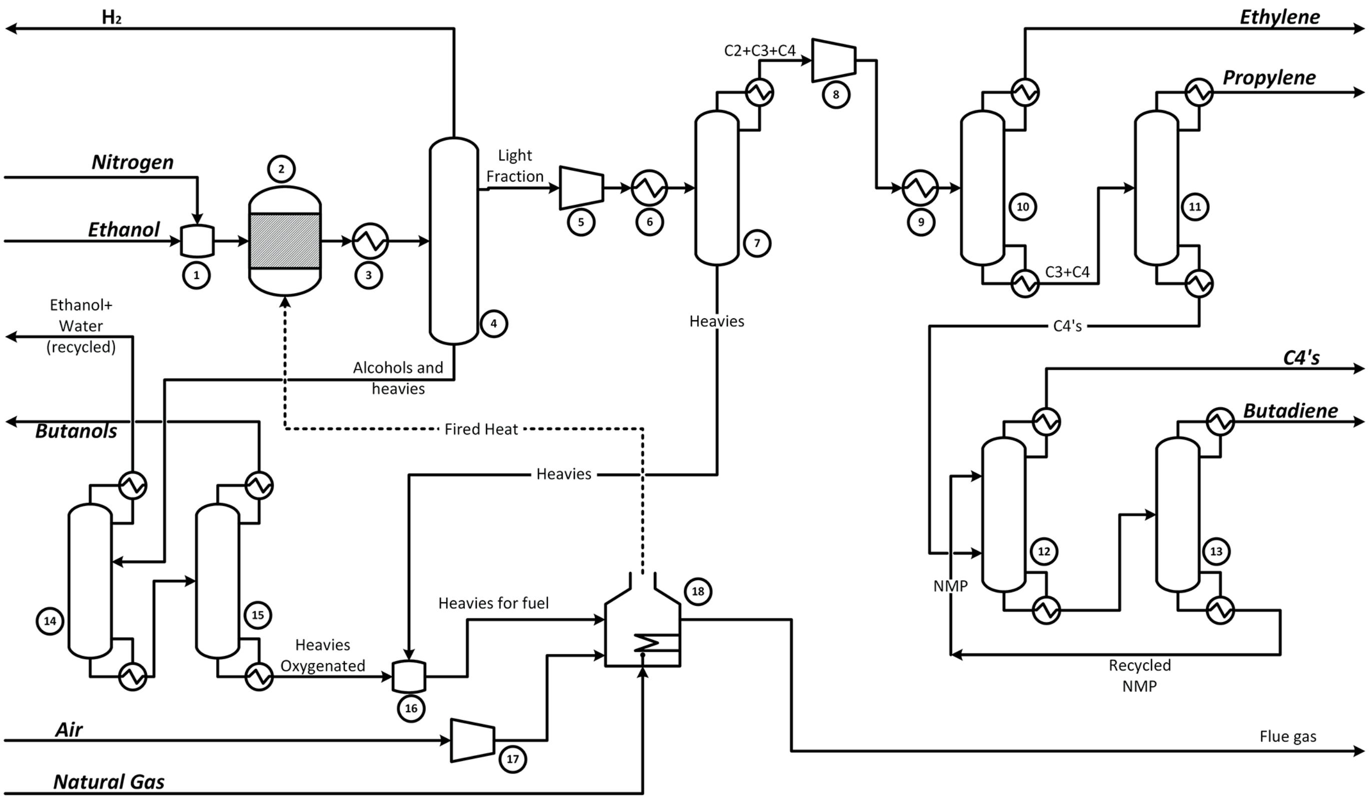


FIGURE 5.4. Simplified flowsheet diagram of the conversion of ethanol into butadiene and downstream processing for the recovery of butadiene and co-products. 1. Set up drum, 2. Reactor, 3. Heat Exchanger, 4. Flash column, 5. Compressor, 6. Heat exchanger, 7. Distillation Column, 8. Compressor, 9. Heat exchanger, 10. Distillation column, 11. Distillation, 12. Extractive distillation column, 13. Distillation column, 14. Distillation column, 15. Distillation column, 16. Mixer drum, 17. Compressor, 18. Furnace.

A fraction of the butanols mixture is recovered at the top of the second column, while the non-recovered heavies at the bottom. The butanol rich stream (mixture of n-butanol and 2-butanol, at 70/30 mass ratio) is not further split due to the complexity to recover the individual butanols (*i.e.,* separation of n-butanol from 2-butanol). This stream was instead assumed as a single product.

The light fraction leaving the flash column (block 4, Figure 5.4) is rich in butadiene, ethylene, diethyl ether, propylene, butenes (assumed as a mixture of C4s) and pentene. This stream is compressed up to 10 bar and cooled to 20 ºC in order to further separate heavier fractions in a distillation column (block 7, Figure 5.4). The bottom stream is rich in diethyl ether and pentane, which are later mixed (block 16, Figure 5.4) with the non-recovered heavies from the butanols recovery section. The complexity of the heavies stream is considered very high for further downstream processing, and therefore, it was assumed that it can be fed to a furnace (block 18, Figure 5.4) to provide the required energy to the reactor. The top stream from block 7 (rich in C2, C3 and C4´s) is compressed to 25 bar and cooled to 20 ºC, before entering a distillation column in which ethylene is recovered as top product (<98 wt%) (see block 10, Figure 5.4). The bottom product, rich in C3 and C4, is sent to a distillation column (block 11, Figure 5.4) where propylene is recovered as top product (<94 wt%). The bottom stream is rich in butenes and butadiene. Due to the similar boiling points, separation using conventional distillation is not possible. In this paper extractive distillation (blocks 12,13, Figure 5.4) was assumed, using aqueous n-methyl-2-pyrrolidone as solvent (NMP) [241]. In the first column, butadiene is recovered as bottom product together with the solvent. The C4 stream leaves as top product and it was considered as a valuable product (composition 49 wt% 1-butene, 31 wt% 2-butene, 20 wt% isobutene). Finally, the solvent is separated from the butadiene and recycled to the extractive distillation column. The butadiene stream is purified up to concentrations above 99 wt%. The processes shown in Figure 5.3 and Figure 5.4 comprise the butadiene production process using C6 sugars as raw material (called Case I).

Caprolactam production process

The process line for caprolactam production is comprised of three main sections: i) levulinic acid production; ii) γ-valerolactone production, and iii) caprolactam production and recovery. Figure 5.5 shows the simplified flowsheet diagram of the production of levulinic acid from C6 sugars. The production of levulinic acid starts with diluting C6 sugars in water and adding sulfuric acid (catalyst) prior to the reaction step. Next, the diluted C6 sugar stream is sent to the reactor which operates at 200 ºC [244]. The reaction systems consists of the dehydration of C6 sugars to Hydroxymethylfurfural (HMF) (humins formed in this step), and its subsequent conversion into levulinic and formic acid. Product yields were estimated by running the kinetic model reported by Girisuta et al., (2006) [244]. Complete conversion of C6 sugars was assumed in this step with a product distribution of 0.52 kg of levulinic acid, 0.20 kg of formic acid and 0.18 kg of humins per kg fed to the reactor. The resulting mixture was sent to a distillation column where formic acid and water were obtained as top products, and levulinic acid and humins as bottom products. The formic acid stream was further dehydrated using a membrane unit and sold as product. The humins were separated from levulinic acid in a second distillation column.

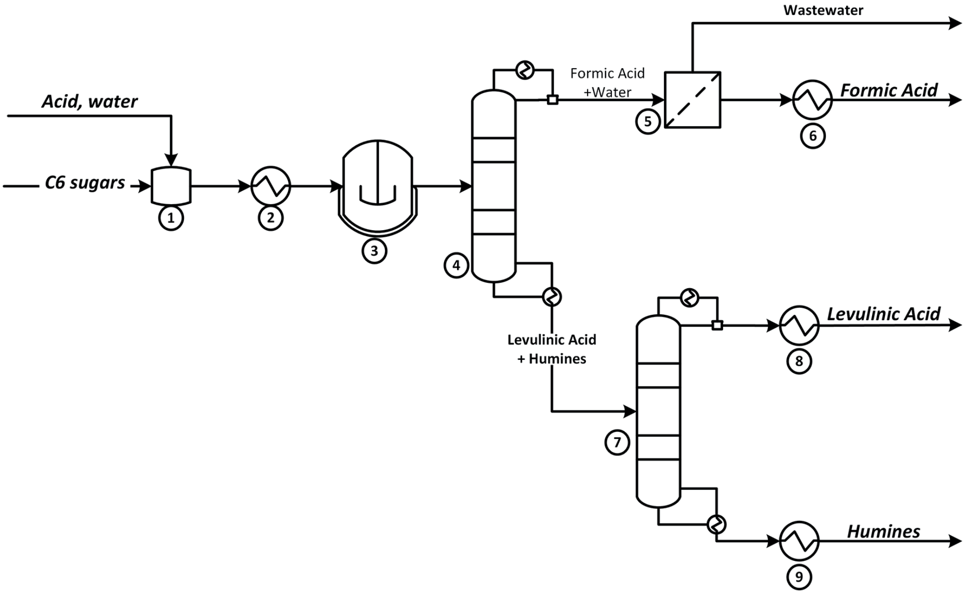


FIGURE 5.5. Simplified flowsheet diagram of the production of levulinic acid from C6 sugars. Equipment list: 1. Set up drum, 2. Heat Exchanger, 3. Reactor, 4. Distillation Column, 5. Membrane unit, 6. Heat exchanger, 7. Distillation column, 8. Heat exchanger, 8. Heat exchanger

Figure 5.6 shows the simplified flowsheet diagram of the production of γ-valerolactone from levulinic acid. The process for producing γ-valerolactone (GVL) from levulinic acid (LA) starts with its dilution in dioxane at a concentration of 10 wt%. The pressure is increased to 10 bar, and the temperature rises to 150 °C at which the reaction takes place. The reaction system was modeled based on data reported by Ftouni et al., (2016) [235]. The reaction is carried out in a Ru/ZrO2 catalyst, at 150 °C. Reactions are listed in able 5.10 in appendix A. The stream leaving the reactor is cooled and passed through a flash column where the unconverted hydrogen is separated and recycled to the reactor. Next, the GVL diluted in dioxane and water is recovered in a distillation column as bottom´s product (with a concentration <97 wt%). The solvent contains small fractions of water, pentanediol and methyltetrahydrofuran, thus, a purge is required before recycling the solvent. The purge stream is considered waste.

The caprolactam production process is itself comprised of three main steps. Step 1 is the production of methyl pentenoates (MPs), which consists of the transesterification of GVL with methanol. This steps starts with mixing GVL with methanol, at a methanol/GVL molar ratio of 1.5 [226]. The catalyst is p-toluenesulfonic acid fed at a ratio of 1 mol per mol of GVL (catalyst is assumed to be recycled to the reactor system). The mixture is heated to 190 ºC, and then directed to the transesterification reactor (block 3, Figure 5.7). For this step, a conservative approach (assuming a mixture of 3-, and 4-MPs) was followed for the base case (Case III), by considering the formation of 3-MP and 4-MP in a molar ratio of 3:1 according to [226]. The reactions and conversions are provided in Table 5.11 in appendix A. The mixture leaving the reaction system is sent to a distillation train, where both unconverted methanol and GLV are recovered and recycled to the reaction system. The mixture of MPs is sent to the second step which consists of the aminolysis of MPs into penteneamides (PAs) with ammonia at 80 ºC (block 8, Figure 5.7). Ammonia is fed at a molar ratio of 5 mol per mol of MPs mixture [226]. Reactions and conversions are also listed in Table 5.11 in appendix A. The mixture leaving the reaction system is passed by a flash column (block 9, Figure 5.7) were ammonia is recovered and later recycled to the reactor. The liquid stream leaving the flash column is sent to a distillation battery where the methanol produced is recovered and recycled to the transesterification unit, while the PAs are recovered and sent to the last conversion step. The last step is the production of caprolactam (CAL) by the hydroformylation of the PAs into unsaturated caprolactam, and after hydrogenation into CAL. The PAs are first diluted in diglyme (concentration of 2 mol/L), heated to 120 ºC and converted into unsaturated caprolactam using syngas ($CO:H_2$ ratio = 1:1, 10 bar) (block 15, Figure 5.7) [226]. The resulting mixture in the hydroformylation step is passed by a flash column to remove excess carbon monoxide (block 16, Figure 5.7). Unsaturated caprolactam is hydrogenated (block 17, Figure 5.7) at 80 ºC using pure hydrogen at 80 bar [226]. The reactions of the caprolactam system were modeled (see Table 5.11 in appendix A) according to [226]. The stream containing caprolactam is passed by a distillation train (blocks 18 and 19, Figure 5.7), where diglyme is recovered and recirculated. The solvent free caprolactam rich stream is passed through a series of distillation/adsorption columns (blocks 20 and 21, Figure 5.7), where valeramide and caprolactam are recovered as products. From this step, the residue stream is sent to a combustion chamber (mixed with excess carbon monoxide from hydroformylation reaction) to produce steam (blocks 22 and 23, Figure 5.7) for consumption in the process. The processes shown in Figure 5.5, Figure 5.6 and Figure 5.7 make up the caprolactam production process using C6 sugars as raw material (Case III).

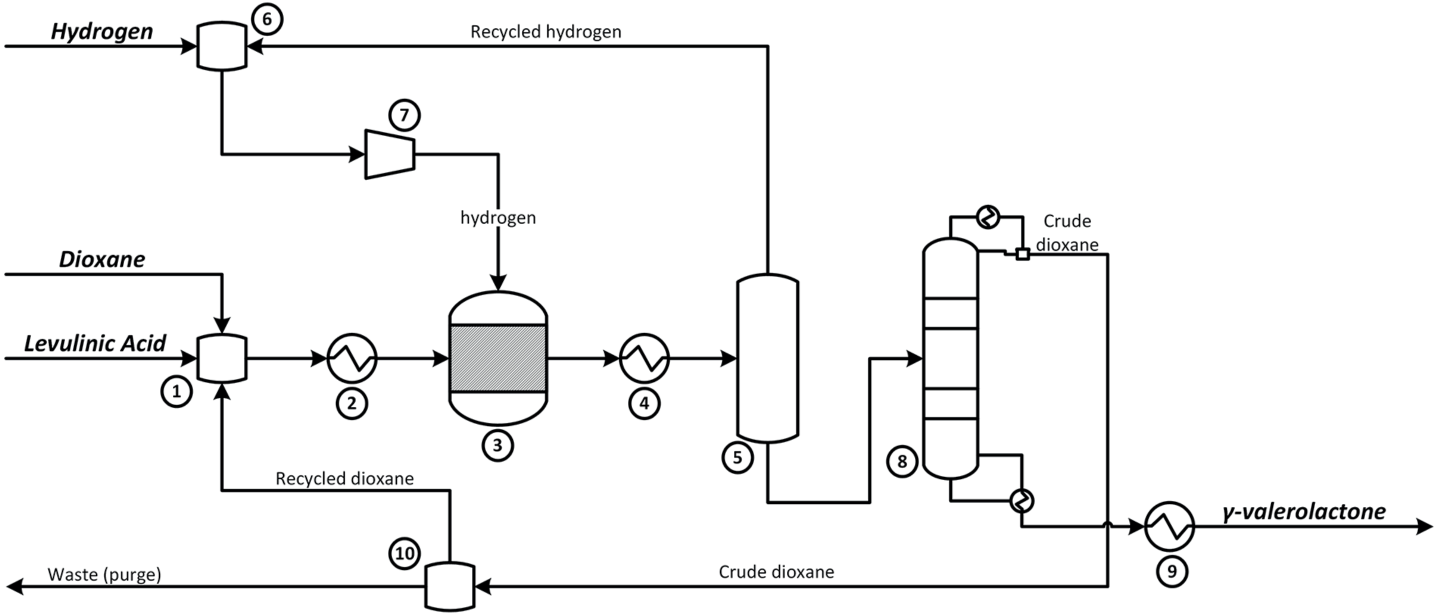


FIGURE 5.6. Simplified flowsheet diagram of the production of **γ-valerolactone** from levulinic acid. Equipment list. 1. Set up drum, 2. Heat Exchanger, 3. Reactor, 4. Heat Exchanger, 5. Flash Column, 6. Mixer drum, 7. Compressor, 8. Distillation Column, 9. Heat Exchanger, 10. Mixer drum.

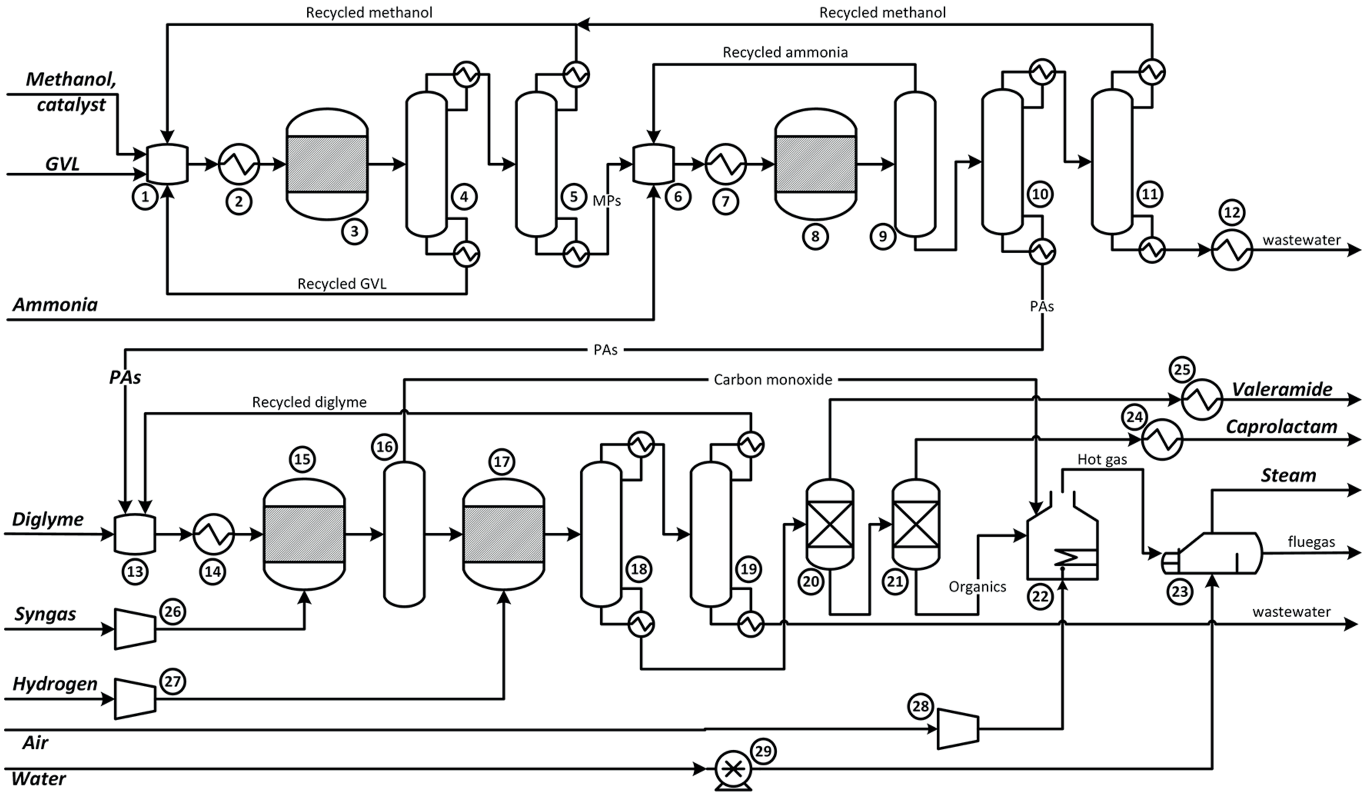


FIGURE 5.7. Simplified flow diagram of the production of caprolactam from **γ-valerolactone. Equipment list:** 1. Set up drum, 2. Heat Exchanger, 3. Reactor, 4. Distillation Column, 5. Distillation Column, 6. Set up drum, 7. Heat Exchanger, 8. Reactor, 9. Flash Column, 10. Distillation Column, 11. Distillation Column, 12. Heat Exchanger, 13. Set up drum, 14. Heat Exchanger, 15. Reactor, 16. Flash Column, 17. Reactor, 18. Distillation Column, 19. Distillation Column, 20. Distillation Column, 21. Adsorption Column, 22. Combustion chamber, 23. Boiler, 24. Heat Exchanger, 25. Heat Exchanger, 26. Compressor, 27. Compressor, 28. Compressor, 29. Pump.

5.2.3. Process cases and humins valorization

For both butadiene and caprolactam systems, two cases per process line were considered for the techno-economic assessment. The objective of including two cases per process (*i.e.,* two cases for butadiene and two cases for caprolactam) was to assess the effect of possible changes on the overall performance of both butadiene and caprolactam production. Table 5.1 summarizes the process cases assessed in this study, where cases I and II correspond to the butadiene production line, and cases III and IV correspond to the caprolactam production line.

For the butadiene production line, case I (base case) corresponds to the description provided above, while case II uses a different set of data on the conversion of ethanol into butadiene [243]. In this case, the reactor operates at 250 ºC and 1 bar. Reactions and ethanol conversion are listed in Table 5.9 in the appendix. Taking into account that the number of products leaving the reactor differ in comparison to those of Case I, the downstream processing is also modified, where columns 11, 14 and 15 shown in Figure 5.4 were left out of the scheme. For both cases I and II, ethanol production section remains identical.

For the caprolactam production line, case III (base case) corresponds to the description provided above. Case IV uses different process sequences in the step from GVL into CAL, where 3-MP is separated from the 4-MP prior to the aminolysis step. The 3-MP are separated from the 4-MP by selective azeotropic distillation (incorporated between blocks 5 and 6 in Figure 5.7) and recycled back to the reaction system (transesterification with methanol) to isomerize the 3-MP into 4-MP, and thus increase the yield of 4-PA and subsequently that of caprolactam per GVL fed to the system. This possible improvement is based on the description provided by Raoufmoghaddam et al., (2014) [226]. Reactions are shown in Table 5.11 in the appendix.

TABLE 5.1. Process cases assessed in this study

Process cases	Butadiene Process	Caprolactam process
Case I (base case)	x	
Case II (process with possible improvement)	x	
Case III (base case)		x
Case IV (process with possible improvement)		x

In addition to the cases described in Table 5.1, the valorization of humins to produce electricity and heat was considered. Humins are only produced in the caprolactam production process (in the levulinic acid production stage). However, it was assumed that the electricity and heat produced was distributed between the butadiene and caprolactam processes at the same ratio as the input C6 sugar stream was distributed (see section 5.2.2). This means that production costs of electricity and heat production from humins are distributed between the two process lines (i.e., butadiene and caprolactam). The production of heat and electricity from humins was estimated assuming combined heat and power unit with power and heat efficiencies of 41% and 49%, respectively. Calculations were based on the heating value of humins (23 MJ/kg [245]). The effect of humins valorization is accounted as part of the sensitivity analysis of the cases shown in Table 5.1. Allocation of heat and power produced from humins are based on the distribution of C6 sugars to each production line.

5.2.4. Economic assessment

The economic assessment comprises estimating the capital (CAPEX) and operating (OPEX) expenditures of the processing lines. These expenditures were estimated using information (equipment list, mass and energy flows) generated in the process modeling stage. In all cases, CAPEX is based on adding up equipment costs (estimated using Aspen Economic Analyzer v8.4) and using typical factors for capital investment according to Peters et al., (2003)[246]. The factors used in this study can be found in appendix B. All costs were updated to 2014 prices using the Chemical Engineering Plant Cost Index (CEPCI) and are expressed in Euros. When necessary an average 2014 exchange rate of 0.784 €/USD was applied.

Operational costs (OPEX) include raw materials, utilities, maintenance, labor, fixed & general and overheads, and capital depreciation (CAPEX). Raw materials costs were based on the mass balances, and unit prices (see Table 5.2). Utilities costs were estimated using energy balances and prices calculated using the equations reported by Ulrich & Vasudevan, (2006) [247] and updated to 2014 prices (using 2014 CEPCI). Labor costs consisted of operating labor cost (3 shifts of 8 hours each, 10 operators per shift for both butadiene and caprolactam processes), operating supervision cost and laboratory charges cost [246]. The yearly wage was assumed at 50,000 €/y per person for all operators of the biorefinery. Additional cost categories such as maintenance, fixed & general, and plant overhead were included in the analysis. Estimating these categories was carried out using typical factors as shown in appendix B [246]. These g. Green premiums, CO_2 credits and subsidies were not taken into account in the analysis. Capital depreciation was estimated using the straight line method for a depreciation time of 10 years based on suggestions by Peters et al., [246].

To assess the profitability of each system, the Net Present Value (NPV) was used as indicator. The NPV was estimated for a 20 year period using information on capital investment, operating costs and revenues from products by calculating discounted cash flows. The discount rate was set to 10% and income tax of 25% for the Netherlands (NPV calculations after taxes). Each step considered in NPV calculations was based on those reported by Peters et al., [246]. Prices and main economic input parameters used in the assessment are displayed in Table 5.2.

TABLE 5.2. Price inputs used in the economic assessment of the processes butadiene and caprolactam production.

Feature	Value	Unit	Reference
C6 sugars [a]	300	€/tonne	[239]
Sulfuric Acid [a]	220	€/tonne	Average from [151]
Ammonia [a]	180	€/tonne	Average from [151]
Yeast [a]	1000	€/tonne	[152]
Dioxane [a]	1670	€/tonne	Average from [151]
Methanol [a]	240	€/tonne	[248]
Diglyme [a]	2000	€/tonne	Average from [151]
Petrochemical Syngas [a]	200	€/tonne	Estimated based on [249]
Butadiene	900	€/tonne	Price index, [250]
Ethylene	950	€/tonne	Price index, [250]
Propylene	950	€/tonne	Price index, [250]
C4s	520	€/tonne	Average price of C4 stream, [250]
Hydrogen [a]	1700	€/tonne	[220]
Butanols [a]	500	€/tonne	Average from [151]
Cell biomass [a]	10	€/tonne	Assumed as anaerobic digestion digestate based on [251]
Formic Acid [a]	370	€/tonne	Average from [151]
Caprolactam	2000	€/tonne	[252]
Valeramide [a]	300	€/tonne	Conservative estimation based on amide prices [151]
Cooling Water [b]	0.12	€/m^3	Estimated using equations of [247] and updated to 2014 price
Low-pressure Steam [b]	40	€/tonne	Estimated using equations of [247] and updated to 2014 price
Mid-pressure Steam [b]	46	€/tonne	Estimated using equations of [247] and updated to 2014 price
Wastewater treatment [b]	0.08	€/m^3	Estimated using equations of [247] and updated to 2014 price
Process water [b]	0.10	€/m^3	Estimated using equations of [247] and updated to 2014 price
Solid disposal [b]	23	€/tonne	Estimated using equations of [247] and updated to 2014 price
Refrigerant [b]	21	€/GJ	Estimated using equations of [247] and updated to 2014 price

[a] Prices assumed to be representative for 2014.

[b] Prices calculated using the equations proposed by [247], updated to 2014 prices using the CE PCI, and using natural gas as fuel source in the Netherlands (11 €/GJ, [194]).

To have a better understanding of the systems, a sensitivity analysis was carried out to identify which economic parameters affect the NPV the most. Changes on inputs were considered up to ±50% of the reference values shown in Table 5.2. As part of the sensitivity analysis, the distribution of C6 sugars to caprolactam and butadiene was also assessed, to evaluate the effect of varying the process capacities on the overall economic performance of butadiene and caprolactam production. Escalations of costs were considered linear for OPEX, while for CAPEX components the six-tenth rule of thumb was applied. The production of electricity and heat from humins was also considered as part of the sensitivity analysis.

5.3. RESULTS AND DISCUSSION

5.3.1. Process modeling

Butadiene Process

Table 5.3 shows the mass balances of the butadiene process for cases I (base case) and II. All mass balances are expressed on a wet basis, to show all input and output streams for each system. The mass balances provide an indication on the consumption of raw materials and the efficiency of the technology to obtain butadiene and co-products. When comparing the mass balances of the two cases it is noted that the input streams are almost identical with exception of air and demineralized water (lower in case II), which are used to provide extra energy to the reactor. Comparing the outputs of co-products, it is seen that the flowrates of products are different with a higher yield of butadiene in case II in comparison to case I. For both cases, the product with the highest yield (excluding LP steam) is butadiene with 122 and 168 kg per tonne of C6 sugars for cases I and II, respectively. Only 12% and 17% of the initial mass of C6 sugars is converted into butadiene. The product with the second highest yield (kg per tonne C6 sugars) is cell biomass with 99 kg per tonne (for both cases) accounting for approximately 10% of the initial mass of C6 sugars, showing that a large amount of carbon from C6 sugars is lost within ethanol production. In fact, 48% of the initial mass of C6 sugars is converted into CO_2. This aspect can be critical for the subsequent economic and environmental analyses as the overall butadiene processing yield (kg butadiene/tonne C6 sugars) is rather low for such a complex system.

Table 5.4 shows the energy requirements for the two cases. The total energy requirement of case I (including ethanol and butadiene sections for all utilities type) corresponds to approximately 50 MJ/kg of butadiene (not allocated). The total energy requirement of case II (including ethanol and butadiene sections for all utilities type) corresponds to 35 MJ/kg of butadiene (not allocated), which is 29% lower than total energy requirements of case I.

TABLE 5.3. Mass balances accounting for key material inputs and outputs of cases I and II of butadiene production, expressed in ktonne/year.

Cases	Case I		Case II	
Stream	**Inputs, ktonne/y**	**Outputs, ktonne/y**	**Inputs, ktonne/y**	**Outputs, ktonne/y**
Raw Materials				
C6 sugars [a]	200	-	200	-
Water	998	-	998	-
Ammonia [b]	6	-	6	-
Yeast	$2*10^{-1}$	-	$2*10^{-1}$	-
Demineralized water	32	-	25	-
Air	111	-	97	-
Products				
Butadiene [c]	-	24	-	34
Ethylene [d]	-	11	-	9
Propylene [e]	-	1	-	-
C4s [f]	-	3	-	1
Hydrogen	-	1	-	2
Butanols [g]	-	6	-	-
LP steam [h]	-	32	-	25
Cell biomass [i]	-	20	-	20
Waste streams				
CO_2 from fermentation	-	95	-	95
Waste Water	-	1,033	-	1,032
Fluegas [j]	-	121	-	110
Total	**1,348**	**1,348**	**1,327**	**1,327**

[a] Stream free of water, C6 sugars purity 100%.
[b] Ammonia concentration 25 wt% in water
[c] Butadiene purity 99.7 wt%
[d] Ethylene purity 98.5 wt%
[e] Propylene purity 94.2 wt%
[f] C4's composition: 49 wt% 1-butene, 31 wt% 2-butene, 20 wt% isobutene
[g] Butanols concentration: 70 wt% n-butanol, 30 wt% 2-butanol
[h] LP steam pressure: 3 bar. Product integrated within the process in the energy balance.
[i] Cell biomass produced from ethanol fermentation
[j] Flue gas composition: water 11 wt%, CO_2 16 wt%, O_2 1 wt%, N_2 72 wt%.

This can also be due to higher butadiene yield in case II compared to case I. Cooling water and refrigerant consumption levels were slightly lower in the butadiene section. A main difference can be seen in LP steam consumption, as that produced in the butadiene process is not sufficient to cover 100% of the demand in the ethanol process. Electricity consumption is 24% higher in case II compared to case I, mostly due to higher compression requirements for the downstream processing of the gaseous components and air compression as input for the furnace. Note that bio-based butadiene production is still at early development stages and therefore there is high uncertainty on the overall processing efficiencies. Figure 5.8 shows the contribution of total energy requirements by utility type and process sections for both cases I and II, highlighting the large contribution of cooling water and the large energy requirements to produce ethanol.

TABLE 5.4. Energy requirements of cases I and II of butadiene production, expressed by utility type and process section in TJ/year.

Butadiene production cases		**Case I**			**Case II**		
Utility Type	**Unit**	**Ethanol Section**	**Butadiene Section**	**Total**	**Ethanol Section**	**Butadiene Section**	**Total**
Cooling Water [a]	TJ/y	495	245	**740**	495	205	**700**
LP Steam [b]	TJ/y	398	-	**398**	404	-	**404**
MP Steam [b]	TJ/y	-	-	**-**	-	-	-
Electricity	TJ/y	$1*10^{-1}$	38	**38**	$1*10^{-1}$	48	**48**
Refrigerant	TJ/y	-	33	**33**	-	30	**30**
Total	**TJ/y**	**893**	**316**	**1209**	**899**	**283**	**1182**

[a] Cooling water heat capacity: 50 kJ/kg

[b] Latent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg

[c] Natural gas lower heating value (LHV): 47.1 MJ/kg

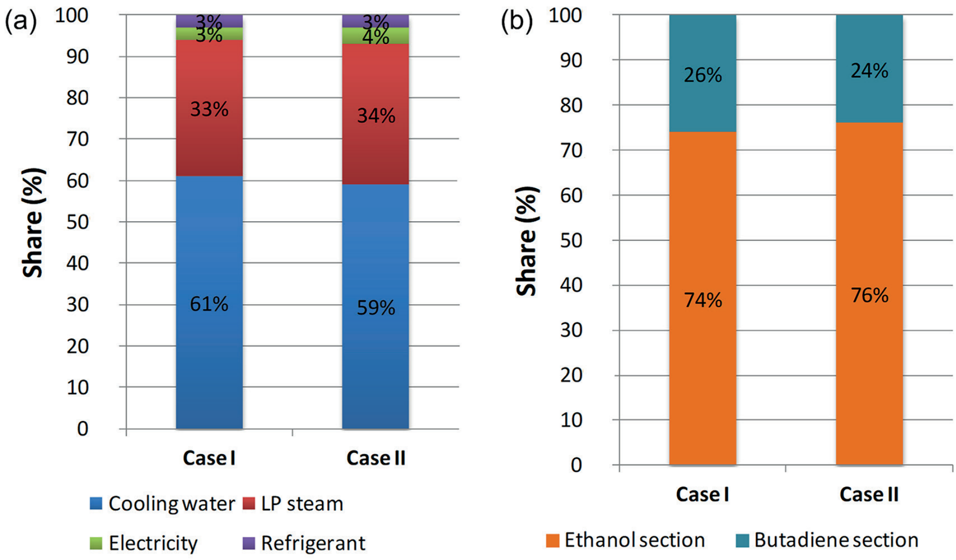


FIGURE 5.8. Distribution of total energy requirements for cases I and II, shown by: a) utility type, b) process section.

When comparing the total energy requirement with literature (including all utilities type), Cespi et al., (2016) [232] reports a consumption range of 8-10 MJ per kg of butadiene (consumption only for the ethanol to butadiene step of Ostromisslensky and Lebedev processes, respectively), while this study reports of 13 MJ/kg of butadiene for case I and 8 MJ/kg of butadiene for case II (consumption only for the butadiene section). Case I shows higher energy requirements (than those reported by Cespi et al., (2016) [232]) by a factor range of 1.3 to 1.6. Case II shows that the energy requirements are within the range reported by Cespi et al., (2016) [232].

Caprolactam Process

Table 5.5 shows the mass balances of the caprolactam process for cases III (base case) and IV (3MPs isomerized to 4MPs before aminolysis step). In both cases, the annual intake of C6 sugars is identical. By comparing the mass balances of the two cases, the input streams are very similar, with exception of air, water (related to the production of LP steam) and syngas and hydrogen (slightly higher in case IV due to higher unsaturated caprolactam production). When comparing the outputs of the co-products, there is no difference in the flowrate of formic acid and water as the process of C6 sugars to levulinic acid step was assumed identical in both cases. What varies the most is the flowrates of caprolactam, valeramide and LP steam. This is due to the fact that the conversion into caprolactam is higher for 4PA in comparison to 3PA. Therefore there is higher selectivity to caprolactam in case IV than in case III. LP steam production is correlated to the non-recovered organics used to feed the combustion chamber (Lower in case IV due to an increase in caprolactam yield). In case IV, the overall production of caprolactam is 59% higher in comparison to case III, while the production of valeramide is 91% lower.

In case III, the product with the highest yield (excluding LP steam and water) is caprolactam with 277 kg per tonne of C6 sugars, followed by formic acid (204 kg per tonne of C6 sugars) and valeramide (145 kg per tonne of C6 sugars). This shows that approximately 28% of the initial mass of C6 sugars is converted into caprolactam. In case IV, the product with the highest yield is also caprolactam with 441 kg per tonne of C6 sugars (59% higher than case III), followed by formic acid (204 kg per tonne of C6 sugars) and valeramide (13 kg per tonne of C6 sugars). In case IV, about 44% of the initial mass of C6 sugars is converted into caprolactam. In terms of waste streams, Case IV shows 19% lower flowrates than those of case III. The humins produced are equal in the two systems since the levulinic acid process is identical.

TABLE 5.5. Mass balances accounting for key material inputs and outputs of cases III and IV of caprolactam production, expressed in ktonne/year.

Cases	**Case III**		**Case IV**	
Stream	**Inputs, ktonne/y**	**Outputs, ktonne/y**	**Inputs, ktonne/y**	**Outputs, ktonne/y**
Raw Materials				
C6 sugars [a]	200	-	200	-
Sulfuric Acid	$9*10^{-2}$	-	$9*10^{-2}$	-
Water	227	-	148	-
Dioxane	1	-	1	-
Hydrogen	3	-	4	-
Methanol	$3*10^{-3}$	-	$3*10^{-3}$	-
Ammonia [b]	43	-	43	-
Diglyme	$4*10^{-2}$	-	$4*10^{-2}$	-
Syngas [c]	26	-	27	-
Air	147	-	91	-
Products				
Formic Acid	-	41	-	41
Water	-	20	-	20
Caprolactam [d]	-	55	-	88
Valeramide [e]	-	29	-	3
LP Steam [f]	-	181 (192[h])	-	102 (192 [h])
Waste streams				
Humins	-	36	-	36
Waste water	-	117	-	122
Flue gas [g]	-	169	-	101
Total	**648**	**648**	**513**	**513**

[a] This stream is free of water, C6 sugars purity of 100%.[b] Ammonia concentration is 35 wt% in water
[c] Syngas composition 50:50, H_2:CO molar. [d] Caprolactam purity of 99 wt%
[e] Valeramide purity of 99wt%. [f] LP steam pressure: 3 bar. Product integrated within the process in the energy balance.
[g] Flue gas composition: water 6 wt%, CO_2 24 wt%, N_2 67 wt%, NO_2 3 wt%.
[h] Additional LP steam produced when humins valorization is considered.

Table 5.6 shows the energy requirements for cases III and IV. The total energy requirement (including all utilities type) corresponds to 50 MJ/kg of caprolactam for case III (not allocated). The energy requirements are 9% higher in case IV in comparison to case III. Although the annual requirements of energy are higher in case IV than in case III, the energy intensity (including all utilities type, expressed in MJ per kg of caprolactam) is about one third lower in case IV than in case III (34 MJ/kg) due to higher CAL yield in case IV. Cooling water requirement is 4% higher in case IV than in case III, while the requirement of LP steam is 109% higher. These higher utilities requirements are due to additional separation steps to recover the 3Ms and recycle them to the transesterification step for isomerization into 4MP in case IV. The electricity consumption in case IV decreased by 10% in comparison to case III, however, its contribution is low and thus its effect is marginal. Figure 5.9 shows the total energy requirements by utility type and process sections for both cases III and IV, showing high contribution of the cooling utilities and large contribution of the GVL and CAL sections.

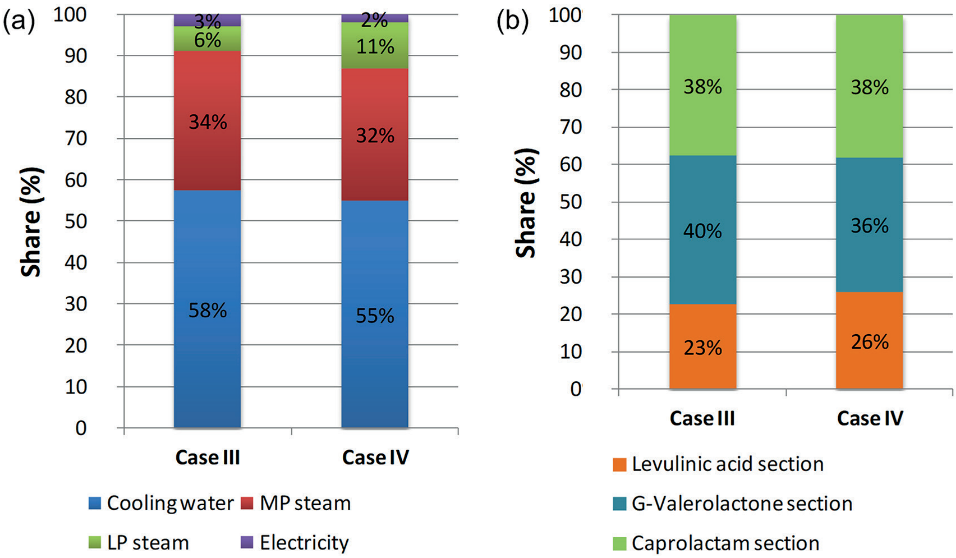


FIGURE 5.9. Distribution of total energy requirements for cases III and IV, shown by: a) utility type, b) process section**.**

Data on energy requirements of bio-based caprolactam production is scarce in open literature, therefore it was not possible to perform a comparison with the results of this work. It should be noted that bio-based caprolactam production is at early stages of development, which brings extra uncertainties to conversion and recovery efficiencies of products and co-products. When considering electricity production from humins, the produced amount is able to cover 100% of electricity requirements in cases I and II of butadiene production and III and IV of caprolactam production. The surplus electricity is considered as a by-product (227 TJ/y).

TABLE 5.6. Energy requirements of cases III and IV, expressed by utility type and process section in TJ/year.

Caprolactam production cases		**Case III**				**Case IV**			
Utility Type	**Unit**	**LA Section**	**GVL Section**	**CAL Section**	**Total**	**LA Section**	**GVL Section**	**CAL Section**	**Total**
Cooling Water [a]	TJ/y	468	544	581	**1594**	468	544	645	**1657**
LP Steam [b]	TJ/y	153	-	-	**153** **(-408 [c])**	321	-	-	**321** **(-408 [c])**
MP Steam [b]	TJ/y	-	522	415	**937**	-	522	452	**974**
Electricity	TJ/y	1	31	44	**76** **(-341 [c])**	1	31	37	**69** **(-341 [c])**
Total	**TJ/y**	**622**	**1098**	**1040**	**2760**	**790**	**1098**	**1133**	**3021**

[a] Cooling water heat capacity: 50 kJ/kg

[b] Latent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg

[c] Total electricity and LP steam produced in humins valorization. Negative symbol indicates a production of instead of consumption.

5.3.2. Economic Analysis

Butadiene process

Table 5.7 shows the CAPEX, OPEX, revenues and NPV for each case. In cases I and II, the fixed capital investment of the ethanol section remained equal (55 M€). The fixed capital investment of the butadiene section is 75 M€ for case I and 80 M€ in case II (6% higher). This difference is basically due to higher butadiene production rate in case II, despite the reduction in process units (columns 11, 14 and 15 shown in Figure 5.4 were left out of the scheme). Note that the bio-based butadiene process is still at early development stages, thus bringing large uncertainties in capital costs. Literature reporting capital costs of ethanol associated with the butadiene process is limited, confirming the importance to include this as part of the sensitivity analysis. In the two cases, the aspects that contribute the most to OPEX are raw materials, and utilities. OPEX are rather similar for cases I and II. In terms of revenues, case II shows slightly higher values, with butadiene as the major contributor, and in both cases ethylene as the second major contributor. This shows the high correlation between the revenues of butadiene and the feasibility of the system. Note that an important amount of cell biomass is produced in the ethanol process and, as previously mentioned, it is the product with the second highest yield (after butadiene). However, from an economic perspective its contribution to revenues is marginal due to its low price. Another option to improve the overall economics of the butadiene process is to capture the CO_2 produced in the ethanol process (*i.e.,* during fermentation) and generate additional income (*e.g.,* bio-CCS, CO_2 utilization), however, this is outside the scope of the current assessment (This might also represent additional CAPEX).

TABLE 5.7. Annualized operational costs, revenues, fixed capital investment and Net Present Value of cases I and II of butadiene production.

Feature	Case I		Case II	
	M€/year	Share	M€/year	Share
Operating costs (OPEX)				
Raw Materials	61.4	63%	61.4	62%
Utilities	11.2	11%	11.4	12%
Maintenance	9.0	9%	9.3	9%
Labor	1.95	2%	1.95	2%
Fixed & General	8.4	9%	8.7	9%
Overhead	5.7	6%	5.9	6%
Total	**97.7**	**100%**	**98.7**	**100%**
Revenues				
Butadiene	22.0	55%	30.2	71%
Ethylene	10.5	26%	8.5	20%
Propylene	1.1	3%	0.0	0%
C4s	1.5	4%	0.5	1%
Hydrogen	1.5	4%	3.1	7%
Butanols	3.1	8%	0.0	0%
Cell biomass	0.2	0%	0.2	0%
Total	**40.0**	**100%**	**42.6**	**100%**
Fixed capital investment (CAPEX)				
M€	130		135	
Net present value after taxes[a]				
M€	-647		-642	

[a] NPV at the end of project's lifetime

The NPV results (see Table 5.7) show negative values for cases I and II, implying that with the data considered in this study, both processes are economically unfeasible. OPEX are much higher than revenues in cases I and II, and added to capital investment, economic unfeasibility is seen. Note that both butadiene processes show similar NPV values, thus suggesting robustness on the unfeasibility of butadiene production from C6 sugars at current butadiene prices. To reach break-even (assuming all other parameters fixed, such as co-products prices), the selling price of butadiene needs to be 4369 €/tonne for case I and 3406 €/tonne for case II. This represents an increase of a factor 3.8-4.9 in comparison to the reference price (900 €/tonne, see Table 5.7). The literature also discusses instances where the production cost price of butadiene is higher than its reference (market) price. For instance, Farzad et al., (2017) [233] reported higher production cost prices than market butadiene prices by factor 3.0-3.3.

Sensitivity Analysis

The sensitivity analyses focuses on the NPV. The results for case I (see Figure 5.10a) suggest that the parameters that influence the NPV most are C6 sugars price, capital investment and butadiene price. The effect of C6 sugars price and capital investment is similar, where increases over the reference values will lead to even more unfeasible scenarios, while decreases may bring the system closer to break-even point. However, even at drastic decreases of 100% of these two parameters (independently of each other), the system is not able to reach break-even. The effect of both butadiene and ethylene prices is not that high in comparison to C6 sugars and capital investment of the butadiene section. As mentioned previously, the price of butadiene needs to be up to 380-490% higher than the reference value to reach break-even. This is very unlikely since a price increase would only be possible by including high extra premiums, and even fluctuations on butadiene prices are unlikely to reach such a high value.

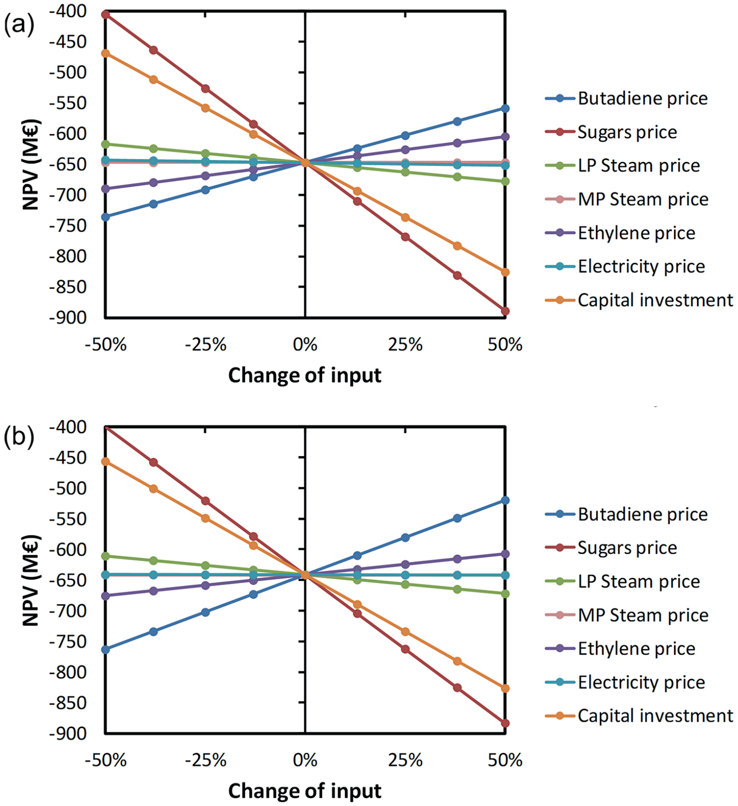


FIGURE 5.10. Results of sensitivity analysis on economic parameters of butadiene production, a):case I, b): case II.

For case II, the results of the sensitivity analysis (see Figure 5.10b) are very similar to those of case I. The parameters that affect the NPV the most are C6 sugars price, capital investment and butadiene price. The effect of changes in C6 sugars price and capital investment follow the same trend as those of case I. The effect of changes in butadiene price is stronger in case II, mostly because the system produces higher butadiene flowrate than in case I. The behavior of the remaining parameters is similar. Overall, cases I and II are very sensitive to changes in most economic parameters, thus, suggesting higher risks to implement this technology. The butadiene production process appears not robust in economic terms.

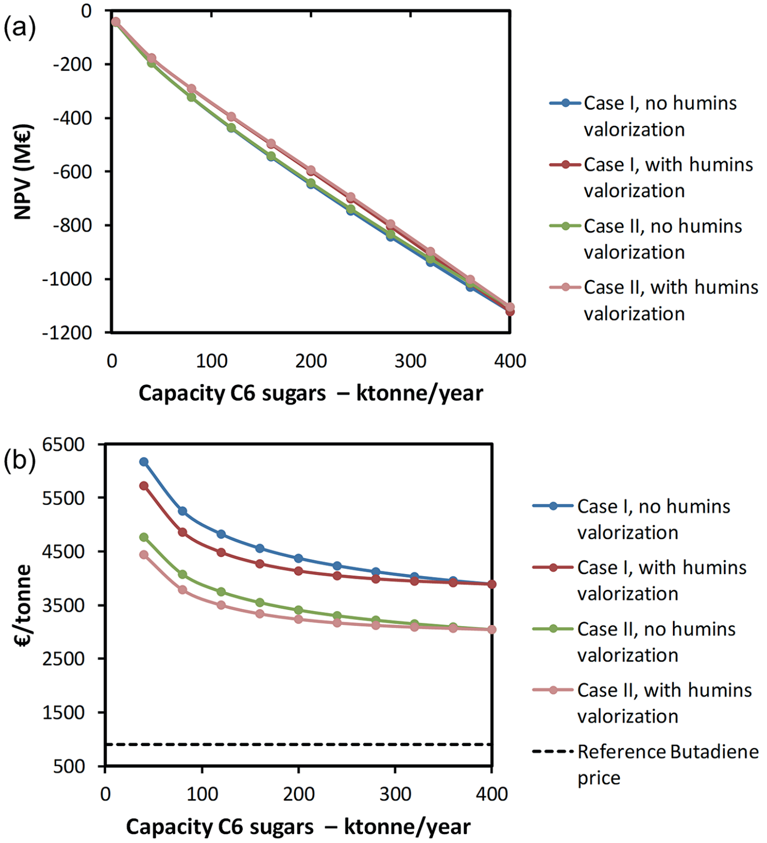


FIGURE 5.11. Results of sensitivity analysis on varying the C6 sugars capacity to the butadiene process. a): effect on NPV, b): effect on production cost price (reference price 900 €/tonne).

Figure 5.11 shows the effect of varying the distribution of C6 sugars to the butadiene and caprolactam processes. The production cost price (Figure 5.11b) of butadiene may be lower when the intake capacity of C6 sugars increases. For instance, when 100% of C6 sugars to butadiene and caprolactam are sent to the butadiene process (400 ktonne/year C6 sugar), the production cost price of butadiene decreases in comparison to the base case (3887 €/tonne for case I and 3042 €/tonne for case II). This suggests benefits of the economies of scale. However, costs prices are still a factor 3.4-4.3 higher than the reference price of butadiene. Therefore, even by increasing the plant capacity to take advantage of economies of scale, is not sufficient to compensate for the high costs related to the butadiene process cases. This therefore implies that the NPV gets even more negative when the process capacity increases (Figure 5.11a). In terms of butadiene's production costs price (At NPV=0, see Figure 5.11b), it tends to decrease when higher capacities are used. Nevertheless, cost prices are always above the butadiene reference market price for all cases. Humins valorization of humins does not show to have a strong effect on the systems, and the difference in NPV when electricity from humins is included is barely noticeable.

Caprolactam process

Table 5.8 shows the CAPEX, OPEX, revenues and NPV for cases III and IV of caprolactam production. In the two cases, the fixed capital investment of the levulinic acid and GVL sections are identical (19 and 38 M€, respectively). The fixed capital investment of the caprolactam section varies from case III to case IV, with case IV being higher by 32% (case III: 81M€, case IV: 107 M€). This increase is due to inclusion of additional process steps to isolate the 3MP from the MPs mixture, and recycle the 3MP for isomerization into 4MP prior to the aminolysis step.

In both cases, the aspects that contribute the most to OPEX are raw materials and utilities (although not surprising for a chemical process). When comparing OPEX, those of case IV are slightly higher than those of case III due to higher cost of utilities related to the additional process steps to recover the 3MP fraction of the transesterification step. In terms of revenues, the product that contributes the most is caprolactam with 82% and 92% in cases III and IV, respectively. When comparing cases, case IV has 43% higher revenues than case III due to the effect of producing more caprolactam as a consequence of the isomerization of 3MP into 4MP prior to the aminolysis step. Note that in case III (see Table 5.8), revenues are lower than OPEX, although, in case IV revenues are higher than OPEX. The latter suggests that case IV has a better outlook for economic feasibility. Nevertheless, it should be taken into account that the effect of CAPEX on the NPV can be stronger than OPEX.

TABLE 5.8. Annualized production costs, revenues and Net Present Value of cases III and IV of caprolactam production.

Feature	Case III		Case IV	
	M€/year	Share	M€/year	Share
Operating costs (OPEX)				
Raw Materials	80.0	58%	80.4	55%
Utilities	32.5	23%	36.5	25%
Maintenance	9.5	7%	11.3	8%
Labor	1.95	1%	1.95	1%
Fixed & General	8.9	6%	10.5	7%
Overhead	6.0	4%	6.9	5%
Total	**138.8**	**100%**	**147.5**	**100%**
Revenues				
Formic Acid	15.1	11%	15.1	8%
Caprolactam	110.6	82%	176.4	92%
Valeramide	8.7	6%	0.8	0%
Total	**134.4**	**100%**	**192.3**	**100%**
Fixed capital investment (CAPEX)				
M€	138		164	
Net present value after taxes [a]				
M€	-229		67	

[a] NPV at the end of project's lifetime

The NPV results (see Table 5.8) show a negative value for case III (unfeasible) and positive for case IV (feasible). For case III, to reach break-even (assuming all other parameters fixed, such as co-products prices), the production cost price of caprolactam needs to be 2595 €/tonne, which is 30% higher than the reference price (2000 €/tonne). The production cost price remains higher than the reference caprolactam price, however, it is in a more reasonable range in comparison the higher cost price of butadiene compared to its reference price. Reductions in OPEX may bring the system (case III) to be economically feasible. In case IV, the production cost price of caprolactam is 1875 €/tonne, which is 6% lower than the reference caprolactam price. NPV results suggest that including 3MP for isomerization into 4MP prior the aminolysis step, represents an important improvement for caprolactam production.

Sensitivity Analysis

The results for case III (see Figure 5.12a) suggest that the parameters that influence NPV the most are caprolactam and C6 sugar prices, and CAPEX. The effect of changes in caprolactam price is clearly stronger than that for other parameters. An increase of caprolactam price above 30% will lead the system to be economically feasible. Similarly, to reach break-even, the price of C6 sugars needs to be 57% lower than the reference value shown in Table 5.2, while increasing the price leads to a more unfeasible case. The effects of the remaining parameters are similar and do not strongly affect the system economic feasibility. The results of the sensitivity analysis of case IV show a rather similar trend of those of case III, but with a positive NPV at 0% change. The results for case IV (see Figure 5.12b), indicate that the parameter that influences NPV the most is the caprolactam price. The effect of caprolactam price is clearly stronger in case IV than in case III. A decrease of the caprolactam price over 5%, results in an unfeasible scenario. However, increases above the reference price will improve the overall economic performance of the system. The effect of C6 sugars price and CAPEX is almost identical, and increases over 25% of any of these two parameters (independently of each other and leaving the others fixed), lead to an unfeasible scenarios. However, a decrease of C6 sugar prices would further benefit the system's economic performance. The effect of the remaining parameters is rather similar and does not have a strong influence on the system. Summarizing, case III and IV for caprolactam production show to be robust and basically depend on the state of the caprolactam market instead of multiple undeveloped markets of other co-products. However, this also imposes some risk in case that prices of caprolactam are not kept equal or above the reference price considered in this study. Improvements in NPV would ultimately represent a decrease on cost price of caprolactam.

Figure 5.13a shows the effect of varying the capacity of C6 sugars intake to the caprolactam process on the NPV. This analysis also includes the effect of humins valorization for heat and power production. The results suggest that case IV benefits from the economies of scale operating at larger capacities than those of the base case (200 ktonne/y of C6 sugars). At an input of C6 sugars capacities lower than 148 ktonne/y the system starts to be unfeasible. For case III, the system remains unfeasible, however, the trend of the curves suggests that in case that C6 sugar intake capacity could be increased, the system may reach break-even operation if valorization of humins is included. The effect of heat and power production from humins starts to be noticeable when the capacity of C6 sugars intake is above 120 ktonne/y (applies for both cases III and IV). This has to do with the availability of humins and the synergy between the butadiene and caprolactam processes (see Figure 5.2), since as assumed in this study, the intake C6 sugar capacity of the butadiene process decreases when the intake of the caprolactam process increases (distribution of C6 sugars). Therefore, if caprolactam is produced in larger quantities more humins are available for heat and power production. The effect of humins valorization shows to have a positive effect on the overall economic performance of both cases III and IV. The main reason is due to the savings in purchased steam and electricity (see Table 5.6), which reduces utilities costs (savings up to 2.3 M€/y for cases I to IV, at base case C6 sugars distribution).

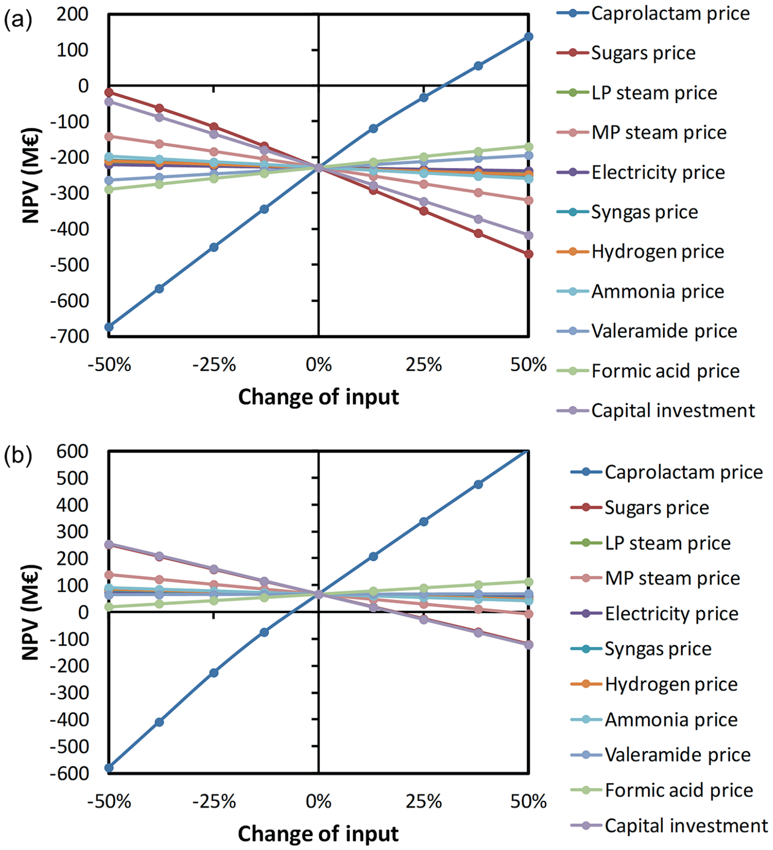


FIGURE 5.12. Results of sensitivity analysis on economic parameters of caprolactam production, a): case III, b): case IV.

Additionally, the revenues of surplus electricity represent an extra 5 M€/y (at base case conditions) to cases I and II, and 5 M€/y to the revenues of cases III and IV. Nevertheless, it should be taken into account that 16 M€ of additional CAPEX are required to produce heat and power from humins. The increase in CAPEX is allocated to both butadiene and caprolactam processes depending on the distribution of C6 sugars to each process, which in base case conditions is 50% (*i.e.,* extra CAPEX of 8 M€ to the butadiene process and 8 M€ to the caprolactam process). Although the production trains were analyzed separately, the strategy of a multiproduct biorefinery system was considered as core to this study. Figure 5.13b shows how the production cost price (at NPV=0) of caprolactam decreases as the input capacity of C6 sugars increases. For case IV (with and without humins valorization), the production cost price starts to be higher than the reference price at capacities lower than 130 ktonne/y In case III, the production cost price is always higher than the reference price, but getting closer as the production capacity increases. Both cases III and IV are highly benefitted by the economies of scale and by the valorization of humins to produce heat and electricity.

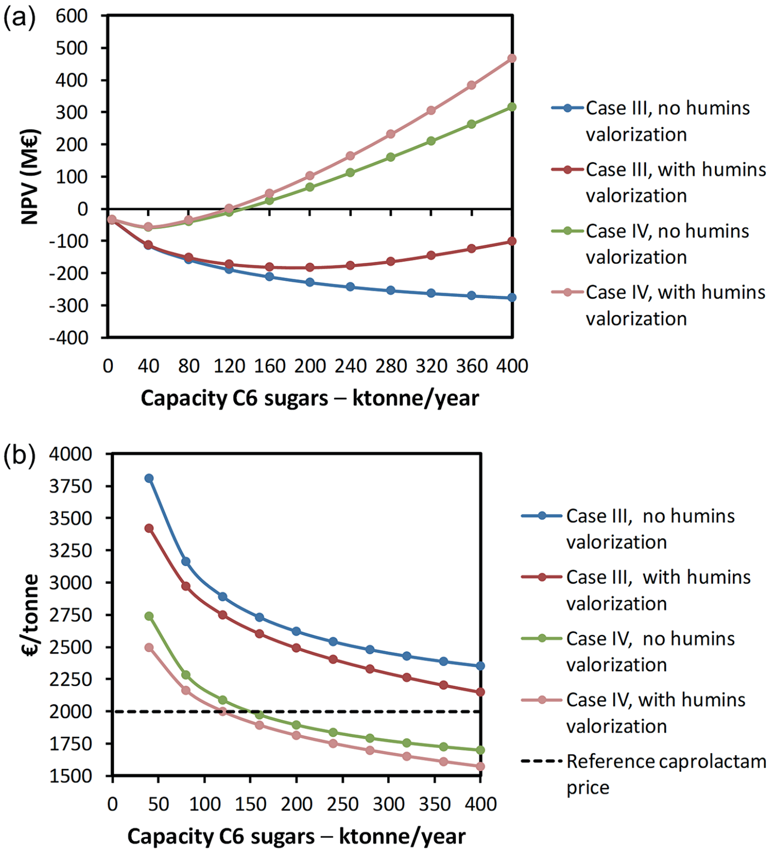


FIGURE 5.13. Results of sensitivity analysis on varying the C6 sugars capacity to the caprolactam process, a): effect on NPV, b): effect on minimum selling price (reference price 2000 €/tonne).

5.4. CONCLUSIONS

The aim of this study was to investigate the techno-economic performance of the production lines for butadiene and caprolactam from C6 sugars, and assess which of the two was economically attractive. In terms of energy intensity, both production lines perform similarly ranging from 34-50 MJ/kg of main product (depending on conditions). In terms of process yields (expressed as kg of product per kg of C6 sugars), that of caprolactam is a factor 1.6-3.6 higher than that of butadiene. In the butadiene process, large amount of the carbon mass of C6 sugars goes into the cell biomass and carbon dioxide (both produced during the ethanol production process), which are streams with low value added.

From an economic point of view, the butadiene process shows a negative performance even when the system is improved (case II) to enhance the selectivity to butadiene and to reduce the number of co-products (implying reduction in energy intensity and capital investment, compared to case I). The economic performance of the butadiene process is highly dependent on the revenues of butadiene and ethylene, and highly sensitive to changes in C6 sugars prices and capital investment. However, even at drastic changes of these parameters, the butadiene production line remains unfeasible. Butadiene production cost is a factor 3-5 (depending on the conditions) in comparison to the reference price used in this study (900 €/tonne), which is very high taking into account the current market. This highlights the big efforts needed to improve the overall efficiency of the butadiene process, and to find alternatives to promote the bio-based butadiene market such as policy incentives (*e.g.,* green premiums). Additionally, the use of cheaper raw materials also plays a crucial role on the economic performance of chemicals such as butadiene, for instance by directly starting from lignocellulosic biomass instead of C6 sugars. This would help on reducing extra logistics costs of dealing with intermediate platform chemicals, and take advantage of co-products revenues of the pre-treatment stage. This integration approach could also be beneficial in the case of additional heat and mass integration strategies which can play a major role on decreasing OPEX. Nevertheless, it should be taken into account that this integration strategy may only be representative to specific countries/regions where availability of biomass is not a major issue.

At base case conditions (case III), caprolactam production also seems unfeasible, however, changes in prices such as decrease in feedstock and increase in caprolactam prices may turn the system to be feasible. Caprolactam production cost for case III is 30% higher than its reference selling price (2000 €/tonne). Moreover, in the case in which the processing line of caprolactam improves its yield (case IV, yield improved by

60% compared to case III), the system becomes economically feasible with production costs 6% lower than its reference market price (2000 €/tonne). Additional integration strategies can also work for the case of caprolactam.

Including heat and power production from humins seems to have a positive effect on the overall economic performance of the caprolactam production process (independently of the case), and production costs are further decreased by savings on external utilities (*i.e.,* heat and power) purchases and revenues by electricity surplus. Production costs of both butadiene and caprolactam were decreased when the processing capacity of C6 sugars was increased, reflecting benefits of the economies of scale. However, only those of caprolactam are lower than the reference price. From an integrated biorefinery perspective, a biorefinery co-producing butadiene from C6 sugars is not economically interesting, however, open for improvements and analysis in other contexts. Overall, the caprolactam production line shows higher economic potential in comparison to that of butadiene.

Acknowledgements

This research has been performed within the framework of the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science. Project number 053.70.381.

APPENDIX

Appendix A. Data inputs used in process modeling

Table 5.9 shows the set of reactions considered in the conversion of ethanol into butadiene modeled in Aspen Plus.

TABLE 5.9. Reactions modeled in butadiene production from ethanol. Case I: Reactor conditions: 425 ºC, 1 bar. Data gathered from direct communication with experts from Delft University of Technology (TUDelft). Case II: Reactor conditions: 250 ºC, 1 bar. Data gathered from [243].

Reactions	Case I	Case II
	Conversion	Conversion
2 ethanol --> butadiene + hydrogen + 2 water	40.29%	33.00%
Ethanol --> ethylene + water	17.75%	1.00%
2 ethanol --> diethyl ether + water	9.26%	0.00%
2 ethanol --> acetaldehyde + hydrogen + ethylene + water	0.00%	15.00%
3 ethanol --> 2 propylene + 3 water	1.79%	0.00%
2 ethanol --> 1-butene + 2 water	2.23%	1.00%
2 ethanol --> isobutene + 2 water	0.95%	0.00%
2 ethanol --> 2-butene + 2 water	1.41%	0.00%
5 ethanol --> 2 pentene + 5 water	1.00%	0.00%
3 ethanol --> hexane + 3 water	0.00%	0.00%
2 ethanol --> 2-butanol + water	2.26%	0.00%
2 ethanol --> n-butanol + water	5.27%	0.00%
4 ethanol --> octanol + 3 water	1.75%	0.00%

Table 5.10 shows the set of reactions considered in the conversion of levulinic acid into γ-valerolactone modeled in Aspen Plus. Table 5.11 shows the reactions considered in the production of caprolactam from GVL.

TABLE 5.10. Reactions modeled in GVL production from levulinic acid. Reactor conditions: 150ºC, 30 H_2 bar, LA concentration 10% wt% in dioxane. Data gathered from [253].

Reactions	Conversion
Levulinic Acid + hydrogen --> γ-valerolactone + water	100%
γ-valerolactone + 2 hydrogen --> 1,4-pentanediol	4%
1,4-pentanediol --> methyltetrahydrofuran + water	50%

TABLE 5.11. Reactions modeled in the different steps for producing caprolactam based on data reported by [226].

Reactions	Case III	Case IV
	Conversion	Conversion
GVL Transesterification with methanol		
GVL + methanol → 3-methyl pentenoate + water	72.75%	72.75%
GVL + methanol → 4-methyl pentenoate + water	24.25%	24.25%
Aminolysis with ammonia		
3-methyl pentenoates + Ammonia → 3-Pentenamides + methanol	100%	100%
4-methyl pentenoates + Ammonia → 4-Pentenamides + methanol	96%	96%
Hydroformylation [a]		
3-Pentenamide + hydrogen → Valeramide	32.67%	3.00%
4-Pentenamide + hydrogen → Valeramide	32.67%	3.00%
3-pentenamide + carbon monoxide + hydrogen → unsaturated caprolactam + water	56.43%	90.00%
4-pentenamide + carbon monoxide + hydrogen → unsaturated caprolactam + water	56.43%	90.00%
3-pentenamide + carbon monoxide + hydrogen → 4L ($C_6H_{13}NO_2$)	0.99%	1.00%
4-pentenamide + carbon monoxide + hydrogen → 4L ($C_6H_{13}NO_2$)	0.99%	1.00%
3-pentenamide + carbon monoxide + hydrogen → 1B ($C_6H_{13}NO_2$)	8.91%	6.00%
4-pentenamide + carbon monoxide + hydrogen → 1B($C_6H_{13}NO_2$)	8.91%	6.00%
Hydrogenation		
unsaturated caprolactam + H_2 → Caprolactam	98.25%	98.25%

[a] Catalyst: Rh/POP-Xantphos

Appendix B. Economic Assessment additional data inputs and factors

Table 5.12 displays the factors used for the estimation of capital investment. Table 5.13 shows the factors used for the estimation of operating costs.

TABLE 5.12. Factors used for the estimation of capital investment according to [246].

Purchased equipment	Percentage of purchased equipment [a]
Direct Costs	
Purchased equipment installation	39%
Instrumentation and Controls (installed)	26%
Piping (installed)	31%
Electrical systems (installed)	10%
Buildings (including services)	29%
Yard improvements	12%
Service facilities (installed)	55%
Total Direct	***202%***
Indirect Costs	
Engineering and supervision	32%
Construction expenses	34%
Legal expenses	4%
Contractor's fee	19%
Contingency	37%
Total Indirect	***126%***
Working capital	75%

[a] Purchased equipment includes delivery costs (10%)

TABLE 5.13. Factors used for the estimation of additional features of operating costs [246].

Category	Feature	Factor
Labor costs	Operating supervision	15% of operating labor
	Laboratory charges	15% of operating labor
Maintenance costs	Maintenance	6% of fix capital investment
	Operating supplies	15% of maintenance
Fixed & general costs	Taxes	2% of fix capital investment
	General	20% of labor, supervision and maintenance
Plant overhead	Plant overhead	60% of labor, supervision and maintenance

CHAPTER 6

Integrated production of 1,3-Butadiene and ε-Caprolactam from C6 sugars: Life cycle assessment

Submitted to a scientific journal:
Moncada J., Vural Gursel I., Worrell E., Ramírez A. 2018.

ABSTRACT

This work assesses the environmental performances of producing 1,3-butadiene and ε-caprolactam from C6 sugars, in comparison to their petrochemical counterpart. A cradle-to-gate prospective life cycle assessment was carried out for five impact categories: Non-renewable energy use (NREU), climate change potential (CCP), water depletion potential (WDP), agricultural land occupation potential (ALOP), and human toxicity potential. Two approaches for distributing the environmental to the main products were considered: i) no allocation, ii) mass allocation. C6 sugars from corn and spruce woodchips were considered to as feedstocks. Results indicate that bio-based butadiene does not show clear advantages over fossil-based butadiene for up to 4 (CCP, HTP, ALOP and WDP) out of the 5 impact categories higher for the bio-based system (with exception of NREU). In the case of caprolactam for 3 (NREU, CCP, HTP) out of the 5 the impact categories, the bio-based caprolactam systems showed better performance than the petrochemical reference system. The application of allocation showed to have large impact on the results and their interpretation as in some cases the direction of some impact categories shifted. For both, butadiene and caprolactam, C6 sugars derived from spruce offered a better performance than C6 sugars derived from corn. Energy produced from humins had a positive effect on the overall environmental performance of both caprolactam and butadiene, but did not change the conclusions.

6.1. INTRODUCTION

Biorefineries are complex systems that can use different types of biomass feedstock such as crops, lignocellulose material, microalgae and macroalgae [214, 215]. The primary conversion step of these feedstocks leads to the production of platform chemicals (*e.g.,* carbohydrates, syngas, lignin) that are today's cornerstone for the production of fuels, chemicals and materials [214, 215]. Among the different platforms, carbohydrates offer large versatility to be converted, either catalytically or biochemically, into valuable products with application in sectors such as fuels, chemicals, pharma, materials and food [217-219].

Among the many chemicals that can be produced from carbohydrates, in previous works [254] the authors have found 1,3-Butadiene and ε-caprolactam to be interesting derivatives with applications as bio-based materials. Butadiene is widely used for producing synthetic rubbers, with about 70% in tires manufacturing. Traditionally, butadiene is obtained in an olefins plant mostly from the steam cracking of naphtha [223, 224]. Caprolactam is the precursor of the nylon-6, with broad applications in the textile industry[226]. Traditionally, caprolactam is produced in a four step process starting from benzene with cyclohexane, cyclohexanone and cyclohexanone oxime as intermediates [226, 227].

In the case of butadiene, a possible bio-based production pathway is via ethanol (produced from the fermentation of sugars). Many authors have studied and reported reaction mechanisms and conditions [228-230]. However, there are limited number of studies assessing the environmental performance of butadiene production from carbohydrates. Cespi et al., (2016) [232] carried out a multi-criteria assessment including techno-economic and environmental indicators, of several processes of butadiene production from ethanol. The main conclusion of their work was that under specific conditions (*e.g.,* by using woody residues as feedstock) bio-based butadiene may have benefits over its petrochemical counterpart. However, results showed to be very sensitive to changes in feedstock which could result in no benefits of bio-based butadiene over the petrochemical route. Farzad et al., (2017) [233] carried out a detailed techno-economic and environmental assessment of butadiene production from sugarcane bagasse (with ethanol as intermediate and co-product). They conclude that considering the integrated production of butadiene (starting from bagasse and including co-production of heat and power), the environmental performance of bio-based butadiene was better than that of the petrochemical system.

In the case of caprolactam, an interesting bio-based pathway is via the conversion of γ-valerolactone (produced from levulinic acid which is first obtained by the dehydration of C6 sugars). Several studies have reported yields and conditions of this pathway [226, 234-236], however, literature is very scarce on environmental assessments reporting on the impacts of caprolactam production starting from C6 sugars. Roes et al., [255] carried out an ex-ante environmental assessment of caprolactam catalysis, concluding on that bio-based caprolactam has better environmental performance than the petrochemical counterpart for the non-renewable energy use and climate change potential impact categories.

The scope of the studies reporting on the environmental impacts of butadiene and caprolactam starts either from an intermediate (from ethanol [232]), or directly from lignocellulosic biomass [233], and sugarcane and starch [255]. However, given the importance of the carbohydrate platform for the bio-based economy, it is important to carry out the assessment starting from C6 sugars, and to investigate the effect of the choice of feedstock (either from sugar crops or lignocellulosic biomass). Given the scarcity of literature on ex-ante environmental assessments of both butadiene and caprolactam production and their potential to possibly substitute fossil counterparts, study the aims: (i) to investigate the cradle-to-gate environmental impacts of producing butadiene and caprolactam using C6 sugars from corn and from spruce, (ii) to identify process bottle necks, to assess the synergies of common streams, and to investigate how each process performs in comparison to their fossil counterparts.

6.2. MATERIALS AND METHODS

In this study, a life cycle assessment of the production of bio-based 1,3-butadiene and ε-caprolactam was conducted. The assessment was carried out following the guidelines of the International Standardization Organization (ISO) in their ISO 14040 series [198].

6.2.1. Process description and modeling

Figure 6.1 shows a simplified block diagram of the integrated production of butadiene and caprolactam from C6 sugars. The capacity of C6 sugars was set to 400 ktonne per year, assuming that this flowrate was equally distributed to feed butadiene and caprolactam processes (200 ktonne/year of C6 sugars), according to Moncada et al., [254]. Butadiene production is composed by two main sections i) ethanol production; ii) butadiene production and recovery. The ethanol section was modeled based on the description provided by Quintero et al., (2008) [240] which included fermentation (assuming an ethanol yield: 0.43 kg/kg C6 sugars), distillation, and dehydration for obtaining ethanol product at 99.7 wt% (details can be found in the work of Moncada et al., [254].). The butadiene section was modeled based on the description provided in Moncada et al., [254] in which ethanol is converted into butadiene and co-products (mainly ethylene) in a reactor operating at 250 ºC and 1 bar, (reaction data and conversions gathered from Shylesh et al., [243]). Butadiene is later recovered in a complex downstream process (overall butadiene yield: 0.17 kg per kg of C6 sugars).

Caprolactam production is comprised of three main sections: i) levulinic acid production; ii) γ-valerolactone (GVL) production, and iii) caprolactam production and recovery. The levulinic acid (LA) production step was modeled based on the kinetic model kinetic model reported by Girisuta et al., (2006) [244]. During the LA acid production step humins (important waste stream) are produced at a rate of 0.18 kg of humins per kg C6 sugars. Later, the conversion of LA into GVL was modeled based on data reported by Ftouni et al., (2016) [235] (reactor operating at 10 bar and 150 ºC). Both the LA and GVL processes considered the downstream processes proposed by Moncada et al. [254]. The caprolactam production step is itself divided into three main steps. Step 1 is the production of methyl pentenoates (MPs), which consists of the transesterification of GVL with methanol (reaction taking place at 190 ºC). Step 2 consists of the aminolysis of MPs into penteneamides (PAs) with ammonia at 80 ºC. The 3 step is the production of caprolactam (CAL) by the hydroformylation of the PAs into unsaturated caprolactam (at 120 ºC and 10 bar), and after hydrogenation into CAL (at 80 ºC and 80 bar). All reaction steps of the conversion of GVL into CAL were modeled based on the data reported by Raoufmoghaddam et al.,[226]. The downstream processing considered the description by Moncada et al. [254] (overall caprolactam yield: 0.44 kg per kg of C6 sugars). Detailed description of the technologies can be found in [254].

As humins are produced as waste in the production line of caprolactam, its valorization was taken into account for the production of heat and power. The production of heat and electricity from humins was estimated assuming combined heat and power unit with power and heat efficiencies of 41% and 49%, respectively. Calculations were based on the heating value of humins (23 MJ/kg [245]). It was assumed that heat and power produced from humins were equally distributed (following same distribution pattern than C6 sugars to each process line) to both the butadiene and caprolactam process. Surplus electricity was considered as additional product.

Based on the technology descriptions provided above, the overall inputs and outputs of both processes (*i.e.,* mass and energy flows) were estimated by developing process models in the commercial package Aspen Plus v8.4 (Aspen Technology, Inc., USA), assuming continuous mode and whole year operation (i.e., 8000 h/year).

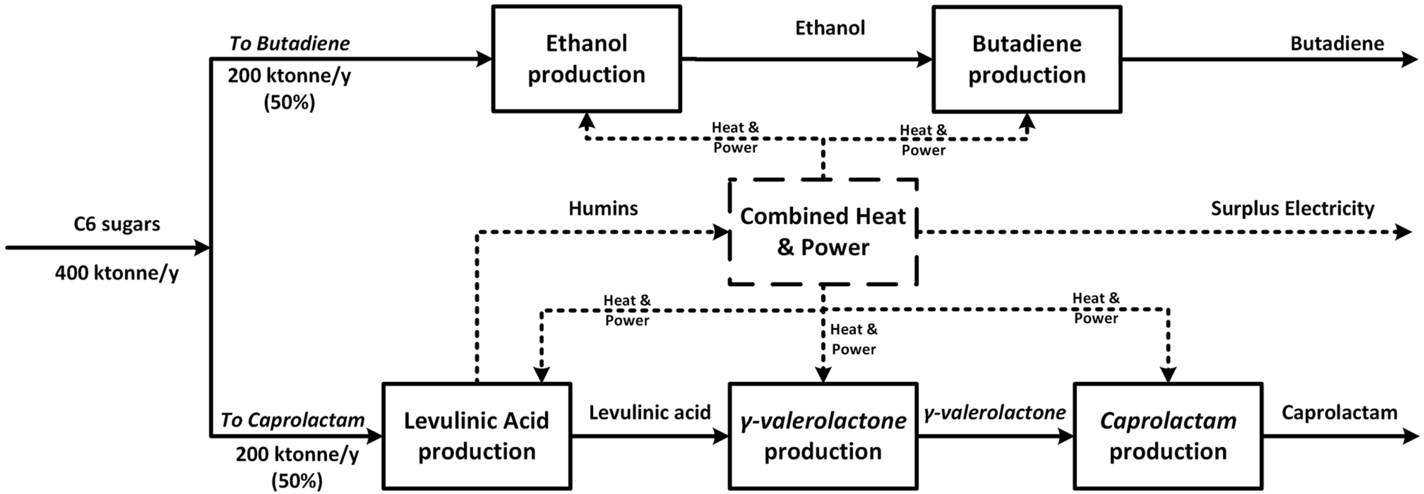


FIGURE 6.1 Simplified block diagram of butadiene and caprolactam production from C6 sugars.

6.2.2. Goal definition and systems boundaries

The system considering the integrated production of butadiene and caprolactam shows that both products have equivalent petrochemical counterparts (See Figure 6.1). To carry out an LCA considering the entire integrated production system and compare it to the reference petrochemical system, would require the development of a fossil based benchmark co-producing caprolactam and butadiene. This is however not possible as the fossil production lines of butadiene (produced from naphtha [256]) and caprolactam (produced from benzene [257]) do not have a common feedstock. Therefore, to overcome this, a subdivision approach was here applied to divide the systems boundaries of the integrated process (see Figure 6.1) into the two individual production processes. This allows accounting for the two functional units of the system and compared each with their respective fossil counterparts. (*i.e.,* 1 kg of butadiene and 1kg of caprolactam).

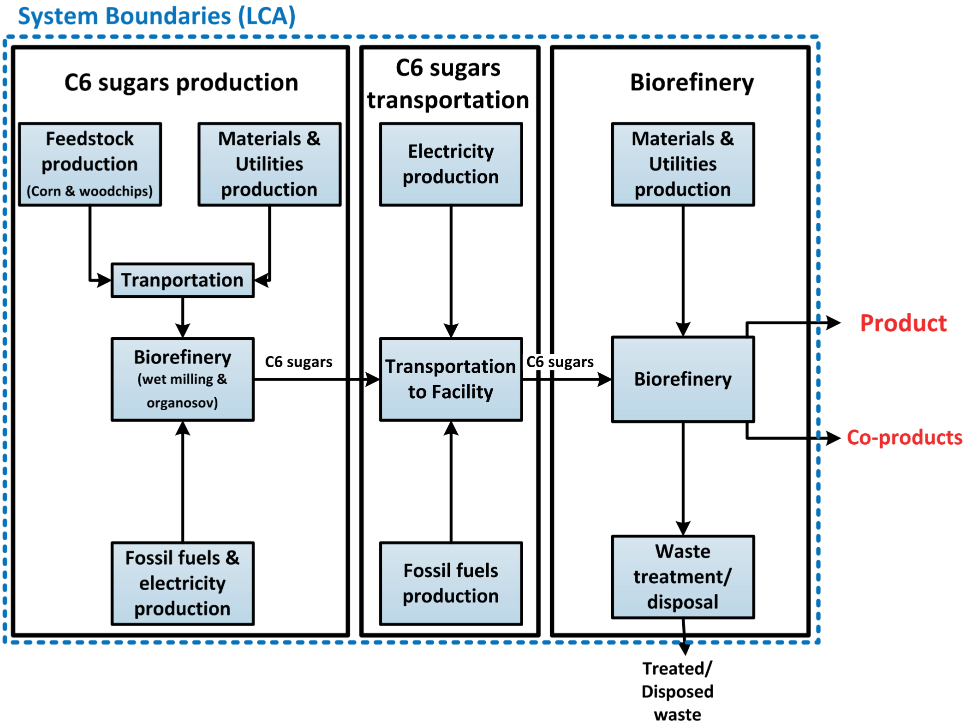


FIGURE 6.2. Main process steps involved in the production of i) butadiene and ii) caprolactam from C6 sugars. Each box (solid black boxes) represents a process module. The system boundaries for the LCA correspond to the aggregation of all process modules (blue dotted line).

Each production process is divided into three main process modules (stages of the life cycle): feedstock production (*i.e.,* C6 sugars), feedstock transportation (*i.e.,* transportation from the pretreatment biorefinery to the conversion biorefinery) and biorefinery (*i.e.,* feedstock processing). Utilities production, auxiliary raw materials production (*e.g.,* solvents, other reactants) and waste treatment/disposal are included. The system boundaries correspond to the aggregation of all process modules depicted in Figure 6.2 for butadiene and caprolactam processes.

The C6 sugars production step was investigated in detail in previous work describing cradle-to-gate environmental impacts of C6 sugars production [239]. This study included the production of biomass, the transport of biomass from the farm gate into the pretreatment (primary) biorefinery gate, and the conversion of the biomass into C6 sugars. The source of C6 sugars can be either from spruce woodchips (scenario 1) and corn (scenario 2).

Despite that the systems boundaries were sub-divised into the two production processes (*i.e.,* butadiene and caprolactam), each of them are still multiproduct systems (*e.g.,* ethylene co-produced in the butadiene process, formic acid co-produced in the caprolactam process). This implied multi-functionality, thus requiring allocation of the environmental impacts over the different products. In this study, two main approaches were considered:

a) All environmental impacts are allocated to butadiene or caprolactam.

b) Impacts are distributed over the main product (*i.e.,* butadiene and caprolactam in their respective processes) and co-products. Mass allocation is preferred over economic and energy allocation, since the mass flowrates of the products will exclusively depend on the technical performance of each technology. Economic allocation is avoided due to the high uncertainty on prices assigned to each product. Energy allocation is avoided since the products obtained in each system have material functionality rather than energy. Allocation factors were calculated using equation 1. In case that electricity appears as additional product (produced from humins), mass allocation is not directly possible. Therefore, the mass of humins used for electricity production was used as mass input for calculating the mass allocation factor of electricity

$$AF_i = \frac{m_i}{\sum_{j=1}^{n} m_j} \tag{6.1}$$

Where, *AF* are the allocation factors of each product*,* and are the product flowrates, *i,j* counters for the products.

Five impact categories were considered in the assessment. Four impact categories using the ReCiPe characterization method [199]: climate change potential (CCP), water depletion potential (WDP), agricultural land depletion potential (ALOP), and human toxicity potential (HTP), and the non-renewable (Non-renewable energy use, NREU) section of the cumulative energy demand characterization method [200].

6.2.3. Life cycle inventory and data

As displayed in Figure 6.2, each process is divided into three main modules. A brief explanation of the inputs and assumptions for each stage is provided below.

C6 sugars production

The environmental impacts of producing C6 sugars either from woodchips or corn, was taken from previous work reported in [239]. Data related to C6 sugars was generated for the 5 impact categories assessed in this study. Since in that work data for C6 sugars from both spruce and corn is available for two allocation approaches (*i.e.,* data when no allocation was considered, and data when mass allocation was applied), we followed here the most conservative approach by *using the values when no allocation was considered*. The effect of using data derived from the upstream mass allocation to C6 sugars was included and presented as supplementary results. Summary of the data inputs related to C6 sugars production can be found in Appendix A (Table 6.7).

C6 sugars transportation

The transportation of C6 sugars from the preatment biorefinery to the conversion biorefinery was assumed at 20 km transported of trucks of 20 tonne according to the Ecoinvent v3.3 database[258]. This is based on the assumption that biomass pretreatment to produce C6 sugars is assumed to be in the same area where the C6 sugars are converted into caprolactam and butadiene (defined as port of Rotterdam in [239]).

Conversion of C6 sugars into butadiene and caprolactam

The data related to conversion of C6 sugars into butadiene and caprolactam is based on the modeling of the processes described in section 2.1. Summary of inputs and outputs of the processes can be found in Appendix A (see Table 6.8, Table 6.9 and Table 6.10). Data from the Ecoinvent v3.3 database [258] were used to complete the life cycle inventory. It includes characterization factors related to auxiliary raw materials and energy carriers such as steam, natural gas (for fired heat) and waste disposal/treatment impacts.

Petrochemical counterparts (reference systems)

Both butadiene and caprolactam production were compared against the conventional petrochemical counterparts. Butadiene was assumed to be produced from naphtha. Franklin- associates [256] reported the inputs and outputs (mass an energy flows) of the petrochemical process to produce butadiene from naphtha (see Table 6.11 in appendix A). This information was used to generate a life cycle inventory and calculate the environmental impacts of petrochemical based butadiene production. Characterization factors of the inputs were gathered from the Ecoinvent v3.3 database [258]. In the case of petrochemical caprolactam production, Hong et al.,[257] reported the inputs and outputs of caprolactam production from benzene (see Table 6.12 in appendix A). This information was used to generate the life cycle inventory and calculate the environmental impacts of petrochemical based caprolactam production. Environmental impacts of the inputs were also gathered from the Ecoinvent v3.3 database [258]. For both petrochemical systems, the allocation approaches mentioned above were also applied (no allocation and mass allocation).

6.3. RESULTS AND DISCUSSION

This section presents the results of the life cycle environmental impacts, focusing on three main aspects: general trends, effect of humins valorization, impact of allocation.

6.3.1. General trends

The results presented in this section are split for the butadiene and caprolactam processes. The results discussed in this section do not include the production of heat and electricity from humins.

Butadiene process

Table 6.1 shows the results for no allocation and when mass allocation is used. In this study, a conservative approach was used by assuming that all upstream impacts are allocated to C6 sugars, thus, the results and discussion are based on this assumption. For comparison purposes the results when using mass allocation of upstream operations are presented in Appendix B.

Overall, when allocation is not applied (approach 1), 2 out of the 5 impact categories showed lower impacts for the bio-based systems than those of the petrochemical reference system. In contrast, 3 out of the 5 impact categories showed higher or similar impacts for the bio-based systems than those of the petrochemical systems. However, when allocation was applied, this picture changed and only 1 out of the 5 impact categories shows lower impacts for the bio-based systems in comparison to the petrochemical system. The remaining 4 impact categories show higher impacts, with a relative large difference, for bio-based butadiene in comparison to petrochemical butadiene. Our results differ from those reported by Farzad et al,.[233] which reports environmental advantages of bio-based butadiene over petrochemical butadiene. However, the main reason for this discrepancy is the level of integration in their technological scheme [233], which included the use of cogeneration, onsite biorefining of the feedstock (including the sugars production step), the difference in feedstocks to produce the sugars for fermentation (to obtain ethanol before butadiene), and strong methodological differences, i.e. the use of economic allocation in contrast to mass allocation.

TABLE 6.1. Environmental impacts expressed per kg of butadiene (functional unit) when no allocation is considered (conservative approach assuming all impacts are allocated to butadiene) and when mass allocation is considered (allocation factors 37% bio-based, 6% petrochemical).

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	69.60	113.03	1329.58
CCP	$kg\ CO_{2eq}$	5.05	9.27	18.79
HTP	$kg\ 1,4\text{-}DB_{eq}$	0.72	0.73	0.95
ALOP	m^2a	36.83	6.75	0.11
WDP	m^3	1.02	0.64	0.33
Mass allocation				
NREU	MJ_{eq}	35.88	58.27	76.72
CCP	$kg\ CO_{2eq}$	2.61	4.78	1.08
HTP	$kg\ 1,4\text{-}DB_{eq}$	0.37	0.38	0.06
ALOP	m^2a	18.98	3.48	0.01
WDP	m^3	0.53	0.33	0.02

When no allocation among co-products is used, NREU is 95 and 91% lower for scenarios 1 and 2 compared to the petrochemical system, respectively (see Figure 6.3a). In the case of CCP (using allocation approach 1), the potential environmental impact of scenarios 1 and 2 are 73 and 51% lower than that of the petrochemical system. When applying mass allocation among butadiene and co-products, the direction of the impacts is not affected for NREU (*e.g.,* lower values for scenarios 1 and 2 in comparison to the petrochemical case), however, the relative difference to the petrochemical case is not that high as when the impacts are not distributed between the co-products (see Figure 6.3b). In the case of CCP allocation shifted the results from lower to higher than the petrochemical counterpart. The main reason is the difference in allocation factors among the bio-based and the petrochemical processes (see Table 6.2).

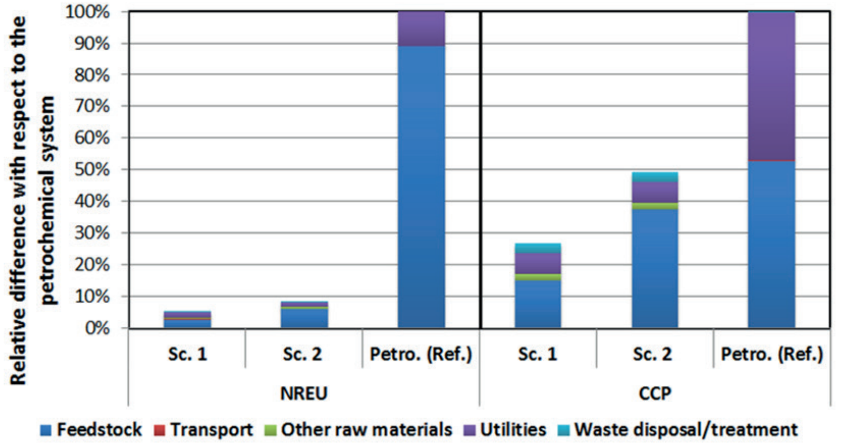
TABLE 6.2. Allocation factors used in each approach for assessing the environmental impacts of butadiene production.

Allocation factors	Approach 1: No allocation		Approach 2: Mass allocation	
	Bio-based (Sc.1 and Sc.2)	Petrochemical	Bio-based (Sc.1 and Sc.2)	Petrochemical
Cell biomass	0%	-	30%	-
Butadiene	100%	100%	52%	6%
Ethylene	0%	0%	14%	40%
Propylene	0%	0%	-	19%
C4s	0%	-	4%	-
Hydrogen	0%	0%	3%	1%
Butanols	0%	-	-	-
Aromatics and C4s	-	0%	-	17%
Methane	-	0%	-	17%

The NREU is higher than those reported in literature[49]. There could be multiple reasons for this difference, and one reason can be the source of C6 sugars and the data related to those. Cespi et al., [49] used data reported for ethanol in three different locations (*i.e.,* USA, Brazil, Europe), which are generally based on allocation of impacts for all upstream operations (upstream impacts of ethanol production distributed among ethanol and co-products). In this case, the impacts of the upstream operations of 100% are allocated to C6 sugars. If data related to C6 sugars from mass allocation was used instead (see Table 6.8), the NREU of butadiene ranges between 24-45 MJ/kg which is much closer to the range reported by [49]. Another possible reason is the difference in product distribution which eventually leads to different allocation factors. In terms of CCP, our findings show a range of 3-5 kg CO_{2eq}/kg of butadiene which partly falls within the range of 1-4 kg CO_{2eq}/kg of butadiene reported by [49].

Figure 6.4 shows that there are no clear advantages of bio-based butadiene production over its fossil counterparts for the categories ALOP and WDP. The results for ALOP show that the impact of both scenarios 1 and 2 are factors 470 and 87 higher than those of the petrochemical counterpart, respectively. For ALOP, the impacts are mostly driven by the feedstock production step. In the case of WDP, the impact of scenarios 1 and 2 are factor 3 and 2 higher than those of the petrochemical case, respectively. The main difference can be attributed to the higher cooling water consumption in the bio-based process in comparison to the petrochemical process. Also, the large water requirements in the upstream operations to produce C6 sugars play an important role in the comparison to the fossil feedstock. When using allocation approach 2 (*i.e.,* mass allocation, See Figure 6.4b), the direction of the impacts of ALOP and WDP do not change (*i.e.,* impacts higher than reference system) when comparing with allocation approach 1. Nevertheless, the relative difference is much larger, meaning that the impacts for the bio-based systems are much higher than those of the petrochemical counterparts. By comparing scenarios 1 and 2, butadiene based on C6 sugars from woodchips seems to perform better than butadiene based on C6 sugars from corn. The main difference is reflected in the upstream impacts of the feedstocks and processes to produce the C6 sugar stream [239].

a) No allocation



b) Mass allocation

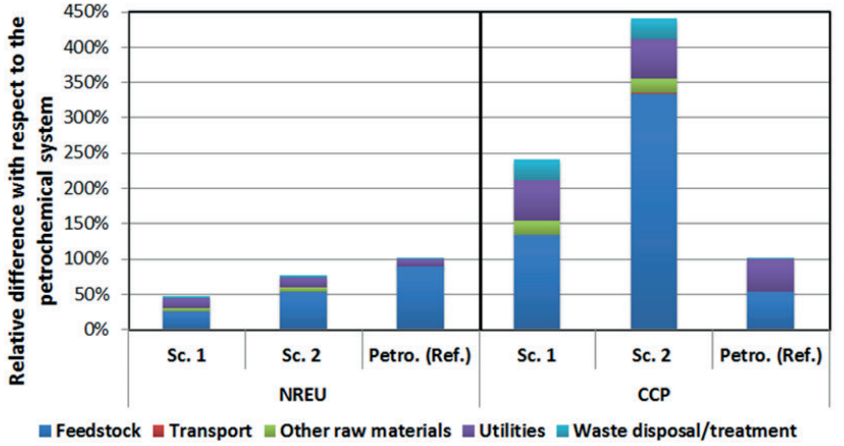
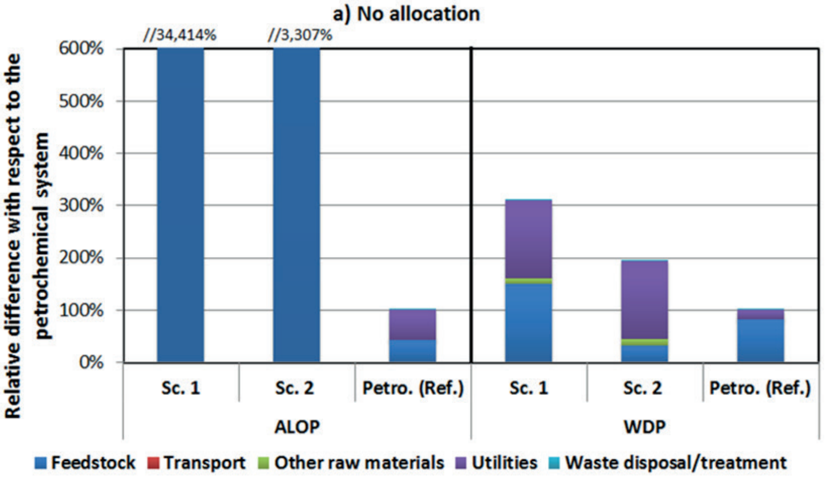


FIGURE 6.3. Environmental impacts for non-renewable energy use (NREU) climate change potential (CCP) relative to the reference system (Petrochemical) for butadiene production. Each system is divided into contributions from feedstock production, feedstock transportation, consumption of auxiliary raw materials, utilities and waste treatment/disposal. a) Results when no allocation is applied (100% of environmental impacts allocated to butadiene); b) mass allocation applied to butadiene and co-products.



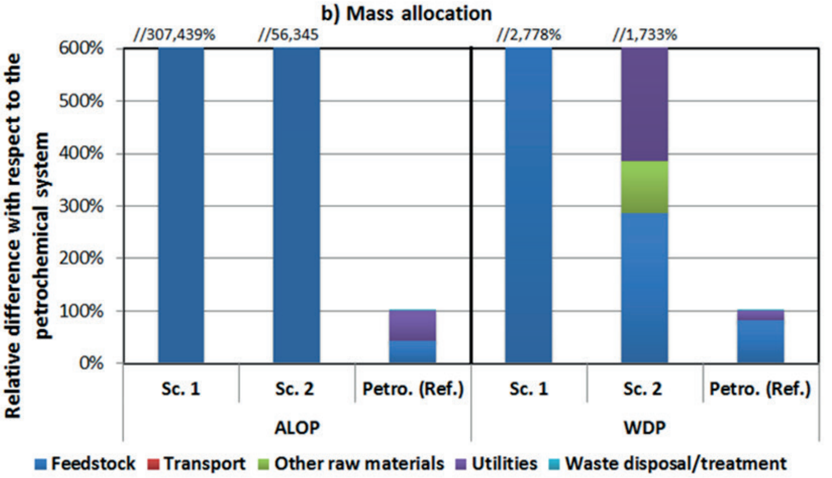


FIGURE 6.4. Environmental impacts for ALOP and WDP relative to the reference system (Petrochemical) for butadiene production. Each system is divided into contributions from feedstock production, feedstock transportation, consumption of auxiliary raw materials, utilities and waste treatment/disposal. a) Results when no allocation is applied (100% of environmental impacts allocated to butadiene), b) mass allocation applied to butadiene and co-products.

HTP shows (see Figure 6.5) to be 25% lower for scenarios 1 and 2 in comparison to the petrochemical counterpart, before allocation is applied. However, when allocation is applied, the impacts of the bio-based systems (scenarios 1 and 2) turn out to be higher than the reference system by a factor 7. When allocation is applied the impacts per kg of butadiene turned shifted from positive to negative.

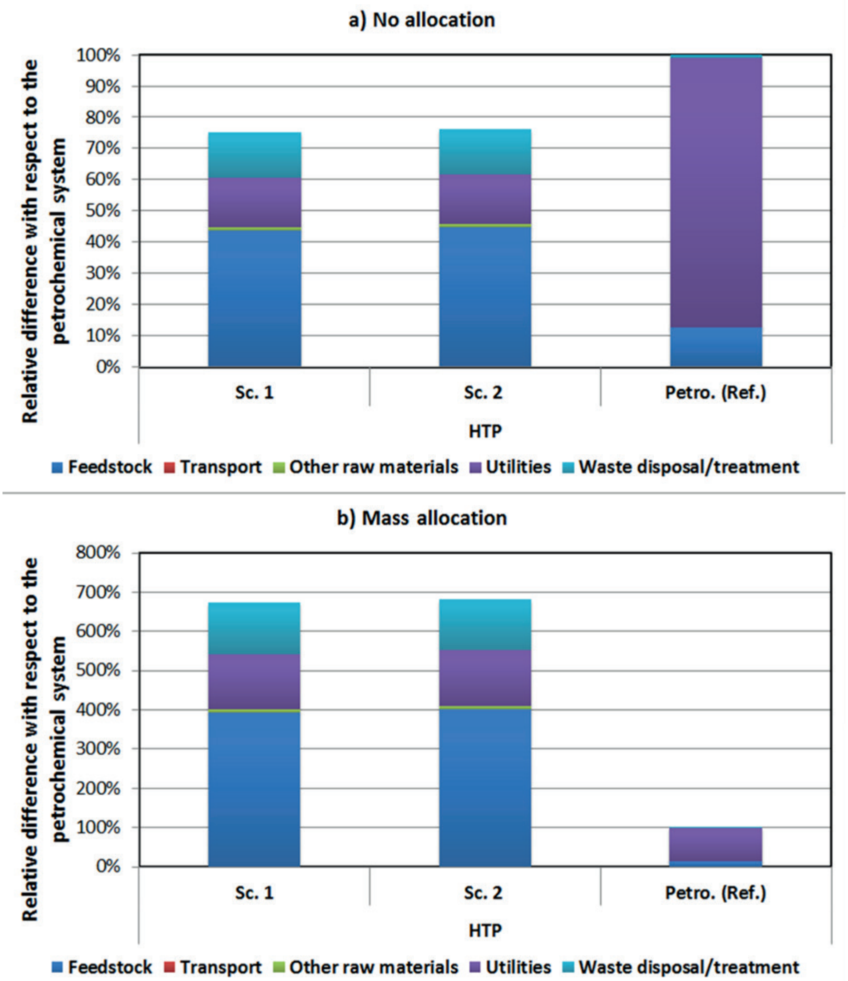


FIGURE 6.5. Environmental impacts for HTP relative to the reference system (Petrochemical) for butadiene production. Each system is divided into contributions from feedstock production, feedstock transportation, consumption of auxiliary raw materials, utilities and waste treatment/disposal. a) Results when no allocation is applied (100% of environmental impacts allocated to butadiene), b) mass allocation applied to butadiene and co-products.

Caprolactam process

Table 6.3 shows the results for no allocation and when mass allocation is used for caprolactam production. Similar to the butadiene cases, the data related to upstream operation was selected by assuming that all impacts are allocated to C6 sugars (details discussed in [239]). The absolute values of the impacts of caprolactam production when using C6 sugars data derived from mass allocation of upstream operations are presented in Appendix C.

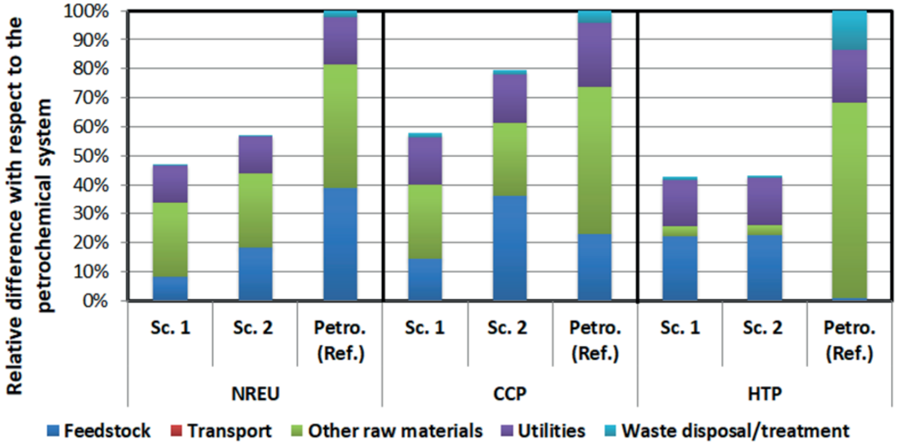
TABLE 6.3. Environmental impacts expressed per kg of caprolactam (functional unit) when no allocation is considered (conservative approach assuming all impacts are allocated to butadiene) and when mass allocation is considered (allocation factors 67% bio-based, 100% petrochemical).

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	77.77	94.30	165.69
CCP	kg CO_{2eq}	4.30	5.91	7.43
HTP	kg 1,4-DB_{eq}	0.31	0.31	0.72
ALOP	m^2a	14.03	2.58	0.05
WDP	m^3	0.66	0.52	0.31
Mass allocation				
NREU	MJ_{eq}	52.07	63.14	165.69
CCP	kg CO_{2eq}	2.88	3.96	7.43
HTP	kg 1,4-DB_{eq}	0.20	0.21	0.72
ALOP	m^2a	9.40	1.73	0.05
WDP	m^3	0.44	0.35	0.31

Independently of the allocation approach used, 3 (NREU, CCP and HTP) out of the 5 assessed impact categories show lower impacts for the bio-based routes than the fossil counterpart. In summary, caprolactam derived from woodchips showed a relatively better cradle-to-gate environmental performance than that from corn. However, independent of the source of C6 sugars, bio-based caprolactam seems promising in terms of environmental performance compared to petrochemical caprolactam.

Figure 6.6 shows the contribution analysis for NREU, CCP and HTP. When no allocation among co-products is used (Allocation approach 1), NREU is 53 and 44% lower in scenarios 1 and 2 than in the petrochemical systems. CCP is 42 and 20% lower in scenarios 1 and 2 than in the petrochemical case, respectively. It is worth noting that for both NREU and CCP, the contribution of other raw materials is important (ranging from 31-55%), mainly due to the use of ammonia in the aminolysis step and later the use of hydrogen in the hydrogenation step[254]. This highlights that although caprolactam can be obtained from renewable sources like C6 sugars, its production still depends partly on molecules that traditionally are produced by the chemical industry such as hydrogen and ammonia. For HTP, there is clear advantage of scenarios 1 and 2 over the petrochemical counterpart with 57% lower impacts (for both scenarios in comparison to the petrochemical counterpart). It is also important to note that for the petrochemical counterpart, the use of ammonia, hydrogen and hydrogen peroxide have a large contribution on the three impacts. When applying allocation (approach 2), NREU, CCP and HTP do not change in direction, but their relative difference with respect to the petrochemical system is further increased.

a) No allocation



b) Mass allocation

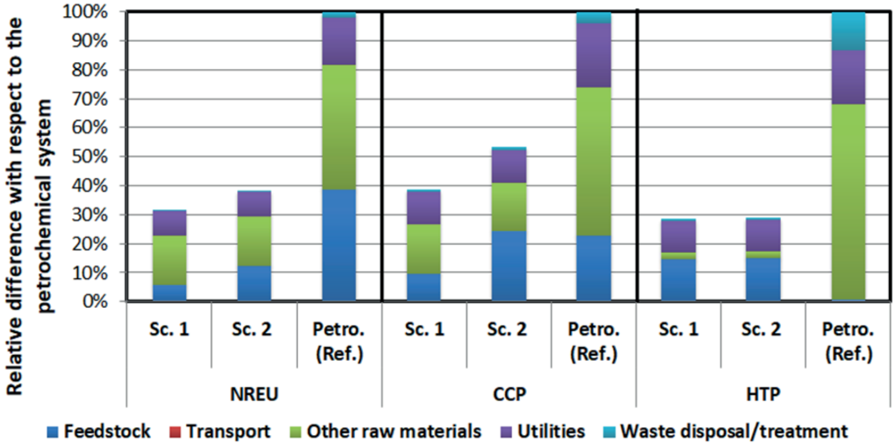
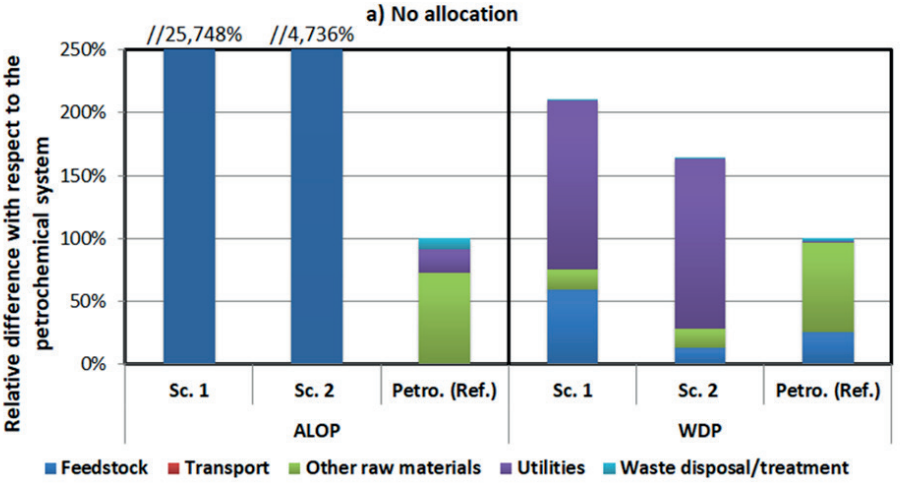


FIGURE 6.6. Environmental impacts for NREU, CCP and HTP relative to the reference system (Petrochemical) for caprolactam production. Each system is divided into contributions from feedstock production, feedstock transportation, consumption of auxiliary raw materials, utilities and waste treatment/disposal. a) Results when no allocation is applied (100% of environmental impacts allocated to caprolactam); b) mass allocation applied to caprolactam and co-products.

The impacts are lower than those of the petrochemical system by 47 to 71%. This decrease is also an effect applying allocation, which increases the relative difference in benefit of the bio-based scenarios in comparison to the petrochemical system (see allocation factors in Table 6.4).

TABLE 6.4. Allocation factors used in each approach for producing caprolactam.

Allocation factors	Approach 1: No allocation		Approach 2: Mass allocation	
	Bio-based (Sc.1 and Sc.2)	Petrochemical	Bio-based (Sc.1 and Sc.2)	Petrochemical
Caprolactam	100%	100%	67%	100%
Formic Acid	0%	-	31%	-
Valeramide	0%	-	2%	-



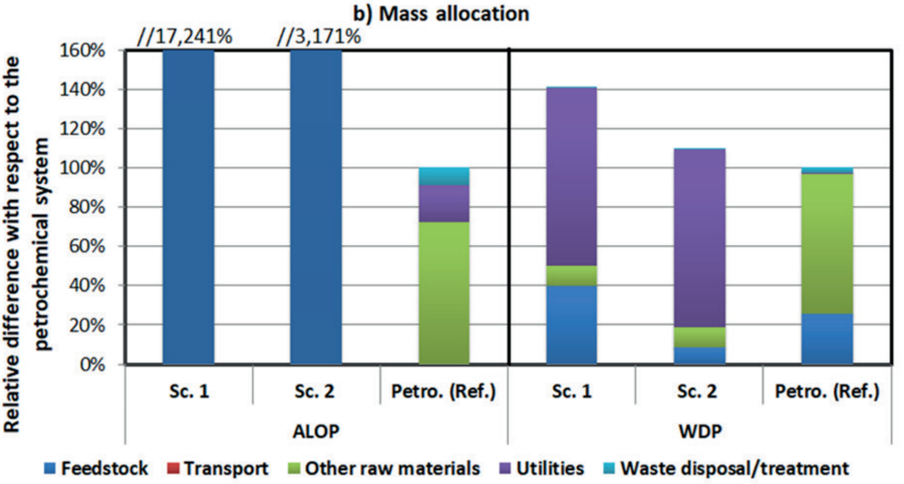


FIGURE 6.7. Environmental impacts for ALOP and WDP relative to the reference system (Petrochemical) for caprolactam production. Each system is divided into contributions from feedstock production, feedstock transportation, consumption of auxiliary raw materials, utilities and waste treatment/disposal. a) Results when no allocation is applied (100% of environmental impacts allocated to caprolactam); b) mass allocation applied to caprolactam and co-products.

When comparing with literature the CCP and NREU of the bio-based routes mentioned here are far from the values reported by Roes et al., [255] for caprolactam derived from sugarcane and starch. The main reason of this deviation is that in principle the sugars conversion route is different (fermentation in Roes et al., [255], and catalytic conversion in this work).

Figure 6.7 shows the contribution analysis for ALOP and WDP. ALOP is 257 and 47 times higher in scenarios 1 and 2 in comparison to fossil caprolactam, respectively. ALOP shows the largest difference among the bio-based systems in comparison to the petrochemical reference. However, the results are not surprising due to the differences of the bio-based feedstocks and benzene for the petrochemical system. In the case WDP, the impacts for scenario 1 and 2 are 2.1 and 1.6 higher than that of the petrochemical counterpart, respectively. The major contributor to water depletion is the use of cooling water in the bio-based systems. This can be improved with a water recycling system, however, this was not considered as part of the current study. When using mass allocation (see Figure 6.7b), the direction of the impacts does not change (*i.e.,* impacts higher than reference system) when comparing with allocation approach 1.

6.3.2. Effect of humins valorization

This section focuses on the effect of valorizing humins for producing heat and power for own biorefinery consumption for both butadiene and caprolactam cases.

Effect of humins valorization on butadiene production

Table 6.5 shows the values of the environmental impacts of butadiene production including electricity and steam production from humins, for no allocation and mass allocation approaches, respectively. Results when using C6 sugars data derived from mass allocation of upstream operations can be found in Appendix D. Allocation factors including surplus electricity as product can also be found in Appendix D.

By comparing butadiene production without and with humins valorization and no allocation, the production of energy from humins benefits the categories NREU, CCP and HTP with reductions between by 7-15%. As part of the energy produced by valorizing humins (steam and electricity) is used to partly or completely offset outsourced energy inputs. Benefits are not clear for ALOP and WDP, which are categories dominated by the feedstock production stage and the use of water inputs (*e.g.,* cooling and washing water), respectively. When mass allocation is considered, all categories are benefitted by the production of energy from humins, with reductions from 21 to 33% for both scenarios. These reductions are related to the distribution of the impacts among more products, i.e. electricity now shares 22% of the impacts of the system. Although the use of humins for energy production seems to help to reduce the environmental impacts, the direction of results is not affected when compared to the petrochemical reference case.

TABLE 6.5. Environmental impacts expressed per kg of butadiene (functional unit) when no allocation is considered (conservative approach assuming all impacts are allocated to butadiene) and when mass allocation is considered (allocation factors 40% bio-based, 6% petrochemical). Results including the valorization of humins.

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	59.22	102.65	1329.58
CCP	kg CO_{2eq}	4.42	8.64	18.79
HTP	kg 1,4-DB_{eq}	0.67	0.68	0.95
ALOP	m^2a	36.82	6.75	0.11
WDP	m^3	1.03	0.64	0.33
Mass allocation				
NREU	MJ_{eq}	23.89	41.41	76.72
CCP	kg CO_{2eq}	1.78	3.48	1.08
HTP	kg 1,4-DB_{eq}	0.27	0.27	0.06
ALOP	m^2a	14.86	2.72	0.01
WDP	m^3	0.41	0.26	0.02

Effect of humins valorization on caprolactam production

Table 6.6 shows the values of the environmental impacts of caprolactam production including electricity and steam production from humins, for no allocation and mass allocation approaches, respectively. Results when using C6 sugars data derived from mass allocation of upstream operations can be found in Appendix D. Allocation factors, including surplus electricity as product, can also be found in Appendix D.

When analyzing the production of caprolactam without and with humins valorization and no allocation, the results follow a similar trend to that discussed for butadiene, benefiting the categories NREU, CCP and HTP with reductions of 5-10%. ALOP and WDP do not benefit from the production of steam and electricity from humins. Also, similar to the case of butadiene, by applying allocation, all categories benefit from the valorization of humins, with reductions from 11 to 20% for both scenarios. Although the positive effect on valorizing humins for energy production, the direction of results is not affected and the behavior follows that explained without humins valorization.

TABLE 6.6. Environmental impacts expressed per kg of caprolactam (functional unit) when no allocation is considered (conservative approach assuming all impacts are allocated to butadiene) and when mass allocation is considered (allocation factors 67% bio-based, 100% petrochemical).

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	72.97	89.51	165.69
CCP	kg CO_{2eq}	3.94	5.55	7.43
HTP	kg 1,4-DB_{eq}	0.28	0.28	0.72
ALOP	m^2a	14.03	2.58	0.05
WDP	m^3	0.66	0.52	0.31
Mass allocation				
NREU	MJ_{eq}	42.96	52.69	165.69
CCP	kg CO_{2eq}	2.32	3.27	7.43
HTP	kg 1,4-DB_{eq}	0.16	0.17	0.72
ALOP	m^2a	8.26	1.52	0.05
WDP	m^3	0.39	0.30	0.31

6.3.3. Impact of allocation

Due to the multiple possible approaches for distributing the environmental impacts among all products, and the possible deviations that this may bring to the objectivity of the comparison of the systems, the approach of allocating all impacts to the main product products allows a better understanding of the processes from a systems perspective rather than from a product perspective. The understanding at the system level is key to understand how allocation may affect the results when providing insights at the product level. So far, results show that the application of allocation can drastically change the perception on the relative performance of a technology playing an important role on the interpretation of results. An example of this can be seen when the production of electricity from humins was included. For both butadiene and caprolactam production on one hand, from a total systems perspective (when no allocation is used), valorization of humins show slight improvements in three out of the five impact categories (NREU, CCP, HTP). On the other hand, when using mass allocation, the five impact categories benefit. Therefore, the results need to be carefully interpreted as other products share the environmental burden of the systems itself, and the message that categories such as ALOP and WDP benefit from the production of energy from humins (when applying allocation) could be misleading. Instead, the benefits are obtained due to the methodological approach to distribute the burdens between the main product and co-products.

As stated by Moncada et al. [239], in biorefineries, the use of allocation is controversial as it is affected by the number of products and by the allocation approach. For instance, one can argue the use of a different approach to allocate environmental impacts, such as economic allocation. A good example of this in the context of the current work is that there could be products which share large environmental impacts by using mass allocation but with low economic value (*e.g.,* cell biomass from C6 sugars fermentation into ethanol). In that case, the use of economic allocation might result in a better representation of the impacts between all products. Nevertheless, it should be taken into account that this can even bring more subjectivity to the analysis as economic allocation factors depend on market prices, which for many bio-based products remain uncertain or have varied historically.

6.4. CONCLUSIONS

The aim of this study was to investigate the environmental performance of the production of butadiene and caprolactam from C6 sugars, and to compare them to the petrochemical counterparts. Bio-based butadiene does not show clear advantages over fossil-based butadiene. The butadiene system is highly affected when allocation is applied and in some cases the environmental impacts favors the petrochemical system over the bio-based routes. The butadiene system do not show evident advantages over the petrochemical system, with up to 4 (CCP, HTP, ALOP and WDP) out of the 5 impact categories assessed higher for the bio-based systems with only NREU lower for bio-based in comparison to fossil. This highlights that bio-based butadiene is not currently an interesting option over its traditional production route. Caprolactam production seems to be more robust to changes in allocation approach. In 3 (NREU, CCP, HTP) out of the 5 the impact categories, the bio-based caprolactam systems showed better performance than the petrochemical reference system.

For both, butadiene and caprolactam, C6 sugars derived from spruce offered a better performance than C6 sugars derived from corn. When humins valorization is taken into account, the production of energy has a positive effect on the overall environmental performance of both caprolactam and butadiene. However, the relation to the petrochemical counterparts is not affected and remains intact to the case when no humins are valorized.

From a life cycle assessment methodological perspective, results show that the use of allocation has a large influence on the outcome and most importantly on the interpretation of results. This work shows that not only the use of allocation itself can bring a lot of uncertainties to the analysis, but also how the upstream burden is distributed between products and co-products along the supply chain. In principle, biorefineries are multifunctional systems where the use of allocation cannot be avoided. Thus, the understanding of bio-based systems following a complete view (no allocation) is key to identify hotspots in comparison to the reference benchmark systems. This also allows having a clearer picture on the interpretation of results compared to when allocation is applied, as in many cases allocation can mistakenly provide insights into the relative difference of a system compared to its benchmark.

Acknowledgements

This research has been performed within the framework of the CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science. Project number 053.70.381.

APPENDIX

Appendix A

This appendix provides a summary of the inventory data used for assessing the environmental impacts of butadiene and caprolactam production. Table 6.7, shows the summary of the data inputs related to C6 sugars production. Table 6.8, shows the inventory data of the process to produce butadiene from C6 sugars. Table 6.9, shows the inventory data of the process to obtain caprolactam from C6 sugars, while Table 6.10 shows the inventory data of the humins valorization process. Table 6.11 and Table 6.12 show the inventory data for the petrochemical butadiene and caprolactam processes, respectively.

TABLE 6.7. Environmental impacts of all categories expressed per kg of C6 sugars when no allocation is considered (conservative approach assuming all impacts are allocated to the C6 sugars stream), and when mass allocation was considered. Data gathered from [239].

Impact Category	Unit	No allocation		Mass allocation [a]	
		C6 sugars fromSpruce	C6 sugars from corn	C6 sugars fromSpruce	C6 sugars from corn
NREU	MJ_{eq}	6.13	13.43	2.29	9.01
CCP	kg CO_{2eq}	0.47	1.18	0.18	0.79
HTP	kg 1,4-DB_{eq}	$7.01 \cdot 10^{-2}$	$7.19 \cdot 10^{-2}$	$2.61 \cdot 10^{-2}$	$4.82 \cdot 10^{-2}$
ALOP	m^2a	6.18	1.13	2.30	0.76
WDP	m^3	$8.24 \cdot 10^{-2}$	$1.77 \cdot 10^{-2}$	$2.61 \cdot 10^{-2}$	$4.82 \cdot 10^{-2}$

[a] Allocation factors to C6 sugars: 37% from Spruce, 67% from Corn.

TABLE 6.8. Inventory data of the process to obtain butadiene from C6 sugars. Data gathered from [254]

Feature	Unit	Inputs	Outputs
Raw materials			
C6 sugars[a]	kg/kg butadiene	5.96	-
Water	kg/kg butadiene	29.72	-
Ammonia[b]	kg/kg butadiene	0.19	-
Yeast	kg/kg butadiene	0.01	-
Demineralized water	kg/kg butadiene	0.75	-
Air	kg/kg butadiene	2.90	-
Products			
Butadiene [c]	kg/kg butadiene	-	1.00
Ethylene [d]	kg/kg butadiene	-	0.27
Propylene [e]	kg/kg butadiene	-	-
C4s [f]	kg/kg butadiene	-	0.03
Hydrogen	kg/kg butadiene	-	0.05
Butanols[g]	kg/kg butadiene	-	-
LP steam [h]	kg/kg butadiene	-	0.75
Cell biomass [i]	kg/kg butadiene	-	0.59
Waste streams			
CO_2 (biogenic from fermentation)	kg/kg butadiene	-	2.84
Waste Water	kg/kg butadiene	-	30.72
Fluegas[j]	kg/kg butadiene	-	3.27
Energy inputs			
Cooling water[k]	MJ/kg butadiene	20.84	-
LP Steam[l]	MJ/kg butadiene	12.04	-
MP Steam[l]	MJ/kg butadiene	0.00	-
Electricity	MJ/kg butadiene	1.42	-
Refrigerant	MJ/kg butadiene	0.90	-

[a] Stream free of water, C6 sugars purity 100%.
[b] Ammonia concentration 25 wt% in water
[c] Butadiene purity 99.7 wt%
[d] Ethylene purity 98.5 wt%
[e] Propylene purity 94.2 wt%
[f] C4's composition: 49 wt% 1-butene, 31 wt% 2-butene, 20 wt% isobutene
[g] Butanols concentration: 70 wt% n-butanol, 30 wt% 2-butanol
[h] LP steam pressure: 3 bar. Product integrated within the process in the energy balance and not considered for the calculation of allocation factors.
[i] Cell biomass produced from ethanol fermentation
[j] Flue gas composition: water 11 wt%, CO_2 16 wt%, O_2 1 wt%, N_2 72 wt%.
[k] Cooling water heat capacity: 50 kJ/kg
[l] Latent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg

TABLE 6.9. Inventory data of the process to obtain caprolactam from C6 sugars. Data gathered from [254]

Feature	Unit	Inputs	Outputs
Raw materials			
C6 sugars[s]	kg/kg caprolactam	2.27	-
Sulfuric Acid	kg/kg caprolactam	9.68E-04	-
Water	kg/kg caprolactam	1.68	-
Dioxane	kg/kg caprolactam	8.95E-03	-
Hydrogen	kg/kg caprolactam	3.97E-02	-
Methanol	kg/kg caprolactam	3.19E-05	-
Ammonia[b]	kg/kg caprolactam	0.48	-
Diglyme	kg/kg caprolactam	4.85E-04	-
Syngas[c]	kg/kg caprolactam	0.30	-
Air	kg/kg caprolactam	1.03	-
Products			
Caprolactam[d]	kg/kg caprolactam	-	1.00
Formic Acid	kg/kg caprolactam	-	0.46
Water[e]	kg/kg caprolactam	-	0.23
Valeramide[f]	kg/kg caprolactam	-	0.03
Lp Steam[g]	kg/kg caprolactam	-	1.15
Waste Streams			
Humins	kg/kg caprolactam	-	0.41
Waste water	kg/kg caprolactam	-	1.39
Fluegas[h]	kg/kg caprolactam	-	1.15
Energy inputs			
Cooling water[i]	MJ/kg caprolactam	18.79	-
LP Steam[j]	MJ/kg caprolactam	3.64	-
MP Steam[j]	MJ/kg caprolactam	11.04	-
Electricity	MJ/kg caprolactam	0.78	-
Refrigerant	MJ/kg caprolactam	-	-

[a] This stream is free of water, C6 sugars purity of 100%.
[b] Ammonia concentration is 35 wt% in water.
[c] Syngas composition 50:50, H_2:CO molar.
[d] Caprolactam purity of 99 wt%
[e] Product not considered in the calculation of allocation factors
[f] Valeramide purity of 99wt%.
[g] LP steam pressure: 3 bar. Product integrated within the process.
[h] Flue gas composition: water 6 wt%, CO_2 24 wt%, N_2 67 wt%, NO_2 3 wt%.
[i] Cooling water heat capacity: 50 kJ/kg
[j] Latent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg

TABLE 6.10. Inventory data of the process to obtain electricity from humins (humins valorization). Data gathered from [254].

Feature	Unit	Humins valorization	
		Inputs	Outputs
Raw Materials			
Humins[a]	kg/kg humins	1.00	-
Air	kg/kg humins	5.20	-
Waste streams			
Fluegas[b]	kg/kg humins	-	6.20
Energy outputs			
LP Steam[c,d]	MJ/kg humins	-	11.27
Electricity [d]	MJ/kg humins	-	9.43

[a]Humins formula assumed in calculations $C_6H_{10}O_5$. Low heating value 23 MJ/kg [245]
[b] Flue gas composition: water 9wt%, CO_2 26wt%, N_2 64wt%
[c] Latent heat steam: LP steam 2120 kJ/kg
[d] Steam and electricity calculated using power and heat effiencies of 41% and 49%, respectively [254].

TABLE 6.11. Inventory data of the process to obtain butadiene from Naphtha (Petrochemical reference system). Data gathered from [256]

Feature	Unit	Petrochemical	
		Inputs	Outputs
Raw materials			
Naphtha	kg/kg butadiene	22.2	-
Products			
Butadiene	kg/kg butadiene	-	1.00
Ethylene	kg/kg butadiene	-	7.00
Propylene	kg/kg butadiene	-	3.22
Aromatics	kg/kg butadiene	-	2.89
Methane	kg/kg butadiene	-	3.00
Hydrogen	kg/kg butadiene	-	0.22
Waste streams			
Waste Water	kg/kg butadiene	-	4.87
Energy inputs			
Cooling water [a]	MJ/kg butadiene	1.98	-
Natural gas [b]	MJ/kg butadiene	67.60	-
Electricity	MJ/kg butadiene	21.49	-

[a]Cooling water heat capacity: 50 kJ/kg
[b]Natural gas heating value: 47.14 MJ/kg

TABLE 6.12. Inventory data of the process to obtain caprolactam from Benzene (Petrochemical reference system). Data gathered from [257]

Feature	Unit	Petrochemical	
		Inputs	Outputs
Raw materials			
Benzene	kg/kg caprolactam	0.95	-
Hydrogen	kg/kg caprolactam	8.63E-02	-
Sodium Hydroxide	kg/kg caprolactam	0.16	-
Toluene	kg/kg caprolactam	5.00E-04	-
Tert-Butyl alcohol	kg/kg caprolactam	5.00E-04	-
Hydrogen peroxide [a]	kg/kg caprolactam	1.26	-
Nitric Acid [b]	kg/kg caprolactam	1.43E-02	-
Sulfuric Acid	kg/kg caprolactam	1.17	-
Water	kg/kg caprolactam	16.72	-
Products			
Caprolactam	kg/kg caprolactam	-	1.00
Waste streams			
Waste Water	kg/kg caprolactam	-	8.38
Gypsum	kg/kg caprolactam	-	1.56
Sodium Carbonate	kg/kg caprolactam	-	0.12
Energy inputs			
LP Steam[c]	MJ/kg caprolactam	2.78	-
MP Steam[c]	MJ/kg caprolactam	7.96	-
Natural gas [d]	MJ/kg caprolactam	3.15	-
Electricity	MJ/kg caprolactam	3.69	-

[a] Concentration 27.5 wt% in water
[b] Concentration 35 wt% in water
[c] Latent heat steam: LP steam 2120 kJ/kg, MP steam 1899 kJ/kg
[d] Natural gas heating value: 47.14 MJ/kg

Appendix B

This appendix shows the absolute values of the life cycle environmental impacts expressed per kg of butadiene, when data from C6 sugars was gathered assuming mass allocation [1] (the reader is referred to [239]). The impacts are presented by allocation approach and case. The allocation factors are remained equal to those presented in Table 6.2.

TABLE 6.13. Environmental impacts of all categories expressed per kg of butadiene (functional unit) when no allocation is considered (conservative approach assuming all impacts are allocated to the butadiene), and when mass allocation is considered (allocation factors 52% bio-based, 6% petrochemical). C6 sugars data based on mass allocation.

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	46.68	86.70	1329.58
CCP	kg CO_{2eq}	3.29	6.95	18.79
HTP	kg 1,4-DB_{eq}	0.46	0.59	0.95
ALOP	m^2a	13.73	4.53	0.11
WDP	m^3	0.72	0.60	0.33
Mass allocation				
NREU	MJ_{eq}	24.06	44.69	76.72
CCP	kg CO_{2eq}	1.70	3.58	1.08
HTP	kg 1,4-DB_{eq}	0.23	0.30	0.06
ALOP	m^2a	7.08	2.34	0.01
WDP	m^3	0.37	0.31	0.02

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[1] Environmental impacts of C6 sugars production were distributed among the different co-products in upstream operations for producing C6 sugars.

Appendix C

This appendix shows the absolute values of the life cycle environmental impacts expressed per kg of caprolactam, when data from C6 sugars was gathered assuming mass allocation (the reader is referred to [239]). The impacts are presented by allocation approach and case. The allocation factors are remained equal to those presented in Table 6.4.

TABLE 6.14. Environmental impacts of all categories expressed per kg of caprolactam (functional unit) when no allocation is considered (conservative approach assuming all impacts are allocated to the butadiene) and when mass allocation was applied (allocation factors 67% bio-based, 100% petrochemical). C6 sugars data based on mass allocation.

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	69.04	84.28	165.69
CCP	kg CO_{2eq}	3.63	5.03	7.43
HTP	kg 1,4-DB_{eq}	0.21	0.26	0.72
ALOP	m^2a	5.24	1.74	0.05
WDP	m^3	0.54	0.50	0.31
Mass allocation				
NREU	MJ_{eq}	46.23	56.43	165.69
CCP	kg CO_{2eq}	2.43	3.37	7.43
HTP	kg 1,4-DB_{eq}	0.14	0.17	0.72
ALOP	m^2a	3.51	1.16	0.05
WDP	m^3	0.36	0.34	0.31

Appendix D

This appendix shows the absolute values of the impact categories when humins are valorized to produce electricity and steam for both butadiene and caprolactam cases. This appendix also show updated allocation factors when electricity is included as product as well as results when upstream data for C6 sugars is derived from mass allocation.

Butadiene production

TABLE 6.15. Allocation factors used in each approach for estimating the environmental impacts of butadiene production including humins valorization.

Allocation factors	Approach 1: No allocation		Approach 2: Mass allocation	
	Bio-based (Sc.1 and Sc.2)	Petrochemical	Bio-based (Sc.1 and Sc.2)	Petrochemical
Cell biomass	0%	-	24%	-
Butadiene	100%	100%	40%	6%
Ethylene	0%	0%	11%	40%
Propylene	0%	0%	-	19%
C4s	0%	-	1%	-
Hydrogen	0%	0%	2%	1%
Butanols	0%	-	-	-
Aromatics and C4s	-	0%	-	17%
Methane	-	0%	-	17%
Electricity [a]	0%	-	22%	-

[a]Electricity allocation factor calculated based on the mass of humins used to produce it.

TABLE 6.16. Environmental impacts of all categories expressed per kg of butadiene and electricity from humins, when no allocation is considered (conservative approach assuming all impacts are allocated to the butadiene) and when mass allocation is applied (allocation factors 40% bio-based, 6% petrochemical). C6 sugars data based on mass allocation.

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	36.30	76.32	1329.58
CCP	kg CO_{2eq}	2.66	6.32	18.79
HTP	kg 1,4-DB_{eq}	0.41	0.54	0.95
ALOP	m^2a	13.73	4.53	0.11
WDP	m^3	0.72	0.60	0.33
Mass allocation				
NREU	MJ_{eq}	14.64	30.79	76.72
CCP	kg CO_{2eq}	1.07	2.55	1.08
HTP	kg 1,4-DB_{eq}	0.16	0.22	0.06
ALOP	m^2a	5.54	1.83	0.01
WDP	m^3	0.29	0.24	0.02

Caprolactam production

TABLE 6.17. Allocation factors used in each approach for estimating the environmental impacts of caprolactam production including humins valorization.

Allocation factors	Approach 1: No allocation		Approach 2: Mass allocation	
	Bio-based (Sc.1 and Sc.2)	Petrochemical	Bio-based (Sc.1 and Sc.2)	Petrochemical
Caprolactam	100%	100%	59%	100%
Formic Acid	0%	-	27%	-
Valeramide	0%	-	2%	-
Electricity	0%	-	12%	-

[a] Electricity allocation factor calculated based on the mass of humins used to produce it.

TABLE 6.18. Environmental impacts of all categories expressed per kg of caprolactam and electricity from humins, when no allocation is considered (conservative approach assuming all impacts are allocated to the butadiene) and when mass allocation is applied (allocation factors 59% bio-based, 100% petrochemical). C6 sugars data based on mass allocation.

Impact Category	Unit	Scenario 1 (C6 sugars from woodchips)	Scenario 2 (C6 sugars from corn)	Petrochemical (Reference system)
No allocation				
NREU	MJ_{eq}	64.24	79.48	165.69
CCP	kg CO_{2eq}	3.27	4.67	7.43
HTP	kg 1,4-DB_{eq}	0.18	0.23	0.72
ALOP	m^2a	5.24	1.74	0.05
WDP	m^3	0.54	0.50	0.31
Mass allocation				
NREU	MJ_{eq}	37.82	46.79	165.69
CCP	kg CO_{2eq}	1.93	2.75	7.43
HTP	kg 1,4-DB_{eq}	0.11	0.13	0.72
ALOP	m^2a	3.08	1.02	0.05
WDP	m^3	0.32	0.30	0.31

CHAPTER 7

Summary, conclusions and recommendations

7.1. BACKGROUND

Fossil resources are intensively ingrained in today's global economy, and according to the IPCC, they have contributed up to 78% of the increase of global GHG emissions since 1970 [2]. In addition, uncertainties on reserves and geographical distribution of fossil resources have caused growing concerns on energy security. Among the different opportunities to contribute to long-term GHG emission reduction targets and decrease fossil fuel dependency, biomass is expected to have an important role[2, 3]. For instance, it is estimated to contribute with almost half to the EU Renewable Energy targets in 2020 [3]. Today, many countries and regions have set up policies for the production of 1G biofuels [7]. There are however concerns on the use of 1G biomass regarding food security and land use change, which could result in negative impacts on GHG emissions, ecosystems and socio-economic aspects [7-9]. The lessons learned from large scale deployment of 1G biofuels and other traditional uses of biomass, have led the BBE community to focus on new feedstock sources (with high attention to lignocellulosic biomass, 2G) covering a broader range of bio-based products including chemicals and materials [7, 8, 10], and the adoption of biorefineries [11, 12].

Although there are sugar based technologies already at commercial stage [19] for producing chemicals from biomass, there are a large number of innovative technologies at pilot or lab scale. Despite the extensive amount of research activities to explore carbohydrate conversion routes (generally using 2G feedstocks) and develop new catalyst and strains (for fermentation), the commercialization of those technologies remains slow[32]. Understanding and assessing emerging technologies at early development stages can provide useful information early-on to technology developers and policy makers to guide faster commercialization.

The sustainable development of biorefineries requires looking beyond process configurations. The multiple combinations of feedstocks, platforms, processes and products that can appear in any bio-based supply chain, makes biorefineries very complex systems. Due to this and the fact that most of the developments in technologies for biomass conversion are still at early development stages [34, 35], ex-ante assessments have become a powerful approach to understand which feedstocks, technologies and products are interesting to be further developed [35, 36]. Furthermore, biorefineries have often mistakenly been considered as sustainable solely due to the renewable characteristic of biomass [35, 37]. However, as in the case of 1G biofuels, the use of biomass have proven that aspects such *i.e.* land use, ecosystems, costs, food security can seriously affect the sustainability of the options [9, 35]. In this context, the ex-ante assessment of biorefineries at early development stages is relevant to provide useful insights regarding their prospective performance from a sustainability perspective (covering technical, economic and environmental aspects, and in some cases social aspects [9, 35, 36, 38, 39]), even when knowledge and availability of data related to technologies, products, markets, feedstocks is limited [34].

7.2. OBJECTIVES

The main objective of this thesis was to generate in depth insights into the key factors that affect the techno-economic and environmental performances of novel technologies for bio-based chemicals production. This was done by assessing multiple case studies of technologies at early development stages both at screening and detailed level. This thesis focused on aspects that are important to increase the usefulness and soundness of ex-ante assessment of novel technologies for bio-based chemicals production. The following three objectives were formulated:

1. To develop screening methods that can address novel biochemical conversion routes of chemicals production and provide insights into their techno-economic and environmental performances.
2. To assess the importance and challenges of biomass pretreatment in the performance of carbohydrate based biorefineries.
3. To identify and evaluate the trade-offs of standalone vs. integrated configurations for the economic and environmental performances of biorefineries.

Table 7.1 provides an overview of the thesis chapters and the objectives they addressed.

TABLE 7.1. Overview of chapters two to six.

Chapter	Title	Objectives		
		1	2	3
2	Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals	x		
3	Comparative early sustainability assessment of multiproduct biorefinery systems: an application to the isobutanol platform	x	x	
4	Techno-economic and ex-ante environmental assessment of C6 sugars production from lignocellulosic biomass and corn. Comparison of organosolv and wet milling technologies.		x	x
5	1,3-Butadiene and ε-Caprolactam production from C6 sugars: techno-economic analysis			x
6	Integrated production of 1,3-Butadiene and ε-Caprolactam from C6 sugars : ex-ante environmental assessment		x	x

7.3. MAIN FINDINGS AND CONCLUSIONS

This section presents a summary of the main findings and conclusions of this thesis for each objective.

Objective 1

To develop screening methods that can address novel biochemical conversion routes of chemicals production and provide insights into their techno-economic and environmental performances.

Biochemical conversion processes play a vital role in the development of biorefineries, both for fuels and chemicals production. Many early screening methods reported in the literature have, to the author's knowledge, focused on chemical and thermochemical conversion processes for bio-chemicals production technologies. Developing an early stage screening method able to capture the features of thermochemical, chemical *and* biochemical conversion processes can provide knowledge and information to researchers, technology developers and policy makers to steer technology development, *e.g.* by identifying which technologies, products and configurations appear more beneficial. This is even more relevant as the number of options to be assessed increases, with time and resources of stakeholders are limited. This thesis addressed this challenge by adapting and extending an existing early stage screening assessment method [50] to cover the key features of thermochemical *and* biochemical conversion processes (chapter 2). The extended method was tested in a number of case studies including:

- Standalone conversion routes (chapter 2) to identify favorable, promising and unfavorable products (by comparing each product with its petrochemical counterpart) derived from bio-based syngas (chemical conversion), carbohydrates (biochemical conversion), and glycerol (chemical and biochemical conversion)
- Bio-based production of isobutanol (starting from softwood) and its petrochemical counterpart (starting from methane) (chapter 3)
- Integrated multiproduct biorefinery systems (chapter 3) from the conversion of isobutanol into fuels and chemicals (*i.e.,* GTBE, isobutyl acetate, ketones and alkanes).

The robustness of the results to changes in data inputs such as feedstocks and product prices (chapters 2 and 3) was also assessed. In addition, important methodological aspects were also examined including the impact of carrying out the screening solely on economic or environmental terms (chapter 3).

Key results

Chapter 2 showed the usefulness and flexibility of the adapted early stage screening method for assessing bio-based chemicals produced either chemically or biochemically. Figure 7.1 provides an overview of the early screening method, which included three sustainability indicators: economic constraint (EC), energy related impacts of raw materials (EIRM) and process complexity (PC). Both the EC and EIRM indicators remained identical to the original method [85]. The novel element was the re-examination of the PC indicator, which aimed to mimic costs and environmental impacts occurring at the processing stage. The original indicator[85] was designed for catalytic conversion processes in which the concentration of the main product, reaction enthalpy, number of co-products and difference in boiling points were the main features used to qualitatively provide scores reflecting the potential costs and environmental impacts occurring at the processing stage. However, as originally defined not all of these features provide a good enough representation of features inherent to chemical and biochemical conversion processes. This is because in principle not all downstream processes (to recover main products) are based on the coexistence of vapor-liquid phases (*e.g.,* distillation), which is the basis used in the original indicator. For instance, in biochemical conversion processes, the presence of solids (*e.g.,* cell biomass during fermentation) can demand an additional separation stage. The production of intracellular metabolite (*e.g.,* PHA's production) is another example of a process that will require additional downstream processing steps. Complex downstream processing can contribute significantly to higher costs and environmental impacts at the processing stage. To account for those possible situations, a subcategory of the PC indicator called Downstream Processing was developed. It captures the process nature (*i.e.,* catalytic or biochemical), the type of metabolite (*i.e.,* intracellular, extracellular), presence of solids, need of distillation, presence of azeotropes, and the need of complex separation alternatives (*e.g.,* liquid-liquid extraction, adsorption, absorption). Also, the remaining subcategories composing the PC indicator (*i.e.,* product concentration, mass loss index, reaction enthalpy, number of co-products and reaction pressure) were revised and adapted to represent chemical and biochemical conversion processes (See Chapter 2).

The adapted method was tested in 36 routes (chapter 2) for the conversion of bio-based syngas, carbohydrates and glycerol. The indicators were applied to both the bio-based and fossil-based routes and the scores where normalized using the maximum score (*i.e.,* the worst) of the two processes (bio-based vs. fossil-based). The three indicators were then aggregated into a single score by using weighting factors (40% for EC, 30% for EIRM (15% CED, 15% GHG) and 30% for PC), which were based on expert elicitations. Finally, the single aggregated scores of the bio-based and fossil-based routes were related through an index ratio, defined as the score of the bio-based route over the score of the fossil-based route. The index ratio was used as criteria to categorize the bio-based routes into three groups: favorable (Group I), promising (Group II) and unfavorable (Group III). Group I includes those routes with high sustainability potential for the bio-based alternative in comparison to petrochemical (index ratios lower than 0.9). Group II includes those routes for which advantages are not substantial, but where technological and economic improvements could lead to better performance of the bio-based alternatives (Index ratios ranging from 0.9 to 1.2). Group III includes those routes with low sustainability potential for bio-based derivatives (index ratios higher than 1.2) for which, the bio-based routes score lower than petrochemical ones. The type of result that the method can provide is presented in Figure 7.2, allowing distinguishing among the groups categorizing the routes (at the order of magnitude). The method allowed for sensitivity analysis to test the robustness of the index ratios to changes in data inputs (*e.g.,* prices, and yields) and assumptions (*e.g.,* distribution of upstream costs), and scenario analysis to account for specific aspects of the value chains related to each conversion process, such as the impact of feedstock prices in different regions. Table 7.2 provides an example on the categorization of derivatives for the case of EU, USA and China.

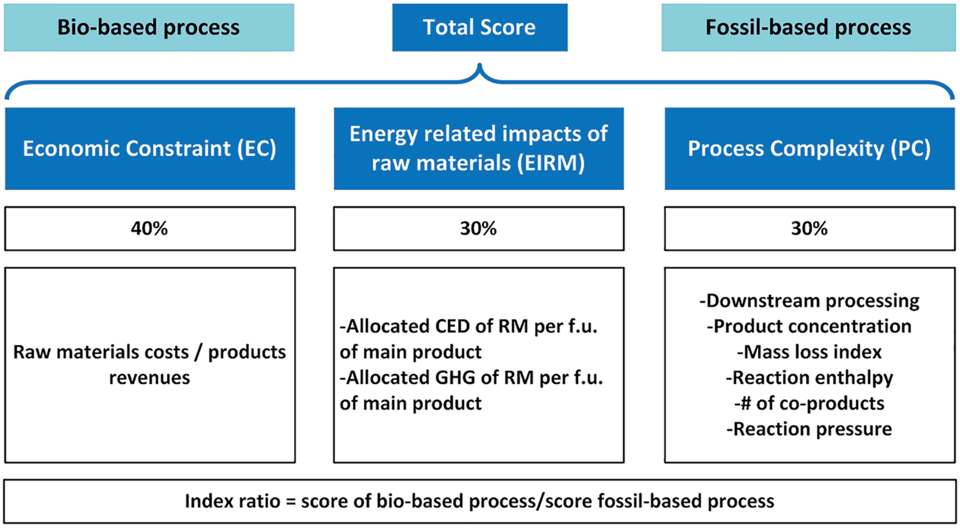

FIGURE 7.1. Overview of the early stage screening method proposed in this thesis

TABLE 7.2. Categorization of sugars (C6 sugars, C5-C6 Mixtures in some cases) derivatives by biochemical conversion

Country/ Region	Succinic Acid **	Succinic Acid	Ethanol ** (C5-C6)	Ethanol (C6) **	Ethanol (C5,C6)	Butanol **	Acetic Acid **	Ethanol (C6)	Acetone **	Butanol	Acetic Acid	Acetone
EU	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-III	G-III	G-III
USA	G-I	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-III
China	G-I	G-I	G-I	G-I	G-I	G-I	G-II	G-II	G-II	G-II	G-II	G-III

G-I: Group I, most favourable compounds to be produced from sugars from lignocellulosic biomass

G-II: Group II, promising derivatives.

G-III: unfavourable derivatives from sugars from lignocellulosic biomass

** Denotes that costs and energy related impact of raw materials were obtained from mass allocation of impacts of lignocellulosic biomass and its further treatment to obtain C5, C6 sugar streams, and lignin.

For derivatives without **, the costs and energy related impacts were obtained via economic allocation assuming a price ratio for C6:C5:lignin of 3:2:1.

C6: denotes fermentation of C6 rich stream. C5, C6: denotes fermentation of C5,C6 mixtures

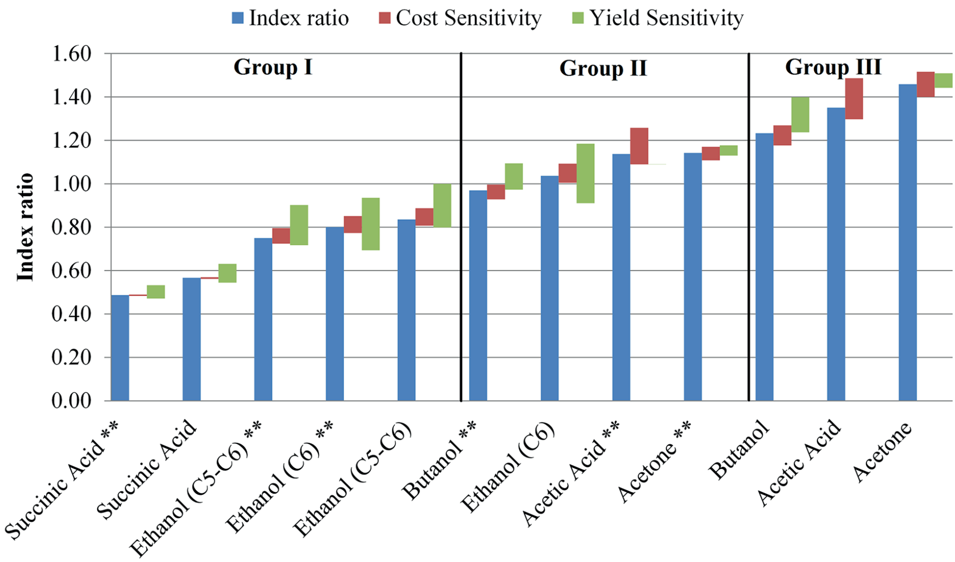

FIGURE 7.2. Index ratio and sensitivity analyses on yields and prices for derivatives from lignocellulosic sugars by biochemical conversion (EU). For derivatives without **, the costs and energy related impacts were obtained via economic allocation assuming a price ratio for C6:C5:lignin of 3:2:1. ** Denotes that costs and energy related impacts of raw materials were obtained from mass allocation of impacts of lignocellulosic biomass and its further treatment to obtain C5-C6 sugar streams, and lignin. C6: denotes fermentation of C6 rich stream. C5-C6: denotes fermentation of C5-C6 mixtures.

In **Chapter 3** we have shown how the developed early screening method was not only applicable to standalone conversion routes, but also to multi-step conversion routes and multiproduct biorefinery systems. The method was first applied to the production of isobutanol by comparing a bio-based route starting from spruce woodchips, to one starting from methane (fossil-based). The results indicated advantages of the bio-based route compared to the fossil one (index ratio 0.8). The method was also applied to three multiproduct systems from the conversion of isobutanol: Case 1: production of isobutyl acetate and glycerol tert-butyl ether (GTBE); Case 2: production of isobutyl acetate and ketones, and Case 3: production of isobutyl acetate and alkanes. The method was effective to compare biorefinery configurations, even when these have multiple conversion steps (in series or parallel) for different products. Furthermore, the method allowed identifying key factors affecting each individual conversion route, and their impact on the overall performance of the integrated multiproduct system. One example of this was when the systems were compared according to the type of auxiliary materials. Specifically, the impact of additional fossil-derived raw materials in some routes led to higher CED and GHG emissions (*e.g.*, acetone for producing ketones and alkanes in cases 2 and 3), which ended up having a significant effect on the overall performance of the multiproduct systems, when compared to those with bio-based auxiliary raw materials (*e.g.,* glycerol for producing GTBE in case 1). This points to the importance of accounting not only for the environmental impacts of the main feedstock but also for the auxiliary raw materials.

The outcome of the early screening assessments relies highly on data inputs such as prices and process yields. Variations in those significantly affect the outcome and in some cases played a major role on which groups to classify the derivatives (*i.e.,* favorable, promising and unfavorable). A clear example of this was provided in chapter 3 were the low price of key co-products (*i.e.,* lignin) had a negative effect on the index ratio. The method also allowed grouping indicators into economic and environmental aspects (see Figure 7.3), and assess the impact of different weightings in the final outcome. The results showed that when there is major weighting to environmental aspects, the bio-based systems tend to show larger advantages than the petrochemical counterparts. In the contrast, when the weighting to economic aspects was increased, the results indicated that the benefits of the bio-based routes compared to the petrochemical routes were limited. This showed that environmental aspects need to be adequately balanced (weighted) in ex-ante assessments to comprehensively understand the advantages and disadvantages of bio-based routes compared to their petrochemical counterparts.

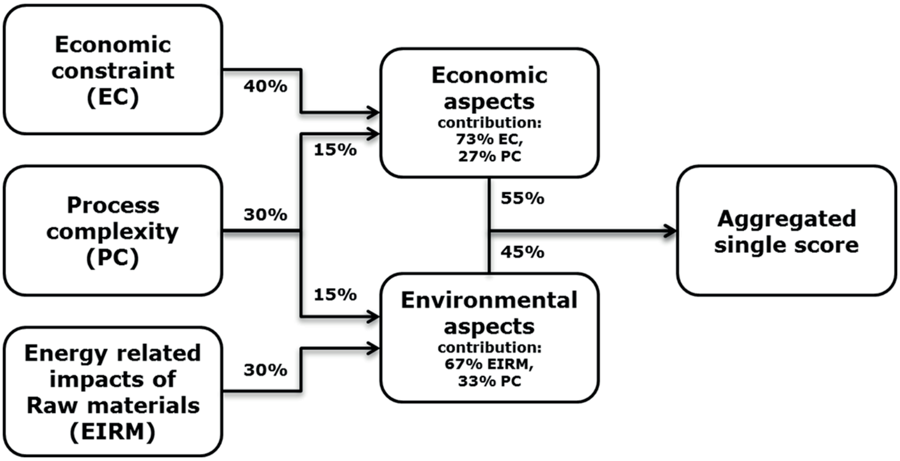

FIGURE 7.3. Overview of weighting and aggregation of indicators into a single sore. Contribution of Economic and Environmental aspects on the aggregated score.

Objective 2

To assess the importance and challenges of biomass pretreatment in the performance of carbohydrate based biorefineries.

The attention for using 2G biomass for fuels and chemicals production has increased as a reaction to the concerns originated by the use of 1G biomass. The use of 2G feedstocks aims to decrease pressure on land use and avoid competition with food [7, 9]. The complexity in the nature of 2G feedstocks (*i.e.,* containing cellulose, hemicellulose and lignin) has been identified as key a barrier as it results in higher energy demand and therefore higher processing costs when compared to 1G feedstocks [8]. In this context, the efficiency of the biomass pretreatment stage plays a key role, as pretreatment is a vital biorefining step to cost-efficiently convert the released sugars into fuels and chemicals [19]. Assessing the techno-economic and environmental performances of biomass pretreatment technologies would allow identifying the main bottlenecks and challenges of using 2G biomass for carbohydrates and chemicals production. Although, some pretreatment technologies such as steam explosion and dilute acid are at demonstration or commercial stages, there are other pretreatment technologies that are being viewed as having potential but are still at early development stages [19]. In this context, this thesis addressed this gap by assessing different cases studies:

- The techno-economic and environmental assessments of the pretreatment of woody biomass using the organosolv technology (Chapter 3 and 4)
- The environmental assessment of chemicals produced from C6 sugars derived from corn and spruce (chapter 6).

Key results

The organosolv technology aims to simultaneously refine woody biomass (with the presence of a catalyst, an organic solvent, high temperature and pressure) into its main components *i.e.,* lignin, hemicellulose hydrolysate (hemicellulose fraction) and cellulose pulp. The pulp stream (rich in cellulose) is used as substrate for further enzymatic hydrolysis (saccharification) into C6 sugars which. The assessment in **Chapter 3** included the organosolv fractionation of spruce as a primary conversion step prior to the saccharification of the pulp, and later the fermentation (of carbohydrates) into isobutanol. The analysis carried out in chapter 3 allowed identifying (at a screening level), the factors that had a major influence on the performance of the organosolv technology: *i.e.,* large requirement of water for dilution (which resulted in low concentration of substrates and products), the need to recover and recycle the solvent, the presence of a non-converted solid fraction of the biomass, high presence of hemicellulose derived sugars with high concentration of inhibitors (considered as wastewater), and the high influence of lignin revenues on the economic performance of the systems (accounting for up to 38% of the total revenues, see chapter 3). **Chapter 4** conducted an in depth assessment that provided insights into the technical, economic and environmental performances of the organosolv technology, compared to the wet milling technology for producing C6 sugars. The assessment was carried out for an organosolv biorefinery that processed 1000 ktonne/y of spruce yielding 359 ktonne/y of C6 sugars (mass and energy balances estimated following a process modeling approach). The capacity of the wet milling process was set to match the C6 sugars flowrate produced by organosolv (to allow a fair comparison). The mass balances of the organosolv system revealed that lignin was the product with the second highest flowrate after C6 sugars (191 ktonne/y), confirming its importance for valorization. The mass balances also revealed that one challenge of the organosolv fractionation of spruce, was that 52% of the initial mass of dry biomass was leaving the system as waste in the form of highly diluted non-converted solids and hemicellulose derived sugars. In an effort to improve the organosolv production system and use these two streams, the production of biogas (to produce heat and power) was included. This improvement showed to have an important impact on the overall energy efficiency of the organosolv process as up to 95% of the required steam, and 100% of the required electricity were covered by biogas. Comparing to the wet milling process, the energy intensity of the organosolv process (without the energy production unit) was higher than that of the wet milling technology by factor 2.5.

The economic analysis carried out in C**hapter 4** showed that operating costs were dominated by raw materials, followed by utilities for both the organosolv systems and wet milling. For organosolv, revenues were dominated by the income from C6 sugars (42-49%), followed by that of lignin (39-46%), and surplus electricity (13% when anaerobic digestion was included). For the wet milling system, revenues were dominated by the income from C6 sugars (69%). The organosolv technology (coupled to biogas production) showed to be feasible with higher positive NPV (238 M€) than that of the wet milling system (168 M€) (at base case prices C6 sugars 300 €/tonne, lignin 630 €/tonne). However, the organosolv technology also showed much higher capital investment needs (236 M€) compared to wet milling (55 M€), which resulted in longer recovery periods of the investment (see Figure 7.4). Sensitivity analyses allowed assessing the robustness of the economic results to changes in input parameters such as prices. The economic performance of the organosolv technology was found to be very sensitive to changes in lignin, C6 sugars and biomass prices, as well as changes in capital investment. The effects of C6 sugars revenues and biomass costs on the economic performance were found to have a typical behavior. However, the effect of both capital investment and incomes by lignin were found to be key factors that need close monitoring for further development of the technology. A difference of up to 126 M€ was found between different literature studies providing capital costs for organosolv (details provided in chapter 4), reflecting on the large uncertainties on equipment needed and their costs at large scales (1000 ktonne/y of wood biomass). This may become an important barrier, as in general, technologies transitioning to higher development stages become generally more expensive due to uncertainties during design phases [259], and for the organosolv technology that would imply a large economic risks. In the case of lignin, even if its price is expected to be higher (compared to kraft or lignosulfonate lignin) due to its potential for high-value applications [260], it is worth noting that market has not been fully developed yet. The findings of the techno-economic analysis carried-out in Chapter 4 suggested that it should be taken into account that 2G technologies are more expensive and with higher risks than 1G technologies and that a transition to 2G systems should be accompanied by incentives to develop (*e.g.*, market incentives, green premiums).

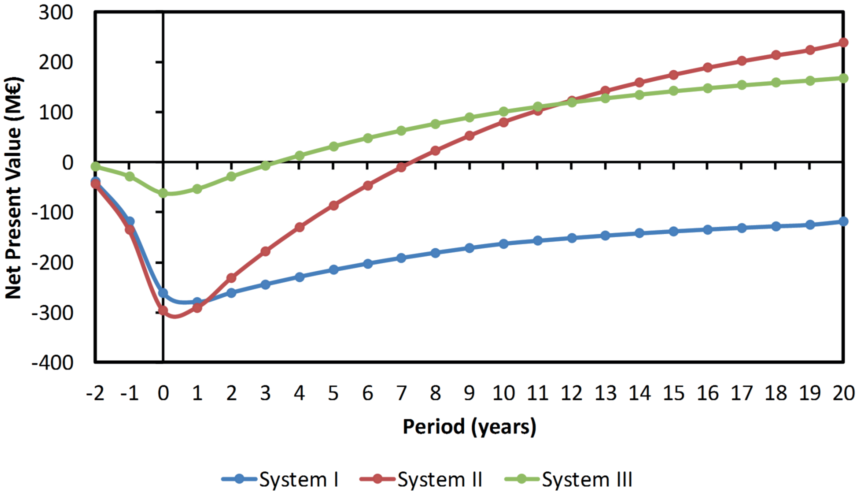

FIGURE 7.4. Cumulative Net Present Value of organosolv and wet milling technologies a project life-time of 20 years. System I: organosolv without anaerobic digestion unit. System II: organosolv with anaerobic digestion unit. System III: wet milling. Lignin price of 630 €/tonne, C6 sugars price (300 €/tonne).

The environmental assessment in **Chapter 4** was carried out following a prospective cradle-to-gate life cycle assessment (LCA) of the organosolv and wet milling technologies to produce C6 sugars. The assessment was carried-out for the impact categories climate change potential (CCP), water depletion potential (WDP), agricultural land depletion potential (ALOP), human toxicity potential (HTP) and non-renewable energy use (NREU). The results showed that improving the energy efficiency of the organosolv system had a positive effect on reducing the environmental impacts of the categories CCP, NREU and HTP, which remained lower than those of the wet milling technology. This shows that energy inputs at the process level were high contributors for these three impact categories. The result showed that for the CCP and NREU categories, the differences were mainly due to the high contribution of corn production in the total aggregation of the impacts in the corn wet milling process, in comparison to the low contribution of woodchips production in the organosolv processes. In the case of ALOP and WDP, the organosolv process showed higher impacts than corn wet milling. For ALOP, this was due to the difference in feedstock flowrates for producing the same amount of C6 sugars, with the organosolv technology requiring 2.1 times more spruce than corn in the wet milling technology for producing 1 kg of C6 sugars. In the case of WDP, the main differences were in the larger requirements of dilution and cooling waters of organosolv compared to wet milling. Overall, the results indicated that the organosolv technology showed a relatively better environmental performance than corn wet milling.

The assessment carried out in **Chapter 6** also followed a prospective cradle-to-gate LCA (for the same impact categories considered in Chapter 4) for the production of butadiene and caprolactam from C6 sugars, which considered the effect of using C6 sugars derived from corn and spruce. This chapter highlighted that the source of C6 sugars had an important impact on the overall environmental performance of the production of butadiene and caprolactam compared to their respective petrochemical counterparts. The results showed that C6 sugars derived from spruce were preferred over those from corn. This highlighted the possible environmental benefits of using 2G technologies over 1G technologies not only at the pretreatment stage level, but also at the downstream conversion level.

Objective 3

To identify and evaluate the trade-offs of standalone vs. integrated configurations for the economic and environmental performances of biorefineries.

One of the characteristics of early assessments of biorefinery systems reported in literature is the strong focus on biofuels and/or standalone technologies focusing on one product only. Integrated multiproduct biorefineries are receiving increasing attention as they can provide a better exploitation of biomass and ultimately improve the competitiveness and reduce environmental impacts when compared to standalone technologies [10]. Identifying the synergies and assessing the trade-offs of integrated biorefinery systems is not straightforward as these are generally case specific. Besides, the early assessments of integrated biorefinery systems generally focus on one or two dimensions (*e.g.,* techno-economic) and rarely on the techno-economic and environmental performances. Thus, carrying out assessments of integrated biorefinery systems including the techno-economic and environmental dimensions, would allow identifying and assessing the key trade-offs to guide on aspects such as the valorization of waste streams and the co-production of utilities (*e.g.,* heat and power). This thesis addressed this assessing the following case studies:

- The techno-economic and environmental assessments of the organosolv technology for producing C6 sugars and co-products (chapter 4)
- The techno-economic and environmental assessments of the integrated production of 1,3-butadiene and ε-caprolactam from C6 sugars (chapters 5 and 6)

Key results

The techno-economic and environmental assessment carried out in **Chapter 4** provided insights into the impact of valorizing waste streams as an option to improve the competitiveness and environmental performances of biomass conversion systems. In chapter 4, the use of the non-converted solids and hemicellulosic sugars for producing steam and electricity, showed to be effective for decreasing the energy intensity of the organosolv processes. This implied reducing the need of outsourced energy inputs and therefore, operating costs and impact categories such as CCP, NREU and HTP were also reduced. The assessment allowed identifying trade-offs, both economically and environmentally. For instance, the intensification of the process (by including the production of heat and power) implied that higher investment needs were required (up to 12% higher compared to the base case). In the specific case of the organosolv technology, the increased capital costs did not negatively affect its economic performance as the reduction of operating costs and revenues by the surplus electricity produced, allowed recovering the investment within the project's life time (see Figure 7.4). It should be taken into account that this is not always the development direction for each biorefinery configuration aiming to integrate new processing lines and/or add value to onsite produced streams. One of the recommendations is for instance, to assess the economic trade-offs between capital needs, operating costs and revenues of the envisioned integration option. This would allow understanding whether the extra investment needs are actually compensated by savings in operating costs. Another example is to evaluate whether there could be conflicting results in the assessed environmental categories considered (*i.e.,* reductions in some categories, and increase in other categories).

Chapter 5 assessed the techno-economic performance of the integrated production of butadiene and caprolactam from C6 sugars. The analysis was carried out for base case conversion systems, and for systems where the overall selectivity to the targeted products was increased (2 systems assessed for butadiene, and 2 systems assessed for caprolactam). Figure 7.5 shows the simplified flow diagram and process steps for producing butadiene and caprolactam from C6 sugars. The results showed that in terms of energy intensity, both the butadiene and caprolactam processes performed similarly (ranging from 34-50 MJ/kg). Nevertheless, the caprolactam process showed higher (factor 1.6-3.6) product yield per unit of C6 sugars input than butadiene. One of the identified bottlenecks of the butadiene production systems, was that a large portion of the carbon mass of C6 sugars went into the cell biomass and carbon dioxide (both produced during the ethanol production process), which are streams with low value added (if any). Besides, in the step of converting ethanol into butadiene several co-products were obtained. This resulted in the need to develop a complex downstream process to recover butadiene and co-products (*e.g.,* ethylene). The butadiene process showed a negative economic performance (with negative NPV values for the assessed cases), with production costs up to 3-5 times higher than its reference market price (900 €/tonne). The sensitivity analysis allowed identifying the dependence of the economic performance of the butadiene process on the revenues of butadiene and ethylene, and high sensitivity to changes in C6 sugars prices and capital investment. This emphasizes on efforts that still are needed to improve the overall efficiency of the butadiene process, and the need to find alternatives to promote the bio-based butadiene market by considering for instance policy incentives (*e.g.,* green premiums). The analysis also showed, at base case conditions, that the caprolactam process was unfeasible. Nevertheless, improving the selectivities of the γ-valerolactone into caprolactam step (yield improved by 60% compared to the base case) resulted in economic benefits with production costs 6% lower than the reference market price (2000 €/tonne). During the levulinic acid conversion step (part of the caprolactam processing line), 18% of the initial mass of C6 sugars ended up in the form of humins. Humins are a group of organic compounds with no commercial value which were considered waste. Similar to the approach followed in Chapter 4, the production of heat and power from the combustion of humins was considered in Chapter 5 (see **Figure 7.5**). Results indicated that by following this integrated approach (*i.e.,* including humins combustion), production costs of both butadiene and caprolactam decreased. This was due to the contribution of surplus electricity on revenues and savings on utilities costs (by using the produced steam and electricity to cover the process needs). One of the key findings was that by changing the distribution (sensitivity analysis) of the C6 sugars input to increase the capacity of the caprolactam process, the benefits of including humins valorization were stronger (by decreasing further the production costs).

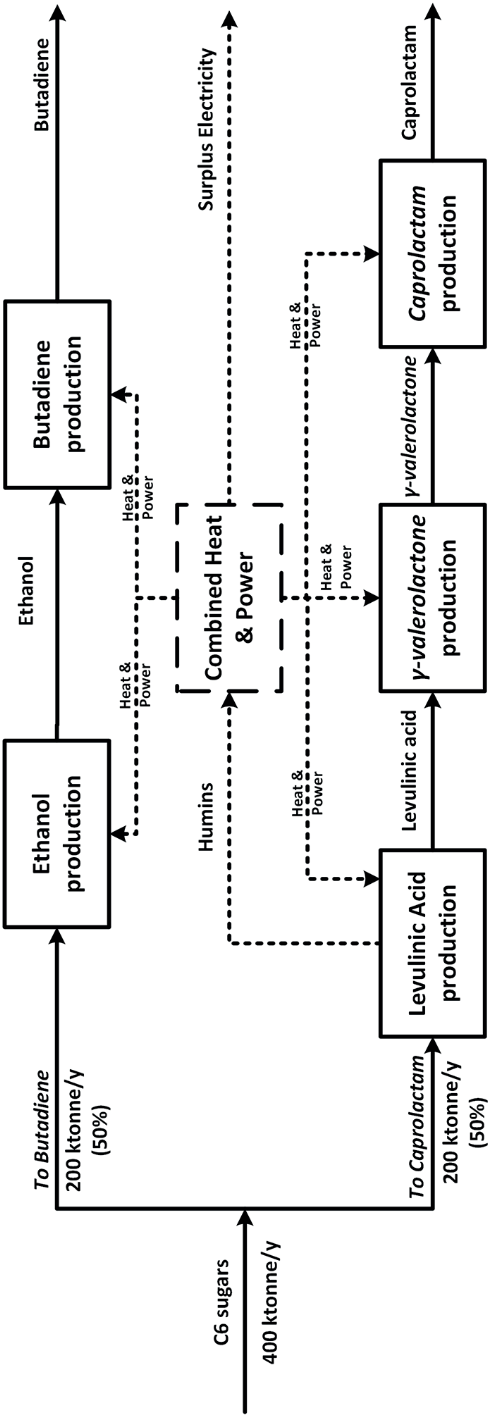

FIGURE 7.5. Simplified block diagram of butadiene and caprolactam production from C6 sugars.

Additionally, the caprolactam process ended up with a high benefit of the economies of scale showing decreased production costs below the reference market price (see Figure 7.6).

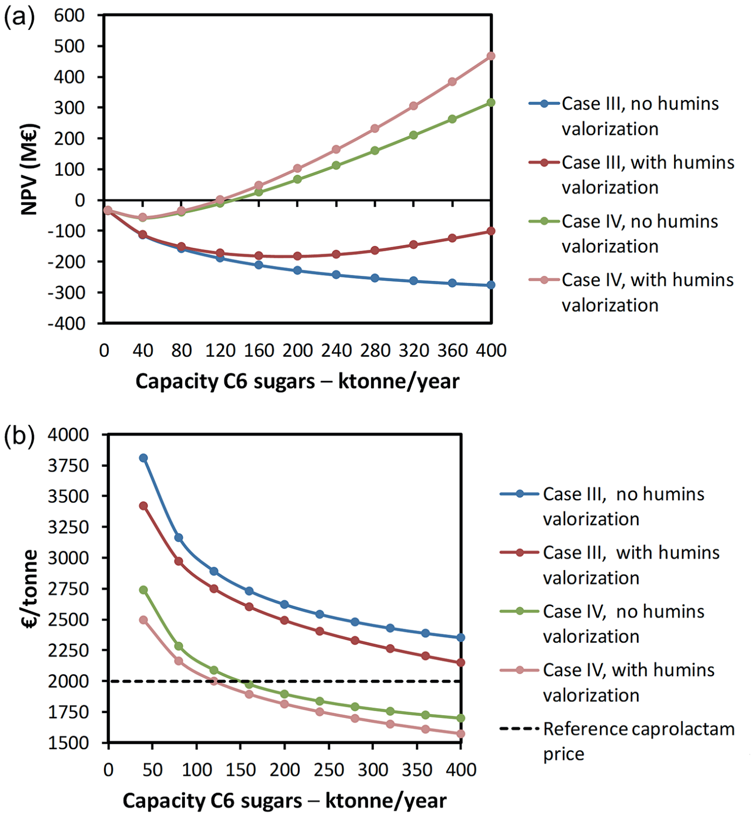

FIGURE 7.6. Results of sensitivity analysis on varying the C6 sugars capacity to the caprolactam process, a): effect on NPV, b): effect on production cost (reference price 2000 €/tonne). Case III: base case conversion. Case IV: improved selectivity.

The environmental assessment in **Chapter 6** was carried out following a prospective cradle-to-gate LCA of the production of butadiene and caprolactam from C6 sugars. The assessment was carried-out for the CCP, WDP, ALOP, HTP and NREU. The results showed no clear advantages of bio-based butadiene over fossil-based butadiene, with 4 (CCP, HTP, ALOP and WDP) out of the 5 impact categories scoring higher for the bio-based systems. Only NREU was lower for bio-based in comparison to fossil. Results also showed that bio-based caprolactam performed better than its petrochemical counterpart in 3 (NREU, CCP, HTP) out of the 5 impact categories (ALOP and WDP performing worse).

When heat and power were produced from humins, benefits were obtained for the NREU, CCP and HTP impact categories, however, the benefits were not strong enough to change the direction of results (*e.g.,* improving the butadiene process to outperform its petrochemical counterpart). Results of the LCA also indicated that the application of allocation shifted the direction of results for some impact categories, which strongly influenced the interpretation of results. In general, assessing different impact categories allowed a better understanding of the technologies. This is important to be mentioned as many LCAs reported in literature have a very strong focus on climate change [34], but other impact categories can have a large impact on the environmental perspective of a technology for producing bio-based chemicals.

In general, the results of this thesis confirmed that even if there is technical potential to convert biomass into *"interesting"* chemicals, in some cases the economic and environmental performances were not necessarily better than their petrochemical counterparts. This, therefore, highlights and confirms why ex-ante assessments of biorefineries are necessary for identifying and communicating the risks, challenges and opportunities of novel technologies to guide technology developers (to improve performance) and for policy makers (to built a roadmap on the potential long term uses of biomass). Moreover, the results provided in chapters 4 to 6 confirmed that the integration of utilities production systems (to produce heat and power) using biorefinery waste streams can positively improve the overall techno-economic and environmental performances of non-integrated biorefineries. Biorefineries are energy intensive processes that need careful integration (both in the form of mass and energy) for the proper management of resources [45] to the improve the techno-economic and environmental performances.

7.4. LIMITATIONS OF THE RESEARCH

In this thesis several methodological particularities and limitations were identified. One common aspect, was the impact of the use of allocation on the results and interpretation. The impact of allocation can be summarized on two main levels: the effect of the upstream allocation of the environmental impacts of the raw materials on the environmental performance of the downstream products, and the use of allocation within the system boundaries of the assessed systems.

For the first level, chapters 2, 3 and 6 showed that upstream data reporting of the cradle-to-gate impacts for raw materials was required. This data is generally derived from the analysis of upstream operations, which in the case of biorefineries can be multifunctional systems (*e.g.,* pretreatment stage). In this thesis, the allocation of the upstream environmental impacts to the raw materials inputs showed to have a significant effect on the outcome of the analysis. A clear example of this can be found in chapter 2 where the upstream costs, CED and GHG emissions of carbohydrates (before their conversion into the targeted chemicals) were allocated following two approaches (mass allocation and economic allocation) providing quite different results. This effect is also seen in Chapter 6 where the approach of allocating the upstream environmental impacts to C6 sugars (main feedstock) affected the final comparison of the downstream products *(i.e.,* caprolactam and butadiene), compared to the petrochemical counterparts. These results suggested that understanding the impact of upstream allocation of environmental impacts needs to be taken into account for two reasons: first to avoid providing a misleading message, and second to account for transparency when reporting on the weaknesses of the assessment methods and applied allocations.

For the second level, chapters 4 and 6 showed that the use of allocation has a large influence on the results and most importantly on their interpretation. Biorefineries are multifunctional systems where the use of allocation cannot, in most cases, be avoided. Assessing the environmental performance at the system level (when no allocation was applied) allowed identifying the major hotspots and bottle-necks of the technologies in comparison to the reference benchmark systems. Besides, this also allowed getting a clearer picture on the interpretation of results when allocation was applied, as in some cases the use of allocation mistakenly increased the relative difference of a product compared to its benchmark. An example of this was provided in chapter 6 where production of electricity from a waste stream seemed to favor the reduction of ALOP and WDP when applying allocation. Nevertheless, this message could be misleading as those benefits were obtained due to fact that the number of products increased (by including electricity as an additional function) and consequently the allocation factor for the main function decreased. Thus, a recommendation is that before applying allocation, the understanding of the performance of the system is required to avoid biases (as much as possible) in the interpretation of results.

Also, the assessments of the multiproduct systems allowed identifying key challenges for the approaches to apply allocation in multiproduct integrated systems as those were more complex than the assessment of standalone processes for one product. In this thesis, the techno-economic evaluations of complex multiproduct systems were carried out by means of analyzing the individual production lines that the integrated multiproduct system had. For instance, in chapter 5, butadiene and caprolactam were the main process lines, however sharing feedstocks and utilities production systems (when humins were valorized). This implied the need to apply an internal subdivision approach to distinguish the system boundaries of each process. This was done by means of allocating the C6 sugar input and utilities based on the capacity of each process. One can argue that the evaluation of multiproduct systems should be done by considering all inputs and outputs and calculating a common NPV, and later allocating the production costs to the individual products. However, that approach can also be problematic as it may not allow identifying whether an individual production line is economically attractive. For instance, it may be possible that the benefits of a high-value added option are decreased due to the co-existence of a low (negative performing) value-added option. However, that approach has been used in literature for systems including high value-added products at low volumes combined with biofuels production, and when the integration of materials and energy is very complex not allowing straight forward subdivision [45].

For the environmental assessments, to subdivide individual production lines within an integrated multiproduct system is a complex task. This has to do with the fact that the LCAs carried out in this thesis aimed to present the advantages and disadvantages of products compared to the petrochemical counterparts. For instance, the system considering the integrated production of butadiene and caprolactam showed that both products have equivalent petrochemical counterparts. To carry out LCA to evaluate the entire integrated production system and later compare it to the reference benchmark, would require the development of a fossil based benchmark co-producing caprolactam and butadiene. This was not possible as the fossil production lines of butadiene (produced from naphtha) and caprolactam (produced from benzene) do not have a common feedstock. This implied considering a subdivision approach (identical to the one followed in the techno-economic evaluation) to divide the systems boundaries of the integrated process into two individual production lines to account for the two functional units for the comparison of the petrochemical counterparts (*i.e.,* kg of butadiene and kg of caprolactam). Note that this approach is analogous to the concept of system expansion applied in standalone systems, but then applied to multiproduct systems. Nevertheless, the use of allocation was still needed for the individual sub-divided processing lines as other co-products were also obtained in each (*e.g.,* ethylene in the butadiene line, formic acid in the caprolactam line). The advantage of using this approach was that the individual (main functions) of the systems were able to be compared to the equivalent petrochemical systems. Nonetheless, it should be noted that the application of this subdivision approach can be challenging when the level of mass and energy integration increases, and when the number of functions is larger.

In this thesis, the estimation of mass and energy balances of the assessed technologies was a key methodological step to provide inputs to both economic and environmental assessments. This estimation was carried out by process modeling, which implied in some cases the need to combine process design to complete the features of many of the assessed technologies. Clear examples of this can be seen in chapter 4 by designing the solvent recovery system of the organosolv technology and in chapter 5 in the complex downstream processing design to recover both butadiene and caprolactam. Despite that process design and modeling is aimed to be carried-out at the highest possible resolution, it depends on the expertise and skills of the analyzer. This may bring subjectivity to the estimation of the efficiency of the design, on which equipment is actually needed, the size of the equipment and the required materials among many others, that affect the quality of the data generated during that step. This was noticed, for instance, to have a large effect on the estimation of the capital costs related to the assessed technologies. Therefore, it is strongly recommended to identify which technical aspects have the most influence on the outcome of the assessments.

7.5. RECOMMENDATIONS

The results presented in this thesis allowed identifying recommendations for policy makers and research.

7.5.1. Policy

- The assessment of the **environmental performance of biorefinery systems** should not only focus on the reduction potential of greenhouse gas (GHG) emissions, but also on other environmental aspects such as land use and water depletion across the biomass value chain. Reduction of GHG emissions does not necessarily imply that the environmental outlook of biorefineries is positive.
- **The deployment of integrated multiproduct biorefinery systems** offers attractive economic and environmental benefits over the deployment of standalone technologies. However, the economic and environmental trade-offs of the different levels of integration and the inclusion of processing lines for waste valorization should be closely monitored.
- **The development of early market scenarios of novel bio-based products** needs to be accounted for when assessing the economic potential of multiproduct biomass deployment technologies. The economic sustainability of multiproduct biorefinery systems highly relies on the incomes from product, which markets are still uncertain. Therefore, early identification of potential applications and market penetration of novel products would allow identifying additional risks and opportunities for the development of novel bio-based systems.

- **The assessment of the uncertainties of novel technologies in biorefineries** needs to be accounted for reporting the risks associated to the transition from early development to higher development stages. Aspects such as uncertainties in capital costs estimates need to be closely monitored.

7.5.2. Further research

- Additional work is needed to understand the **synergies and impacts of biomass supply** on the techno-economic and environmental performances of large scale multiproduct biorefinery systems. Despite research ongoing on biomass supply to identify bottle necks and hotspots related to biomass collection and logistics, most of its attention is focused on bioenergy production. However, it would be helpful to understand biomass supply requirements to secure the operability of multiproduct biorefineries at large scales. This would allow assessing the economic and environmental impacts of biomass supply related to aspects such as seasonality, feedstock accessing and contracting, limitations in transport infrastructure, multi-feedstock operability and labor intensity among others. This type of analysis would allow contextualizing new emerging technologies to specific countries/regions.
- Challenges remain present to assess and understand **the end-of-life environmental impacts of bio-based chemicals.** The development of scenarios of the use phase of chemicals derived from biomass is required to assess whether there are long term mitigation potentials of novel bio-based products compared to traditional bio-based products and to fossil products with similar functionalities.
- Investigating the **methodological implications of the use of allocation** of multiproduct biorefineries needs to be continued. The insights provided in this thesis allow identifying the large influence of allocation on the results. Thus, the impact of multiple allocation approaches for assessing the environmental impacts of highly integrated biorefinery systems with multiple functions would allow developing a methodological guideline on the environmental assessment of complex biorefineries.

CHAPTER 8

Samenvatting, conclusies en aanbevelingen

8.1. ACHTERGROND

De kennis ontwikkeld door de grootschalige inzet van 1G biobrandstoffen en andere traditionele gebruiksvormen van biomassa hebben ervoor gezorgd dat de gemeenschap van de 'bio-based economy' zich concentreert op nieuwe bronnen voor grondstoffen (met veel aandacht voor lignocellulosische biomassa, 2G), de bredere range van 'bio-based' producten, waaronder chemicaliën en materialen [7, 8, 10], en de adoptie van bioraffinages [11, 12].

De duurzame ontwikkeling van bioraffinages vereist een blik breder dan procesconfiguraties. Bovendien zijn bioraffinages vaak foutief als duurzaam bestempeld slechts op basis van het hernieuwbare aspect van biomassa [35, 37]. In deze context, de ex-ante beoordeling van bioraffinages in vroege ontwikkelingsstadia is relevant om nuttige inzichten te verschaffen met betrekking tot de toekomstige prestatie op het gebied van duurzaamheid (op het gebied van technische, economische en milieu aspecten, en in sommige gevallen sociale aspecten [9, 35, 36, 38, 39]), zelfs als kennis en beschikbaarheid van data over technologieën, producten, markten en grondstoffen beperkt is [34].

8.2. DOELSTELLINGEN

Het hoofddoel van deze thesis was om diepgaand inzicht te verschaffen over de belangrijkste factoren die van invloed zijn op de techno-economische en milieu prestatie van nieuwe technieken voor de productie van 'bio-based' chemicaliën. De volgende doelstellingen zijn opgesteld:

1. Het ontwikkelen van 'screening' methods die nieuwe biochemische conversie routes kunnen behandelen en inzichten verschaffen in de bijbehorende techno-economische en milieu prestaties.
2. Het vaststellen van het belang van voorbehandeling van biomass voor de prestatie van koolhydraat-gebaseerde bioraffinages.
3. Het identificeren en evalueren van de trade-off van 'standalone' ten opzichte van geïntegreerde configuraties van de economische en milieu prestaties van bioraffinages.

Tabel 7.1 geeft een overzicht van de hoofdstukken in deze thesis en de doelstellingen die behandeld worden.

8.3. BELANGRIJKSTE RESULTATEN EN CONCLUSIES

Deze sectie geeft een samenvatting van de belangrijkste resultaten en conclusies van deze thesis voor elke doelstelling.

Doelstelling 1

Ontwikkeling van een 'screening' methode die nieuwe biochemische conversiepaden voor de productie van chemicaliën behandeld en inzicht geeft in de bijbehorende techno-economische en milieu prestaties.

Belangrijkste resultaten

Hoofdstuk 2 beschreef het nut en de flexibiliteit van de aangepaste 'early stage screening' methode voor de evaluatie van voor zowel chemisch en biochemisch geproduceerde 'bio-based' chemicaliën. Figuur 7.1 geeft een overzicht van de 'early screening' methode, deze omvatte drie indicatoren voor duurzaamheid: economische beperking ('Economic constraint', EC), energie gerelateerde impact van de grondstoffen ('energy related impacts of raw materials', EIRM) en proces complexiteit (PC). Zowel de EC als de EIRM indicatoren bleven identiek aan de originele methode [85]. Het vernieuwende element was een nieuwe evaluatie van de PC indicator, die gericht is op het nabootsen van kosten en milieu impacts gedurende het verwerkingsproces. Zoals eerder gedefinieerd, niet alle 'downstream' processen (om de hoofdproducten te herstellen) zijn gebaseerd op de co-existentie van de damp-vloeistof fases (bv. destillatie), wat de basis is die gebruikt wordt in de originele indicator. Complexe 'downstream' verwerking kunnen significant bijdragen aan hogere kosten en milieu impacts in de verwerkingsfase. Om rekenschap te geven aan deze mogelijke situaties is een subcategorie van de PC indicator ontwikkeld, genaamd 'Downstream verwerking'. De resterende subcategorieën die de PC indicator vormen (d.w.z. product concentratie, massa verlies index, reactie enthalpie, aantal co-producten en reactie druk) zijn aangepast om de chemische en biochemische conversie processen weer te geven (zie hoofdstuk 2).

De aangepaste methode is getest in 36 routes (hoofdstuk 2) voor de conversie van 'bio-based' syngas, koolhydraten en glycerol. De routes zijn gecategoriseerd in drie groepen: gunstig (groep I), veelbelovend (groepII) en ongunstig (groep III). Groep I bevat routes met een hoge potentie voor duurzaamheid van de 'bio-based' optie ten opzichte van de petrochemische. Groep II bevat routes waarvan de voordelen niet erg groot zijn, maar waarvan de technologische en economische verbeteringen kunnen resulteren in een betere prestatie van de 'bio-based' alternatieven. Groep III omvat routes waarvan het duurzaamheidspotentieel laag is voor 'bio-based'derivaten. De methode omvat een gevoeligheidsanalyse om de robuustheid te testen van de resultaten (categorisatie) voor veranderingen in data input (o.a. prijzen en opbrengst) en aannames (o.a. distributie van 'upstream' kosten) en scenario analyse om rekening te houden met specifieke aspecten van de waardeketen gerelateerd aan elk conversie proces, zoals de impact van de prijs van grondstoffen in de verschillende regios.

Hoofdstuk 3 toonde hoe de ontwikkelde vroege screeningsmethode niet alleen van toepassing was op onafhankelijke conversieroutes, maar ook op multi-stap conversieroutes en multi-product bioraffinage systemen. De methode werd voor het eerst toegepast op de productie van isobutanol door een bio-gebaseerde route te vergelijken, beginnend met vurenhoutsnippers, tot één die begon met methaan (op basis van fossiele brandstoffen). De resultaten wezen op voordelen van de bio-gebaseerde route in vergelijking met de fossiele route. De methode werd ook toegepast op drie multi-product systemen van de omzetting van isobutanol: Geval 1: productie van isobutylacetaat en glycerol-tert-butylether (GTBE); Geval 2: productie van isobutylacetaat en ketonen, en Geval 3: productie van isobutylacetaat en alkanen. De methode was effectief om bioraffinageconfiguraties te vergelijken. Bovendien, de methode heeft de identificatie van belangrijke, die van invloed zijn op elke individuele conversieroute, mogelijk gemaakt. Op dezelfde manier werd de impact op de algehele prestaties van het geïntegreerde multi-product systeem geïdentificeerd.

Met de methode konden indicatoren worden gegroepeerd in economische en milieuaspecten (zie figuur 7.3) en de impact van verschillende wegingen in het eindresultaat te beoordelen. De resultaten toonden aan dat wanneer er een grote weging naar milieuaspecten is, de biobased systemen hebben meestal grotere voordelen dan de petrochemische tegenhangers. In tegenstelling hiermee, toen de weging naar economische aspecten werd verhoogd, gaven de resultaten aan dat de voordelen van de biobased routes beperkt waren in vergelijking met de petrochemische routes. Dit toonde aan dat milieuaspecten voldoende afgewogen (gewogen) moeten zijn in ex-ante beoordelingen om de voordelen en nadelen van biobased routes ten opzichte van hun petrochemische tegenhangers volledig te begrijpen.

Doelstelling 2

Het belang van en de uitdagingen in het voorbehandelen van biomassa beoordelen bij koolhydraat- bioraffinaderijen.

Belangrijkste resultaten

In **Hoofdstuk 3** werd organosolv fractionering van spar-biomassa als primaire conversiestap vooraf de versuikering van het pulp en opvolgende fermentatie (van koolhydraten) naar isobutanol beoordeeld. Door de daar uitgevoerde analyse was het mogelijk om de factoren te identificeren die het meeste invloed hadden op de prestaties van de gebruikte organosolv technologie, namelijk: de onverwacht grote waterbenodigdheden voor de verdunning (wat ervoor zorgde dat er een lage concentratie van substraten en producten werd geleverd), de noodzaak om het oplosmiddel op te vangen en te hergebruiken, de aanwezigheid van een fractie biomassa dat niet wordt omgezet, het frequente voorkomen van suikers afkomstig uit hemicellulose die een hoge dichtheid aan remmers bevat (te beschouwen als afvalwater), en de hoge invloed van lignine-inkomsten op de economische prestaties van het systeem (die wel tot 38% verantwoordelijk kunnen zijn voor de totale inkomsten). In **Hoofdstuk 4** werd er een diepte analyse uitgevoerd op de organosolv technologie waarbij ze werd vergeleken met de natte maling-technologie die wordt gebruikt om C6-suikers te produceren. Deze analyse bracht belangrijke inzichten in de technische, economische en milieu-prestaties van organosolv technologie voort. De massavergelijking tussen de twee technologieën liet ook zien dat bij organosolv fractionering van spar-biomassa 52% van de oorspronkelijke biomassa het systeem verlaat in de vormen van zwaar verdunde, niet-omgezette vaste fracties en hemicellulose-gebaseerde suikers. Dit is een belangrijke uitdaging voor de organosolv technologie. In het streven om het organosolv systeem te verbeteren werden deze twee vormen gebruikt om biogas te produceren, wat weer gebruikt kon worden als verwarmings- en krachtbron. Deze uitbreiding zorgde voor een belangrijke verbetering van de energie-efficiëntie van het gehele organosolv proces, waar tot 95% van de benodigde stoom en 100% van de benodigde energie kon worden opgewekt uit het biogas.

De organosolv technologie (in combinatie met de biogas productie) bleek haalbaar met een hogere hogere Net Present Value dan dat van de natte maling-technologie (238 M€ versus 168 M€; uitgaande van 630 €/ton lignine en 300 €/ton C6-suikers). De organosolv technologie bleek echter een veel hogere kapitaalinvestering nodig te hebben in vergelijking met de natte maling-technologie (236 M€ versus 55 M€), wat resulteerde in een langere terugverdientijd (zie Figure 7.4). de haalbaarheid en de terugverdientijd bleken erg gevoelig te zijn voor schommelingen in de vraagprijs voor lignine, C6-suikers en de kostprijs van biomassa. Hierbij zijn de kapitaalinvestering en het inkomsten uit de verkoop van lignine belangrijke factoren die moeten worden meegenomen in de verdere ontwikkeling van de organosolv technologie. Gerapporteerde kapitaalkosten voor de organosolv technologie in de literatuur verschilde tot wel 126 M€, wat een reflectie is van de grote onzekerheden in materiaalkosten en benodigdheden wanneer op een grotere schaal wordt gewerkt (hier 1000 kton biomassa/jaar). Deze onzekerheden zouden een grote drempel kunnen gaan vormen in de invoering van organosolv technologie, gezien organosolv technologie zich sterk ontwikkeld en over het algemeen ontwikkelende technologieën duurder zijn vanwege onzekerheden binnen de ontwerp fase van een technologie [259]. Het is hier echter belangrijk om te signaleren dat lignine nu al een hogere verwachte verkoopprijs heeft dan kraft of lignosulfaat vanwege de toepassingspotentie [260], terwijl de markt zich nog niet volledig heeft ontwikkeld. De techno-economische analyse in **Hoofdstuk 4** stelt dat tweede generatie (2G) technologieën hogere kosten en hogere risico's met zich meebrengen dan eerste generatie technologieën en dat om de transitie naar 2G-systemen gepaard zal moeten gaan met prikkels (bijvoorbeeld markt prikkels, groene premies).

De milieu-impact beoordeling in **Hoofdstuk 4** van de organosolv en natte maling technologieën omsloeg een *cradle-to-gate life cycle assesment* (LCA). Hierbij werd er gekeken naar de potentie ot klimaatsverandering (CCP), de potentie tot water depletie (WDP), de potentie van landbouwareaal depletie (ALOP), de potentie voor toxische werking op mensen (HTP) en het niet-herbruikbare energiegebruik (NREU). De resultaten lieten zien dat de verbetering van de energie-efficiënte van het organosolv systeem een positief effect had op het terugdringen van CCP, NREU en HTP, die allen lager bleven dan bij het natte maling-systeem (van Maïs). Over het geheel gaven de resultaten aan dat de organosolv technologie relatief beter presteerde op milieuvlak dan natte maling technologie (van maïs). In Hoofstuk 6 werd er ook eenzelfde LCA uitgevoerd maar dan voor de productie van butadieen en caprolactam uit C6-suikers uit zowel Maïs als Spar. Hieruit bleek dat C6-suikers uit Spar te prefereren zijn boven die uit Maïs.

Doelstelling 3

Het identificeren en evalueren van de voor- en nadelen van opzichzelfstaande tegenover geïntegreerde configuraties voor de economische en milieuprestaties van bioraffinaderijen.

Belangrijkste resultaten

De technisch-economische en milieubeoordeling uitgevoerd in **Hoofdstuk 4** gaf inzichten in de invloed van het valoriseren van afvalstromen als optie om het concurrentievermogen en de milieuprestaties van biomassaconversiesystemen te verbeteren. Het gebruik van niet-omgezette vaste stoffen en hemicellulose koolhydraten voor het produceren van stoom en elektriciteit bleek effectief te zijn in het verlagen van het energieverbruik van het "organosolv" proces. Dit resulteerde in een vermindering van de uitgaande energievraag, met als gevolg dat de operationele kosten en impactcategorieën zoals CCP, NREU en HTP ook werden gereduceerd. Via de beoordeling konden zowel de economische als de milieutechnische voor- en nadelen worden geïdentificeerd. Ter illustratie, de intensivering van het proces (het meewegen van de hitte en stroomproductie) resulteerde in hogere investeringsbehoeften (tot 12% meer in vergelijking met het referentiescenario). Er moet rekening mee worden gehouden dat de ontwikkelingsstrategie van bioraffinaderijen niet altijd is gericht op het integreren van nieuwe proceslijnen en/of het toekennen van waarde aan ter plaatse geproduceerde stromen. Eén van de aanbevelingen is bijvoorbeeld om een economische afweging te maken van de kapitaalbehoeften, operationele kosten en inkomsten van de beoogde integratie optie. Hierdoor wordt inzicht verkregen of de extra investeringsbehoeften daadwerkelijk gecompenseerd worden de besparingen in de operationele kosten.

Hoofdstuk 5 beoordeelde de technisch-economische prestatie van de integreerde productie van butadieen en caprolactam van C6-suikers. Het butadieenproces had een negatieve economische prestatie (negatieve NPV waardes in de onderzochte scenario's), met productiekosten tot 3-5 hoger dan de referentie marktprijs (900 €/ton). Uit de gevoeligheidsanalyse bleek de afhankelijkheid van de economische prestaties van het butadieenproces op de inkomsten van butadieen en ethyleen, en de hoge gevoeligheid voor schommelingen in C6-suikerprijzen en kapitaalinvestering. Daarnaast kwam uit de analyse naar voren dat het caprolactamproces onhaalbaar was in het referentiescenario. Desalniettemin, het verbeteren van de selectiviteiten van de γ-valerolacton in de caprolactamstap (de opbrengst vermeerderde met 60% ten opzichte van het referentiescenario) resulteerde in economische baten met productiekosten 6% lager dan de referentie marktprijs (2000 €/ton). Tijdens het levulinezuur omzettingsproces (onderdeel van de caprolactamverwerkingslijn) transformeerde 18% van de initiële

C6-suiker massa naar humin. Humin zijn een groep organische verbindingen zonder commerciële waarde, die als afval worden beschouwd. Vergelijkbaar met de aanpak in Hoofdstuk 4, was de productie van hitte en stroom van de verbranding van humin beschouwd in **Hoofdstuk 5**. De resultaten duidden dat met het volgen van deze geïntegreerde aanpak (i.e., het meewegen van huminenverbranding), de productiekosten van zowel de butadieen en het caprolactam afnamen. Eén van de belangrijkste bevindingen was dat bij het veranderen van de C6-suikertoevoerverdeling (gevoeligheidsanalyse) om zo de capaciteit van het caprolactamproces te vergroten, de baten van het meewegen van de huminenvalorisatie groeiden (doordat de productiekosten verder verlaagd werden). Bovendien, het caprolactamproces kreeg grotere baten door schaalvoordelen met verlaagde productiekosten onder de referentie markprijs.

De milieubeoordeling in **Hoofdstuk 6** was uitgevoerd door middel van een toekomstige "van wieg tot poort" LCA voor de productie van butadieen en caprolactam van C6-suikers. De beoordeling was toegespitst op de impactcategorieën CCP, WDP, ALOP, HTP en NREU. Uit de resultaten bleken geen duidelijke voordelen van bio-gebaseerde butadieen ten opzichte van butadieen op basis van fossiele grondstoffen, waarbij vier (CCP, HTP, ALOP en WDP) van de vijf impactcategorieën hoger scoorden voor het bio-gebaseerde systeem. Alleen NREU was lager voor bio-gebaseerd in vergelijking met fossiel als basis. Daarnaast wezen de resultaten erop dat bio-gebaseerde caprolactam beter presteerde dan de petrochemische tegenhanger in drie (NREU, CCP, HTP) van de vijf impactcategorieën (ALOP en WDP presteerden slechter). Wanneer warmte en stroom van huminen werden geproduceerd, werden er baten gegenereerd voor de NREU, CCP en HTP impactcategorieën. Echter, deze baten waren niet voldoende om de richting van de resultaten te veranderen (e.g., verbeteren van het butadieenproces om zo de petrochemische tegenhanger te overtreffen). De resultaten van de LCA laten ook zien het toepassen van toewijzingen de richting van sommige impactcategorieën verschoof, wat de interpretatie sterk beïnvloed.

Samenvattend, de resultaten van deze thesis bevestigen dat ook al is het technisch mogelijk om biomassa om te zetten in "interessante" chemicaliën, in sommige gevallen de economische en milieuprestaties niet noodzakelijk beter zijn dan die van de petrochemische tegenhanger. Hiermee wordt derhalve benadrukt en bevestigt waarom ex-antebeoordeling van bioraffinaderijen noodzakelijk is voor het identificeren en communiceren van risico's, uitdagingen en kansen van nieuwe technologieën om zo sturing te geven aan technologieontwikkelaars (ter verbetering van prestaties) en beleidsmakers (ter creatie van een stappenplan voor het lange termijngebruik van biomassa).

8.4. BEPERKINGEN VAN HET ONDERZOEK

In dit proefschrift werden verschillende methodologische bijzonderheden en beperkingen geïdentificeerd. Een gemeenschappelijk aspect was de impact van het gebruik van allocatie op de resultaten en interpretatie. Het effect van allocatie kan worden samengevat op twee hoofdniveaus: het effect van de stroomopwaartse allocatie van de milieueffecten van de grondstoffen op de milieuprestaties van de stroomafwaartse producten, en het gebruik van allocatie binnen de systeemgrenzen van de beoordeelde systemen.

De hoofdstukken 2, 3 en 6 toonden voor het eerste niveau aan dat het rapporteren van stroomopwaartse data van de levenscyclusimpact van grondstoffen was vereist. In dit proefschrift bleek de allocatie van de stroomopwaartse milieueffecten aan de grondstoffen een significant effect te hebben op de uitkomst van de analyse. Een duidelijk voorbeeld hiervan is te vinden in hoofdstuk 2, waarin de stroomopwaartse kosten, de CED en de uitstoot van broeikasgassen van koolhydraten (vóór hun omzetting in de beoogde chemicaliën) werden toegewezen volgens twee benaderingen (massa allocatie en economische allocatie), welke gepaard gingen met beduidend verschillende resultaten. Dit effect is ook duidelijk in hoofdstuk 6, waar de aanpak van de allocatie van de stroomopwaartse milieueffecten aan C6-suikers (de voornaamste grondstof) invloed had op de uiteindelijke vergelijking van de stroomafwaartse producten (d.w.z. caprolactam en butadieen) met de petrochemische tegenhangers.

Voor het tweede niveau toonden de hoofdstukken 4 en 6 aan dat het gebruik van allocatie een grote invloed heeft op de resultaten en vooral op de interpretatie hiervan. Bioraffinaderijen zijn multifunctionele systemen waarbij het gebruik van allocatie in de meeste gevallen niet kan worden vermeden. Het beoordelen van de milieuprestaties op systeemniveau (wanneer er geen allocatie werd toegepast) maakte het mogelijk om de belangrijkste brandhaarden en knelpunten van de technologieën in vergelijking met de referentiesystemen te identificeren. Bovendien maakte dit het ook mogelijk om een duidelijker beeld te krijgen van de interpretatie van resultaten wanneer allocatie werd toegepast, omdat in sommige gevallen het gebruik van allocatie ten onrechte het relatieve verschil van een product ten opzichte van het referentieproduct verhoogde.

De beoordelingen van de multiproduct-systemen maakten het ook mogelijk om de belangrijkste uitdagingen in de toepassing van allocatie in geïntegreerde systemen met meerdere producten te identificeren, omdat deze complexer waren dan de beoordeling van op zichzelf staande processen voor één product. In dit proefschrift werden de techno-economische evaluaties van complexe multiproduct-systemen uitgevoerd door middel van het analyseren van de individuele productielijnen binnen het geïntegreerde multiproduct-systeem. In hoofdstuk 5 waren bijvoorbeeld butadieen en caprolactam de belangrijkste proceslijnen, maar deelden deze gezamenlijke grondstoffen en ondersteunende productiesystemen (wanneer humins werden gevaloriseerd). Dit impliceerde de noodzaak om een interne indelingsbenadering toe te passen om de systeemgrenzen van elk proces te onderscheiden. Dit gebeurde door middel van het alloceren van de C6-suikerinput en utiliteiten op basis van de capaciteit van elk proces. Men zou kunnen stellen dat de evaluatie van systemen met meerdere producten moet gebeuren door alle in- en uitgangen te beschouwen en een gemeenschappelijke NPV te berekenen en later de productiekosten aan de afzonderlijke producten toe te wijzen. Een dusdanige aanpak kan echter ook problematisch zijn, omdat hierdoor mogelijk niet kan worden vastgesteld of een individuele productielijn economisch aantrekkelijk is.

Voor het beoordelen van milieuprestaties is het een complexe taak om individuele productielijnen onder te verdelen in een geïntegreerd multiproduct-systeem. Dit heeft te maken met het feit dat de LCA's die in dit proefschrift zijn uitgevoerd erop gericht waren de voor- en nadelen van producten te presenteren in vergelijking met de petrochemische tegenhangers. Het systeem dat de geïntegreerde productie van butadieen en caprolactam in aanmerking nam, toonde bijvoorbeeld aan dat beide producten gelijkwaardige petrochemische tegenhangers hebben. Voor het uitvoeren van een LCA om het gehele geïntegreerde productiesysteem te evalueren en later te vergelijken met de referentiebenchmark, zou de ontwikkeling van een op fossielen gebaseerde benchmark, waarin zowel coprolactam als butadieen geproduceerd worden, vereist zijn. Dit was niet mogelijk omdat de fossiele productielijnen van butadieen (geproduceerd uit nafta) en caprolactam (geproduceerd uit benzeen) geen gemeenschappelijke grondstof hebben. Dit impliceerde dat een onderverdelingsbenadering werd overwogen (identiek aan die in de techno-economische evaluatie) om de systeemgrenzen van het geïntegreerde proces in twee afzonderlijke productielijnen te verdelen om rekening te houden met de twee functionele eenheden voor de vergelijking van de petrochemische tegenhangers (dwz, kg butadieen en kg caprolactam). Deze benadering is analoog aan het concept van systeemuitbreiding toegepast in zelfstandige systemen, maar dan toegepast op multiproduct-systemen. Het gebruik van allocatie was niettemin nog steeds nodig voor de afzonderlijke onderverdeelde verwerkingslijnen omdat ook andere nevenproducten werden verkregen in elke lijn (bijvoorbeeld ethyleen in de butadieen productielijn, mierenzuur in de caprolactam productielijn). Het voordeel van deze benadering was dat de individuele (hoofd) functies van de systemen konden worden vergeleken met de equivalente petrochemische systemen. Echter moet worden opgemerkt dat de toepassing van deze onderverdelingsbenadering een uitdaging kan zijn wanneer het niveau van massa- en energie-integratie toeneemt, en wanneer het aantal functies groter is.

In dit proefschrift was de schatting van de massa en energiebalansen van de beoordeelde technologieën een belangrijke methodologische stap om input te leveren voor zowel economische als milieutechnische beoordelingen. Procesmodellering werd uitgevoerd voor het maken van deze schatting, wat in sommige gevallen de noodzaak impliceerde om het proces te ontwerpen om de kenmerken van veel van de beoordeelde technologieën te voltooien. Het procesontwerp en -modellering moeten worden uitgevoerd met de hoogst mogelijke resolutie, maar dit hangt af van de expertise en vaardigheden van de uitvoerder. Dit kan een subjectieve invloed hebben op o.a. de inschatting van de efficiëntie van het ontwerp, welke apparatuur feitelijk nodig is, de grootte van de apparatuur en de benodigde materialen, wat van invloed kan zijn op de kwaliteit van de gegevens die tijdens die stap worden gegenereerd.

8.5. AANBEVELINGEN

De in deze dissertatie gepresenteerde resultaten maken aanbevelingen voor beleidsmakers en de wetenschap mogelijk.

8.5.1. Beleid

- De beoordeling van de **milieuprestaties van bioraffinagesystemen** moet zich niet alleen concentreren op het reductiepotentieel van broeikasgassen, maar ook op andere milieuaspecten in de biomassa waardenketen, zoals landgebruik en verdroging. Het terugbrengen van broeikasgassen (*greenhouse gases;* GHGs) leidt niet noodzakelijk tot een positief oordeel van de bioraffinages.
- **De realisatie van bioraffinagesystemen met meervoudige geïntegreerde producten** biedt aantrekkelijke economische en milieuvoordelen boven de implementatie van 'standalone' technologieën.
- **De ontwikkeling van vroege marktscenario's voor bio-based producten** moeten meegenomen worden in de beoordeling van de economische potentie van op multiproduct biomassa-implementatietechnologieën. De economische duurzaamheid van multiproduct bioraffinagesystemen hangt in grote mate af van de inkomsten van het product, waarvan de markten nog steeds onzeker zijn. Derhalve zou de vroege identificatie van potentiële applicaties en marktpenetratie van nieuwe producten het mogelijk maken bijkomende risico's van en kansen voor de ontwikkeling van nieuwe bio-based systemen te identificeren.
- **De beoordeling van onzekerheden van nieuwe technologieën in bioraffinages**

moet benoemd worden in de rapportage van risico's behorende bij de transitie van vroege naar late ontwikkelingsstadia. Aspecten zoals onzekerheden in schattingen van kapitaalkosten moeten nauwlettend gevolgd worden.

8.5.2. Verder onderzoek

- Aanvullend werk is nodig voor het begrijpen van de **synergieën in en de impact van biomassatoevoer** op de techno-economische en milieuprestaties van grootschalige multiproduct bioraffinagesystemen. Ondanks lopend onderzoek over biomassatoevoer voor het identificeren van knelpunten en hotspots gerelateerd aan biomassawinning en –logistiek, gaat de meeste aandacht uit naar het genereren van bio-energie. Het zou echter waardevol zijn de toevoereisen van biomassa te begrijpen om de grootschalige bruikbaarheid van multiproduct bioraffinages te verzekeren. Dit zou de beoordeling mogelijk maken van de en milieu- en economische impact van aan biomassatoevoer gerelateerde aspecten zoals (onder anderen) seizoensgebondenheid, contracteren van en toegang tot grondstoffen, limitaties in transportinfrastructuur, meervoudige grondstofoperabiliteit en arbeidsintensiteit. Dit type analyse zou het mogelijk maken nieuwe opkomende technologieën in de context van specifieke landen/regio's te plaatsen.
- Uitdagingen om **end-of-life milieu-impact van bio-based chemicaliën** te beoordelen en te begrijpen blijven aanwezig. De ontwikkeling van scenario's van de gebruiksfase van chemicaliën afgeleid van biomassa is nodig voor het beoordelen van het mitigatiepotentieel op de lange termijn van nieuwe bio-based producten in vergelijking met traditionele bio-based producten en fossiele producten met vergelijkbare functionaliteit.
- Het onderzoeken van de **methodologische implicaties van het gebruik van allocatie** van multiproduct bioraffinages moet worden voortgezet. De in deze dissertatie verschafte inzichten maken het identificeren van de grote invloed van de allocatie op de resultaten mogelijk. De impact van meerdere allocatiebenaderingen voor het beoordelen van milieu-impacts van sterk geïntegreerde bioraffinagesystemen met meerdere functies, maakt het aldus mogelijk een methodologische richtlijn te ontwikkelen voor de milieubeoordeling van complexe bioraffinages.

CHAPTER 9

Resumen, conclusiones y recomendaciones

9.1. ANTECEDENTES

Las lecciones aprendidas por el uso a grande escala de biocombustibles de 1G y otros usos tradicionales de biomasa, han llevado a la comunidad BBE (bioeconomía) a enfocarse en nuevas fuentes de materias primas (con alta atención en biomasa lignocelulósica, 2G) cubriendo un alto rango de bioproductos incluyendo materiales y químicos [7, 8, 10], y la adopción de biorefinerías [11, 12].

El desarrollo sostenible de biorefinerías requiere mirar más allá de las configuraciones de proceso. Además, las biorefinerías han sido frecuentemente y erróneamente consideras sostenibles solo por la característica renovable de la biomasa [35, 37]. En este contexto, la evaluación ex-ante de biorefinerías en etapas tempranas de desarrollo es relevante para proveer aportes útiles respecto a su desempeño prospectivo desde una perspectiva de sostenibilidad (cubriendo aspectos técnicos, económicos y ambientales, y en algunos casos aspectos sociales [9, 35, 36, 38, 39]), incluso cuando el conocimiento y disponibilidad de información relacionada con las tecnologías, productos, mercado, materias primas es limitada [34].

9.2. OBJETIVOS

El objetivo principal de esta tesis era generar aportes detallados de los factores clave que afectan el desempeño tecno-económico y ambiental de nuevas tecnologías para la producción de bioquímicos. Los siguientes tres objetivos fueron formulados,

1. Desarrollar métodos de evaluación y selección que puedan abordar nuevas rutas de conversión bioquímica para la producción de químicos y proveer aportes respecto a sus desempeños tecno-económicos y ambientales.
2. Evaluar la importancia y los retos del pretratamiento de biomasa en el desempeño de biorefinerías basadas en carbohidratos.
3. Identificar y evaluar los compromisos de configuraciones independientes vs. integradas en el desempeño económico y ambiental de biorefinerías.

La Tabla 7.1 muestra un resumen de los capítulos de la tesis y los objetivos que estos abordan.

9.3. RESULTADOS PRINCIPALES Y CONCLUSIONES

Esta sección muestra un resumen de los principales resultados y conclusiones de esta tesis por cada objetivo.

Objetivo 1

Desarrollar métodos de evaluación y selección que puedan abordar nuevas rutas de conversión bioquímica para la producción de químicos y proveer aportes respecto a sus desempeños tecno-económicos y ambientales.

Resultados clave

El **capitulo 2** mostro el uso y la flexibilidad del método a etapas tempranas de evaluación y selección para evaluar bioquímicas producidos tanto ruta química como ruta bioquímica. La Figura 7.1 muestra un resumen del método en etapas tempranas de evaluación y selección, el cual incluye tres indicadores de sostenibilidad: restricción económica (EC, siglas en ingles), impactos relacionados con energía de las materias primas (EIRM, siglas en ingles) y complejidad del proceso (PC, siglas en ingles). Ambos, los indicadores EC y EIRM se mantuvieron idénticos como en el método original [85]. El elemento novedoso fue la re-exanimación del indicar PC, el cual tenía como objetivo imitar los costos e impactos ambientales que ocurren en la etapa de procesamiento. Como se definió originalmente, no todos los procesos de separación (para recuperar los productos principales) están basados en la coexistencia de la fase liquido-vapor (*p.ej.,* destilación), cuyo criterio fue usado en el indicador original. Procesos complejos de separación pueden significativamente contribuir al incremento de costos e impactos ambientales en la etapa de procesamiento. Para tener en cuenta estas posibles situaciones, se desarrolló una subcategoría del indicador PC llamada Procesos de Separación (Downstream Processing). Además, las sub-categorías restantes del indicador PC (es decir, concentración de producto, índice de pérdida de masa, entalpia de reacción, número de co-productos y presión de reacción) fueron revisados y adaptados para que fuesen representativos para procesos de conversión química y bioquímica (ver el capítulo 2).

El método adaptado fue probado en 36 rutas (capitulo 2) para la conversión de bio-gas de síntesis, carbohidratos y glicerol. Las rutas fueron categorizadas en tres grupos: favorable (Grupo I), promisorio (Grupo II) y desfavorable (Grupo III). El grupo I incluye rutas que tienen alto potencial de sostenibilidad para la alternativa bio en comparación a la petroquímica. El grupo II incluye rutas para las cuales las ventajas no son substanciales, pero donde mejoras tecnológicas y económicas puedan conllevar a un mejor desempeño para las alternativas bio. El grupo III incluye rutas con bajo potencial de sostenibilidad para las alternativas bio. El método permitió incluir análisis de sensibilidad para probar la solidez de los resultados (categorización) a cambios en datos de entrada (p ej., precios y rendimientos) y suposiciones (p ej., distribución de costos de operaciones previas), y análisis de escenarios para tener en cuenta los aspectos específicos de las cadenas de valor relacionadas con cada proceso de conversión, como el impacto de los precios de las materias primas en diferentes regiones.

El **capítulo 3** mostró como el método a etapas tempranas de evaluación y selección fue no solamente aplicable a rutas de conversión independientes, sino también a rutas con múltiples etapas de conversión y biorefinerías multi-producto. El método fue primero aplicado a la producción de isobutanol comparando la ruta bio usando astillas de picea como materia prima, con la ruta fósil que usa metano como materia prima. Los resultados indicaron ventajas de la ruta bio en comparación con la fósil. El método también fue aplicado a tres sistemas multiproducto a partir de la conversión de isobutanol: Caso 1: producción de acetato de isobutilo y glicerol tert-butil éter (GTBE); Caso 2: producción de acetato de isobutilo y cetonas, y Caso 3: producción de acetato de butilo y alcanos. El método fue efectivo para comparar configuraciones de biorefinerías. Además, el método permitió la identificación de los factores clave que afectan cada ruta de conversión individual, y su impacto sobre el desempeño general del sistema integrado multiproducto.

El método permitió agrupar los indicadores en aspectos económicos y ambientales (ver Figura 7.3), y evaluar el impacto de diferentes pesos en el resultado final. Los resultados mostraron que cuando hay mayor peso a los aspectos ambientales, los sistemas bio tienden a mostrar más ventajas que las contrapartes petroquimicas. En cambio, cuando se incrementó el peso hacia aspectos económicos, los resultados indicaron que los beneficios de las rutas bio fueron limitados en comparación con las rutas petroquímicas. Esto mostró que los aspectos ambientales necesitas estar adecuadamente balanceados en las evaluaciones ex-ante para comprensivamente entender las ventajas y desventajas de las rutas bio en comparación con las rutas fósiles.

Objetivo 2

Evaluar la importancia y los retos del pretratamiento de biomasa en el desempeño de biorefinerías basadas en carbohidratos.

Resultados clave

La evaluación en el **capítulo 3** incluyo el fraccionamiento organosolv de picea como etapa de conversión primaria antes de la sacarificación de la pulpa, y despúes fermentación (de los carbohidratos) hacia isobutanol. El análisis llevado a cabo en el capítulo 3 permitió la identificación (al nivel de selección), los factores que tenían la mayor influencia en el desempeño de la tecnología organosolv: altos requerimientos de agua para diluciones (lo cual resulto en baja concentración de sustratos y productos), la necesidad de recuperar y recircular el solvente, la presencia de una fracción solida de biomasa no transformada, alta presencia de azucares derivados de la hemicelulosa con alta concentración de inhibidores (considerado como agua residual), y la alta influencia de las ventas de lignina en el desempeño económico de los sistemas (sumando hasta el 38% de las ventas totales, ver el capítulo 3). En el **capítulo 4** se llevó a cabo un análisis detallado que brindo conocimiento acerca de los desempeños técnico, económico y ambiental de la tecnología organosolv en comparación a la tecnología de molienda en húmedo del maíz, para la producción de azucares C6. Los balances de materia revelaron que uno de los retos del fraccionamiento de epicea era que el 52% de la masa inicial de biomasa seca estaba saliendo del sistema como residuo en la forma de solidos no convertidos y azucares de hemicelulosa altanamente diluidos. En un esfuerzo para mejorar el sistema organosolv y hacer uso de esas dos corrientes, la producción de biogás (para producir calor y energía eléctrica) fue incluida. Esta mejora mostro tener un importante impacto en la eficiencia energética del proceso organosolv pues hasta el 95% del vapor requerido, y 100% de la electricidad requerida fueron cubiertas por el biogás.

La tecnología organosolv (acoplada con la producción de biogás) mostro ser viable con NPV positivo (238 M€) que aquel del sistema de molienda húmeda (168 M€) (a precios base de azucares 300 €/tonelada y lignina 630 €/tonelada, ver capítulo 4). Sin embargo, la tecnología organosolv también mostro una más alta inversión de capital (236 M€) comparado con la molienda húmeda (55 M€), lo cual resulta en periodos más prolongados para recuperar la inversión (ver Figura 7.4). Se encontró que el desempeño económico de la tecnología organosolv es muy sensible a cambios en los precios de lignina, azucares C6 y precios de biomasa, al igual que cambios en inversiones de capital. El efecto de ambos, inversiones de capital y ventas de lignina fueron encontrados como factores clave que necesitan monitoreo para promover el desarrollo de la tecnología. En literatura, se encontró que estudios reportando los costos de capital para organosolv mostraban una diferencia de hasta 126 M€ (detalles en el capítulo 4), reflejando la gran incertidumbre en los equipos requeridos y sus costos a largas escalas (1000 ktoneladas/año). Esto puede convertirse en una barrera importante, pues en general, las tecnologías que transicionan a etapas de desarrollo mayores son más costosas debido a las incertidumbres durante las fases de diseño [259], y para la tecnología organosolv esto implicaría un alto riesgo económico. En el caso de lignina, incluso si su precio se espera que sea mayor (comparado con lignina kraft o lignosulfonada) por su alto potencial para aplicaciones con alto valor agregado [260], vale la pena mencionar que su mercado no está aun totalmente desarrollado. Los resultados del análisis tecno-económico llevado a cabo en el capítulo 4 sugirieron que se debe tener en cuenta que tecnologías de 2G son más costosas y con mayores riesgos que las tecnologías de 1G, y que la transición a sistemas de 2G deben estar acompañados por incentivos para su desarrollo (p ej., incentivos de mercado, primas verdes).

La evaluación ambiental del **capítulo 4** se llevo a cabo siguiendo un análisis de ciclo de vida (LCA siglas en ingles) de la cuna-a la-puerta prospectivo, de las tecnologías organosolv y molienda húmeda para producir azucares C6. El análisis se llevo a cabo para las categorías de impacto potencial de cambio climático (CCP), potencial de agotamiento de agua (WDP), potencial de ocupación de tierra agrícola (ALOP), potencial de toxicidad humana (HTP) y uso de energía no-renovable (NREU). Los resultados mostraron que mejorando la eficiencia energética del sistema organosolv tenía un efecto positivo en la reducción de los impactos ambientales de las categorías CCP, NREU y HTP, las cuales se mantenían más bajas que aquellas de la tecnología de molienda húmeda. En general, los resultados indicaron que la tecnología organosolv mostraba un desempeño ambiental relativamente mejor que la tecnología de molienda húmeda del maíz. El análisis llevado a cabo en el **capítulo 6** también siguió un LCA prospectivo de la cuna-a la- puerta (para las mismas categorías de impacto que en el capítulo 4), para la producción de butadieno y caprolactam a partir de azucares c6, el cual considero el efecto de usar azucares derivados de maíz y picea. Los resultados mostraron que los azucares C6 derivados de picea fueron preferidos por encima de los derivados de maíz.

Objetivo 3

Identificar y evaluar los compromisos de configuraciones independientes vs. integradas en el desempeño económico y ambiental de biorefinerías.

Resultados clave

Las evaluaciones tecno-económicas y ambientales llevadas a cabo en el **capítulo 4** brindaron conocimiento en referencia al impacto de la valorización de corrientes residuales como una opción para mejorar la competitividad y el desempeño ambiental de sistemas de conversión de biomasa. En el capítulo 4, el uso de los sólidos no-convertidos y azucares de hemicelulosa para producir vapor y electricidad, mostro ser efectivo para disminuir la intensidad energética del proceso organosolv. Esto implico la reducción en el uso de fuentes de energía externa y por lo tanto, los costos operacionales y las categorías de impacto como CCP, NREU y HTP también se redujeron. La evaluación permitió la identificación de los compromisos tanto ambientales como económicos. Por ejemplo, la intensificación del proceso (incluyendo la producción de vapor y electricidad) implico que mayores inversiones eran requeridas (hasta el 12% mayor en comparación al caso base). Se debe tener en cuenta que esta no es siempre la dirección en el desarrollo de cada configuración que desee integrar nuevas líneas de proceso y/o agregar valor a corrientes producidas en el mismo. Una de las recomendaciones es por ejemplo, evaluar los compromisos económicos entre los requerimientos de capital, costos operacionales y ventas en la opción proyectada integrada. Esto permite entender si los costos de inversión adicional son realmente compensados por los ahorros en costos operacionales.

El **capitulo 5** evaluó el desempeño tecno-económico de la producción integrada de butadieno y caprolactam a partir de azucares C6. El proceso de butadieno mostro un desempeño económico negativo (con valores de NPV negativos para los casos evaluados), con costos de producción hasta 3-5 veces mayores que los precios de referencia en el mercado (900 €/tonelada). El análisis de sensibilidad permitió la identificación de la dependencia del desempeño económico del proceso de butadieno en las ventas de butadieno y etileno, y la alta sensibilidad a cambios en los precios de azucares C6 e inversión de capital. El análisis también mostro, que a condiciones base, que el proceso de caprolactam fue inviable. Sin embargo, mejorando las selectividades de la etapa γ-valerolactona a caprolactama (rendimiento mejorada hasta 60% comparado con el caso base) resulto en beneficios económicos con costos de producción hasta 6% menores que el precio de referencia en el mercado (2000 €/tonelada). Durante la etapa de conversión a acido levulínico (parte de la línea de proceso de caprolactama), 18% de la masa inicial de azucares C6 terminaron en la forma de humins. Humins son un grupo de compuestos orgánicos con no valor comercial los cuales se consideraron como residuos. De forma similar al enfoque seguido en el capítulo 4, la producción de electricidad y vapor a partir de la combustión de humins fueron considerados en el capítulo 5. Los resultados indicaron que siguiendo este enfoque de integración (es decir, incluyendo la combustión de humins), los costos de producción de ambos butadieno y caprolactam disminuyeron. Uno de los resultados clave fue que cambiando la distribución (análisis de sensibilidad) del flujo de entrada de los azucares C6 para aumentar la capacidad del proceso de caprolactam, los beneficios de incluir la valorización de humins fue más fuerte (disminuyendo mas los costos de producción). Adicionalmente, el proceso de caprolactam se beneficio altamente de la economía de escala mostrando costos de producción por debajo del precio de referencia en el mercado.

La evaluación ambiental en el capítulo 6 se llevo a cabo siguiendo un análisis de ciclo de vida prospectivo de la cuna-a la-puerta de la producción de butadieno y caprolactam a partir de azucares C6. La evaluación fue llevada a cabo para CCP, WDP, ALOP, HTP y NREU. Los resultados mostraron que no hay claras ventajas de bio-butadieno sobre fósil-butadieno, con 4 (CCP, HTP, ALOP y WDP) de las 5 categorías de impacto con valores mayores para los sistemas bio. Solo NREU fue menor para la ruta bio en comparación con la fósil. Los resultados también mostraron que bio-caprolactam tuvo un mejor desempeño que su contraparte petroquímica en 3 (NREU, CCP y HTP) de las 5 categorías de impacto (ALOP y WDP con desempeños negativos). Cuando se produjo calor y electricidad a partir de humins, los beneficios no fueron lo suficientemente fuertes para cambiar la dirección de los resultados (p ej., mejorando el proceso de butadieno para que tenga un mejor desempeño que su contraparte fósil). Los resultados del LCA también indicaron que la aplicación de distribución (allocation en ingles) cambio la dirección de los resultados en algunas categorías de impacto, lo cual afecto fuertemente la interpretación de los resultados.

En general, los resultados de esta tesis confirmaron que incluso si hay potencial técnico para la conversión de biomasa hacia químicos *“interesantes”,* en algunos casos el desempeño económico y ambiental no fueron necesariamente mejores que sus contrapartes de petróleo. Esto, por lo tanto, refleja y confirma por que las evaluaciones ex-ante de biorefinerías son necesarias para identificar y comunicar los riegos, retos y oportunidades de nuevas tecnologías para guiar a desarrolladores (para mejorar su desempeño) y para creadores de políticas (para construir un mapeo del potencial a largo plazo de los usos de biomasa).

9.4. LIMITACIONES DE LA INVESTIGACIÓN

En esta tesis varias particularidades metodológicas y limitaciones fueron identificadas. Un aspecto común fue el impacto del uso de distribución (allocation) en los resultados y en su interpretación. El impacto de distribución puede resumirse en dos niveles principales: el efecto de la distribución de impactos ambientales en operaciones previas (upstream), y el uso de distribución (allocation) dentro de los limites de los sistemas evaluados.

Para el primer nivel, los capítulos 2, 3 y 6 mostraron que era requerida información reportando los impactos de la cuna-a la-puerta de las materias primas. En esta tesis, la distribución de los impactos ambientales en operaciones previas atribuidas a las materias primas mostro tener un efecto significativo en los resultados del análisis. Un claro ejemplo de esto se puede encontrar en el capítulo 2 donde los costos de operaciones previas, CED y emisiones GHG de carbohidratos (antes de su conversión hacia químicos seleccionados) fueron distribuidos siguiendo dos enfoques (distribución basada en masa y valores económicos) lo cual brindo resultados bastante diferentes. Este efecto también se ve en el capítulo 6 donde el enfoque de distribución de los impactos ambientales en operaciones previas atribuidos a los azucares C6 (materia principal) afecto la comparación final de los productos evaluados (es decir, caprolactama y butadieno), y a su vez su comparación con las contrapartes de petróleo.

Para el segundo nivel, los capítulos 4 y 6 mostraron que el uso de distribución (allocation) tiene una amplia influencia en los resultados y mas importante en su interpretación. Las biorefinerías son sistemas multifuncionales donde el uso de distribución no se puede evitar en la mayoría de casos. Evaluando el desempeño ambiental al nivel del sistema (cuando no se aplica distribución) permitió identificar los mayores puntos calientes y cuellos de botella de las tecnologías en comparación a los sistemas de referencia. Además, esto permitió obtener una clara imagen en la interpretación de los resultados cuando se aplico distribución, pues en algunos casos el uso de distribución erróneamente incremento la diferencia relativa de un producto comparado con su producto de referencia.

Igualmente, las evaluaciones de sistemas multiproducto permitieron la identificación de retos clave en los enfoques para aplicar distribución en sistemas integrados pues estos son más complejos que la evaluación de sistemas independientes para un producto. En esta tesis, las evaluaciones tecno-económicas de sistemas multiproducto complejos se llevaron a cabo analizando las líneas de producción individual que los sistemas integrados tenían. Por ejemplo, en el capítulo 5, butadieno y caprolactam fueron las líneas de proceso principales, sin embargo compartiendo materias primas y sistemas de producción de servicios (cuando humins fueron valorizados). Esto implico la necesidad de aplicar un enfoque de subdivisión interna para distinguir los límites del sistema de cada proceso. Esto fue llevado a cabo distribuyendo el flujo de entrada de azucares C6 y los servicios en base a la capacidad de cada proceso. Uno puede discutir que la evaluación de sistemas multiproducto se debe realizar considerando todas las entradas y salidas y calcular un NPV común, y después distribuir los costos de producción a los productos individuales. Sin embargo, ese enfoque puede también ser problemático pues este puede no permitir la identificación de si una línea de producción es económicamente atractiva.

Para las evaluaciones ambientales, para subdividir las líneas de producción individuales contenidas en un sistema multiproducto es una tarea compleja. Esto tiene que ver con el hecho que los LCAs llevados a cabo en esta tesis tenían como objetivo mostrar las ventajas y desventajas de productos comparados con sus contrapartes petroquímicas. Por ejemplo, el sistema que considera la producción integrada de butadieno y caprolactama mostro que ambos productos tienen una contraparte petroquímica equivalente. Para llevar a cabo LCA para evaluar el sistema de producción integrado completo y después compararlo con el sistema de referencia, requeriría el desarrollo de un sistema de referencia fósil que co-produzca caprolactam y butadieno. Esto no fue posible pues las líneas de producción fósil de butadieno (producido de nafta) y caprolactama (producido de benceno) no tienen una materia prima común. Esto implico considerar un enfoque de subdivisión (idéntico al mismo seguido en la evaluación tecno-económica) para dividir los límites del sistema del proceso integrado en dos líneas de producción individual para tener en cuenta las dos unidades funcionales para la comparación de las contrapartes petroquímicas (es decir, kg de butadieno y kg de caprolactama). Nótese que este enfoque es análogo al concepto de expansión del sistema aplicado a sistemas independientes, pero aquí aplicado a sistemas multiproducto. Sin embargo, el uso de distribución fue igualmente requerido para las líneas de proceso sub-divididas pues otros co-productos fueron también obtenidos en cada una (p ej., etileno en la línea de butadieno, acido fórmico en la línea de caprolactama. La ventaja de usar este enfoque fue que las funciones (principales) individuales de los sistemas se pudieron comparar con los sistemas petroquímicos equivalentes. Sin embargo, se debe tener en cuenta que la aplicación del enfoque de subdivisión puede ser complejo cuando el nivel de integración masica y energética incrementa, y cuando el número de funcionalidades es mayor.

En esta tesis, la estimación de los balances de materia y energía de las tecnologías evaluadas fue una etapa metodológica clave para brindar los datos de entrada para ambas las evaluaciones económicas y ambientales. La estimación fue llevada a cabo a través modelamiento de procesos, el cual implico en algunos casos combinar con diseño de procesos para completar aspectos de muchas de las tecnologías evaluadas. A pesar de que el diseño de procesos y su modelamiendo se intento llevar a cabo a la mayor resolución posible, este depende de la experticia y habilidades del analizador. Esto puede traer subjetividad a la estimación de la eficiencia del diseño, que equipos son realmente requeridos, el tamaño de los equipos y las materias primas requeridas entre muchos otros, que afectan la calidad de la información generada en esta etapa.

9.5. RECOMENDACIONES

Los resultados presentados en esta tesis permitieron identificar recomendaciones para desarrolladores de políticas e investigación.

9.5.1. Políticas

- La evaluación de el **desempeño ambiental de sistemas de biorefinerías** no debe solo enfocarse en la reducción del potencial de emisiones de gases de efecto invernadero (GHG), sino también en otros aspectos ambientales como el uso de tierra y agotamiento de agua a través de la cadena de valor de biomasa. La reducción de emisiones GHG no necesariamente implica que la perspectiva ambiental de biorefinerías es positiva.
- **El uso de sistemas de biorefinerías integrado multiproducto** ofrece beneficios económicos y ambientales sobre el uso de tecnologías independientes. Sin embargo, los compromisos económicos y ambientales de los diferentes niveles de integración y la inclusión de líneas de proceso para la valorización de residuos deben monitorearse cercanamente.
- **El desarrollo de escenarios tempranos de mercado de productos bio novedosos** se debe tener en cuenta cuando se evalúa el potencial económico de tecnologías que usan biomasa hacia múltiples productos. La sostenibilidad económica de sistemas multiproducto de biorefinerías dependen altamente en las ventas de productos cuyos mercados aun son inciertos. Por lo tanto, la identificación temprana de potenciales aplicaciones y penetración en el mercado de productos novedosos permitiría la identificación de riesgos adicionales y oportunidades para el desarrollo de nuevos sistemas bio.
- **La evaluación de incertidumbres de nuevas tecnologías en biorefinerías** se debe tener en cuenta cuando se reportan los riesgos asociados a la transición desde etapas

de desarrollo tempranas hacia etapas mayores. Aspectos como incertidumbres en la estimación de costos de capital necesitan ser monitoreados cercanamente.

9.5.2. Investigación futura

- Trabajo adicional es requerido para entender las **sinergias e impactos del suministro de biomasa** sobre los desempeños tecno-económicos y ambientales de sistemas de biorefinerías multiproducto. A pesar que actualmente se está llevando a cabo investigación acerca de suministro de biomasa para identificar cuellos de botella y puntos calientes relacionados con la colección de biomasa y su logística, la gran parte de su atención esta focalizada en la producción de bioenergía. Sin embargo, sería de gran ayuda entender los requerimientos de suministro de biomasa para asegurar la operatividad de biorefinerías multiproducto a largas escalas. Esto permitiría la evaluación de los impactos económicos y ambientales relacionados con aspectos como el efecto de las temporadas (estaciones), contratación y accesibilidad a las materias primas, limitaciones en infraestructuras de transporte, operatividad con múltiples materias primas e intensidad laboral entre otras. Este tipo de análisis permitiría la contextualización de nuevas tecnologías emergentes a países/regiones específicas.
- Aun existen retos presentes para evaluar y entender **los impactos ambientales al final-de-vida de bioquímicos.** El desarrollo de escenarios de la fase de uso de químicos derivados de biomasa es requerido para evaluar si hay potencial de mitigación a largo plazo de nuevos productos bio en comparación a productos bio tradicionales y productos fósiles con funcionalidades similares.
- La investigación de las **implicaciones metodológicas del uso de distribución (allocation)** en biorefinerías multi-producto debe continuarse. El conocimiento proporcionado en esta tesis permite la identificación de la gran influencia de distribución en los resultados. Por lo tanto, el impacto de múltiples enfoques de distribución para evaluar los impactos ambientales de sistemas de biorefinerías altamente integradas con múltiples funcionalidades, permitiría el desarrollo de una directriz metodológica acerca la evaluación ambiental de biorefinerías complejas.

Acknowledgements

The support and involvement of many people was a key factor to go through this exciting journey of completing this PhD thesis. I am very thankful to my supervisors, partners in all the projects I participated, colleagues, friends and family who have helped me to keep on track on my research and to find happiness in the minor details of life.

I would like to thank the reading committee for reading and assessing my PhD thesis.

Andrea, as my promotor, you were always enthusiastic, optimistic and always kept my motivation high in the difficult moments. The critical discussions with you were always enlightening and encouraging towards the end of the road. I admire your capacity to make time and keep the quality and critical discussion with your students, even when you were not working at Utrecht University. I specially thank you for all the trust you deposited in me to deal with projects and bring my own ideas into my research. This gave an extra boost to my experience in the academic world. Nothing of my thesis would have been possible without your help. Thank you for everything,

Ernst, I am especially thankful with you for joining this PhD journey as my promotor. The open and critical discussions towards the completion of my PhD thesis were very important to me. I truly appreciate your support during the final moments to keep my motivation high and finish the final bits. I admire your capacity in your your speed to provide feedback with an eye on the great picture and the happiness and optimism that you always reflect. I particularly enjoyed our meetings which generally finished a laugh after a short anecdote about the Dutch weather. Thank you for all your support.

Iris, I have enjoyed our discussions and meetings regarding all the work done to shape the ideas on my thesis. Thanks for joining as my co-promotor, even if that was in the middle of the road. Thanks for your trust and for discussing with me the ideas I was bringing onto the table for both research and supervision of master students. Thank you for your patience and for keeping a critical eye on the details of my research.

I would also like to thank John who was very important to shape the foundations of my thesis. I am really thankful for your trust and your availability to discuss on the roadmap of biorefinery assessments. I have enjoyed working with you and special thanks for your large contribution in this thesis. Thank you for giving me the opportunity to work with you.

I am also thankful for the contributions of all people involved in the projects in which I have participated. Sjaak, Adrie, Raimo, Ana (IBPR), Jan Wilco, Wouter, Marija, Paul, Constantino (Catchbio), Miklos, Ana, Fabian, Ben, Hans, Marcel, Aurora, José, Ana, Jordan, Balaz (MAB 2.0), and all others: Thank you very much.

I would also like to thank to the people at the Energy & Resources group within the Copernicus Institute of Sustainable Development at Utrecht University. The group is a massive moving machine which works so well due to the great quality of researchers and staff, but most importantly due to the great human beings that are part of it. I have enjoyed both academic and non-academic moments which enhanced my experience working for Utrecht University. I would like to thank to Ana, Steven, Hu Jing, Tarek, Blanca, CS, Pannos, Ric, Floor, Birka, Bhavya, Martin J, Marnix, Martijn, Ioannis L, Ioannis T, Odysseas, Marc, Gert-Jan J, Niels, Barbara, Carina, Rosalien, Bas, Wil, Pita, Christian, Sierk, Mijndert, Lotte, Geert, and all the others. My Dutch colleagues who helped me to translate my conclusions from English into Dutch deserve a special mention here. Thanks a lot for your help Wouter Schakel, Wouter Schram, Anna, Gijs and Mariska. I would also to thank Aisha for all her mental support and always being kind to help me in all the administrative issues. I also thank to Fiona and Siham for helping me with all my questions and paper work when I needed it.

During my time as PhD I have the opportunity to contribute in courses and supervision of master students. Li, thank you for trusting me and allowing me to contribute with my ideas to both your courses and supervision of a master thesis. I enjoyed and learned a lot working with you. Evert, I have enjoyed participating in your courses both assisting in exercise classes and home assignments. I have learned a lot. Special thanks to Katelin and Simone. I enjoyed and learned a lot supervising your master theses.

I am grateful to have shared an office with great colleagues. Thank you Cora, Jana, Hans, Asier, Kostis, Mariska and Alexa. I enjoyed the great working environment and the multicultural discussions we had across the road.

I am very grateful to my paranymphs Jorge and Jesus, as we are not only colleagues but also good friends with whom I have shared very good moments.

Beyond the university world, there are many people who supported me and helped me to keep my mental health. Thanks a lot to John, Diana, Jorge, Ana, Yeczain, Valeria, Vanessa, Sebastian, Diego, Monika, Simone, David, Rody, Sanny, Anja, Karine, Kiera, Markus, Mike, Clem and all others. Thanks for sharing holidays, dinners, drinks, parties, concerts, festivals, world cups and memorable times.

En la distancia se encuentra un grupo de personas que han sido uno de los ejes fundamentales de mi vida, mi Familia. Mi familia me ha apoyado incondicionalmente en todos los momentos de mi doctorado y ha sido vital para mantener la estabilidad emocional y mental al mudarme a un nuevo país. Les agradezco con todo mi corazón por su apoyo y ayuda. Un especial agradecimiento a mi padre Marino, a mi madre Adiela, a mis hermanas Carolina y Paola, a mi sobrino José David y a mi abuela Ines. Gracias por no dejarme desfallecer pero sobre todo por haberme guiado en una vida que siempre ha tenido los valores como fundamento. Quiero también dar un especial agradecimiento a mi más reciente familia por preocuparse por mi bienestar. Martha Nury, José Hernán, Camila, Jorge Hernán, Nancy y Valentina. Infinitas gracias.

Mis amigos de la vida han contribuido de una manera muy importante en todos los momentos especiales y esta no es una excepción. Quiero hacer un agradecimiento especial a David Angulo, quien ha seguido desde el colegio un camino académico similar al mío, y con quien he tenido la fortuna de hacer las más grandes locuras en Europa. A mis amigos David D, Sergio, Daniel, Cesar, Ángela I, Sebastián A, Alejandro y Esteban gracias por siempre estar ahí.

Last but most importantly, I would like to thank and dedicate this work to my beloved wife Ximena. She has always been a light to me. Thank you for supporting me in all moments of stress, for helping me everyday to be a better man, and for coping with all my feelings and emotions about my research. This thesis would have not been possible without all your patience and comprehension. Thanks a lot for always being there. This PhD means a lot to both as it gave us the opportunity to rejoin our journeys once again. Je t'aime.

About the author

Jonathan Moncada Botero was born on February 12, 1988 in Manizales, Colombia. He completed the BSc program in Chemical Engineering at the National University of Colombia in Manizales (graduated in 2011). At the same University, he completed the MSc program in Chemical Engineering, with a *cum laude* thesis (graduated in 2013). In 2014, he became junior researcher/PhD candidate at the Energy & Resources group of the Copernicus Institute of Sustainable Development at Utrecht University. He was involved in four research projects (2014-2017) mostly on the techno-economic and environmental assessments of technologies for producing biobased chemicals, materials and fuels. During his academic career, he has published several articles in scientific journals. As of January 2018, he became consultant for the Food and Agricultural Organization of the United Nations (FAO).

PUBLICATIONS

Publications involved in this thesis

Moncada J., Vural Gursel I., Worrell E., Ramirez A. 2018. Production of 1,3-Butadiene and ε-Caprolactam from C6 sugars. Techno-economic analysis. In press. Biofuels, bioproducts & biorefining.

Moncada J., Vural Gursel I., Huijgen WJJ., Dijkstra JW., Ramirez A. 2018. Techno-economic and ex-ante environmental assessment of C6 sugars production from spruce and corn. Comparison of organosolv and wet milling technologies. Journal of Cleaner Production, 170, p610-624

Moncada J., Posada JA., Ramirez A. 2017. Comparative early stage assessment of multiproduct biorefinery systems: An application to the isobutanol platform. Bioresource technology, 241, p44-53.

Moncada J., Posada JA., Ramirez, A. 2015. Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals. Biofuels, Bioproducts & Biorefining, 9, p722-748.

Other publications (selected)

Moncada J., Aristizabal V., Cardona CA. 2016. Design strategies for sustainable biorefineries. Biochemical Engineering Journal, 116, p122-134.

Moncada J., Cardona CA., Higuita JC., Vélez JJ., López-Suarez FE. 2016 Wood residue (*Pinus patula* bark) as an alternative feedstock for producing ethanol and furfural in Colombia: experimental, techno-economic and environmental assessments. Chemical Engineering Science, 140, p309-318.

Moncada J., Tamayo JA., Cardona CA. 2014. Integrating first, second, and third generation biorefineries: Incorporating microalgae into the sugarcane biorefinery. Chemical engineering science, 118, p126-140.

Moncada J., Tamayo JA., Cardona CA. 2014. Evolution from biofuels to integrated biorefineries: techno-economic and environmental assessment of oil palm in Colombia. Journal of cleaner production, 81, p51-59.

Moncada J., El-Halwagi MM., Cardona CA. 2013. Techno-economic analysis for a sugarcane biorefinery: Colombian case. Bioresource Technology, 135 (Special Issue: Biorefineries), p533-543.

References

1. IEA. International Energy Agency. Key World Energy Statistics. 2017;Paris, France:1-95.
2. IPCC. Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Geneva, Switzerland. 2014.
3. Scarlat N, Dallemand J-F, Monforti-Ferrario F, Nita V. The role of biomass and bioenergy in a future bioeconomy: Policies and facts. Environmental Development. 2015;15:3-34.
4. OECD. The bioeconomy to 2030: designing a policy agenda, main findigs. OECD Observer. 2009;Organization for Economic Cooperation and Development (OECD), Paris, France.
5. de Besi M, McCormick K. Towards a bioeconomy in Europe: National, regional and industrial strategies. Sustainability. 2015;7(8):10461-78.
6. EC. European Commission. Innovating for Sustainable Growth: A Bioeconomy for Europe, Brussels, Belgium. 2012.
7. Havlík P, Schneider UA, Schmid E, Böttcher H, Fritz S, Skalský R, et al. Global land-use implications of first and second generation biofuel targets. Energy Policy. 2011;39(10):5690-702.
8. Parajuli R, Dalgaard T, Jørgensen U, Adamsen APS, Knudsen MT, Birkved M, et al. Biorefining in the prevailing energy and materials crisis: a review of sustainable pathways for biorefinery value chains and sustainability assessment methodologies. Renewable and Sustainable Energy Reviews. 2015;43:244-63.
9. Moncada B J, Aristizábal M V, Cardona A CA. Design strategies for sustainable biorefineries. Biochemical Engineering Journal. 2016;116:122-34.
10. Moncada J, Tamayo J, Cardona CA. Evolution from biofuels to integrated biorefineries: techno-economic and environmental assessment of oil palm in Colombia. Journal of Cleaner Production. 2014;81:51-9.
11. Cherubini F. The biorefinery concept: using biomass instead of oil for producing energy and chemicals. Energy Convers Manage. 2010;51(7):1412-21.
12. Cherubini F, Jungmeier G, Wellisch M, Willke T, Skiadas I, Van Ree R, et al. Toward a common classification approach for biorefinery systems. Biofuels Bioprod Bioref. 2009;3(5):534-46.
13. Maity SK. Opportunities, recent trends and challenges of integrated biorefinery: Part II. Renewable and Sustainable Energy Reviews. 2015;43:1446-66.
14. Chowdhury R, Ghosh S, Debnath B, Manna D. Indian Agro-wastes for 2G Biorefineries: Strategic Decision on Conversion Processes. In: De S, Bandyopadhyay S, Assadi M, Mukherjee DA, editors. Sustainable Energy Technology and Policies: A Transformational Journey, Volume 1. Singapore: Springer Singapore; 2018. p. 353-73.
15. Krzyżaniak M, Stolarski MJ, Waliszewska B, Szczukowski S, Tworkowski J, Załuski D, et al. Willow biomass as feedstock for an integrated multi-product biorefinery. Industrial Crops and Products. 2014;58:230-7.
16. Cherubini F, Strømman AH. Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems. Biofuels Bioprod Bioref. 2011;5(5):548-61.
17. Kudakasseril Kurian J, Raveendran Nair G, Hussain A, Vijaya Raghavan G. Feedstocks, logistics and pre-treatment processes for sustainable lignocellulosic biorefineries: A comprehensive review. Renewable Sustainable Energy Rev. 2013;25:205-19.
18. de Jong E, Higson A, Walsh P, Wellisch M. Bio-based Chemicals Value Added Products from Biorefineries. IEA Bioenergy, Task42 Biorefinery. 2012.

19. Taylor R, Nattrass L, Alberts G, Robson P, Chudziak C, Bauen A, et al. From the sugar platform to biofuels and biochemicals. Final report for the European Commission Directorate-General Energy NENER. C2/423-2012/SI2. 673791, 2015.
20. Jung KA, Lim S-R, Kim Y, Park JM. Potentials of macroalgae as feedstocks for biorefinery. Bioresource technology. 2013;135:182-90.
21. Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "top 10" revisited. Green Chem. 2010;12(4):539-54.
22. Luo L, van der Voet E, Huppes G. Life cycle assessment and life cycle costing of bioethanol from sugarcane in Brazil. Renewable and Sustainable Energy Reviews. 2009;13(6–7):1613-9.
23. Kudakasseril Kurian J, Raveendran Nair G, Hussain A, Vijaya Raghavan GS. Feedstocks, logistics and pre-treatment processes for sustainable lignocellulosic biorefineries: A comprehensive review. Renewable and Sustainable Energy Reviews. 2013;25:205-19.
24. Menon V, Rao M. Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. Progress in Energy and Combustion Science. 2012;38(4):522-50.
25. Zakzeski J, Bruijnincx PC, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. Chemical reviews. 2010;110(6):3552-99.
26. Schutyser W, Renders T, Van den Bosch S, Koelewijn SF, Beckham GT, Sels BF. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chemical Society Reviews. 2018;47(3):852-908.
27. Harun R, Danquah MK. Enzymatic hydrolysis of microalgal biomass for bioethanol production. Chemical Engineering Journal. 2011;168(3):1079-84.
28. Lozano FJ, Lozano R. Assessing the potential sustainability benefits of agricultural residues: Biomass conversion to syngas for energy generation or to chemicals production. Journal of Cleaner Production. 2018;172:4162-9.
29. Benalcázar EA, Deynoot BG, Noorman H, Osseweijer P, Posada JA. Production of bulk chemicals from lignocellulosic biomass via thermochemical conversion and syngas fermentation: a comparative techno-economic and environmental assessment of different site-specific supply chain configurations. Biofuels, Bioproducts and Biorefining. 2017;11(5):861-86.
30. Cai CM, Zhang T, Kumar R, Wyman CE. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. Journal of Chemical Technology and Biotechnology. 2014;89(1):2-10.
31. Aristizábal V, Gómez Á. Biorefineries based on coffee cut-stems and sugarcane bagasse: Furan-based compounds and alkanes as interesting products. Bioresource technology. 2015;196:480-9.
32. Mika LT, Cséfalvay E, Németh Á. Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. Chemical Reviews. 2018;118(2):505-613.
33. Sheldon RA. Green and sustainable manufacture of chemicals from biomass: state of the art. Green Chemistry. 2014;16(3):950-63.
34. Broeren ML, Zijp MC, Waaijers-van der Loop SL, Heugens EH, Posthuma L, Worrell E, et al. Environmental assessment of bio-based chemicals in early-stage development: a review of methods and indicators. Biofuels, Bioproducts and Biorefining. 2017.

35. Palmeros Parada M, Osseweijer P, Posada Duque JA. Sustainable biorefineries, an analysis of practices for incorporating sustainability in biorefinery design. Industrial Crops and Products. 2017;106:105-23.
36. Sandén BA, Pettersson K. Systems Perspectives on Biorefineries. Göteborg, Sweden Chalmers University of Technology; 2013. 155 p.
37. Pfau SF, Hagens JE, Dankbaar B, Smits AJ. Visions of sustainability in bioeconomy research. Sustainability. 2014;6(3):1222-49.
38. Azapagic A. Sustainability considerations for integrated biorefineries. Trends in biotechnology. 2014;32(1):1-4.
39. Parada MP, Asveld L, Osseweijer P, Posada JA. Setting the design space of biorefineries through sustainability values, a practical approach. Biofuels, Bioproducts and Biorefining. 2018;12(1):29-44.
40. Bao B, Ng DK, Tay DH, Jiménez-Gutiérrez A, El-Halwagi MM. A shortcut method for the preliminary synthesis of process-technology pathways: An optimization approach and application for the conceptual design of integrated biorefineries. Computers & Chemical Engineering. 2011;35(8):1374-83.
41. Martinez-Hernandez E, Campbell G, Sadhukhan J. Economic value and environmental impact (EVEI) analysis of biorefinery systems. Chemical Engineering Research and Design. 2013;91(8):1418-26.
42. Cheali P, Gernaey KV, Sin G. Toward a Computer-Aided Synthesis and Design of Biorefinery Networks: Data Collection and Management Using a Generic Modeling Approach. ACS Sustainable Chemistry & Engineering. 2014;2(1):19-29.
43. Santibañez-Aguilar JE, González-Campos JB, Ponce-Ortega JM, Serna-González M, El-Halwagi MM. Optimal planning and site selection for distributed multiproduct biorefineries involving economic, environmental and social objectives. Journal of Cleaner Production. 2014;65:270-94.
44. El-Halwagi MM. Chapter 11 - Overview of Optimization. Sustainable Design Through Process Integration (Second Edition): Butterworth-Heinemann; 2017. p. 307-46.
45. Moncada J, Tamayo JA, Cardona CA. Integrating first, second, and third generation biorefineries: Incorporating microalgae into the sugarcane biorefinery. Chemical Engineering Science. 2014;118:126-40.
46. Posada JA, Patel AD, Roes A, Blok K, Faaij AP, Patel MK. Potential of bioethanol as a chemical building block for biorefineries: Preliminary sustainability assessment of 12 bioethanol-based products. Bioresour Technol. 2013;135:490-9.
47. Kelloway A, Daoutidis P. Process synthesis of biorefineries: optimization of biomass conversion to fuels and chemicals. Industrial & Engineering Chemistry Research. 2013;53(13):5261-73.
48. Kokossis AC, Yang A, Tsakalova M, Lin T-C. A systems platform for the optimal synthesis of biomass based manufacturing systems. Computer Aided Chemical Engineering. 28: Elsevier; 2010. p. 1105-10.
49. Cespi D, Passarini F, Vassura I, Cavani F. Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry. Green Chemistry. 2016;18(6):1625-38.
50. Patel AD, Meesters K, den Uil H, de Jong E, Blok K, Patel MK. Sustainability assessment of novel chemical processes at early stage: application to biobased processes. Energy & Environmental Science. 2012;5(9):8430-44.

51. Patel AD, Meesters K, den Uil H, de Jong E, Worrell E, Patel MK. Early-stage comparative sustainability assessment of new bio-based processes. ChemSusChem. 2013;6(9):1724-36.
52. Sugiyama H, Fischer U, Hungerbühler K, Hirao M. Decision framework for chemical process design including different stages of environmental, health, and safety assessment. AIChE Journal. 2008;54(4):1037-53.
53. Li Q, Zhang Y, Hu G. Techno-economic analysis of advanced biofuel production based on bio-oil gasification. Bioresource technology. 2015;191:88-96.
54. Tan EC, Snowden-Swan LJ, Talmadge M, Dutta A, Jones S, Ramasamy KK, et al. Comparative techno-economic analysis and process design for indirect liquefaction pathways to distillate-range fuels via biomass-derived oxygenated intermediates upgrading. Biofuels, Bioproducts and Biorefining. 2017;11(1):41-66.
55. Brown TR, Wright MM, Román-Leshkov Y, Brown RC. 2 - Techno-economic assessment (TEA) of advanced biochemical and thermochemical biorefineries A2 - Waldron, Keith. Advances in Biorefineries: Woodhead Publishing; 2014. p. 34-66.
56. Persson M, Erdei B, Galbe M, Wallberg O. Techno-Economic Aspects in the Evaluation of Biorefineries for Production of Second-Generation Bioethanol. In: Ruiz HA, Hedegaard Thomsen M, Trajano HL, editors. Hydrothermal Processing in Biorefineries: Production of Bioethanol and High Added-Value Compounds of Second and Third Generation Biomass. Cham: Springer International Publishing; 2017. p. 401-20.
57. Klein BC, Chagas MF, Junqueira TL, Rezende MCAF, Cardoso TdF, Cavalett O, et al. Techno-economic and environmental assessment of renewable jet fuel production in integrated Brazilian sugarcane biorefineries. Applied Energy. 2018;209:290-305.
58. Klein BC, Silva JFL, Junqueira TL, Rabelo SC, Arruda PV, Ienczak JL, et al. Process development and techno-economic analysis of bio-based succinic acid derived from pentoses integrated to a sugarcane biorefinery. Biofuels, Bioproducts and Biorefining. 2017;11(6):1051-64.
59. Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, et al. Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: dilute-acid pretreatment and enzymatic hydrolysis of corn stover. National Renewable Energy Laboratory (NREL), Golden, CO., 2011.
60. Davis R, Tao L, Tan E, Biddy M, Beckham G, Scarlata C, et al. Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons: dilute-acid and enzymatic deconstruction of biomass to sugars and biological conversion of sugars to hydrocarbons. National Renewable Energy Laboratory (NREL), Golden, CO., 2013.
61. Hernández V, Romero-García JM, Dávila JA, Castro E, Cardona CA. Techno-economic and environmental assessment of an olive stone based biorefinery. Resources, Conservation and Recycling. 2014;92:145-50.
62. Nanda S, Azargohar R, Dalai AK, Kozinski JA. An assessment on the sustainability of lignocellulosic biomass for biorefining. Renewable and Sustainable Energy Reviews. 2015;50:925-41.
63. González-García S, Hospido A, Agnemo R, Svensson P, Selling E, Moreira MT, et al. Environmental Life Cycle Assessment of a Swedish Dissolving Pulp Mill Integrated Biorefinery. Journal of Industrial Ecology. 2011;15(4):568-83.
64. Cherubini F, Strømman AH. Life cycle assessment of bioenergy systems: State of the art and future challenges. Bioresource Technology. 2011;102(2):437-51.

65. Wang B, Gebreslassie BH, You F. Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: Integrated life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. Computers & Chemical Engineering. 2013;52:55-76.

66. Jacquemin L, Pontalier P-Y, Sablayrolles C. Life cycle assessment (LCA) applied to the process industry: a review. The International Journal of Life Cycle Assessment. 2012;17(8):1028-41.

67. Weiss M, Haufe J, Carus M, Brandão M, Bringezu S, Hermann B, et al. A Review of the Environmental Impacts of Biobased Materials. Journal of Industrial Ecology. 2012;16(s1):S169-S81.

68. Borrion AL, McManus MC, Hammond GP. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. Renewable and Sustainable Energy Reviews. 2012;16(7):4638-50.

69. ISO. ISO, 14040: Environmental Management - Life Cycle Assessment - Principles and Framework. . Geneva, Switzerland. 2006.

70. ISO. ISO, 14044: Environmental Management - Life Cycle Assessment- Requirements and Guidelines. Geneva, Switzerland. 2006.

71. Erickson B, Winters P. Perspective on opportunities in industrial biotechnology in renewable chemicals. Biotechnology journal. 2012;7(2):176-85.

72. EASAC. Multi-functionality and sustainability in the European Union's forests. EASAC policy report 32. Availble at: wwweasaceu. 2017.

73. Meerman JC, Ramírez A, Turkenburg WC, Faaij APC. Performance of simulated flexible integrated gasification polygeneration facilities. Part A: A technical-energetic assessment. Renewable Sustainable Energy Rev. 2011;15(6):2563-87.

74. Haro P, Villanueva Perales ÁL, Arjona R, Ollero P. Thermochemical biorefineries with multiproduction using a platform chemical. Biofuels Bioprod Bioref. 2014;8(2):155-70.

75. Munasinghe PC, Khanal SK. Biomass-derived syngas fermentation into biofuels: opportunities and challenges. Bioresour Technol. 2010;101(13):5013-22.

76. Werpy T, Holladay J, White J. Top value added chemicals from biomass: I. results of screening for potential candidates from sugars and synthesis gas. University of Pennsylvania Law Review. 2004;154(3):477.

77. Novalin S, Zweckmair T. Renewable resources–green biorefinery: separation of valuable substances from fluid–fractions by means of membrane technology. Biofuels Bioprod Bioref. 2009;3(1):20-7.

78. Zakzeski J, Bruijnincx PC, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. Chem Rev. 2010;110(6):3552-99.

79. Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy. 2012;38:68-94.

80. Zondervan E, Nawaz M, de Haan AB, Woodley JM, Gani R. Optimal design of a multi-product biorefinery system. Comput Chem Eng. 2011;35(9):1752-66.

81. Ponce-Ortega JMa, Pham V, El-Halwagi MM, El-Baz AA. A disjunctive programming formulation for the optimal design of biorefinery configurations. Ind Eng Chem Res. 2012;51(8):3381-400.

82. Posada JA, Rincón LE, Cardona CA. Design and analysis of biorefineries based on raw glycerol: addressing the glycerol problem. Bioresour Technol. 2012;111:282-93.

83. Vlysidis A, Binns M, Webb C, Theodoropoulos C. A techno-economic analysis of biodiesel biorefineries: Assessment of integrated designs for the co-production of fuels and chemicals. Energy. 2011;36(8):4671-83.
84. Sugiyama H, Fischer U, Hungerbühler K, Hirao M. Decision framework for chemical process design including different stages of environmental, health, and safety assessment. AlChE J. 2008;54(4):1037-53.
85. Patel AD, Meesters K, den Uil H, de Jong E, Blok K, Patel MK. Sustainability assessment of novel chemical processes at early stage: application to biobased processes. Energy Environ Sci. 2012;5(9):8430-44.
86. Smith RM. Chemical process: design and integration. West Sussex: John Wiley & Sons; 2005.
87. Douglas JM. Conceptual design of chemical processes. New York: McGraw-Hill Book Co.; 1988.
88. Mussatto SI, Roberto IC. Acid hydrolysis and fermentation of brewer's spent grain to produce xylitol. J Sci Food Agric. 2005;85(14):2453-60.
89. Abdel-Rahman MA, Tashiro Y, Sonomoto K. Lactic acid production from lignocellulose-derived sugars using lactic acid bacteria: overview and limits. J Biotechnol. 2011;156(4):286-301.
90. Adhikari S, Fernando S, Gwaltney SR, Filip To S, Mark Bricka R, Steele PH, et al. A thermodynamic analysis of hydrogen production by steam reforming of glycerol. Int J Hydrogen Energy. 2007;32(14):2875-80.
91. Jungbluth N, Chudacoff M, Dauriat A, Dinkel F, Doka G, Faist Emmenegger M, et al. Life cycle inventories of bioenergy. Ecoinvent Report No. 17. Swiss Centre for Life Cycle Inventories, Dübendorf, CH. 2007.
92. IndexMundi. Commodity Prices. http://www.indexmundi.com/commodities/. [Accessed: March, 2014].
93. Moncada J, El-Halwagi MM, Cardona CA. Techno-economic analysis for a sugarcane biorefinery: Colombian case. Bioresour Technol. 2013;135:533-43.
94. Quispe CA, Coronado CJ, Carvalho Jr JA. Glycerol: Production, consumption, prices, characterization and new trends in combustion. Renewable Sustainable Energy Rev. 2013;27:475-93.
95. Clausen LR, Elmegaard B, Houbak N. Technoeconomic analysis of a low CO2 emission dimethyl ether (DME) plant based on gasification of torrefied biomass. Energy. 2010;35(12):4831-42.
96. He J, Zhang W. Techno-economic evaluation of thermo-chemical biomass-to-ethanol. Applied Energy. 2011;88(4):1224-32.
97. Dutta A, Hensley J, Bain R, Magrini K, Tan ECD, Apanel G, et al. Technoeconomic Analysis for the Production of Mixed Alcohols via Indirect Gasification of Biomass Based on Demonstration Experiments. Industrial & Engineering Chemistry Research. 2014;53(30):12149-59.
98. Su L-W, Li X-R, Sun Z-Y. The consumption, production and transportation of methanol in China: A review. Energy Policy. 2013;63:130-8.
99. Pinazo JM, Domine ME, Parvulescu V, Petru F. Sustainability metrics for succinic acid production: A comparison between biomass-based and petrochemical routes. Catalysis Today. 2015;239(0):17-24.

100. Delhomme C, Weuster-Botz D, Kühn FE. Succinic acid from renewable resources as a C 4 building-block chemical—a review of the catalytic possibilities in aqueous media. Green Chem. 2009;11(1):13-26.

101. Guerrero-Pérez MO, Bañares MA. Metrics of acrylonitrile: From biomass vs. petrochemical route. Catalysis Today. 2015;239(0):25-30.

102. Marinas A, Bruijnincx P, Ftouni J, Urbano FJ, Pinel C. Sustainability metrics for a fossil- and renewable-based route for 1,2-propanediol production: A comparison. Catalysis Today. 2015;239(0):31-7.

103. Xu B-Q, Sachtler WM. Rh/NaY: A selective catalyst for direct synthesis of acetic acid from syngas. J Catal. 1998;180(2):194-206.

104. Lee S, Sardesai A. Liquid phase methanol and dimethyl ether synthesis from syngas. Top Catal. 2005;32(3-4):197-207.

105. Xu-Longya W-Q. Promotion effect of K20 and MnO additives on the selective production of light alkenes via syngas over Fe/silicalite-2 catalysts. Catal Lett. 1995;31:253-66.

106. Maciel CG, Silva TdF, Assaf EM, Assaf JM. Hydrogen production and purification from the water–gas shift reaction on $CuO/CeO_2–TiO_2$ catalysts. Appl Energy. 2013;112(0):52-9.

107. Knifton JF, inventor; Texaco Development Corp., White Plains, NY., assignee. Manufacture of ethylene glycol from synthesis gas. United States1981.

108. Xiang M, Li D, Li W, Zhong B, Sun Y. Synthesis of higher alcohols from syngas over K/Co/β-Mo_2C catalysts. Catal Commun. 2007;8(3):503-7.

109. Kondo T, Kondo M. Efficient production of acetic acid from glucose in a mixed culture of *Zymomonas mobilis* and *Acetobacter* sp. J Ferment Bioeng. 1996;81(1):42-6.

110. Guettler MV, Jain MK, Rumler D, inventors; Michigan Biotechnology Institute, Lansing, Mich, assignee. Method for making succinic acid, bacterial variants for use in the process, and methods for obtaining variants. United States patent 5,573,931. 1996.

111. Qureshi N, Blaschek H, editors. Butanol production using *Clostridium beijerinckii* BA101 hyper-butanol producing mutant strain and recovery by pervaporation. Twenty-First Symposium on Biotechnology for Fuels and Chemicals; 2000: Springer.

112. Rivera EC, Costa AC, Atala DI, Maugeri F, Maciel MRW, Maciel Filho R. Evaluation of optimization techniques for parameter estimation: Application to ethanol fermentation considering the effect of temperature. Process Biochem. 2006;41(7):1682-7.

113. Leksawasdi N, Joachimsthal EL, Rogers PL. Mathematical modelling of ethanol production from glucose/xylose mixtures by recombinant *Zymomonas mobilis*. Biotechnol Lett. 2001;23(13):1087-93.

114. Zhang B, Tang X, Li Y, Xu Y, Shen W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. Int J Hydrogen Energy. 2007;32(13):2367-73.

115. Kurosaka T, Maruyama H, Naribayashi I, Sasaki Y. Production of 1, 3-propanediol by hydrogenolysis of glycerol catalyzed by $Pt/WO_3/ZrO_2$ Catal Commun. 2008;9(6):1360-3.

116. Yuan Z, Wang J, Wang L, Xie W, Chen P, Hou Z, et al. Biodiesel derived glycerol hydrogenolysis to 1, 2-propanediol on Cu/MgO catalysts. Bioresour Technol. 2010;101(18):7088-92.

117. Tsukuda E, Sato S, Takahashi R, Sodesawa T. Production of acrolein from glycerol over silica-supported heteropoly acids. Catal Commun. 2007;8(9):1349-53.

118. Szymanowska-Powa D, Bia W. Scale-up of anaerobic 1, 3-propanediol production by Clostridium butyricum DSP1 from crude glycerol. BMC Microbiol. 2014;14(1):45.
119. Shams Yazdani S, Gonzalez R. Engineering *Escherichia coli* for the efficient conversion of glycerol to ethanol and co-products. Metab Eng. 2008;10(6):340-51.
120. Zhang A, Yang S-T. Propionic acid production from glycerol by metabolically engineered *Propionibacterium acidipropionici*. Process Biochem. 2009;44(12):1346-51.
121. Alibaba. Prices of chemicals. http://www.alibaba.com/Chemicals_p8. [Accessed: February, 2014].
122. Platts. McGraw Hill Financial, Petrochemicals - Price Index. http://www.platts.com/commodity/petrochemicals. [Accessed: April, 2014].
123. Methanex. Methanol Price. https://www.methanex.com/our-business/pricing. [Acessed: January, 2014].
124. ICISpricing. Indicative Chemical Prices A-Z. http://www.icis.com/chemicals/channel-info-chemicals-a-z/. [Accessed: March, 2014].
125. Erickson B, Nelson, Winters P. Perspective on opportunities in industrial biotechnology in renewable chemicals. Biotechnol J. 2012;7(2):176-85.
126. Hahn H-D, Dämbkes G, Rupprich N, Bahl H, Frey GD. Butanols. Ullmann's Encyclopedia of Industrial Chemistry: Wiley-VCH Verlag GmbH & Co. KGaA; 2000.
127. Lan EI, Liao JC. Microbial synthesis of n-butanol, isobutanol, and other higher alcohols from diverse resources. Bioresour Technol. 2013;135:339-49.
128. Butamax. Butamax and Gevo Enter into Global Patent Cross-License and Settlement Agreements to Accelerate Development of Markets for Bio-based Isobutanol and End All Litigation. Butamax press releases. 2016;Available at: http://www.butamax.com/Portals/0/pdf/Butamax%20Gevo%20Press%20Release%2008-24-15.pdf(Accesed: November 2015).
129. Sutter M, Silva ED, Duguet N, Raoul Y, Métay E, Lemaire M. Glycerol Ether Synthesis: A Bench Test for Green Chemistry Concepts and Technologies. Chem Rev. 2015;115(16):8609-51.
130. Lin Z, Nikolakis V, Ierapetritou M. Alternative approaches for p-xylene production from starch: techno-economic analysis. Ind Eng Chem Res. 2014;53(26):10688-99.
131. Smith Jr LA, Loescher ME, Adams JR, Gelbein AP. Catalyzing the reaction in the presence of an acid catalyst and in concurrent flow, forming isooctane from isobutene. Google Patents; 2008.
132. Davidson GJ, Arsenault G, Foellinger T, Schenkel R-I, Kulbaba K, Watson JL. Polymers of isobutene from renewable sources. Google Patents; 2015.
133. West RM, Liu ZY, Peter M, Dumesic JA. Liquid Alkanes with Targeted Molecular Weights from Biomass-Derived Carbohydrates. ChemSusChem. 2008;1(5):417-24.
134. Breitkreuz K, Menne A, Kraft A. New process for sustainable fuels and chemicals from bio-based alcohols and acetone. Biofuels, Bioproducts and Biorefining. 2014;8(4):504-15.
135. Muñoz R, Montón JB, Burguet MC, de la Torre J. Separation of isobutyl alcohol and isobutyl acetate by extractive distillation and pressure-swing distillation: Simulation and optimization. Sep Purif Technol. 2006;50(2):175-83.
136. Moncada J, Posada JA, Ramírez A. Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals. Biofuels, Bioprod Biorefin. 2015;9(6):722-48.

137. Minty JJ, Singer ME, Scholz SA, Bae C-H, Ahn J-H, Foster CE, et al. Design and characterization of synthetic fungal-bacterial consortia for direct production of isobutanol from cellulosic biomass. Proceedings of the National Academy of Sciences. 2013;110(36):14592-7.
138. Tao L, Tan ECD, McCormick R, Zhang M, Aden A, He X, et al. Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol. Biofuels, Bioprod Biorefin. 2014;8(1):30-48.
139. Wildschut J, Smit AT, Reith JH, Huijgen WJJ. Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose. Bioresour Technol. 2013;135:58-66.
140. Constant S, Wienk HL, Frissen AE, de Peinder P, Boelens R, van Es DS, et al. New insights into the structure and composition of technical lignins: a comparative characterisation study. Green Chemistry. 2016;18(9):2651-65.
141. Pan X, Arato C, Gilkes N, Gregg D, Mabee W, Pye K, et al. Biorefining of softwoods using ethanol organosolv pulping: Preliminary evaluation of process streams for manufacture of fuel-grade ethanol and co-products. Biotechnol Bioeng. 2005;90(4):473-81.
142. Sutter J. Life Cycle Inventories of Petrochemical Solvents. Ecoinvent report No 22. 2007.
143. Mountraki A, Tsakalova M, Panteli A, Papoutsi AI, Kokossis AC. Integrated Waste Management in Multiproduct Biorefineries: Systems Optimization and Analysis of a Real-Life Industrial Plant. Ind Eng Chem Res. 2016;55(12):3478-92.
144. Moncada J, Tamayo J, Cardona CA. Evolution from biofuels to integrated biorefineries: techno-economic and environmental assessment of oil palm in Colombia. J Cleaner Prod. 2014;81:51-9.
145. Di Serio M, Casale L, Tesser R, Santacesaria E. New Process for the Production of Glycerol tert-Butyl Ethers†. Energy & Fuels. 2010;24(9):4668-72.
146. Wooley R, Putsche V. Development of an ASPEN PLUS physical property database for biofuels components. National Renewable Energy Laboratory, Golden, CO, USA. 1996:38.
147. Posada JA, Patel AD, Roes A, Blok K, Faaij APC, Patel MK. Potential of bioethanol as a chemical building block for biorefineries: Preliminary sustainability assessment of 12 bioethanol-based products. Bioresour Technol. 2013;135:490-9.
148. ISO. ISO 14044:2006. Environmental management - Life cycle assessment - Requirements and guideline. 2006.
149. Ecoinvent. Ecoinvent Database v2.2. www.ecoinvent.ch. 2010.
150. Skogsstyrelsen. Swedish Forest Agency. Prices. 2013;Available at: http://www.skogsstyrelsen.se/en/AUTHORITY/Statistics/Subject-Areas/Prices/Prices/ (Accesed: July 2015).
151. Alibaba. Average Prices of Chemicals. Available at: https://wwwalibabacom/Chemicals_p8. 2015;Accesed: July 2015.
152. Nitzsche R, Budzinski M, Gröngröft A. Techno-economic assessment of a wood-based biorefinery concept for the production of polymer-grade ethylene, organosolv lignin and fuel. Bioresour Technol. 2016;200:928-39.
153. IEA. International Energy Agency. Key World Energy Statistics. Prices. 2014;Paris, France:42-3.
154. Ulrich GD, Vasudevan PT. How to estimate utility costs. Chem Eng. 2006;113(4):66.
155. Platts. McGraw Hill Financial, Petrochemicals - Price Index. . Available at: http://wwwplattscom/commodity/petrochemicals. 2015;Accessed: April, 2014.

156. Platts. McGraw Hill Financial, Petrochemicals - Price Index. . Available at: http://wwwplattscom/news-feature/2015/petrochemicals/pgpi/propylene. 2015;Accesed: July 2015.
157. Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, Davis MF, et al. Lignin valorization: improving lignin processing in the biorefinery. Science. 2014;344(6185):1246843.
158. Constant S, Wienk HL, Frissen AE, de Peinder P, Boelens R, van Es DS, et al. New insights into the structure and composition of technical lignins: a comparative characterisation study. Green Chem. 2016;18(9):2651-65.
159. Huijgen W, Linden R, Reith J, Uil H. Development of a Lignocellulose Biorefinery Concept based on Organosolv Pretreatment. Jaen, Spain. 10 – 12 April 2013;2013:33.
160. Di Serio M, Casale L, Tesser R, Santacesaria E. New Process for the Production of Glycerol tert-Butyl Ethers†. Energy Fuels. 2010;24(9):4668-72.
161. Breitkreuz K, Menne A, Kraft A. New process for sustainable fuels and chemicals from bio-based alcohols and acetone. Biofuels, Bioprod Biorefin. 2014;8(4):504-15.
162. Cherubini F. The biorefinery concept: using biomass instead of oil for producing energy and chemicals. Energy Conversion and Management. 2010;51(7):1412-21.
163. Cherubini F, Jungmeier G, Wellisch M, Willke T, Skiadas I, Van Ree R, et al. Toward a common classification approach for biorefinery systems. Biofuels, Bioproducts and Biorefining. 2009;3(5):534-46.
164. Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy's "Top 10" revisited. Green Chemistry. 2010;12(4):539-54.
165. Maity SK. Opportunities, recent trends and challenges of integrated biorefinery: Part I. Renewable and Sustainable Energy Reviews. 2015;43:1427-45.
166. Ramirez EC, Johnston DB, McAloon AJ, Yee W, Singh V. Engineering process and cost model for a conventional corn wet milling facility. Industrial Crops and Products. 2008;27(1):91-7.
167. Renouf MA, Wegener MK, Nielsen LK. An environmental life cycle assessment comparing Australian sugarcane with US corn and UK sugar beet as producers of sugars for fermentation. Biomass and Bioenergy. 2008;32(12):1144-55.
168. Bhaumik P, Dhepe PL. Efficient, stable, and reusable silicoaluminophosphate for the one-pot production of furfural from hemicellulose. ACS Catalysis. 2013;3(10):2299-303.
169. Nitzsche R, Budzinski M, Gröngröft A. Techno-economic assessment of a wood-based biorefinery concept for the production of polymer-grade ethylene, organosolv lignin and fuel. Bioresource Technology. 2016;200:928-39.
170. Karlsson H, Börjesson P, Hansson P-A, Ahlgren S. Ethanol production in biorefineries using lignocellulosic feedstock – GHG performance, energy balance and implications of life cycle calculation methodology. Journal of Cleaner Production. 2014;83:420-7.
171. Wiloso EI, Heijungs R, de Snoo GR. LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice. Renewable and Sustainable Energy Reviews. 2012;16(7):5295-308.
172. Eerhart AJJE, Patel MK, Faaij APC. Fuels and plastics from lignocellulosic biomass via the furan pathway: an economic analysis. Biofuels, Bioproducts and Biorefining. 2015;9(3):307-25.

173. Bernardi A, Giarola S, Bezzo F. Spatially explicit multiobjective optimization for the strategic design of first and second generation biorefineries including carbon and water footprints. Industrial & Engineering Chemistry Research. 2013;52(22):7170-80.

174. Miret C, Chazara P, Montastruc L, Negny S, Domenech S. Design of bioethanol green supply chain: Comparison between first and second generation biomass concerning economic, environmental and social criteria. Computers & Chemical Engineering. 2016;85:16-35.

175. Watanabe MD, Chagas MF, Cavalett O, Guilhoto JJ, Griffin WM, Cunha MP, et al. Hybrid Input-Output Life Cycle Assessment of First-and Second-Generation Ethanol Production Technologies in Brazil. Journal of Industrial Ecology. 2015;20(4):764-74.

176. Tsiropoulos I, Cok B, Patel MK. Energy and greenhouse gas assessment of European glucose production from corn–a multiple allocation approach for a key ingredient of the bio-based economy. Journal of Cleaner Production. 2013;43:182-90.

177. Bakker RRC, Elbersen HW, Poppens RP, Lesschen JP. Rice Straw and Wheat Straw - Potential feedstocks for the Biobased Economy. Utrecht: NL Agency, 2013.

178. Palgan YV, McCormick K. Biorefineries in Sweden: Perspectives on the opportunities, challenges and future. Biofuels, Bioproducts and Biorefining. 2016;10(5):523-33.

179. Wildschut J, Smit AT, Reith JH, Huijgen WJJ. Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose. Bioresource Technology. 2013;135:58-66.

180. Ennaert T, Op de Beeck B, Vanneste J, Smit AT, Huijgen WJJ, Vanhulsel A, et al. The importance of pretreatment and feedstock purity in the reductive splitting of (ligno)cellulose by metal supported USY zeolite. Green Chemistry. 2016;18(7):2095-105.

181. Thornley P, Chong K, Bridgwater T. European biorefineries: Implications for land, trade and employment. Environmental Science & Policy. 2014;37:255-65.

182. Viell J, Harwardt A, Seiler J, Marquardt W. Is biomass fractionation by Organosolv-like processes economically viable? A conceptual design study. Bioresource Technology. 2013;150:89-97.

183. Wooley RJ, Putsche V. Development of an ASPEN PLUS physical property database for biofuels components. Golden, Colorado: National Renewable Energy Laboratory (NREL); 1996. p. 1-32.

184. van der Linden R, Huijgen W, Reith J. Ethanol-based organosolv biorefineries: feedstock-flexibility & economic evaluation. In: Niemelä K, editor. NWBC 2012, The 4th Nordic Wood Biorefinery Conference; 23–25 October; Helsinki, Finland: VTT Technical Research Centre of Finland; 2012. p. 199-204.

185. Constant S, Wienk HL, Frissen AE, de Peinder P, Boelens R, van Es DS, et al. New insights into the structure and composition of technical lignins: a comparative characterisation study. Green Chemistry. 2016;18(9):2651-65.

186. Michels J. "Lignocellulose Biorefinery – Phase 2" – final scientific and technical report of all project partners. DECHEMA Gesellschaft für Chemische Technik und Biotechnologie. . Available online: http://edok01tibuni-hannoverde/edoks/e01fb15/837304261pdf. 2014;Accessed: May 2016.

187. Moncada J, El-Halwagi MM, Cardona CA. Techno-economic analysis for a sugarcane biorefinery: Colombian case. Bioresource Technology. 2013;135(Biorefineries):533 - 43.

188. Rincón LE, Becerra LA, Moncada J, Cardona CA. Techno-economic analysis of the use of fired cogeneration systems based on sugar cane bagasse in south eastern and mid-western regions of Mexico. Waste and biomass valorization. 2014;5(2):189-98.

189. Peters M, Timmerhaus K, West R. Plant Design and Economics for Che- mical Engineers. McGraw Hill, New York. 2003.

190. Ulrich GD, Vasudevan PT. How to estimate utility costs. Chemical Engineering. 2006;113(4):66.

191. Skogsstyrelsen. Swedish Forest Agency. Prices. 2014;Available at: http://pxweb.skogsstyrelsen.se/pxweb/en/Skogsstyrelsens%20statistikdatabas/Skogsstyrelsens%20statistikdatabas__Rundvirkespriser/JO0303_1_20160128.px/?rxid=0762e9f1-f8c9-46e3-9135-97ca4631f207(Accesed: July 2015).

192. Platts. McGraw Hill Financial, Petrochemicals - Price Index. . Available at: http://wwwplattscom/news-feature/2015/petrochemicals/pgpi/propylene. 2016;Accesed: July 2016.

193. Torres AI, Daoutidis P, Tsapatsis M. Continuous production of 5-hydroxymethylfurfural from fructose: a design case study. Energy & Environmental Science. 2010;3(10):1560-72.

194. IEA. Key World Energy Statistics. International Energy Agency. 2015.

195. Gebrezgabher SA, Meuwissen MPM, Prins BAM, Lansink AGJMO. Economic analysis of anaerobic digestion—A case of Green power biogas plant in The Netherlands. NJAS - Wageningen Journal of Life Sciences. 2010;57(2):109-15.

196. Indexmundi. Commodity Price Indices. Available at: http://wwwindexmundicom/. 2015;Accesed: July 2015.

197. U.S.Grains. U.S. Grains Council. FOB Price Charts. Available at: http://wwwgrainsorg/market-data/charts-tables. 2015;Accesed: July 2015.

198. ISO. ISO 14044:2006. Environmental management -- Life cycle assessment -- Requirements and guideline. 2006.

199. Goedkoop MJ, Heijungs R, Huijbregts M, De Schryver A, Struijs J, Van Zelm R. ReCiPe 2008, A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level. First edition Report I: Characterisation. 2009;Available at: http://www.lcia-recipe.net.

200. Hischier R, Weidema B, Althaus H-J, Bauer C, Doka G, Dones R, et al. Implementation of Life Cycle Impact Assessment Methods. Ecoinvent report No 3, v22 Swiss Centre for Life Cycle Inventories. 2010;Dübendorf, Switzerland.

201. Giuntoli J, Agostini A, Edwards R, Marelli L. Solid and gaseous bioenergy pathways: input values and GHG emissions. Report EUR 26696. 2014.

202. UIC, IEA. Railway Handbook. Energy consumption and CO2 emissions. Focus on Infrastructure. 2014.

203. Sea-distances. Port-to-port sea distances. available at: http://wwwsea-distancesorg/. 2015;Accesed: July 2015.

204. Michael W, May W, Hong H. Life-cycle energy and greenhouse gas emission impacts of different corn ethanol plant types. Environmental Research Letters. 2007;2(2):024001.

205. van der Linden R, Huijgen WJJ, Reith JH. Ethanol-based organosolv biorefineries: feedstock-flexibility & economic evaluation. In: Niemelä K, editor. NWBC 2012, The 4th Nordic Wood Biorefinery Conference; 23–25 October; Helsinki, Finland: VTT Technical Research Centre of Finland; 2012. p. 199-204.

206. Laure S, Leschinsky M, Fröhling M, Schultmann F, Unkelbach G. Assessment of an organosolv lignocellulose biorefinery concept based on a material flow analysis of a pilot plant. Cellulose Chemistry and Technology. 2014;48:793-8.

207. Pan X, Arato C, Gilkes N, Gregg D, Mabee W, Pye K, et al. Biorefining of softwoods using ethanol organosolv pulping: Preliminary evaluation of process streams for manufacture of fuel-grade ethanol and co-products. Biotechnology and bioengineering. 2005;90(4):473-81.

208. Huijgen WJJ, Linden Rvd, Reith JH, Uil Hd, editors. Development of a Lignocellulose Biorefinery Concept based on Organosolv Pretreatment. 2nd Iberoamerican Congress on Biorefineries,; 2013; Jaen, Spain, 10 – 12 April 2013. .

209. de la Torre MJ, Moral A, Hernández MD, Cabeza E, Tijero A. Organosolv lignin for biofuel. Industrial Crops and Products. 2013;45:58-63.

210. Michels J. “Lignocellulose Biorefinery – Phase 1” – final scientific and technical report of all project partners. DECHEMA Gesellschaft für Chemische Technik und Biotechnologie. . Available online: http://wwwfnr-serverde/ftp/pdf/berichte/22014406pdf. 2009;Accessed: May 2016.

211. Klein-Marcuschamer D, Oleskowicz-Popiel P, Simmons BA, Blanch HW. The challenge of enzyme cost in the production of lignocellulosic biofuels. Biotechnology and bioengineering. 2012;109(4):1083–7.

212. Johnson E. Integrated enzyme production lowers the cost of cellulosic ethanol. Biofuels, Bioproducts and Biorefining. 2016;10(2):164-74.

213. Cherubini F. The biorefinery concept: using biomass instead of oil for producing energy and chemicals. Energy Convers Manage. 2010;51(7):1412-21.

214. Hossain GS, Liu L, Du GC. 1 - Industrial Bioprocesses and the Biorefinery Concept. Current Developments in Biotechnology and Bioengineering: Elsevier; 2017. p. 3-27.

215. Moncada J, Tamayo JA, Cardona CA. Integrating first, second, and third generation biorefineries: Incorporating microalgae into the sugarcane biorefinery. Chem Eng Sci. 2014;118:126-40.

216. Cherubini F, Jungmeier G, Wellisch M, Willke T, Skiadas I, Van Ree R, et al. Toward a common classification approach for biorefinery systems. Biofuels Bioprod Bioref. 2009;3(5):534-46.

217. Dusselier M, Mascal M, Sels BF. Top Chemical Opportunities from Carbohydrate Biomass: A Chemist’s View of the Biorefinery. In: Nicholas KM, editor. Selective Catalysis for Renewable Feedstocks and Chemicals. Cham: Springer International Publishing; 2014. p. 1-40.

218. Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy’s “Top 10” revisited. Green Chem. 2010;12(4):539-54.

219. Moncada J, Posada JA, Ramírez A. Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals. Biofuels Bioprod Bioref. 2015;9:722–48.

220. Posada JA, Patel AD, Roes A, Blok K, Faaij AP, Patel MK. Potential of bioethanol as a chemical building block for biorefineries: preliminary sustainability assessment of 12 bioethanol-based products. Bioresour Technol. 2013;135:490-9.

221. Hayes DJ, Fitzpatrick S, Hayes MHB, Ross JRH. The Biofine Process – Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks. Biorefineries-Industrial Processes and Products: Wiley-VCH Verlag GmbH; 2008. p. 139-64.

222. Hayes DJ, Fitzpatrick S, Hayes MH, Ross JR. The Biofine process-Production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks. Biorefineries–Industrial Processes and Product. 2006;1:139-64.

223. Angelici C, Weckhuysen BM, Bruijnincx PC. Chemocatalytic conversion of ethanol into butadiene and other bulk chemicals. ChemSusChem. 2013;6(9):1595-614.

224. Makshina EV, Janssens W, Sels BF, Jacobs PA. Catalytic study of the conversion of ethanol into 1,3-butadiene. Catal Today. 2012;198(1):338-44.

225. Kim T-W, Kim J-W, Kim S-Y, Chae H-J, Kim J-R, Jeong S-Y, et al. Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported spherical silica catalysts for circulating fluidized bed. Chem Eng J. 2015;278:217-23.

226. Raoufmoghaddam S, Rood M, Buijze FK, Drent E, Bouwman E. Catalytic Conversion of γ-Valerolactone to ε-Caprolactam: Towards Nylon from Renewable Feedstock. ChemSusChem. 2014;7(7):1984-90.

227. Hong J, Xu X. Environmental impact assessment of caprolactam production–a case study in China. J Cleaner Prod. 2012;27:103-8.

228. Wang Y, Liu S. Butadiene production from ethanol. J Bioproc Eng Bioref. 2012;1(1):33-43.

229. Kyriienko PI, Larina OV, Soloviev SO, Orlyk SM, Dzwigaj S. High selectivity of TaSiBEA zeolite catalysts in 1,3-butadiene production from ethanol and acetaldehyde mixture. Catal Commun. 2016;77:123-6.

230. Chae H-J, Kim T-W, Moon Y-K, Kim H-K, Jeong K-E, Kim C-U, et al. Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported ordered mesoporous silica catalysts. Appl Catal, B. 2014;150:596-604.

231. Patel AD, Meesters K, den Uil H, de Jong E, Blok K, Patel MK. Sustainability assessment of novel chemical processes at early stage: application to biobased processes. Energy Environ Sci. 2012;5(9):8430-44.

232. Cespi D, Passarini F, Vassura I, Cavani F. Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry. Green Chem. 2016;18(6):1625-38.

233. Farzad S, Mandegari MA, Görgens JF. Integrated techno-economic and environmental analysis of butadiene production from biomass. Bioresour Technol. 2017;239:37-48.

234. Girisuta B, Heeres HJ. Levulinic Acid from Biomass: Synthesis and Applications. In: Fang Z, Smith JRL, Qi X, editors. Production of Platform Chemicals from Sustainable Resources. Singapore: Springer Singapore; 2017. p. 143-69.

235. Ftouni J, Muñoz-Murillo A, Goryachev A, Hofmann JP, Hensen EJM, Lu L, et al. ZrO2 Is Preferred over TiO2 as Support for the Ru-Catalyzed Hydrogenation of Levulinic Acid to γ-Valerolactone. ACS Catal. 2016;6(8):5462-72.

236. Abdelrahman OA, Heyden A, Bond JQ. Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form γ-valerolactone over Ru/C. ACS Catal. 2014;4(4):1171-81.

237. Han J. Biorenewable Strategy for Catalytic ε-Caprolactam Production Using Cellulose- and Hemicellulose-Derived γ-Valerolactone. ACS Sustainable Chem Eng. 2017;5(2):1892-8.

238. Wooley RJ, Putsche V. Development of an ASPEN PLUS physical property database for biofuels components. Citeseer; 1996.

239. Moncada J, Vural Gursel I, Huijgen WJ, Dijkstra JW, Ramírez A. Techno-economic and ex-ante environmental assessment of C6 sugars production from spruce and corn. Comparison of organosolv and wet milling technologies. J Cleaner Prod. 2018;170:610-24.
240. Quintero J, Montoya M, Sánchez OJ, Giraldo O, Cardona C. Fuel ethanol production from sugarcane and corn: comparative analysis for a Colombian case. Energy. 2008;33(3):385-99.
241. White WC. Butadiene production process overview. Chem Biol Interact. 2007;166(1–3):10-4.
242. Eldridge RB. Olefin/paraffin separation technology: a review. Ind Eng Chem Chem Res. 1993;32(10):2208-12.
243. Shylesh S, Gokhale AA, Scown CD, Kim D, Ho CR, Bell AT. From Sugars to Wheels: The Conversion of Ethanol to 1, 3-Butadiene over Metal-Promoted Magnesia-Silicate Catalysts. ChemSusChem. 2016.
244. Girisuta B, Janssen L, Heeres HJ. Green chemicals: A kinetic study on the conversion of glucose to levulinic acid. Chem Eng Res Des. 2006;84(5):339-49.
245. Mija A, Van Der Waal J, Pin J-M, Guigo N, De Jong E, editors. Humins as promising material for producing sustainable polyssacharide-derived building materials. First International Conference on Bio-based Building Materials; 2015.
246. Peters M, Timmerhaus K, West R. Plant Design and Economics for Chemical Engineers. McGraw Hill, New York. 2003.
247. Ulrich GD, Vasudevan PT. How to estimate utility costs. Chem Eng. 2006;113(4):66.
248. Methanex. Methanol price. Available at: https://wwwmethanexcom/our-business/pricing. 2016;Accesed, June 2016.
249. Pei P, Korom SF, Ling K, Nasah J. Cost comparison of syngas production from natural gas conversion and underground coal gasification. Mitig Adapt Strategies Glob chang. 2016;21(4):629-43.
250. Platts. Platts price index. Available at: http://wwwplattscom/commodity/petrochemicals. 2014.
251. Gebrezgabher SA, Meuwissen MPM, Prins BAM, Lansink AGJMO. Economic analysis of anaerobic digestion—A case of Green power biogas plant in The Netherlands. NJAS - Wag J Life Science. 2010;57(2):109-15.
252. ICIS. ICIS pricing: Prices for chemicals. Available at: wwwiciscom. 2014.
253. Ftouni J, Muñoz-Murillo A, Goryachev A, Hofmann JP, Hensen EJM, Lu L, et al. ZrO2 Is Preferred over TiO2 as Support for the Ru-Catalyzed Hydrogenation of Levulinic Acid to γ-Valerolactone. ACS Catalysis. 2016;6(8):5462-72.
254. Moncada J, Vural Gursel I, Worrell E, Ramirez A. Production of 1,3-Butadiene and ε-Caprolactam from C6 sugars. Techno-economic analysis. Biofuels Bioprod Bioref. 2018;Accepted(In Press).
255. Roes AL, Patel MK. Ex-ante environmental assessments of novel technologies – Improved caprolactam catalysis and hydrogen storage. Journal of Cleaner Production. 2011;19(14):1659-67.
256. Franklin-Associates. Cradle-to-gate life cycle inventory of nine plastic resins and four polyurethane precursors. In: https://plastics.americanchemistry.com/LifeCycle-Inventory-of-9-Plastics-Resins-and-4-Polyurethane-Precursors-APPS-Only/ Aa, editor.: Eastern Research Group, INC. Prairie Village, KS, USA; 2011.
257. Hong J, Xu X. Environmental impact assessment of caprolactam production–a case study in China. Journal of Cleaner Production. 2012;27:103-8.

258. Ecoinvent. Ecoinvent Database v3.3. www.ecoinvent.ch. 2013.

259. van der Spek M, Ramirez A, Faaij A. Challenges and uncertainties of ex ante techno-economic analysis of low TRL CO2 capture technology: Lessons from a case study of an NGCC with exhaust gas recycle and electric swing adsorption. Applied Energy. 2017;208:920-34.

260. Bajpai P. Value-Added Products from Lignin. Biotechnology for Pulp and Paper Processing. Singapore: Springer Singapore; 2018. p. 561-71.