

Methodology for the identification of promising integrated biorefineries

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Abstract

Steady increase in global energy consumption, greenhouse gas emissions, and depletion of fossil energy resources, together with increased attention towards sustainable development has prompted researchers to discover economical and environmentally competitive non-petroleum alternatives and biomass is considered to be one of the most promising renewable sources of energy and carbon of this matter to address the aforementioned issues within a biorefinery platform. A biorefinery is an integrated processing facility that converts biomass into transportation fuels, value-added chemicals, heat, and electricity via biochemical and thermochemical conversion routes. Integrated biorefineries are capable of mimicking petroleum refineries via application of advanced process synthesis methods including modeling, simulation, integration and optimization techniques.

This thesis presents a comprehensive synthesis methodology for the integration of bioprocessing technologies in biorefineries by addressing techno-economic and environmental sustainability analysis. The proposed systematic design approach combines advanced process modeling approaches, process integration techniques, and multi-objective optimization algorithms to assess the performance of the overall system with respect to economic, environmental, and energetic indicators.

The design strategy is applied based on different case studies. Results indicate that multi-product processes can yield significant cost and environmental benefits. Additionally, the integration of biochemical and catalytic processes with thermochemical conversion pathways results in increased carbon efficiency and economic and environmental competitiveness. Synergies between biorefineries and energy system are assessed by integrating industrial plants with a cogeneration system producing biofuels and process heat. In doing so, system efficiency is increased by coupling the proposed cogeneration system with carbon capture and sequestration (CCS) and power-to-gas technologies to store the renewable intermittent electricity in the form of biofuels.

The results exhibit that through system expansion, integrated biorefinery systems allow us to imitate fossil refineries with a large spectrum of bio-based products. This further increases the resource efficiency while offering a promising solution to mitigate CO₂ emissions and hence reaching the longer-term decarbonization target set by the Paris Agreement.

Keywords

Biomass conversion, multi-product biorefineries, combined heat and fuel plant, bioenergy with CO₂ capture and storage, conceptual process design, process integration, multi-objective optimization

Résumé

La demande croissante des besoins énergétiques mondiaux, couplée à la consommation des hydrocarbures fossiles, a entraîné une augmentation significative des émissions de gaz à effet de serre. La diminution des réserves de ces combustibles fossiles ainsi qu'une sensibilité environnementale grandissante justifient l'intérêt accru pour des alternatives économiquement viables et plus propres. La biomasse est considérée comme l'une des sources d'énergie renouvelable les plus prometteuses. Elle peut être transformée en biocarburants, en produits chimiques à valeur ajoutée, en chaleur et en électricité dans des bioraffineries, par voie thermochimique ou biochimique. La conception de ces installations industrielles, similaires à des raffineries pétrolières, pose un certain nombre de défis en raison du grand nombre de technologies disponibles. Afin de minimiser les coûts et impacts environnementaux totaux, il est nécessaire d'utiliser des méthodes avancées de synthèse et d'optimisation de procédés. La contribution principale de cette thèse est le développement d'une méthodologie complète de conception et d'intégration des bioraffineries. Cette dernière se base sur des modèles avancés de procédés, des outils de programmation mathématique pour l'intégration énergétique, ainsi que sur des algorithmes d'optimisation à objectifs multiples. Chaque solution est évaluée de manière systématique en s'appuyant sur des indicateurs de performance thermodynamiques, économiques et environnementaux. La méthodologie proposée est illustrée et validée avec plusieurs cas d'études. Les résultats indiquent que la génération simultanée de produits énergétiques et chimiques (polygénération) peut permettre une réduction importante des impacts environnementaux et des coûts de production. L'ajout de procédés biochimiques et catalytiques aux procédés de conversion thermochimique permet une meilleure valorisation du carbone présent dans la biomasse, entraînant de facto une meilleure compétitivité des bioraffineries. Les synergies entre ces installations et le système énergétique sont également évaluées. Un procédé de cogénération novateur, produisant des biocarburants et de la chaleur, est proposé. L'efficacité du système énergétique est améliorée en couplant cette nouvelle installation avec des procédés de capture et séquestration du CO₂ (CCS) et de conversion d'électricité en gaz (P2G). Cette stratégie permet le stockage d'énergie renouvelable et intermittente sous forme de biocarburants. Ce travail démontre que les systèmes intégrés de bioraffinerie sont analogues aux raffineries pétrolières classiques. Ils proposent un large éventail de produits d'origine biologique et permettent la conversion efficace de ressources énergétiques. Leur implémentation à grande échelle peut jouer un rôle important dans la transition énergétique, avec, comme objectif, la réduction des émissions de CO₂ dans le cadre de

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l'Accord de Paris sur le réchauffement climatique.

Mots-clefs

Conversion de la biomasse, bioraffineries multiproduits, usine de production combinée de chaleur et de combustible, bioénergie avec captage et stockage du CO₂, conception du procédé, intégration du procédé, optimisation multiobjectif.

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Nomenclature

Abbreviations

CBP	Consolidated bioprocessing
CC	Composite curve
CCS	Carbon capture and storage
CEPCI	Chemical engineering plant cost index
CFB	Circulating fluidized bed
CHF	Combined heat and fuel
CHP	Combined heat and power
CO ₂	Carbon dioxide
COP	Conference of parties
DME	Dimethyl ether
EF	Entrained flow
environomic	environmental and economic
EU	European Union
FICFB	Fast internally circulating fluidized bed
FT	Fischer-Tropsch
GCC	Grand composite curve
GWP	Global warming potential
ICC	Integrated composite curve
IPCC	International panel on climate change
LCA	Life cycle assessment
LCIA	Life cycle impact assessment
LHV	Lower heating value
MD	Middle distillate
MEOH	Methanol
MER	Minimum energy requirements
MILP	Mixed integer linear programming
MSP	Minimum selling price

Nomenclature

NG	Natural gas
PSA	Pressure swing adsorption
SNG	Synthetic natural gas
US	United States of America
WGS	Water-gas shift

Symbols

ϵ	Energy efficiency	
A	Area	[m ²]
c_p	Heat capacity	[kJ/kg°C]
ΔT	Temperature difference	[°C]
\dot{E}	Electrical flow	[kW]
h	Enthalpy	[kJ/kg]
i	Interest rate	[%]
\dot{m}	Mass flow	[kg/s]
n	Lifetime	[y]
P	Pressure	[bar]
\dot{Q}	Heat flow	[kW]
s	Entropy	[kJ/kg°C]
T	Temperature	[°C]
U	Overall heat transfer coefficient	[W/m ² °C]

Introduction

Overview

- Global energy perspective, global warming and energy transition
- Integrated biorefineries as coping strategy for climate change
- Objectives and outline of the thesis.

Today's research community is focusing on a future without fossil resources due to the undesired rates of global warming, rising demand for transportation fuels, heat, power and raw products together with the need for sustainable development.

Global warming may be considered as the biggest challenge of the 21st century since climate change has many ecological, physical and health impacts. The major threats are rising sea levels, increase in average global temperature and severe weather events (such as heat waves, droughts, storm surges, intense rainfalls and floods). It also has drastic consequences on food security and water supply [1]. The most important drivers of global warming are the anthropogenic greenhouse gas (GHG) emissions. The Sankey flow diagram in Figure 1 shows the global energy supply and consumption flows in 2016 as published by International Energy Agency (IEA) [2]. From the figure, it can be deduced that, the current energy mix is dominated by fossil resources (coal, oil and natural gas). CO₂ emissions from fossil fuel combustion and other industrial processes are the primary sources of greenhouse gas emissions accounting 65% of total emissions. Over the past 25 years, global energy-related CO₂ emissions from fossil fuel increased by more than 50% [3] (Figure 2). In 2018, energy-related global CO₂ emissions reached a historic high of 33.1 Gt (billion tonnes) CO₂/yr [4]. Without any action taken, total global GHG emissions will increase another 30% by 2040 [5].

The world's population is expected to expand from 7.6 billion today to more than 9 billion by the year 2040 [6]. As the world population grows, the total global energy demand is also expected to increase by 30 % between the years 2016 and 2040 [7]. Today, the industrial sector accounts for 32 % of global energy consumption [8] and it is expected to increase by 18% over the projection [7]. The emissions from industrial sector accounts for 24% of global CO₂ emissions [9]. Widely used diverse range of products such as plastics, advanced materials, cosmetics, composites, cleaning fluids, fabrics, dyes, pharmaceuticals and many more are derived from fossil resources today and the increase in population will severely affect the demand. Producing and using these hydrocarbon products generates numerous debates regarding the negative impact they have on the environment. Chemicals and

Introduction

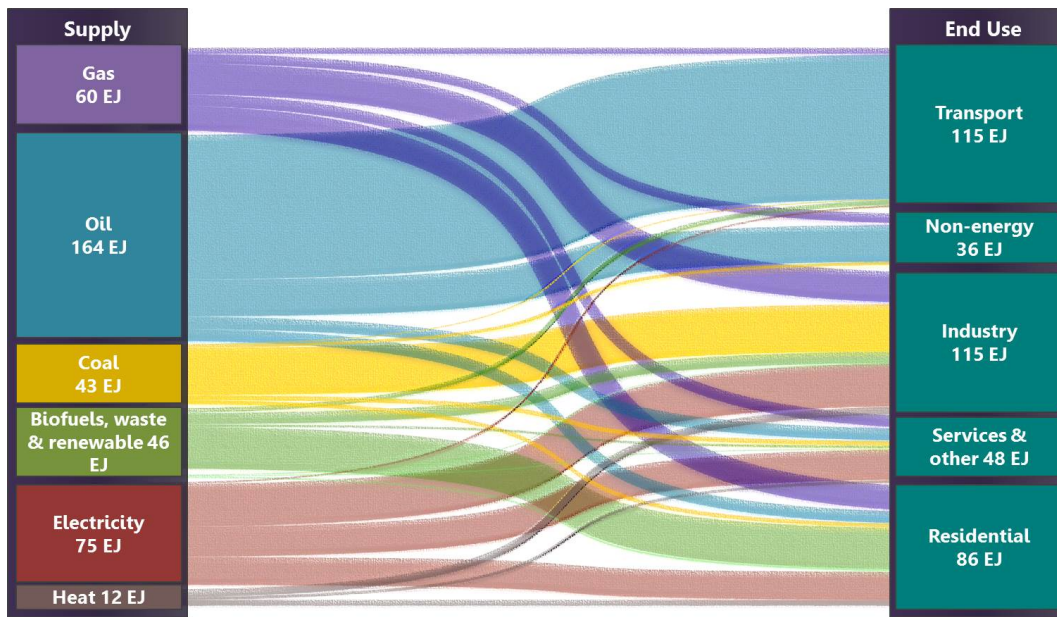


Figure 1: Worldwide energy flows in 2016 published by the International Energy Agency [2].

petrochemicals sector is the largest industrial energy user consuming 30% of industrial final energy and accounts for 17% of industrial CO₂ emissions [10]. Other main challenge for eliminating fossil fuel related emissions is the substitution of fossil fuels in the transportation sector which makes 31% of global final energy demand up [8] and is responsible for 24% of global CO₂ emissions [9].

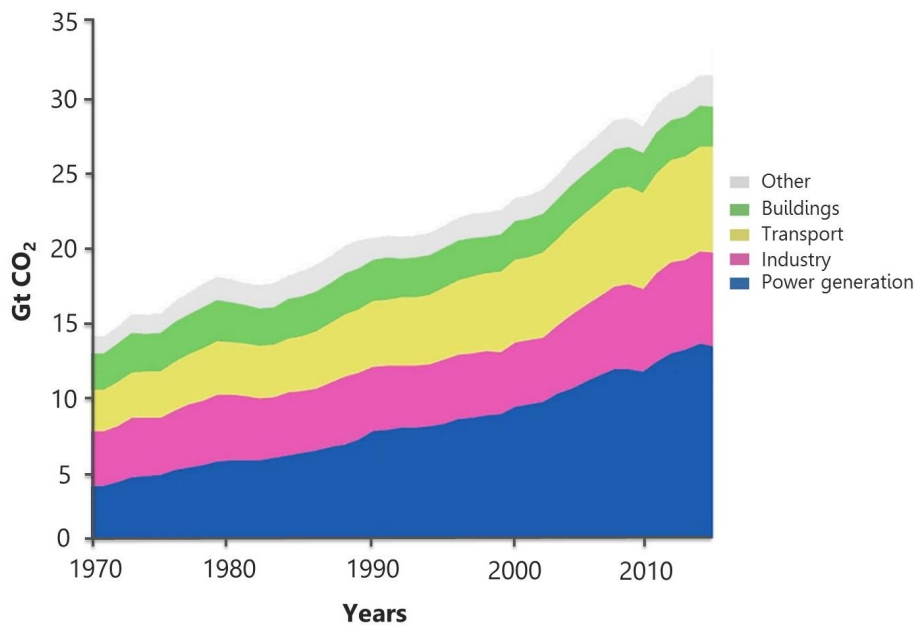


Figure 2: Global energy-related emissions by sector [3].

* Other* includes agriculture, non-energy use (except petrochemical feedstock), oil and gas extraction and energy transformation. International bunkers are included in the transport sector [3].

In the light of evidences, Paris Agreement within the United Nations Framework Convention on Climate Change (UNFCCC) is adopted by 195 states at Paris climate conference (COP21) (21st session of Conference of Parties) in December 2015. The long-term goal of this global climate deal is to limit the average global temperature rise to well below 2°C above pre-industrial levels, and pursuing efforts towards 1.5°C, since this would significantly reduce the effects of climate change. Following up the decision in 2015 Paris Agreement, parties invited Intergovernmental Panel on Climate Change (IPCC) to provide a special report in 2018 on the assessment of the impacts of global warming of 1.5°C. Scenarios show that global greenhouse gas emissions need to be lowered by 49% of 2017 levels by 2030 and then to near-zero by 2050 in order to keep temperature increases below 1.5°C (Figure 3). Even meeting the upper target of limiting the increase in global average temperature to 2°C would require emissions to fall around 20 % by 2030, before reaching near-zero emission target by around 2075. To achieve 1.5°C warming trajectory, rapid and large-scale transformations are necessary in many areas [1].

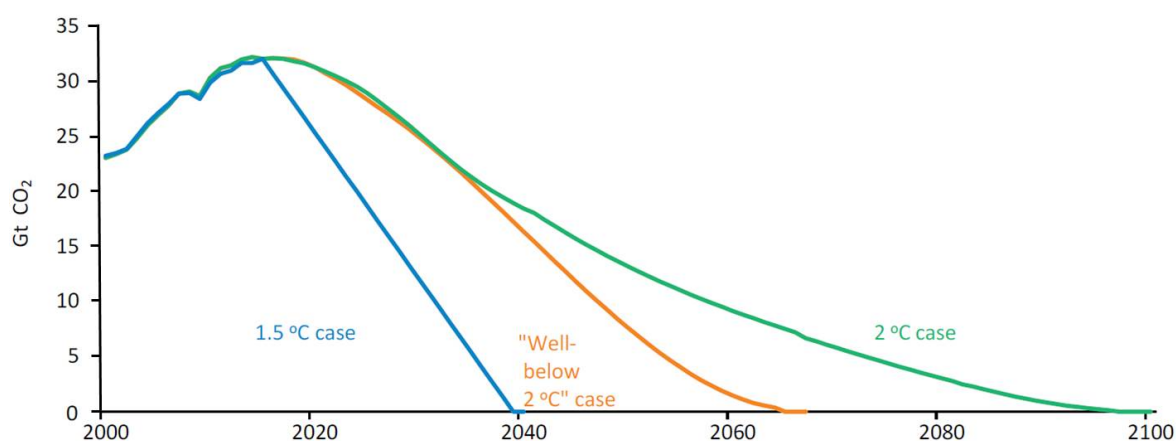


Figure 3: Global energy-related emission trajectories for different decarbonisation pathways (adapted from [8])

Climate change is also challenging our ability to meet the environmental, economic and social objectives that define sustainable development [11]. Since the energy sector is the biggest contributor for the greenhouse gas emissions, it has to be at the center of any climate change and sustainable development strategy. The current energy systems have to eliminate fossil fuels and renewable energy sources have a great potential to mitigate emissions of greenhouse gases from the use of fossil fuels [1]. Incorporating measures such as energy and resource efficiency in industries, increasing the share of renewable energy in all the sectors and development of new conversion technologies are possible solutions to achieve a sustainable future. Furthermore, there is an urgent need for carbon negative solutions, and remaining emissions need to be balanced by removing CO₂ from the atmosphere to achieve near-zero emission target [12].

Biorefineries as a coping strategy with global warming

Biomass is one of the most promising renewable resources since it receives solar energy and stores it in the form of chemical energy by the process of photosynthesis, meaning long term storage of energy. Even though the efficiency of photosynthesis is below 1%, around 3000EJ of energy is captured every year through photosynthesis [13, 14]. The biggest advantage of using biomass derived services is that the carbon cycle can be closed and it can be seen as a carbon neutral or balanced feedstock. Biomass feedstocks store CO₂ from the atmosphere via photosynthesis in a relatively short period of time and the same amount of CO₂ is released into the atmosphere during the decomposition. On the other hand, the storage of CO₂ in fossil fuels happens over millions of years and emits CO₂ by combustion in very short time [15]. Biomass can be used in the manufacturing process of all carbon-based products, including liquid hydrocarbon fuels and energy services [16]. Moreover, IPCC 1.5°C special report state that bioenergy (BE) combined with carbon capture and storage (CCS) is the only large scale technology that is able to achieve net negative emissions and it is essential in the stabilization of the global average temperature [1]. Sustainable biomass potential by 2050 is estimated to be around 150-250 EJ/year which can provide significant amount of energy for the global energy consumption [17].

Lignocellulosic biomass, also known as second generation biomass has been recognized as a valuable commodity since it is a sustainable alternative to fossil resources. It has the advantage of being cheap, abundant and unlike first generation biomass, does not compete with food crops [18]. Despite these advantages, there still remain many technological barriers to overcome, when using lignocellulosic biomass as the primary carbon feedstock. Indeed, the processing of this renewable feedstock is energy intensive and expensive. To alleviate economic and environmental burden of the operation, an efficient processing of biomass into products must be applied.

The transportation sector is currently predominantly powered by oil; therefore, introducing renewable energy sources is essential for the decarbonisation of this sector and for reducing pollutants to improve urban air quality. Contributing to low carbon-transport is possible with rapid expansion of electric mobility (on condition that the electricity, itself, is renewable), the development of electricity storage technologies, the use of alternative fuels such as liquid biofuels (synthetic paraffinic fuels, alcohols, ethers and esters), synthetic natural gas (SNG), upgraded biomethane together with the improvement of the overall energy efficiency of the transport system [19]. The transport sector is subcategorized into four modes; road (light and heavy duty), marine, aviation and rail transport and two types; passenger and freight transport. Electrification of both rail and road transport is now seen as a viable option and its use is increasing. However, aviation, marine transport and certain heavy-duty road vehicles are likely to rely on internal combustion engines and liquid fuels in the near future. In these transportation modes, sustainably produced biofuels are capable of delivering significant life cycle greenhouse gas emission savings as the main alternatives to fossil fuels [20]. IPCC recently indicated that the transport sector must include more biofuels together with electricity in its energy mix to keep track on 1.5°C pathway. The biofuels share should increase by 2%, 5.1%,

and 26.3% by 2020, 2030 and 2050 respectively [1]. However, economically competitive production of biofuels is always a challenging task. Therefore, co-production of high value chemicals can enable the production of economically profitable biofuels. This leads to the concept of biorefinery.

A biorefinery is an integrated processing facility where biomass is converted into a variety of products ranging from fuels, value-added chemicals to heat and power after many physical, chemical, biological and thermal conversion processes [21]. Currently, the attention is increasing on feasible biorefinery concept as well as an inventory of most promising biochemicals due to high environmental impact of petroleum derived products. Biomass is the only renewable energy source which can provide organic carbon to chemical industry in sustainable yield. Therefore, there is a huge potential for bio-based chemicals in the future. Future biorefineries would be multifunctional and able to imitate the energy efficiency of modern petroleum refining via extensive energy integration and co-product development. Overall, combined production of transportation fuels, chemicals, heat and power from biomass creates promising opportunity to satisfy part of their respective markets [22, 23].

Challenges

There are many challenges for process developers as well as opportunities while developing, designing, and commercializing sustainable and cost-effective biorefineries. Biorefinery research is ongoing and there are large number of potential technologies at development stage. These processes need to be evaluated before the data is consolidated. One of the main challenges is the need of a systematic approach to select and integrate processes in a way that market demand of existing and possible new products is satisfied by considering the availability of the biomass feedstocks [24]. In a biorefinery, several feedstocks, various products and a large number of technologies exist and this leads to a complex structure that has different production pathways [25]. Maximizing product and biomass recovery in a sustainable manner is crucial for an integrated biorefinery thus product diversification should be put forward. In addition, the energy balance should be closed with renewable energy and it should be supplied from the waste streams or the feedstocks. The economic competitiveness of the biorefineries is based on the production of high-value co-products together with comparably low-value bioenergy, including biofuels. Moreover, self-sufficiency should be achieved by exchanging material and heat streams within the complex structure, to minimize the energy and material requirements and wastes [26]. There are also concerns about actual sustainability of bio-based products due to consumption of energy and water. It is not possible to identify the overall best biorefining technology. The problem to be solved is to identify the competition between bio-based products; bioenergy in terms of heat and power, biofuels and biochemicals considering economic performance, energy requirement and environmental impact and to analyze the synergies of co-production while maximizing use of biomass resources.

All these aspects bring the requirement of advanced process synthesis and optimization methods to guarantee the economic viability, energy efficiency and minimum environmental impact [27]. These methods are essential to develop, design and commercialize biorefineries. The systematic approach

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for the design of an optimal biorefinery is to integrate process synthesis with process design and analysis. Process synthesis generates design ideas and establishes performance targets. It collects information on different biorefinery process operations and process data and produces economically and energetically efficient flowsheets which have good design characteristics. Process analysis evaluates those design ideas through simulation, integration and optimization approaches to match the design targets, screen alternative designs, enhance design and operational decisions and quantify the real impact to finally reach the optimal biorefinery pathways and designs [28].

Thesis objectives

Main goal of this thesis is to create a computer-aided platform to perform multi-scale design of biorefineries by proposing a combination of computational and thermodynamic tools that offer powerful support for optimal implementation of processes and assist decision-making. In particular, three research questions are addressed;

- *How can we develop a systematic methodology for early stage decision making in the design of biorefineries?*
- *What is the role of biomass in the energy conversion system?*
- *What is the potential of new biorefining technologies integrating consolidated bioprocessing and catalytic upgrading to produce specialty chemicals and jet fuel blend?*

Outline

Chapter 1 introduces the general context of the biorefinery concept and presents a brief state-of-the-art literature review of the advances in the area of process system engineering, available systematic techniques for process synthesis, design, integration, and optimization and their application to biorefineries are introduced. It motivates the choice of the analyzed case study and technologies.

In Chapter 2, a systematic biorefinery design approach is developed for thermo-environmental modeling, analysis and multi-objective optimization. A superstructure of different processes is developed considering biochemical and thermochemical conversion pathways. Optimal energy integration algorithms between process units of biofuels, biochemicals and bioenergy production pathways are implemented and synergies between them are investigated to understand the best combination of products and optimal sizes of process units. Proposed multi-objective optimization methodology combines integer cut constraints with ϵ constraint method to show the trade-offs between economic and environmental objectives and the results provide a set of candidate solutions according to minimum total cost and environmental impact, considering benefit of heat integration between different pathways to obtain energy efficient biorefinery systems with improved process economics and reduced environmental impacts.

Chapter 3 addresses the potential of replacing conventional natural gas fired steam boilers with biomass gasifiers producing heat and several biofuels under CO₂ emission and re-utilization constraints. A system which combines heat and fuel (CHF) production together with CO₂ capture and sequestration and power-to-gas technologies is evaluated using thermo-environmental optimization

methodology to highlight the use of biomass as a source for long term energy storage. Cost of heat is calculated for different scenarios considering carbon dioxide avoidance benefit. To achieve this, a variable CO₂ tax is introduced and breakeven carbon taxes are calculated for different scenarios.

In Chapter 4, the proposed methodology in Chapter 2 is applied on the design of a novel birefinery system which combines a catalytic conversion platform with consolidated bioprocessing focusing on jet fuel blend and alpha olefins production considering both economic and environmental impact criteria. Minimum energy requirements are identified for the processes and heat recovery potentials in the systems are analyzed using pinch analysis. Different gasification configurations are integrated with biological conversion and catalytic upgrading pathways to benefit from the energy synergy between them. Technology comparison is made by calculating minimum selling price and greenhouse gases emissions.

1 Context

Overview

- Context of the biorefinery concept
- State-of-the art review on process systems engineering in biorefineries

Section 1.2 provides a general *state-of-the-art* review of relevant work that have currently been undertaken and the identified gaps in process systems engineering in biorefineries. The chapter is partly published in the book chapter: *Léonard, G., Pfennig, A., Celebi, A.D., Sharma, S. and Maréchal, F., 2017. Industrial Integration of Biotechnological Processes from Raw Material to Energy Integration: Study by Modeling Approach. Microbial Fuels: Technologies and Applications [29]*

1.1 The biorefinery concept

There are several definitions for biorefinery in the literature. The most comprehensive definition is done by International Energy Agency (Bioenergy Tasks, Task 42 on Biorefineries) by saying that biorefining is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat) [30].

Biomass refers to any organic matter available on a renewable basis such as wood and wood residues, agricultural residues, algae, animal or food waste. In order to diversify the products and to increase profit, the renewable carbon source feedstock must be separated into more useful and treatable fractions, that are then further processed through different production lines into chemicals, fuels or electricity [31]. The expression sustainable processing relates to cost effective and efficient transformation of the biomass into products while considering environmental and social impact. For the design of biorefineries, there are multiple degrees of freedom included such as type of biomass feedstocks and their variability in the composition, possible products and the conversion technologies. Figure 1.1 shows the illustration of different categories in the biorefinery systems.

1.1.1 Type of feedstocks

Choice of the biomass feedstock depends on many criteria such as year-round availability, sustainability of the harvesting method, infrastructure for a reliable feedstock supply, choice of plant

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location to minimize transportation distance and looking after the economic and environmental benefits for farmers and other stakeholders. The feedstock must be cheap with high production rate and a low level of contaminants [32]. It also highly depends on the regional availability since it affects the scale of the biorefinery. In United States, economies of scale require a biorefinery size of 100-400 MW_{dry} [33]. While in Switzerland, Steubing et al. showed that a biorefinery focusing on bioenergy should consider a capacity 100–200 MW_{dry} for an economical production scale and the range is between 5–40 MW_{dry} for environmental optima [34].

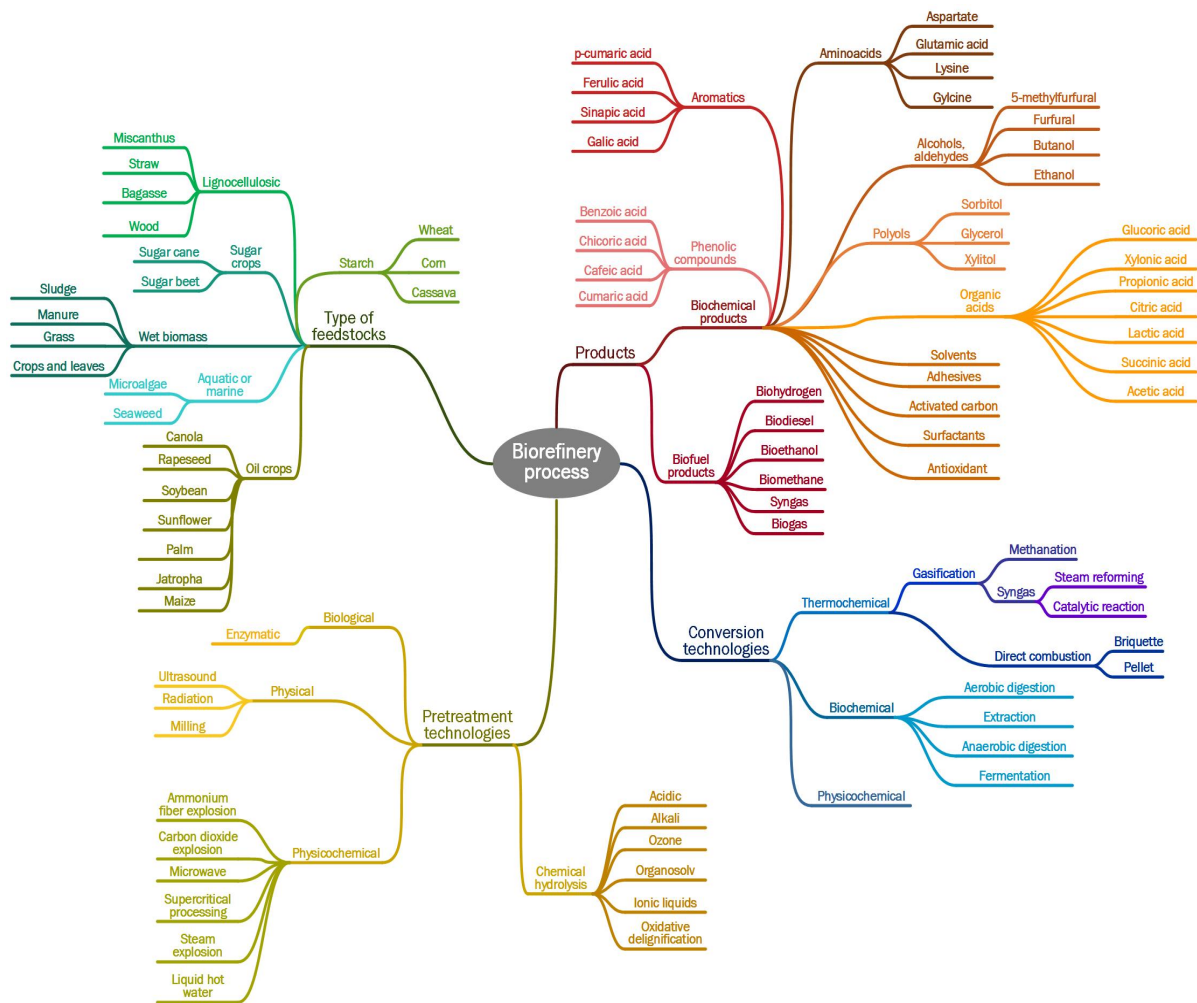


Figure 1.1: Biorefinery systems (adapted from [35]).

Depending on the type of biomass feedstock, biorefineries are classified as first, second and third generation. Example biomass feedstocks and products for each biorefinery classification are shown in Table 1.1 [36].

First generation biorefineries using agricultural biomass (corn, starch, vegetable oils etc.) have the risk of creating a competition with food consumption and biorefinery process using the same

Table 1.1: Biorefinery classification

Generation	Feedstocks	Examples
First generation biorefineries	Sugar crops (sugar cane, sugar beet), starch crops (corn, wheat), vegetable oils or animal fats	Bioalcohols, biodiesel, biogas
Second generation biorefineries	Nonfood crops, bagasse, wheat straw, corn stover, wood, solid waste, energy crops	Bioalcohols, bio-oil, bio Fischer-Tropsch diesel
Third generation biorefineries	Algae	Biodiesel, biomethane

biomass [36]. Second generation biorefineries use mainly lignocellulosic biomass which denotes feedstock derived from agricultural residues (corn stover, crop straws and bagasse), herbaceous crops (switchgrass), short rotation woody crops, forestry residues, waste paper and other wastes (municipal and industrial). Lignocellulosic biomass has been recognized as a sustainable alternative to fossil resources. It has the advantage of being cheap and abundant [18]. It is composed of mainly three polymers; (carbohydrate polymers) cellulose entangled with hemicellulose and trapped by lignin (aromatic polymer) through a variety of covalent bonds. Typical composition of lignocellulosic biomass is 45% cellulose, 25% hemicellulose, 25% lignin and 5% others (ash etc.) [37]. Figure 1.2 shows the structure of lignocellulosic biomass.

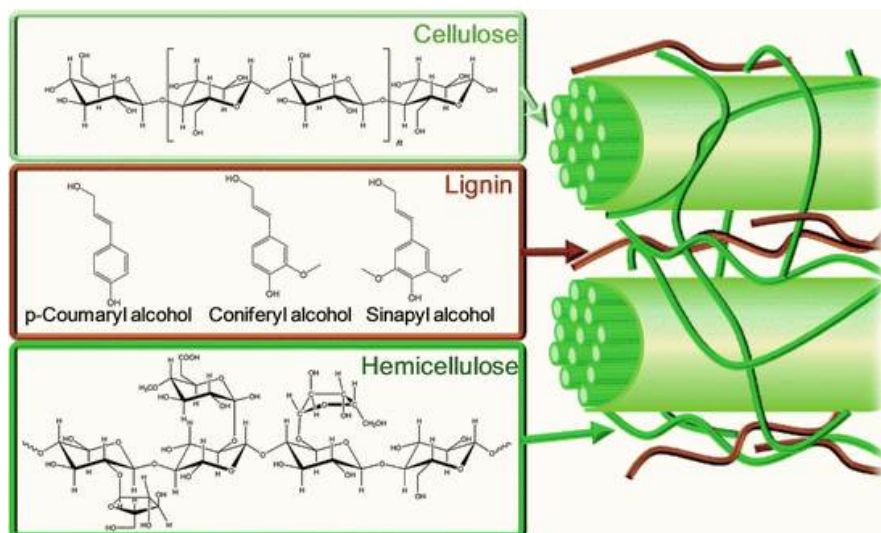


Figure 1.2: Structure of lignocellulosic biomass (taken from [38]).

Cellulose Cellulose is a linear polysaccharide $(C_6H_{10}O_5)_x$ consisting of several thousand of D-glucose linked by β -(1,4)-glucosydic bonds to each other. Cellulose microfibrils are packed tightly linked by strong hydrogen bonds so that this crystalline material is highly recalcitrant, water-insoluble and has high molecular weight. Only agents capable of destroying the glycosidic bonds

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between the glucose residues will solubilize the cellulose [18].

Hemicellulose Hemicellulose is located in secondary cell walls, and has branched heteropolymers containing pentoses (xylose and arabinose) as well as hexoses such as glucose, galactose and mannose. They can relatively easily be hydrolyzed due to their amorphous and branched structure and lower molecular weight [18]. The primary component of hemicellulose is xylan and its composition varies for each feedstock. Therefore, a wide range of enzymes is needed to hydrolyze it completely. A control of operating conditions is necessary to avoid degradation of C5 sugar into furfural products that have inhibitory effects later on enzymatic hydrolysis and fermentation [39].

Lignin Lignin is a complex hydrophobic polymer of aromatic rings coupled via covalent bonds to xylans and it is highly resistant to enzymatic, chemical and microbial hydrolysis due to its extensive cross linking. It plays an essential role in the formation of cell walls, giving stability to the plant cell wall [39, 18].

The composition varies depending on the type, species and the region where it comes from and it affects the yield of bioconversion to intermediates and platforms. Table 1.2 shows main characteristics of different lignocellulosic biomass.

Table 1.2: Characteristics of some lignocellulosic biomass

	Sugarcane bagasse [40, 41]	Wheat straw [40, 42, 43]	Corn stover [39, 44]	Switchgrass [42]	Hardwood [45, 39]	Softwood [46, 39]
Moisture (%)	45-50	16	6-30	40-70	50	45
LHV (MJ/kg) ¹	17.7	18.3	16.9	17.4	18.4	17.9
Bulk density (kg/m ³) ²	50-75	51-97	66-131	65-105	70-100	-
Proximate analysis (%)³						
Volatile matter	83.7	82.1	80.9	73-87	82.8	84.2
Fixed carbon	13.2	11.0	14.1	13-27	16.4	15.5
Ash	3.2		5.06	3-13	0.9	0.3
Ultimate analysis (%)⁴						
C	45.5	43.0	46.8	42-53	49.9	48.8
H	6.0	5.4	5.7	5.2-6.5	6.1	5.8
O	45.3	47.0	41.4	36-49	42.9	44.9
N	0.2		0.7		0.	0.2
Chemical composition (%)						
Cellulose	43.38	33-40	38.3	30-50	45-47	40-45
Hemicellulose	25.63	20-25	25.5	10-40	25-40	25-29
Lignin	23.24	15-20	17.4	5-20	20-25	30-60
Extractive	4.82	-	-	-	0.80	0.50

¹ LHV [MJ/kg daf] = HHV[MJ/kg daf] - 2.442x(8.936xH[wt%]/100)[44].

³ dry basis.

⁴ dry basis, ash free (daf).

² Bulk density ranges are found in Tanger et al. [47].

Woody biomass has many advantages in terms of production, harvesting, storage and transportation compared with herbaceous biomass as a feedstock for the biorefineries. Long term storage problems can be eliminated since it can be cultivated all year-around and it can be produced in large quantities in many regions of the world if the land is managed in a sustainable manner. Having higher lignin content implies higher energy density, thus giving opportunities to use for further processing into bio-based products [48].

1.1.2 Conversion technologies

A biorefinery can employ several pathways with the major ones being biochemical pathways (i.e. sugar platform) and thermochemical pathways (i.e. syngas platform) for the production of biofuels and value-added bio-based chemicals.

1.1.2.1 Thermochemical pathways - syngas platform

Thermochemical pathways consist of complex processes where biomass is converted into syngas or pyrolysis oil using heat and catalysts.

Main thermochemical pathways are:

- i **Pyrolysis:** It consists of thermal degradation of biomass in the absence of any oxidizing agent. It usually occurs at around 300-650°C and can be categorized as slow pyrolysis or rapid/fast pyrolysis depending on the residence time. The outlet consists of liquid, gas and solid matters. The most important product is the liquid part (bio-oil) depending on the process and feedstock [49].
- ii **Torrefaction:** It is milder form of the pyrolysis, hence it occurs at lower temperatures at around 200-320 °C [50].
- iii **Gasification:** It is a high temperature endothermic process resulting in syngas (producer gas) mainly consisting of hydrogen (H₂), carbon monoxide (CO), methane (CH₄), carbon dioxide (CO₂), with traces of light hydrocarbons, water, tars, ash and nitrogen if air is used as gasifying agent. Syngas is an important intermediate in chemicals production and an important fuel source. Gasification technologies can be classified depending on different operation modes (see Table 1.3) [51]. Each technology yields in different syngas compositions with different H₂/CO ratios varying from 0.45 to 2. Depending on the feedstock and technology, the gasification temperatures can range between 800-1500 °C and even higher [50, 42].

To produce biofuels, gasification process is followed by biofuel synthesis. Specific chemical composition is required for a particular biofuel synthesis therefore operating conditions and gasifying agents in gasification are chosen accordingly. For example, steam-blown gasification results in hydrogen and methane rich syngas which can be further used for producing SNG. Raw syngas needs cleaning and conditioning before biofuel synthesis. The contaminants such as tar and sulphur need to be removed from the syngas with technologies such as high-temperature catalytic tar removal, wet scrubbers to remove gas impurities and solid particles, and filters for removal of dust. Syngas conditioning involves catalytic water-gas-shift reaction

Table 1.3: Gasifier types and operating parameters

Parameter	Type	Subtype
Reactor design	Fixed-bed	Downdraft (cocurrent) Updraft (countercurrent)
	Fluidized-bed	Bubbling fluidized-bed (BFB) Circulating fluidized-bed (CFB)
	Entrained-flow (EF)	
Gasifying agent	Air, oxygen, steam	
Heat management	Direct	
	Indirect	
Pressure	Atmospheric	
	Pressurized	

to adjust CO/H₂ ratio, compressors for pressurizing to desired synthesis pressure and CO₂ removal technologies. Then it can be processed in secondary catalytic synthesis of a variety of hydrocarbons to produce transportation biofuels (such as synthetic natural gas via exothermic methanation process, Fischer-Tropsch crude, methanol and dimethyl ether) and chemicals (such as ammonia) or can be used to produce heat and power via a gas turbine [52, 51].

Other thermochemical conversion technologies consist of liquefaction processes which are similar to pyrolysis but in lower temperatures and higher pressure levels and hydrothermal approaches which operate at moderate temperatures (200-600°C) and high pressures (5-40 MPa) [53]. Catalytic hydrothermal gasification creates an opportunity for the utilization of wet biomass such as manure, microalgae, municipal solid waste, woody biomass etc. [54, 55].

1.1.2.2 Biochemical pathways - sugar platform

Biochemical pathways break down biomass using enzymes and bacteria into different types of sugars which are further processed into bio-based products. Bio-conversion of any kind of lignocellulosic biomass consists of following main steps:

- i **Pretreatment:** The main purpose is to break the links of biomass and set free the cellulose and hemicellulose and disrupt the crystalline structure of cellulose so that the acids or enzymes can easily access to cellulosic fibres during the hydrolysis step [56].
- ii **Hydrolysis:** To convert the cellulose and hemicellulose to fermentable sugar like glucose (C6 sugar) and xylose (C5 sugar), respectively.
- iii **Fermentation:** Fermentation processes use yeasts to convert sugars to bio-based products.
- iv **Digestion:** During the anaerobic digestion process, the organic material is decomposed by microorganisms in the absence of oxygen to produce biogas, that is a gas mixture of methane (50-70%) and carbon dioxide with traces of impurities [42].

Pretreatment

Pretreatment breaks the complex matrix of the lignocellulose to make the sugars more accessible to enzymes. Many researchers published reviews on the biomass pretreatment methods. [56, 57, 58].

Pretreatment methods can be classified into different categories: physical, physicochemical, chemical, and biological (fungi). Depending on the biomass composition and by-products produced as a result of pretreatment, different technologies can be chosen [56]. Selecting appropriate pretreatment method is important for the downstream processing, since it will affect the overall conversion in terms of cellulose digestibility, generation of toxic compounds, energy demand, wastewater treatment as well as the economic and environmental impact.

Physical pretreatments

Drying of the biomass prior to processing is an energy conservation method and it requires a large amount of heat to evaporate the water from the biomass feedstock [59]. Steam and air drying are the most common technologies for biomass drying. Usually, operating temperatures are higher in steam dryers so air dryers might be advantageous if heat is available at lower temperatures. Steam dryers have more complex design and even a small leakage can cause big reduction in energy efficiency [60, 61]. The performance should be evaluated depending on the integration with the rest of the processes.

Mechanical comminution is a combination of chipping, grinding and milling treatments which is applied to reduce the size of feedstock and causes a decrease in cellulose crystallinity and increase enzyme accessible surface area of biomass [56].

Physicochemical pretreatments

- ***Steam explosion:*** It is one of the widely used methods for the pretreatment of lignocellulosic material. In steam explosion technology, biomass particles are charged into a reactor, high-pressure saturated steam is injected to biomass and the pressure is suddenly released to atmospheric pressure resulting in an explosive decompression that breaks the structure of the materials.

Steam explosion pretreatment produces a slurry. It combines mechanical forces and chemical effects of hydrolysis of acetyl groups into organic acids that serve as catalyst for hemicellulose hydrolysis helped by acidic properties of water at high temperatures [62]. Time, temperature, particle size and moisture content are the key parameters to configure process severity. Steam explosion dissolves hemicelluloses and results in low sugar degradation [56, 62].

- ***Liquid Hot Water (LHW):*** In LHW, pressure is applied to maintain water in the liquid state at high temperature without rapid pressure release. The products are slurry, consisting of solids (enriched cellulose and water soluble materials) and liquid fraction (water and most of the solubilized hemicelluloses). This pretreatment method is still being developed and indicates a great potential [18, 63].
- ***Ammonia fibre explosion (AFEX):*** Biomass particles are charged into a high-pressure reactor and treated with a liquid ammonia solution at high pressure for a variable period of time. Similar to steam explosion, after retention time, pressure is suddenly reduced, vaporizing ammonia and allowing its recovery. Temperature is the most important factor in AFEX since it determines the amount of ammonia vaporized. AFEX method produces only solid material due to low boiling point of ammonia and it does not liberate sugars directly. It is not very

effective with biomass containing high lignin content [64].

- **CO₂ explosion:** It has a lower temperature than steam explosion and reduces expenses compared to ammonia explosion but the yield of sugars is lower. Biomass pretreatment is facilitated by high pressure. CO₂ pressure is released explosively and cellulose and hemicellulose structure is disrupted. In aqueous solution, CO₂ forms carbonic acid and increases the hydrolysis rate. Since the temperature is low, degradation of monosaccharides caused by acid can be prevented [65, 66].

Chemical pretreatments

- **Concentrated acid pretreatment:** Acid is used as catalyst and results in improvement of enzymatic hydrolysis to release sugars. H₂SO₄ and HCl are the most common used acids [66].
- **Dilute acid pretreatment:** In dilute acid pretreatment, H₂SO₄ below 4 wt% concentration, phosphoric acid and weak organic acids are used at high temperature for cellulose hydrolysis. Since acid is dilute, the process is less expensive. Dilute acid pretreatment removes hemicellulose effectively and recovers as xylose and other sugars. Sugar yield from hemicellulose is 70-95%. Depending on the process temperature some undesirable compounds such as hydroxymethylfurfural (HMF), furfural and aromatic lignin degradation compounds occur [67].
- **Alkaline pretreatment:** Alkali based pretreatment uses some agents such as sodium, potassium, calcium and ammonium hydroxides for the pretreatment of lignocellulosic materials and the effects of the pretreatment depends on the lignin content of the materials. It requires lower temperatures and pressures but the residence times are in hours rather than minutes. Sugar degradation and improvement in cellulose digestibility is lower when compared with the acid pretreatment [66, 68].
- **Oxidation pretreatment:** It uses oxidising agent such as hydrogen peroxide, ozone, oxygen or air and pretreatment results in lignin biodegradation and low cellulose degradation [69]. Hydrogen peroxide is an oxidative compound that is commonly used to achieve 50% dissolution of lignin. Ozonolysis is a pretreatment method focusing on delignification by attacking aromatic rings of lignin structure [70]. Wet oxidation pretreatment utilizes oxygen as an oxidizer for compounds dissolved in water at high temperature and pressures to fractionate biomass by solubilizing hemicellulose and removing lignin about 50% to 70% [71].
- **Organosolv pretreatment:** It uses organic solvents such as ethanol, methanol, ethylene glycol, and acetone, to break internal lignin and hemicellulose bonds and provide more accessible cellulose. Methanol and ethanol are used widely due to their low boiling point, low cost and miscibility with water. The organic solvent is mixed with water and added to biomass with solids ratio ranging from 4:1 to 10:1 (w/w). Some catalysts such as HCl, H₂SO₄, oxalic and salicylic acid can be added if the process is operated at low temperature as 180-210°C to break the hemicellulose bonds [69, 72]. Recycling of the solvent is possible and high quality lignin can be produced. But, the production cost is high with high cost of solvent. Therefore, high value products should be produced to compensate this shortfall. With minimization of

waste streams and providing valuable by-products, organosolv pretreatment might become one of the leading pretreatment technologies despite the fact that it is more expensive than the other pretreatment methods [73].

- ***Ionic liquid (IL) pretreatment:*** Ionic liquids which are salts with melting points below 100°C and exist in liquid form at low temperatures. They are used as solvents to break down the extensive hydrogen bonding network of the polysaccharides and enhance its solubilisation resulting in removal of lignin and hemicellulose [74, 75].

Biological pretreatments

- ***Fungal pretreatment:*** Microorganisms such as brown-, white- and soft-rot fungi are used to degrade hemicellulose and lignin. White and soft rot fungi attack cellulose and lignin while white rot fungus is selectively effective for delignification over cellulose. It is a safe and environmental friendly method [76].

Table 1.4 summarizes the main operating conditions of mentioned pretreatment processes, their advantages and disadvantages.

Hydrolysis

Hydrolysis is a chemical reaction that converts cellulose molecules into simple monosaccharides (glucose). To accomplish this, acids or enzymes are used as catalyst [69].

- ***Acid based hydrolysis:*** For acid based hydrolysis, dilute or concentrated acid is utilized. In concentrated acid hydrolysis, the sugar recovery efficiency is high. Concentrated acid breaks the hydrogen bonds between cellulose chains and results in cellulose decrystallization and forms a gelatin with acid. The advantages of concentrated acid process over dilute acid process are higher efficiency and lower operating temperature (40°C). But since the concentration of acid is between 30-70% which is very high, the concentrated acid hydrolysis is extremely corrosive and requires expensive corrosion-resistant reactors. Also, recovery of acid is an energy consuming process. However, the potential for cost reduction for concentrated acid hydrolysis is bigger. In this process, usually sulphuric acid about 70-77% is added to biomass. For dilute acid hydrolysis, low concentration of sulphuric acid is used at higher temperatures. For hemicellulose hydrolysis, highest yield can be obtained around 190°C while cellulose depolymerizes into glucose at higher temperatures (e.g. 230°C) [66].
- ***Enzymatic hydrolysis:*** Enzymatic hydrolysis reaction is carried out by enzymes to break down the bonds in cellulose and hydrolyse into glucose. Cellulase enzymes are used as catalysts which are commonly produced by fungi and bacteria [69]. Enzymatic hydrolysis reaction takes place at ideal conditions for cellulose enzyme at pH 4.8 and 45-50°C . It requires longer reaction time (several days) while acid hydrolysis process takes a few minutes. Final products of enzymatic hydrolysis are required to be removed to prevent enzyme inhibition. High enzyme cost is the main disadvantage however it is a non-corrosive process [77].

Table 1.4: Overview of different pretreatment methods for lignocellulosic biomass

Method	Conditions	Advantages	Disadvantages	Source
Mechanical comminution	Size after chipping: 10-30 mm, size after milling and grinding: 0.2-2 mm	Reduces cellulose crystallinity	Power consumption is higher than inherent biomass energy	[56]
Steam explosion	No agent, 160-240°C , 10-50 bar , 2-5 minutes	Low environmental impact, low capital investment, less hazardous process chemicals, complete sugar recovery, more potential for energy efficiency	generation of toxic compound	[56, 62]
Liquid hot water	170-230°C , pressure > 50 bar, 45 seconds-15 minutes	Simple, low generation of inhibiting products, high yields, low reactor cost, no catalyst cost, limited corrosion problems	Water recycling prohibitively expensive	[63, 18]
Ammonia fibre explosion	dosage: 1-2 kg of ammonia/kg of dry biomass, 60-100°C , 0.5-3 hours	90% conversion of cellulose and hemicellulose to fermentable sugars,	Limited effects on soft and hardwood, requires high pressure equipment, recycle of ammonia is required	[64]
CO ₂ explosion	CO ₂ as agent, 35°C , 56.2 bar, 10-60 minutes	CO ₂ is non-toxic, leaves no harmful residues, inexpensive and readily available, increases accessible surface area	lower sugar yield than AFEX and steam explosion, very high pressure requirement	[65, 66]
Concentrated acid	H ₂ SO ₄ /HCl as agent	Moderate operating conditions, no enzyme requirement, less operating cost than dilute acid treatment	Needs neutralisation, acid recovery, significant formation of fermentation inhibitors, corrosion problems, conc. acids are toxic, hazardous	[66]
Dilute acid	H ₂ SO ₄ as agent, T > 160°C , continuous, solid loading: 5-10% weight of substrate/weight of rxn mixture, 2-10 min OR T < 160°C	Excellent hemicellulose sugar yields, highly digestible cellulose with low acid loadings	Needs neutralisation, acid recovery, significant formation of fermentation inhibitors, higher cost than physicochemical treatments (e.g. AFEX, steam explosion)	[67]
Alkaline	NaOH/ Ca(OH) ₂ / Ammonia as agent, 70-150°C , 1-13 hours	Alters lignin structure removes hemicellulose and lignin, increases accessible surface area	Costs wastewater treatment are high, generation of inhibitory compounds	[66, 68]
Wet oxidation	O ₂ /air in combination with water as agent, 150-350°C , 5-20 MPa	Removal of lignin, lower production of inhibitors such as HMF and furfural	Costs of reagents and wastewater treatment are high	[69, 71]
Organosolv	Ethanol/methanol/acetone as agent, 100-250°C , 30-150 minutes	Relatively pure lignin as by-product	Cost of solvent recovery is high	[69, 72, 73]
Ionic liquid	Ionic liquid as agent, 90-130°C , 1-24 hours	Mild processing conditions (low temperatures), ability to dissolve high loadings of different biomass types	Costs of reagents and long treatment time, limited data about ILS toxicity and biodegradability	[74, 75]
Fungal	White-, brown-, soft-rot fungi	Low energy requirements, mild environmental conditions, no use of chemicals, no require pressurized reactors, no waste stream	Rate of hydrolysis is very low, longer retention time	[76]

Fermentation

After the hydrolysis step, sugars can be fermented by microorganisms that include yeast and bacteria. Yeast *Saccharomyces cerevisiae* is one of the most commonly used yeasts for ethanol fermentation of glucose and it contains an enzyme called *zymase* that acts as catalyst for fermentation. For pentose fermentation, *C. shehatae*, *P. stipites* and *P. tannophilus* are the most common yeasts [78]. The fermentation process can take place in batch, fed batch or continuous reactors. For batch process, the reaction might be completed in about three days. The fermentation yield depends on the type of feedstock, type of process, and kinetic properties of microorganisms [79]. Depending on the type of strain, the sugars can also be fermented into carboxylic acids (acetic, succinic, butyric acid etc.).

Recovery and purification

The final part of the process is the downstream processing for the recovery and purification of the fermentation products to meet product specifications. Downstream processing involves many stages and technologies such as distillation, filtration, solvent extraction, precipitation, electrodialysis and chromatography which have been widely explained in [80]. For example, a distillation process consists of distillation columns which are required to increase ethanol concentration of the ethanol blend coming from the fermentation step.

1.1.3 Biorefinery products

The term bio-based products refers to any product derived from biomass. Biorefineries can also be categorized as product-driven biorefineries or energy-driven biorefineries depending on the function of the products. A variety of bio-based products can be produced in biorefineries, ranging from biofuels to value-added chemicals. Next sections will give an overview of selected promising bio-based products.

Bio-based chemicals

Promising bio-based chemicals are identified in the review of US Department of Energy [81] in 2010 as well as in the report and roadmap prepared for the European Commission [82, 83].

Selected bio-based chemicals for this thesis are listed in Table 1.5 and their global bio-based market volume in 2014 as well as total production capacity together with fossil-derived products are shown. Bioethanol production dominates the market with the largest production capacity and it is followed by much smaller but still significant market capacities of acetic acid, n-butanol and lactic acid. Xylitol is one of the products without petrochemical alternatives and it has a significant market share.

Market volume of the bio-based products affects their value. Commodities such as bioenergy, biofuels and bulk biochemicals have larger market volume with lower prices while value-added biochemicals and pharmaceuticals have smaller market volume with higher prices [86].

In 2015, bio-based feedstocks covered 10% of the total volume of organic feedstocks used for chemicals production in European Union. Bio-based Industries Consortium (BIC) in EU set an

Chapter 1. Context

Table 1.5: Characteristics and market capacity of selected bio-based products in 2014 [82]

Products	Chemical formula	ΔH_f^0 ¹ [kJ mol ⁻¹]	ΔG_f^0 ² [kJ mol ⁻¹]	% C [kg _C /kg _{product}]	Total production (bio+fossil) [ktonnes/yr]	Market share of bio-based product [%]
Lactic acid	C ₃ H ₆ O ₃ (l)	-694.0	-430.62	0.400	472	100
Ethylene	C ₂ H ₄ (g)	52.4	61.4	0.857	127'200	0.2
Acetic acid	C ₂ H ₄ O ₂ (l)	-484.5	-389.9	0.400	13'570	10
Ethanol	C ₂ H ₆ O(l)	-277.1	-174.9	0.522	76'677	93
Acetone	C ₃ H ₆ O(l)	-248.0	-154.0	0.621	5'500	3.2
n-butanol	C ₄ H ₁₀ O(l)	-327.4	-168.9	0.649	3'000	19.7
Succinic acid	C ₄ H ₆ O ₄ (l)	-940.26	-548.68	0.407	76	50
Xylitol	C ₅ H ₁₂ O ₅ (l)	-1118.6	-700.2	0.395	160	100
HMF	C ₆ H ₆ O ₃ (g)	-333.9	-289.5	0.571	0.1	20

¹ Standard molar enthalpy change of formation at 298 K, data for HMF is taken from [84], remaining data are taken from [85].

² Standard molar Gibbs free energy change of formation at 298 K, data for HMF is taken from [84], remaining data are taken from [85].

aspirational target of increasing biomass feedstock use to 25% [83] by 2030 in 2017 [83].

Figure 1.3 shows the share of bio-based products in EU chemical markets in 2015. Bio-based products' contribution is already large in some chemical groups such as surfactants, paints, coatings, dyes and man-made fibres.

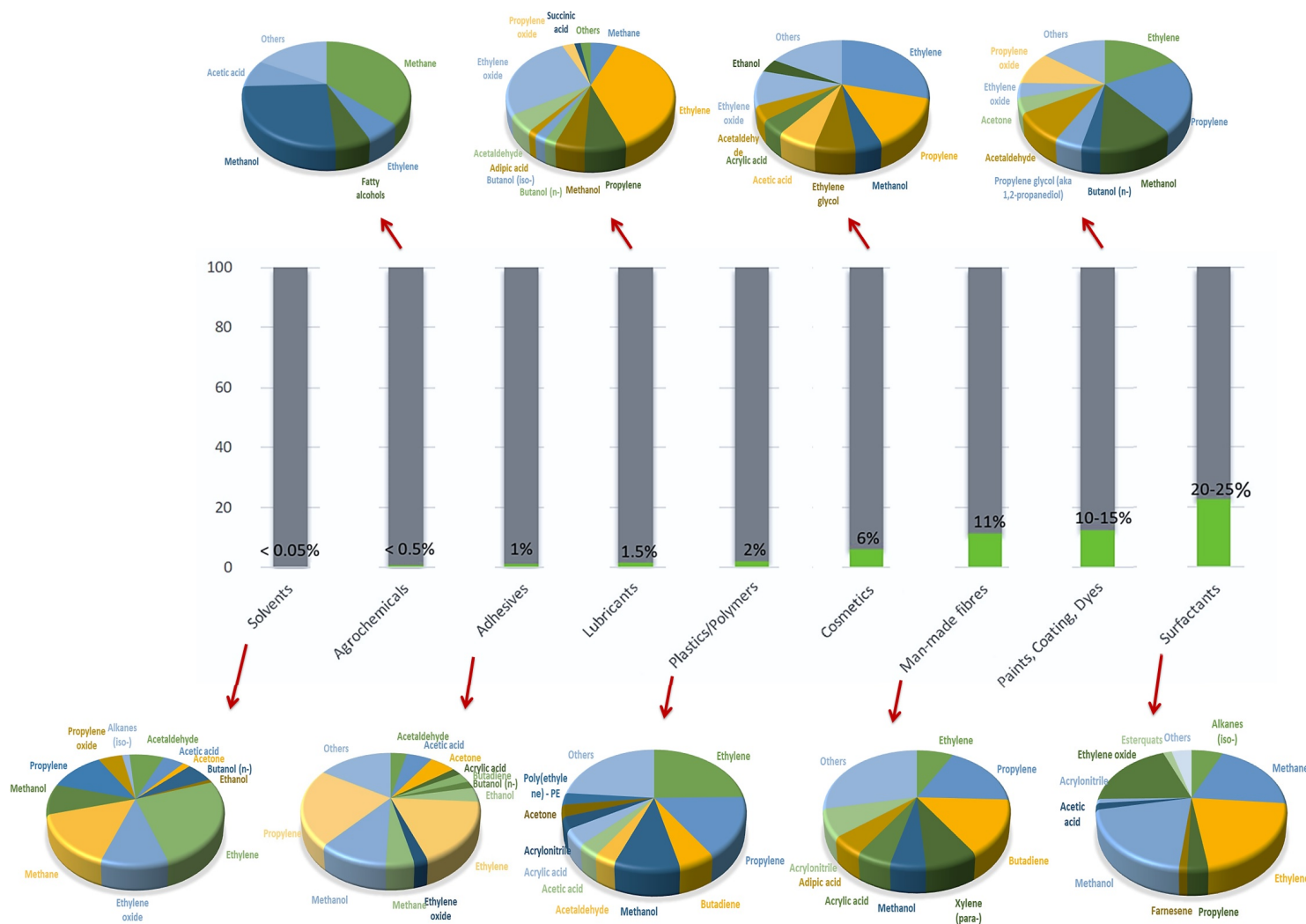


Figure 1.3: Share of bio-based products in EU chemical markets in 2015 and potential bio-based products for substitution in the future (adapted from RoadToBio D1.1 report [83]).

Ethylene: Ethylene is used to produce polyethylene (PE) which is the most widely manufactured plastic in the world and it has overtaken the packaging sector. Polyethylene can be produced by dehydrating ethanol to ethylene and then ethylene undergoes polymerization reaction using lignocellulosic biomass [83].

Lactic acid: Lactic acid from biomass can be produced via fermentation technology using lactic acid bacteria. It is an intermediate-volume specialty chemical which attracts food, pharmaceutical and personal care market. But one of the main driver of lactic acid market growth is polylactic acid (PLA). PLA is manufactured by polymerization of lactic acid and is mainly used as packaging material, insulation foam, fibres and automotive parts [83].

Succinic acid: Bio-based succinic acid is a platform chemical which can be produced via fermentation route and mainly used to replace maleic anhydride in the current industrial processes. It has a wide range of applications such as personal care products, food additives, bio-polymers, plasticizers, polyurethanes, resins, coating. Polybutylene succinate (PBS) is thermoplastic polyester and a potential route for the utilization of succinic acid. It can be produced via the esterification of succinic acid and butane-1,4-diol [83].

Acetic acid: Acetic acid is an organic acid and important chemical reagent, which is used to produce vinylacetate for polymers, synthetic fibres and fabrics, ethylacetate as solvent and it has other uses as food additive in the food industry. It can be produced via fermentation by bacterial strains [83, 87].

Xylitol: Xylitol is a polyol sugar which can be produced by the hydrogenation of xylose. Xylitol attracted the interest as diabetic sweetener and it has potential for use in food applications [88].

HMF: Bio-based 5-HMF is produced via dehydration of sugars and it is a promising feedstock for the production of polymers, fine chemicals (agrochemicals, flavors) and precursor of fuels [89].

Vanillin: The use of lignin for chemical production is so far limited except production of vanillin from lignosulfonate.

Bioenergy: biofuels

Biofuels are biomass derived energy sources used in transportation sector.

Fischer-Tropsch (FT) fuels: Fischer-Tropsch crude is a synthetic diesel that consists of various hydrocarbon liquids with different chain lengths which are produced by converting treated syngas through a Fischer-Tropsch (FT) synthesis process using catalysts. The hydrocarbons in FT fuels are mainly olefins (alkenes) and paraffins (alkanes) consisting of carbon ranges of C₂-C₄, C₅-C₁₂ and C₁₃-C₁₈. It can be used in compression-ignition (diesel) engines or spark ignition (gasoline) engines [45, 90].

Dimethyl ether (DME): DME is a gaseous clean fuel for compression ignition engines and produced by hydration of methanol. It has similar combustion properties to diesel and can be used as a fuel in diesel engines, gasoline engines as a blend of LPG/DME in transportation sector. Its applications also involve power generation via using DME in gas turbines. China has an important contribution to DME market [83, 20].

Synthetic natural gas (SNG): Bio-SNG is produced by synthesis reaction of treated syngas followed

by gas upgrading. It can be used as transportation fuel as well as for combined heat and power (CHP) production [91]. SNG can be in the form of CNG (compressed natural gas) or LNG (liquefied natural gas) to replace gasoline and diesel in internal combustion engines. CNG is stored at high pressure and can be injected in the natural gas distribution pipeline. LNG is suitable to the transportation for longer distances using heavy duty diesel engines such as ships, trains and large trucks due to its higher energy density [20].

Bioethanol: Ethanol is the most widely produced biofuel, accounting more than 90% of the global biofuel consumption. The largest producers of bioethanol are Brazil and US accounting more than 70% of the global production where bioethanol is already used in road vehicles for many years [92]. It is produced by yeast fermentation of sugar-rich and starch-rich biomass like sugarcane (Brazil), maize (North America) or grain crops (Europe). It can be used as transportation fuel in its pure form replacing gasoline or can be blended into gasoline as fuel additive to increase octane number and vehicle emissions. Ethanol can also be used as heating fuel, solvent or as a chemical industry feedstock. 10-20% of global ethanol production is used in the industrial sector and usage as solvent in the manufacture of pharmaceuticals, paints accounts for 60% of the total ethanol consumption in industrial sector [83].

Methanol: Methanol is an alternative fuel to gasoline and can be directly used or blended with gasoline in the vehicles. Treated syngas yields into methanol through catalytic reactions. There is a growing demand to use methanol in the production of DME, which is an alternative gaseous fuel to diesel [83, 50].

Butanol: Biobutanol is produced by acetone, butanol and ethanol (ABE) fermentation of biomass. It is a strong candidate in biofuel market to replace gasoline and it can be blended into gasoline up to 11.5 % volume. When compared to ethanol, it has higher energy density and it is less corrosive. Therefore, biobutanol shows promise as motor fuel to be used in internal combustion engine. It is also an important chemical which shows promises to be used as industrial solvent. It is possible to use biobutanol in many applications such as paintings, coatings, resins, pharmaceuticals and plasticizers. [83].

Table 1.6 and Table 1.7 show the characteristics and the main synthesis reactions for different synthetic fuels production, respectively.

Table 1.6: Characteristics of selected synthetic fuels

Products	Chemical formula	$\Delta H_f^{0\ 1}$ [kJ mol ⁻¹]	$\Delta G_f^{0\ 2}$ [kJ mol ⁻¹]	% C [kgC/kg _{product}]
Synthetic natural gas (SNG)	CH ₄ (g)	-74.9	50.6	0.708
Dimethyl ether (DME)	C ₂ H ₆ O (g)	-184.1	-112.9	0.522
Methanol	CH ₄ O (l)	-238.6	-166.2	0.375

¹ Standard molar enthalpy change of formation at 298 K, data are taken from [93].

² Standard molar Gibbs free energy change of formation at 298 K, data are taken from [93].

Table 1.7: Main synthesis reactions for synthetic fuels production [14]

Name	Reaction	$\Delta \tilde{h}_r^0$ [kJ mol ⁻¹]
Ethanol production (glucose fermentation)	$C_6H_{12}O_6 \rightarrow 2(C_2H_5OH + CO_2)$	-165
Methane synthesis	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-206
Water-gas shift reaction	$CO + H_2O \rightleftharpoons CO_2 + H_2$	-41
Sabatier reaction	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	-165
FT synthesis	$CO + 2H_2 \rightarrow -CH_2 - + H_2O$	-159
Methanol synthesis	$CO + 2H_2 \rightleftharpoons CH_3OH$	-90.1
	$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	-49
DME synthesis (methanol dehydration)	$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$	-23.4
DME synthesis (one-step)	$3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2$	-246.5

Bioenergy : heat and power

Biomass is also used for heat and power production using thermochemical conversion technologies such as combustion, gasification, and pyrolysis as well as biochemical conversion pathways, especially anaerobic digestion. Currently, biomass combustion is the dominant technology to produce heat and it is usually coupled with steam Rankine cycles to co-produce power. Global electricity production from biomass accounted for 2% of worldwide power generation in 2018 while 4% of global heat demand in buildings. Biomass integrated gasification combined cycle (BIG/CC) power plants are promising systems with higher efficiencies and larger plants sizes [94].

Carbon capture and storage (CCS)

Carbon Capture and Storage (CCS) technologies capture waste CO₂ usually from large industrial sources, such using absorption medium and desorb in a separate vessel. CO₂ is usually pressurized and transported for an onshore or offshore storage. CCS processes are attracting technologies to lower the CO₂ emissions [86]. IPCC report suggests coupling bioenergy (BE) with CCS technologies to achieve net negative emissions [1]. There are four different CO₂ capture technologies; post-combustion being the most common, pre-combustion, oxy-combustion and chemical looping. Chemical absorption is the most widely used process as a post-combustion method which uses absorbents such as MEA (monoethanolamine) and ammonia [86].

1.2 Process systems engineering tools for biorefineries

There are several methodologies to solve complex problems in process design and synthesis of chemical plants and energy systems regarding to multiple criteria and decision variables. Integration of the processes and the analysis of the interaction between units are becoming more and more important to improve the efficiency of mass and energy transfer and to reduce the capital and operating cost [95].

A systematic approach for the design of biorefinery, integrates the use of advanced process synthesis, process analysis and optimization methods [24]. Process synthesis methods collect the input

data about different biorefinery processes and produce energetically and economically efficient biorefinery flowsheets with good operating conditions and design specifications. Process modeling and simulation are complementary approaches to analyze different designs obtained from process synthesis for the optimal configurations of biorefineries [28, 96]. Over the last 45 years, researchers have studied in process synthesis area and many have published extensive reviews on this subject [97, 98, 99, 100].

In the next sections, a brief review of advances in the area of process system engineering is provided.

1.2.1 Process synthesis

The approaches are generalized into three categories or some combination thereof

1. methods that use heuristics,
2. methods that use thermodynamic targets and process integration,
3. methods that use superstructures, mathematical programming and optimization.

In hierarchical (or heuristic) approach, one can decide whether the plant will be operated in batch or continuous, type of reactor used, recycle schemes for material, methods and sequence of separations, energy integration applied, etc. In thermodynamic analysis, one has to decide the units and streams which are considered for the heat recovery, thermodynamic targets used and the level of utilities involved. In the optimization approach, the extent of the superstructure, included physical data, employed objective function, as well as constraints and uncertainties to consider, are the features to be decided by engineer [101]. Major contributions in the first two approaches (heuristics and thermodynamic targets) are the hierarchical-conceptual decomposition strategy (Douglas, 1988) [102] and pinch analysis that is used to identify the possible heat recovery (Linnhoff, 1993) [103], which have been applied very successfully in many industrial applications [28]. Recently, researchers focus on combining mathematical programming approach with algorithmic methods based on optimization techniques which can be used effectively in process synthesis [104]. There are three steps in the combined approach: (1) the development of a representation for alternative superstructures, (2) the formulation of a mathematical program for the selection of the configuration and operating levels from the superstructure, and (3) the solution of the optimization model [28].

The main mathematical tool for this purpose is mixed integer programming and it is widely used in areas of utility systems, heat recovery networks and processing systems. The problem can be formulated using a mixed-integer linear programming (MILP) and/or mixed-integer nonlinear programming (MINLP) model for solving optimization problems involving both continuous and discrete variables. For MILP problems, the functions involved in the problem are linear and the standard procedure is branch and bound method [105].

1.2.2 Process modelling

Process models are necessary for simulations in the context of process synthesis. Mathematical models are used for simulations that represent the behavior of the processes. A mathematical process model consists of a set of variables which describes some properties of the process and a

set of equations that builds relationships among variables to explain the behaviour of the system. For complex systems found in many chemical processes in industry, the models present mostly nonlinear behaviours. With the increased interest in process synthesis, the demand for models with increased accuracy of the mathematical description is also growing. One of the main concepts in optimization in process systems engineering is the idea of superstructure. A superstructure contains most (or all) of the alternatives a system can have. Superstructures are defined by the process modeller, and alternative superstructures can be derived for the same process. Then, mathematical optimization approach seeks to find the optimal configuration among the proposed alternatives using different solution algorithms such as branch and bound algorithm, evolution based approaches and hybrid techniques [106].

1.2.2.1 Process integration

Process integration is a design approach that deals with the energy efficiency, waste minimization and an efficient use of raw materials. Process integration is greatly facilitated by the use of process simulations. In biorefineries, process integration plays an important role to study strong tradeoffs [24]. Large scale integration means accounting for process operation of different energy conversion systems and integration of process units. The principle is to identify the possible synergies between processes. An efficient integrated process system will contribute to water savings, reducing waste generation and lowering the emissions, thus reducing the overall cost and environmental impact.

Pinch analysis

Heat integration potentials can be estimated using pinch analysis. Pinch analysis is a very powerful technique based on thermodynamics with a structured approach to identify minimum energy consumption targets for heating and cooling and maximum internal heat recovery within a process (Linnhoff, 1993 [103]; Kemp, 2007 [107]). First law of thermodynamics is used to calculate enthalpy changes in a heat exchange process and close the energy balance while the second law of thermodynamics assures that heat flows from high temperature to low temperature. Therefore, none of the heat exchangers can have a temperature crossover. In practice, the ΔT_{min} value determines the lowest allowable temperature difference between the hot and cold stream in a heat exchanger and ΔT_{min} is determined considering economic criteria. Pinch point shows the temperature level at which ΔT_{min} is observed.

The following rules of pinch analysis are not allowed to be violated:

- No heat transfer across the pinch.
- No hot utility below the pinch.
- No cold utility above the pinch.

The concept of composite curves can provide a view of the problem related to efficient recovery (or re-use) of resources. Composite curves are temperature-enthalpy diagrams constructed by building a heat cascade and calculating the enthalpy content of hot and hot streams in each temperature interval. They are used to predict targets for minimum energy, minimum heat exchanger network

area and minimum number of heat exchanger units. On the composite curves, pinch point shows how closely hot and cold composite curves are pinched [108]. The grand composite curve is another way to graphically represent the heat flows in a temperature-enthalpy diagram using a pinch analysis concept. It shows the net deficit of heat above the pinch point and net surplus of heat below the pinch point, thus they are useful for selecting appropriate levels of utilities to cover all the heating and cooling requirements and show the opportunities for process integration [107]. Figure 1.4 shows the illustrative examples of hot and cold composite curves and grand composite curve. Mathematical contributions related to heat integration are as follows; Maréchal and Kalitventzeff, 1998 [109] developed process integration techniques to study the energy supply and the heat recovery in industrial processes. Duran and Grossmann, 1986 [110] proposed an algorithm for simultaneous heat integration and optimization of chemical processes. This concept is also applicable in other areas in addition to heat recovery whenever an amount (e.g. mass) has a quality (e.g. concentration).

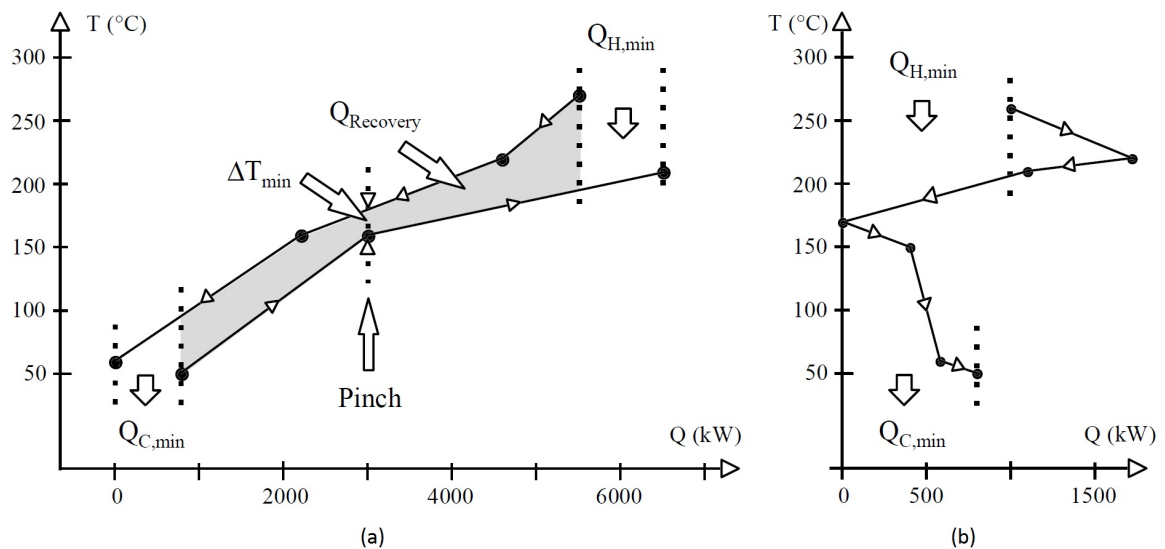


Figure 1.4: Illustrative examples of (a) Hot and cold composite curves and (b) Grand composite curve [108].

1.2.2.2 Costing and life cycle analysis

With the growing interest in sustainability, biorefineries are likely to play significant roles in enhancing the energy security and mitigating the climate changes. Process modelling and simulation are essential for predicting the economic, environmental and social performance of industrial processes [111]. Recently, researchers have been mainly focusing on the development of cost-effective biorefineries. In order to make the biorefinery profitable, production of value added products (e.g., succinic acid, dimethyl ether, etc.), valorisation of waste mass and energy streams, and cogeneration are of significant importance. If a biorefinery is only producing biofuels, environmental incentives may be required. The sustainable growth of biorefineries not only requires cost-effective products, but also energy efficient plants. The environmental assessment of a biorefinery includes land use

changes, greenhouse gas emissions, timing of emissions, waste production, environmental impact of products, etc. Some studies in literature are specifically focusing on the life-cycle assessment of biorefineries [112].

Biorefineries can use many traditional equipments and features from the petrochemical industry (e.g., distillation column, pump, heat exchange, compressors, etc.), and cost functions for these equipment are well established [113]. Conversely, some of the biorefinery processes are underdeveloped (e.g., gasifier, fuel cell, membrane separation, etc.), so their future costs are highly uncertain [114]. Generally, the production cost goes down with an increase in the plant size, and optimal plant capacity depends on economic value of product. Since biomass is diluted and diversified in vast area, supply chain optimization and economic viability study for different sizes of biorefineries is also critical for investment planning.

1.2.3 State-of-the-art : Process synthesis and optimal design of biorefineries

Recently, several researchers have been working in the field of process synthesis and design of large scale biorefinery systems. Various methodologies were presented by Kokossis et al. [115] in designing an integrated biorefinery.

Most studies in the literature addressed the determination of the single best technology for the production of single product, especially bio-fuels such as ethanol production [116, 117], biodiesel production [118] and combined heat and power production [119]. Brunet et al. [120], studied the design of amino acid production through biotechnological processing and optimized the bioprocesses using multi-objective optimization evaluating economics and environmental impact [120]. There are various studies that take into account superstructures and optimization-based performance evaluation with different feedstocks, products and conversion pathways for process synthesis and optimization of biorefinery processes.

Sammons et al. [121] applied a systematic methodology to evaluate integrated biorefineries for product allocation problems in the optimization framework where the candidate configurations are identified based on maximum profitability and ranked according to environmental performance to find the optimal pathway. Ng et al. [122] extended pinch based automated targeting approach of resource conservation networks with maximum fuel production and maximum revenue targets. They considered integrated biofuels production from biochemical and thermochemical platforms as a case study. Santibanez-Aguilar et al. [123] included epsilon constraint method into multi-objective optimization approach to provide a set of optimal solutions in a biorefinery producing ethanol, biodiesel and hydrogen according to profit maximization and environmental impact minimization objective. Kim et al. [124] proposed a framework for superstructure optimization of a multi-product biofuels biorefinery to evaluate the embedded strategies using alternative criteria and calculated minimum energy consumption for the designs. Bao et al. [125] introduced a shortcut method for the conceptual design of biorefineries by defining a chemical species/conversion operator structural representation aiming to maximize the yield or the economic potential. Martin and Grossman [126] applied superstructure optimization formulated as MINLP problem for bioethanol production

via gasification of lignocellulosic biomass to show profitability. Bertran et al. [127] developed a generic methodology for biomass superstructure optimization using a subsequent automated network formulation ensuring feasible connections between individual processing steps, supply chain constraints and processing pathways or pathways and product selection. Murillo-Alvarado et al. [128] applied a multi-objective optimization based on disjunctive programming for the synthesis of biofuels production considering economic and environmental criteria. Alvarado-Morales et al. [129] showed a systematic methodology for biorefinery design and analysis for a case study of bioethanol production. They analyzed cost and sustainability, and generated new design alternatives including downstream processing with the use of the group contribution approach.

Supply chain considerations are also included in biorefinery synthesis problems (Cucek et al. [130], Marvin et al. [131], Garcia and You [132]). You et al. [133] proposed a multi-period and multi-objective optimization formulated as MILP problem with epsilon constraint to address the optimal design and planning of sustainable ethanol supply chains under economic, environmental and social criteria by involving the life cycle assessment. Few studies comprise a holistic view on the matter while taking into account process integration and thermo-environmental optimization for biorefineries.

Pfeffer et al. [117] applied process integration into a bioethanol production plant with an optimization objective of minimization of heat demand. Tay et al. [134] developed fuzzy optimization strategy for bio-fuels production pathways where fuzzy optimization needs to be decoupled with incremental values on both economic and environmental objectives to obtain a Pareto optimal front, and energy recovery is considered via steam and electricity production in the syngas platform. Baliban et al. [135] studied biomass to liquids systems under large-scale mixed-integer nonlinear optimization framework to identify best economically and environmentally superior biofuels production technologies within heat, power and water integration. Ensinas et al. [136] applied multi-objective optimization using evolutionary algorithms to create a set of candidate solutions of different configurations for integrated first and second generations sugarcane biorefinery. Albarelli et al. [137] followed the same methodology for the integrated ethanol and methanol production in sugarcane biorefinery. Gassner and Marechal [138] developed a methodology that can be applied for the conceptual design of bio-fuel plants based on optimization with identification of promising flowsheets and process integration methods; they applied process synthesis on wood gasification processes. Tock et al. [50] applied the same methodology for the production of biofuels. Niziolek et al., [139] solved a global MINLP optimization problem for the production of liquid fuels and C6 - C8 aromatics to analyze the trade-offs between environmental and economic objectives considering heat integration. Duret et al. [140] applied energy integration to gasification process of wood to produce synthetic natural gas. Ahmetovic et al. [141] studied a simultaneous optimization approach to minimize energy consumption and to synthesize an optimal process water network for corn-based bioethanol plants. Gerber et al. [111] integrated life cycle assessment in the environmental optimization strategies combining with process integration and thermoeconomic analysis. They applied this methodology for the production of fuels and electricity from lignocellulosic biomass.

For the reduction of CO₂ emissions on the way to achieve climate targets, design of carbon and energy efficient energy conversion systems is necessary. One way to achieve this is to couple biorefinery systems with other energy technologies. Gencer et al. [142] proposed an integrated system where biomass and natural gas (NG) conversion is converted into liquid fuels. They developed a mixed integer nonlinear programming model (MINLP) for superstructure optimization to identify the process configurations with maximum energy output as liquid fuel. Gassner and Marechal [143] showed that integrating electrolysis unit to SNG fuel production from biomass resulted in higher energy and exergy efficiency while the proposed system is an interesting option to mitigate CO₂ emissions and store electricity in the form of SNG. They analyzed the process design using a multi-objective optimization algorithm. Agrawal et al. [144] showed a promising sustainable alternative to transportation fuels by proposing a hybrid hydrogen-carbon (H₂CAR) process for the production of liquid hydrocarbon fuels. In their design, biomass is the carbon source and hydrogen is supplied converting solar energy to H₂ using photovoltaic (PV) and electrolyzer technologies. The studies discussed in this section are compared in various aspects in Table 1.8.

Table 1.8: State-of-the-art summary of studies in the area of process synthesis and optimal design of biorefineries

source	feedstock	conversion technologies					products			approach				process integration approach		performance criteria		
		supply chain	bio chemical	thermo chemical	CHP	other	single product	multi-product	final products	optimal synthesis	formulation	LCA	uncertainty	energy	mass	other	economic	environmental /social
Bao et al. [125]	sorghum, MSW		•	•			•	gasoline	optimization chemical species/ conversion operator diagram	NLP			•		min. energy consumption			
Martin et al. [126]	switchgrass			•			•	bioethanol	superstructure optimization	MINLP					max. profit			
Bertran et al. [127]	multiple (6 feedstocks)	•	•				•	bioethanol	superstructure optimization	MINLP	•				max. profit	min. GHG emissions		
Alvarado-Morales et al. [129]	hardwood chips		•				•	bioethanol	superstructure optimization (solvent selection)	MINLP	•		•	•	min. energy & waste cons.			
Marvin et al. [131]	multiple (5 feedstocks)	•	•				•	bioethanol	supply chain superstructure optimization	MILP		•			max. NPV			
You et al. [133]	multiple (3 feedstocks)	•	•	•			•	bioethanol	superstructure optimization, MOO with ϵ -constraint	MILP					min. total annual cost	min. GHG emissions, max. accrued jobs		
Pfeffer et al. [117]	wheat/corn		•		•		•	bioethanol	energy integration	MILP			•		min. energy consumption			
Ahmetovic et al. [141]	corn		•				•	bioethanol	superstructure optimization energy and water integration	MINLP			•	•	min. energy & water cons.			
Gencer et al. [142]	biomass, natural gas			•			•	FT fuel	superstructure optimization	MINLP	•		•	•	max. energy of fuel		emissions reduction	
Cucek et al. [130]	multiple (6 feedstocks)	•	•		•		•	bioethanol, heat, electricity	supply chain superstructure optimization	MILP					max. profit	env. impact, GWP		
Sammons et al. [121]	chicken litter			•	•		•	syngas, hydrogen, electricity	superstructure optimization	MINLP	•				max. profit	tot. potential impact score (US-EPA WAR)		
Ng et al. [122]	wood waste, energy crop		•	•			•	methane, bioethanol, FT fuel	MOO with ranking pinch-based targeting	LP				•	max. biofuel yield	max. revenue		
Santibanez-Aguilar et al. [123]	multiple (21 feedstocks)		•	•			•	bioethanol, biodiesel, hydrogen	superstructure optimization	MILP	•				max. profit	min. env. impact, eco-indicator-99		
Kim et al. [124]	multiple (8 feedstocks)		•	•	•		•	bioethanol, SNG, butanol, electricity, FT fuel...	superstructure optimization	MILP		•			max. product yield	min. payback period		
Murillo-Alvarado et al. [128]	multiple (10 feedstocks)		•	•			•	bioethanol, biodiesel, gasoline, hydrogen	superstructure optimization	MILP	•				max. profit	min. GHG emissions		
Garcia et al. [132]	multiple		•	•			•	bioethanol, biodiesel, gasoline	superstructure optimization	NLP	•				max. profit	min. GHG emissions		
Tay et al. [134]	black liquor			•	•		•	DME, FT fuel, mix-OH, electricity	MOO with ϵ -constraint	MINLP			•		max. NPV	min. tot. impact score (US-EPA WAR)		
Baliban et al. [135]	wood chips, residues			•	•		•	FT fuel (gasoline, jet), electricity	energy and water integration	MINLP			•	•	min. total cost			
Ensinas et al. [136]	sugarcane		•	•	•		•	bioethanol, electricity	superstructure optimization	MINLP					max. prod. &			
Tock et al. [50]	wood			•	•		•	DME, MEOH, FT fuels, electricity	energy integration	MILP			•		min. energy consumption			
Niziolek et al. [139]	wood, natural gas			•			•	FT fuel (gasoline, jet), C6-C8 aromatics	superstructure optimization	MINLP					min total negative profit	env. impact, GWP		
Gerber et al. [111]	wood			•	•		•	SNG, electricity	evolutionary MOO	MINLP					max. electricity prod.	min. env. impact, GWP, EI 99, eco-scarcity06		
Pyrgakis et al. [145]	multiple (6 feedstocks)		•	•			•	bioethanol, butanol, HME, nylon, PEF, PEIT, PVC	energy integration	MILP					min. annual energy cost			
Jin et al. [146]	plant waste		•	•	•		•	bioethanol, biodiesel, polyphenols, PHAs, PHB	superstructure optimization	MINLP					cost prod. cost			
Luo et al. [147]	corn stover		•		•		•	bioethanol, succinic acid, acetic acid, electricity	techno-environmental assessment		•				NPV, IRR	eco-efficiency		
Merten et al. [148]	wood residues, sugar beet		•				•	succinic acid	techno-environmental assessment with energy integration	MILP	•		•		max. profit	env. impact, GWP, CED, EI99, hazard		
Gunuluka [149]	wood		•	•			•	furfural, TDO oil	techno-economic assessment						minimum selling price			
Gassner et al. [143]	wood			•	•	electrolysis	•	SNG, electricity, district heating	evolutionary MOO	MINLP			•		max. energy efficiency	min. inv. cost		
Agrawal et al. [144]	biomass			•		PV and electrolysis	•	FT fuel	energy integration conceptual design and assessment				•					

1.2.4 Identified gaps

Most of the studies conducted in the literature do not take into account the systematic process integration approach for maximum energy recovery in the integrated multi-platforms (chemical, thermochemical and biochemical conversion platforms) and multi-product biorefineries. Production of value-added products (e.g., succinic acid, dimethyl ether, etc.), valorization of waste mass and energy streams, and co-generation are significantly important for the sustainability of the biorefineries. Development of a systematic approach to select and integrate these biorefinery processes capable of evaluating processes in terms of efficiency, cost and environmental impact is challenging. For the bigger scale of production, heat and power demand concerns are quite important. Cost-effective integrated biorefineries can be only achieved by optimal process integration. Furthermore, the integration of processes from different platforms and the analysis of the interactions between process units using thermodynamics knowledge are becoming more and more important to improve the efficiency of mass and energy transfer and to reduce the operating cost in the overall energy system. Integration of biorefineries with other renewable energy conversion technologies is the key to achieve the climate goals since it will give the leverage of CO₂ mitigation when coupled with power-to-gas concepts, carbon dioxide storage and sequestration technologies.

2 Assessment of integrated multi-product biorefineries

Overview

- A systematic approach is applied which adopts thermo-environmental optimization together with heat integration to assess the economic performance, environmental impact, and energy requirement of several process options.
- A novel multi-objective optimization methodology is used by combining integer cut constraints with ε -constraint method to address the trade-offs between economic and environmental performance criteria.
- A superstructure of different processes in sugar and syngas platforms is developed considering multiple products (energy services, valuable chemicals and fuels) and those pathways are evaluated to understand the best combination of products and the synergies between them considering benefit of heat integration.

This chapter is an extension of Celebi et al. [150].

2.1 Introduction

In a biorefinery, there is a variety of bio-based products: bioenergy in terms of heat and power, biofuels and biochemicals, and/or their simultaneous production. The problem to be solved is to identify the competition between these products and to analyze the benefit of co-production in terms of energy efficiency and economics. Integration of the co-production units will maximize the use of biogenic carbon or maximize the impact of biomass as an energy source. Furthermore, closing the energy balance of the whole system by renewable energy sources is essential for sustainable bio-based products. These aspects necessitate the application of advanced process synthesis methods, which adopt process integration and optimization techniques to guarantee the economic viability and minimum environmental impact throughout the process [24]. In the biorefinery process design, it is important to implement an algorithm that allows systematic generation, evaluation of energy conversion chains and comparison of the different pathways, by different performance criteria ranking.

In this study, a superstructure of different process alternatives based on biochemical and thermo-chemical conversion pathways is developed. Different pathways are systematically compared with each other and ranked according to the selected objective function with the implementation of integer cut constraints (ICC) methodology for identification of the most promising technologies and finding their optimum configuration and size. Optimal integration algorithms between process units of bio-energy, bio-fuels and bio-chemicals production pathways are developed. Multi-objective optimization is implemented by combining integer cut constraints (ICC) algorithm with ε -constraint method to systematically generate the list of competing options in a Pareto front. The method applied in the current study is fast and powerful and it is appropriate for preliminary process design and comparison in biorefineries.

2.2 Methodology

2.2.1 Thermo-environmental modelling

The thermo-environmental modelling methodology in this thesis is adapted from Gassner et al. [138]. Initially a superstructure is defined which encompasses different biomass-to-fuels and biomass-to-chemical conversion pathways together with their corresponding flowsheet models. The flowsheet calculations are done using simulation software and solving mass and energy balances (see 2.3). The material and energy flow models describe the chemical and physical conversions from feedstock to product, and they consist information about all process streams, physical properties, and mass and energy balances which are used to define the heat and power requirements in the process. The corresponding thermal streams are then extracted to build the energy integration model which is used to compute the heat recovery potential in the system with heat cascade determination. Using pinch analysis approach [109], the minimum energy requirement and the optimal utilities network corresponding to the minimal operating cost are determined, taking into account the overall energetic performance. The energy-flow and the energy integration models are necessary to size the process equipment and to evaluate the performance of the process configurations. The economic models are used to evaluate economic performances of the system, including operating and investment costs which are calculated for the preliminary sized process equipments. Detailed estimation of investment for each piece of equipment is calculated over its lifespan with the methods and correlations available in Turton et al. [113] and Ulrich et al. [151]. To perform a LCIA (Life Cycle Impact Assessment), an environmental layer which represents LCA (Life Cycle Assessment) model is integrated within the thermo-economic model and consequently the thermo-environmental model is conceived. Material and energy flows such as fuel and electricity are modelled by associating each flow to a corresponding LCI (Life Cycle Inventory) Ecoinvent [152] unit process. These are identified according to their functions and the step at which they occur in the process. The models are formulated as Mixed Integer Linear Programming (MILP) models which are solved using CPLEX [105].

2.2.2 Multi-objective optimization (MOO) strategy

The multi-objective optimization methodology allows to address several conflicting objectives simultaneously such as economic and environmental impacts. These are the two main indicators for chemical process design. The approach proposes a set of optimal solutions which are called Pareto optimals. The multi-objective optimization solving strategy is adapted from Fazlollahi et al. [153] which is the application of ε -constraint combined with the integer cut constraints (ICC) method.

In combining ICC and ε -constraint, multi-objective optimization problem is solved in two loops. The outer loop is for integer cut constraints (ICC) dealing with the integer variables, while the inner loop is for ε -constraint dealing with continuous variables. MOO problem is solved to obtain a set of suboptimal solutions in the Pareto frontier, each solution achieving a unique combination. Number of iterations in the outer loop as well as number of subintervals (iterations) in ε -constraint method must be defined in advance. After the first generation of integer cut constraint, an upper limit ε constraint on the second objective function is imposed and optimization problem is solved using different values of ε . After analyzing the performance criteria, the iteration continues as described before, to finally obtain the Pareto set.

2.2.2.1 Epsilon constraint

ε constraint method (parametric optimization), is based on parameterizing one of the objectives into a set of inequality constraints while keeping the other objective as the main objective function. The optimization problem is solved individually for each of the objectives to provide a lower and an upper bound for the ε . Then, the interval of ε is divided into subintervals, solving a set of single objective problems for different values of ε [154].

$$\begin{aligned} \min \quad & f_1(x(\varepsilon_j)) \\ \text{subject to: } & f_2(x(\varepsilon_j)) \leq \varepsilon_j, \quad Axx(\varepsilon_j) \leq b \\ \text{with } & \varepsilon_j = \varepsilon_1, \varepsilon_2, \dots, \varepsilon_n \quad \text{and} \quad Lim_{inf} \leq \varepsilon_j \leq Lim_{sup} \end{aligned} \quad (2.1)$$

where $f_1(x(\varepsilon_j))$ is the first objective function denoting economic objective and $f_2x(\varepsilon_j)$ is the second objective function representing environmental objective. Lim_{inf} is the limit inferior and Lim_{sup} is the limit superior giving the extreme bounds for ε_j .

2.2.2.2 Integer cut constraints (ICC)

Integer cut constraints algorithm is used to generate a set of solutions for the optimization problem with different objectives [155]. Sahinidis [156] studied this concept in the planning of chemical industry. Maronose et al. [157] applied this approach in biorefinery pathways selection. Biorefineries are process networks consisting of different conversion technologies. Evaluation of different alternatives of conversion routes within the same process is crucial. The ICC method allows different conversion pathways to be evaluated inside the superstructure and ordered according to

the objective function values. The methodology is applied to select and rank different pathways according to objective function and is shown in Figure 2.1.

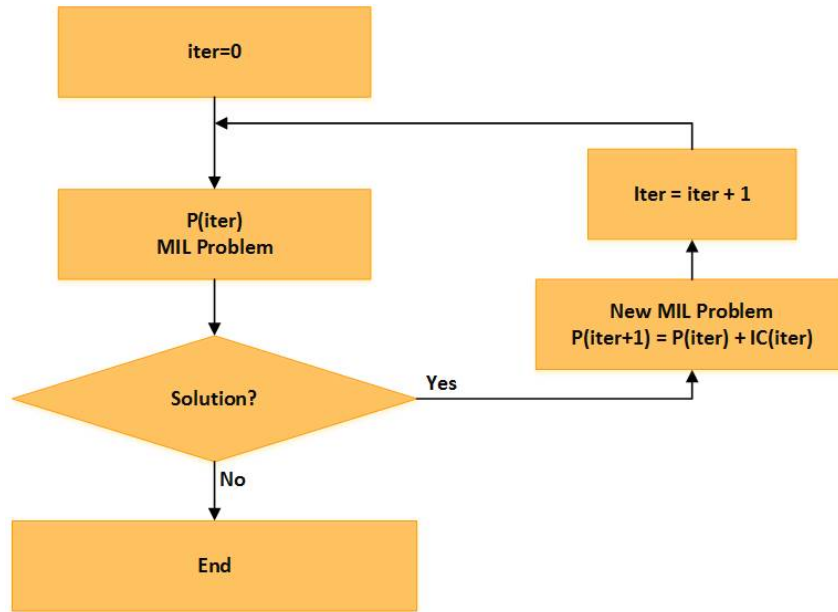


Figure 2.1: Integer cut constraints approach

This method systematically generates a ranked set of pathways and prevents the duplication of past solutions by number of constraints linearly with the new solutions found since a new constraints is added at each iteration [153]. It is formulated as:

$$\sum_{s=1}^{N_s} (2y_s^k - 1)y_s \leq \left(\sum_{s=1}^{N_s} y_s^k \right) - 1 \quad \forall k = 1, \dots, N_{sol} \quad (2.2)$$

where

k	index of the current solution
N_s	the number of subsystem in the model
$s \in 1, \dots, N_s$	index of the subsystem
$y_s^k \in 0, 1$	integer variable for the unit use of unit s at the k -th iteration
$y_s \in 0, 1$	integer variable for the unit use of unit s at the current iteration
N_{sol}	number of solutions

This technique, however, has some computational issues. The application of ICC method may create fake solutions in which one or more units are activated but have small or even zero sizes. This is due to the fact that both unit use and multiplication factor are variables in optimization problem. For example, for an activated subsystem with zero size, the unit use y_s is 0 while the multiplication factor f_s is 1. To avoid fake solutions, unit sizes were ensured not to be zero by implementing minimum sizes for each unit from the literature of available data.

This study, adapts the previously proposed ICC technique [157], is improved by considering white-box energy conversion models of both biochemical and thermochemical conversion pathways.

2.2.3 Optimization framework

Thermo-environmental models are used for energy integration superstructure optimization problem which is solved in the Lua-OSMOSE framework [158]. This framework includes the optimal utility system integration approach developed by Maréchal and Kalitventzeff [109], where a MILP problem is proposed for the optimal selection of energy conversion utilities. The heat cascade layer constraints in the MILP are explained in Appendix A. The platform allows to link several flowsheeting software and provide analysis tools (optimization, sensitivity analysis, etc.). The overall design problem is formulated as mixed integer linear programming (MILP) optimization problem and epsilon-constraint method is combined with integer cut constraints (ICC) algorithm to systematically generate the list of competing options in a Pareto front to show the trade-offs between economic and environmental objectives. The proposed methodology is summarized in figure 2.2.

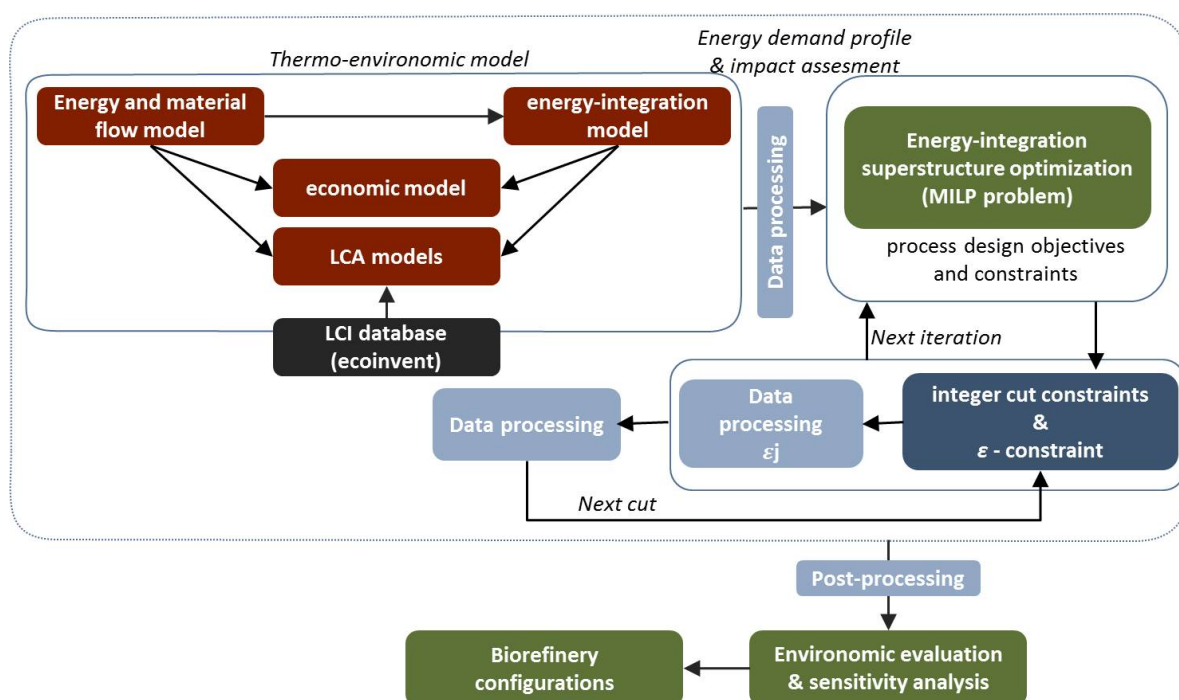


Figure 2.2: Multi-objective optimization methodology with integer cut constraints (ICC) and epsilon constraint

In order to highlight the benefits of this approach, a case study is considered and solved. The mathematical programming model is written in AMPL [159] and solved using the MILP solver AMPL-CPLEX [105]. The results of the proposed approach provide a set of non-dominated solutions (i.e., Pareto front), and each solution shows different biorefinery configuration. They are the feasible

solutions which are capable of achieving design objectives as optimal performance indicators.

2.3 Process description

In this study, a wood biomass plant with a capacity of 200 MW located in Switzerland [34] is considered. The process modelling is performed using flowsheeting software such as Aspen PLUS [160] and Belsim VALI [161]. The processes from wood to products were modelled in the following way: The wood biomass is considered to have a moisture content of 50 wt% and the average elementary composition dry weight basis is: C 49.9%; O 42.9%; H 6.11%; N 0.109%, and has a lower heating value of 18.614 MJ/kg [45]. For the proposed case study, both sugar (biochemical conversion) and syngas (thermochemical conversion) platforms are considered in order to compare processes with output of different nature (energy services, valuable chemicals, fuels). For these reasons, several technologies are considered in a superstructure and the necessary data have been systematically collected from scientific literature and patents. Biochemical routes for biomass conversion have been explored aiming at the valorisation of glucose rich streams (C6 platform) and co-products (C5 and lignin platforms) which are decomposed after biomass pretreatment and saccharification units. The characteristics of these units are given in the Table 2.1.

The summary of the sugar platform products portfolio is given in Table 2.2. The part of the superstructure describing the conversion of sugars into ethanol includes the following units: air drying unit, steam explosion combined with Organosolv pretreatment unit and enzymatic hydrolysis unit, glucose concentration unit, fermentation unit followed by hydrous ethanol production (93 wt%), and ethanol dehydration unit (99.3 wt%). The residual vinasse is used for biogas production through anaerobic digestion. The ethanol production block of units can be followed by ethylene production which has a greater value in the market. The side products of the pre-treatment units linked to sugar platform, such as high purity lignin and xylose, are always converted into vanillin and xylitol. These last two products are high value bio-chemicals and provide an opportunity for profit. One of the main observations in biorefineries is that valorization of by-products (C5 sugars and lignin) is crucial for economic feasibility. The other biochemical products and fuels that are included in the superstructure are: butanol fuel production unit, lactic acid production unit, acetic acid production unit, succinic acid production unit, and HMF production unit.

Concerning thermochemical conversion technologies, several relevant models are also integrated in this case study. The goal is to make a comparison between these technologies, based on their economic and environmental performances. The technologies used in the models for syngas platform basically consists of the following steps: biomass pretreatment, gasification, producer gas cleaning, fuel synthesis and fuel upgrading for the production of synthetic natural gas (SNG), methanol (MeOH), dimethyl ether (DME), and Fischer-Tropsch crude (FT) fuels. More details are provided in Table 2.3. Finally, sugar and syngas platforms are combined in a hybrid superstructure (Figure 2.3) for the analysis of the integration.

2.3. Process description

Table 2.1: Characteristics of biomass pretreatment and saccharification for biochemical conversion pathways

		Process parameters	Source
Drying	Technology	Air drying	[162]
	Air inlet temperature [°C]	200	
	Wood outlet humidity [%]	15	
Pretreatment	Technology	Steam explosion + Organosolv	[163]
	<i>Steam explosion pretreatment</i>		
	Temperature [°C]	278	
	Pressure [bar]	12.5	
	Reactor temperature [°C]	170	
	SO ₂ level [% dry basis]	6.0	
	Hemicellulose-xylose conversion [%]	61.4	
	<i>Organosolv pretreatment</i>		
	Temperature [°C]	170	
	Lignin removal [%]	73.9	
	Hemicellulose-xylose conversion [%]	56.7	
Saccharification	Technology	Enzymatic hydrolysis	[163]
	Temperature [°C]	50	
	Retention time [h]	24	
	Hydrolysis solid loading [%]	6	
	Enzyme loading [mg/g cellulose]	42	
	Cellulose-glucose conversion [%]	93	

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Table 2.2: Summary of sugar platform models used in this study

Products	Production and purification technologies	Source
Butanol	Glucose fermentation to acetone-butanol-ethanol products + liquid-liquid extraction	[164]
Succinic acid	Glucose fermentation using an engineered strain of <i>E.coli</i> + liquid-liquid extraction, crystallization, eletrodialysis	[148]
Lactic acid	Glucose fermentation using standard lactic acid bacteria + esterification, hydrolysis, distillation	[165]
Hydrous ethanol	Glucose fermentation by <i>S.cerevisiae</i> + distillation	[136]
Anhydrous ethanol	Glucose fermentation by <i>S.cerevisiae</i> + distillation, dehydration	[136]
Acetic acid	Catalytic ethanol oxidation + extraction, distillation	[164]
Ethylene	Catalytic ethanol dehydration	[166]
HMF	Dehydration of glucose in the water/methyl isobuthyl ketone (MIBK) biphasic system + extraction, distillation	[89]
Vanillin	Alkaline oxidation lignin to vanillin + supercritical extraction, crystallization	[167]
Xylitol	Hydrogenation of xylose to xylitol	[168, 169]
Biogas	Upflow anaerobic sludge blanket (UASB) biodigester	[170]

Table 2.3: Summary of syngas platform models used in this study

Section	Specification	SNG	FT	MEOH	DME
Drying	Technology		Air drying		
	Air inlet temperature [°C]		200		
	Wood outlet humidity [%]	20	10	20	20
Torrefaction	Temperature [°C]	-	250	-	-
Pyrolysis	Temperature [°C]	-	-	-	260
Gasification	Heating mode	Indirectly heated	Directly heated	Directly heated	Directly heated
	Gasification type	FICFB	EF	CFB	CFB
	Temperature [°C]	850	1350	850	850
	Pressure [bar]	1	30	25	1
	Agent	Steam	Steam-O ₂	Steam-O ₂	Steam-O ₂
	Steam preheat T [°C]	300	400	450	400
	Steam to biomass ratio	0.5	0.6	0.38	0.6
Air separation	Technology	-		Cryogenic distillation	
	Energy consumption [kJ/kg O ₂]	-		1080	
Tar cracking	Technology	-	HT stage	Catalytic reforming	
	Temperature [°C]	-	1350	850	-
	Heating mode	-	directly heated	indirectly heated	
Steam methane reforming	Temperature [°C]	-	-	-	950
Water quench	Temperature [°C]	-	750	-	-
Gas cleaning	Technology	Cold	Cold	Hot	Cold
	Temperature [°C]	150	150	850	150
	Filter pressure drop [mbar]		100		
	Flash temperature [°C]		25		
Water gas shift	Temperature [°C]	-	300	-	443
CO ₂ removal	Technology	TSA & PSA		MEA ¹	
	Amount CO ₂ removed		95%		
Synthesis		Internally cooled	Multi-tubular,	Multi-stage	Slurry phase
	Technology	Fluidized bed reactor	Fixed bed reactor	Fixed bed reactor	reactor
	Catalyst	Ni/Al ₂ O ₃	Co/Zr/SiO ₂	Cu/ZnO/Al ₂ O ₃	ACZ & HZSM-5
	Temperature [°C]	327	220	315	277
	Pressure [bar]	5	25	85	50
Upgrading	Technology	Polysulfone membrane for H ₂ sep., compression	Private data	Flash, distillation (2x)	Flash, distillation (3x)
Fuel specifications		96 vol%	Liquid fuels	99.4 vol %	99.88 vol%
		25°C, 50 bar	25°C, 1 bar	25°C, 1 bar	25°C, 1 bar
Adapted source		[162]	[90]	[50]	[50]

¹ For MEA absorption, reboiler heat demand is fixed at 3.3MJ/kg CO₂ separated at 150°C, 20% of the heat duty is recoverable between 90°C to 40°C. Electricity consumption is fixed at 25 kJ/kg CO₂ [171].

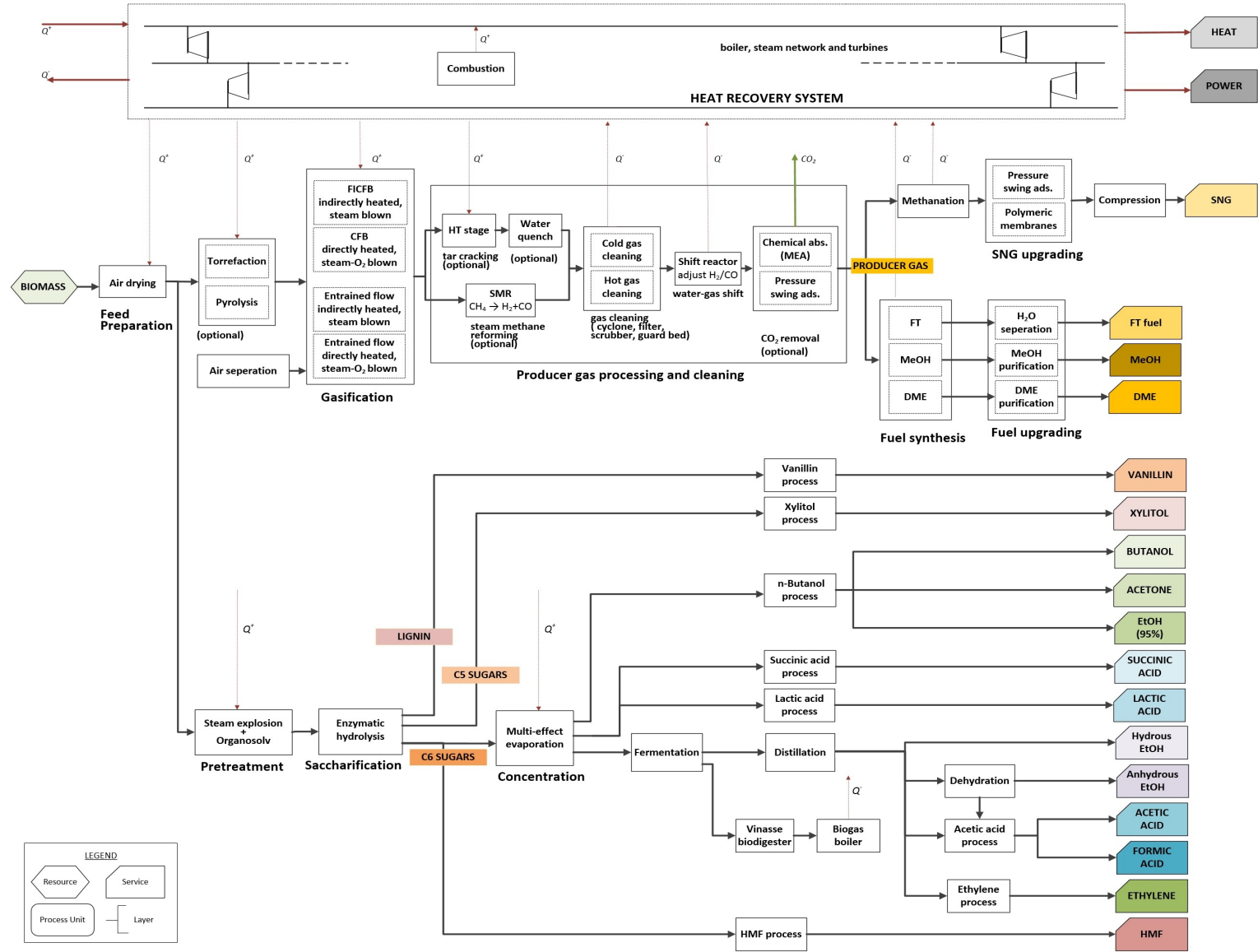


Figure 2.3: Hybrid (biochemical & thermochemical) process superstructure

2.3.1 Performance criteria

The superstructure modeling framework contains feedstock and raw materials (Resources), process conversion technology units (Technologies), products (Services), and mass and energy balances nodes in the system. The system performance criteria are yearly total cost and yearly total emissions. The objective function of the MILP problem was stated as:

min

$$C_{tot} = \sum_{j \in Technologies} (\tau(j)C_{inv}(j) + C_{op\&maint}(j)) + \sum_{i \in Resources} C_{op}(i) - \sum_{k \in Services} C_{rev}(k) \quad (2.3)$$

subject to:

$$\tau(j) = \frac{i(i+1)^{n(j)}}{(1+i)^{n(j)} - 1} \quad \forall j \in Technologies \quad (2.4)$$

$$C_{inv}(j) = c_{inv_1}(j)y(j) + c_{inv_2}(j)f(j) \quad \forall j \in Technologies \quad (2.5)$$

$$C_{op}(i) = c_{op_1}(i)y(i) + c_{op_2}(i)f(i) \quad \forall i \in Resources \quad (2.6)$$

$$C_{rev}(k) = c_{rev_1}(k)y(k) + c_{rev_2}(k)f(k) \quad \forall k \in Services \quad (2.7)$$

$$GWP_{tot} = \sum_{j \in Units} GWP_{const}(j) + \sum_{i \in Resources} GWP_{op}(i) \quad (2.8)$$

$$GWP_{const}(j) = gwp_{const_1}(j)y(j) + gwp_{const_2}(j)f(j) \quad \forall j \in Technologies \quad (2.9)$$

$$GWP_{op}(i) = gwp_{op_1}(i)y(i) + gwp_{op_2}(i)f(i) \quad \forall i \in Resources \quad (2.10)$$

where

C_{tot}	Annual total cost
$\tau(j)$	Annualization factor
$C_{inv}(j)$	Annualized investment cost for technology j
$C_{op\&maint}(j)$	Annual operation and maintenance cost for technology j
$C_{op}(i)$	Cost for resource i
GWP_{tot}	Annual global warming potential impact factor
$GWP_{const}(j)$	Annual impact of construction of technology j
$GWP_{op}(i)$	Annual impact of consumption of resource i
$n(j)$	Lifetime of the plant
$c_{inv}(j)$	Specific investment cost for technology j
$c_{op\&maint}(j)$	Annual specific maintenance cost for technology j
$C_{op}(i)$	Specific operating cost for resource i
$gwp_{const}(j)$	Annual specific impact of construction of technology j
$gwp_{op}(i)$	Annual specific impact of consumption of resource i

The decision variables of the MILP problem are y and f which respectively correspond to the binary value associated to the use of a unit and the multiplication factor which is a real number used to

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size the unit in the size ranges considered for each technology. The cost and impact functions are broken down into a fixed part (c_1, gwp_1) and a variable part (c_2, gwp_2) linearly proportional to f . Parameters gwp_{op} and gwp_{const} are taken from ecoinvent database.

The economic performance criteria (or economic objective function), annualized total cost is calculated by the sum of annualized investment and the total production costs taking into account the operation and maintenance costs, expenses and revenues as Eq. (1). Operation and maintenance cost of units is assumed to be 5% of the total investment cost per year [113]. Table 2.4 gives the main parameters that are used for economic modelling.

Table 2.4: Main economic parameters and assumptions

Parameter	Value	Source	Parameter	Value	Source
Economic assumptions			Market prices of services		
CEPCI index (2015)	568	[172]	Hydrous ethanol [USD/liter]	0.695	[173]
Exchange rate [USD/CHF]	1.12	[174]	Anhydrous ethanol [USD/liter]	0.74	[173]
Exchange rate [USD/EUR]	1.37	[174]	Vanillin [USD/kg]	10	[175]
Interest rate [%]	6		Formic acid [USD/kg]	1	[176]
Plant operation [%]	90		Lactic acid [USD/kg]	1.32	[177]
Plant lifetime [years]	20		n-butanol [USD/kg]	0.6	[178]
Maintenance cost [% C_{GR}]	5		Succinic acid [USD/kg]	5	[178]
Market prices of resources			Acetic acid [USD/kg]	0.9	[178]
Wood [USD/kWh]	0.039	[179]	Acetone [USD/kg]	0.5	[178]
Electricity [USD/kWh]	0.12	[181]	Xylitol [USD/kg]	5.54	[180]
Enzymes [USD/kg]	10.14	[183]	Ethylene [USD/kg]	1.105	[182]
Fresh water [USD/kg]	0.001	[185]	HMF [USD/kg]	2	[184]
Natural gas [USD/kWh]	0.056	[187]	SNG [USD/kg]	0.745	[186]
			FT [USD/kg]	0.487	[188]
			DME [USD/kg]	0.479	[178]
			MEOH [USD/kg]	0.384	[189]

The environmental impact of the whole process (environmental objective function) was calculated in terms of equivalent CO_2 emissions using the GWP100a method which is “IPCC 2013 Global Warming Potential” impact assessment method for time-horizon of 100 years [190]. The proposed superstructure is solved using the methodology described in section 2.2. The utility selection and the sizing of each utility are optimized for minimum total costs and for minimum environmental impact in terms of CO_2 emissions.

Table 2.5 shows the gwp_{op} parameters for main resource units.

2.4 Results

2.4.1 Biorefinery solutions using integer cut constraints (ICC) method

First, by using ICC method, the problem is iteratively solved and a set of 150 solutions is generated for each optimization objective (the minimum total costs and the minimum environmental impact). For a clear representation of the results, only the top 34 out of 150 solutions are presented. Each

Table 2.5: Emission factors of resource units for the evaluation of the environmental objective from Ecoinvent® v3.2 [191]

Resource	Value	Unit
Wood	0.012	kt CO ₂ eq/GWh
Electricity	0.517	kg CO ₂ eq/kg
Enzymes	10	kg CO ₂ eq/kg
Fresh water	0.0002	kg CO ₂ eq/kg
Natural gas	0.267	kt CO ₂ eq/GWh

iteration takes on average 1 CPU second on a single core computer. After solving the proposed case study, the two sets of 34 solutions, one concerning minimum total costs solutions and one minimum environmental impact solutions are analyzed. Comparing process options leads to the selection of the best exploitation of wood resource. Creating a ranking of the possible alternatives can help in the decision making, if two pathways have similar results in terms of one objective function, other indicators can be applied to choose the most suitable pathway. Furthermore, analysis of the prevalence of pathways in the top solutions is an important criterion for the evaluation of multiple solutions. By using the ICC approach, the integrated process options are ranked in terms of their economic objectives (Figure 2.4) and environmental objectives (Figure 2.5). The optimizer determines the amounts of biomass resource fed to the biochemical conversion pathways and to the syngas platform according to the objective function. Application of pinch analysis satisfied process heat demand above the pinch by hot utilities consisting of different fuels. The depleted streams such as dried gases from torrefied biomass, off-gases from ash drums and distillation columns, and the solid carbon along the processing steps can be used as energy sources to satisfy the heat demand. If the combustibles from waste streams are not enough, combustion processes are used. These processes utilize early stage intermediate product streams from the thermochemical conversion processes such as part of producer gas produced after biomass gasification units. Within this approach, no external streams are needed in utilities; the appropriate flows in the conversion processes are chosen based on the quality of integration. The cooling demand is satisfied by three different types of cold utilities including cooling by river water (when process temperatures are not below atmospheric temperatures), and two refrigeration cycles (operating at 5°C and -20°C) are accounted as options to close the energy balance. Additionally, power recovery expansion turbines are added to the superstructure for all gas streams with a pressure of 25 bar. These can contribute to a reduction of the electricity demand of the thermochemical conversion pathways and increase the productivity of the bio-resource. The set of 34 conversion pathways including the corresponding total costs is reported in Figure 2.4. The ranked solutions are represented in terms of their product distribution percentages which are normalized on their respective annual productions. Since the total cost includes the revenues coming from product sales, negative cost values show profitable production pathways. Rank 1 in Figure 2.4 illustrates that the most profitable solution (which has the lowest cost) is the integrated production of DME and succinic acid, while the most promising

Chapter 2. Assessment of integrated multi-product biorefineries

solution in terms of environmental performance is the integrated production of SNG and Fischer-Tropsch (FT) fuels in Figure 2.5. Solutions combining syngas platform products with biofuels from biochemical conversion such as hydrous and anhydrous ethanol, and butanol do not appear in the top solutions when economic criteria is considered as there are more profitable alternatives in the biorefinery superstructure. Selecting only the economic objective (in the optimization problem) results in the production of large volumes of high value chemicals. On the other hand, environmental objectives show that the decision maker has to produce biofuels in large volumes. In Figure 2.5, one can observe that a biorefinery configuration containing a high value chemical, such as succinic acid production combined with SNG fuel production, appears in the top 20 but not in top 10 solutions.

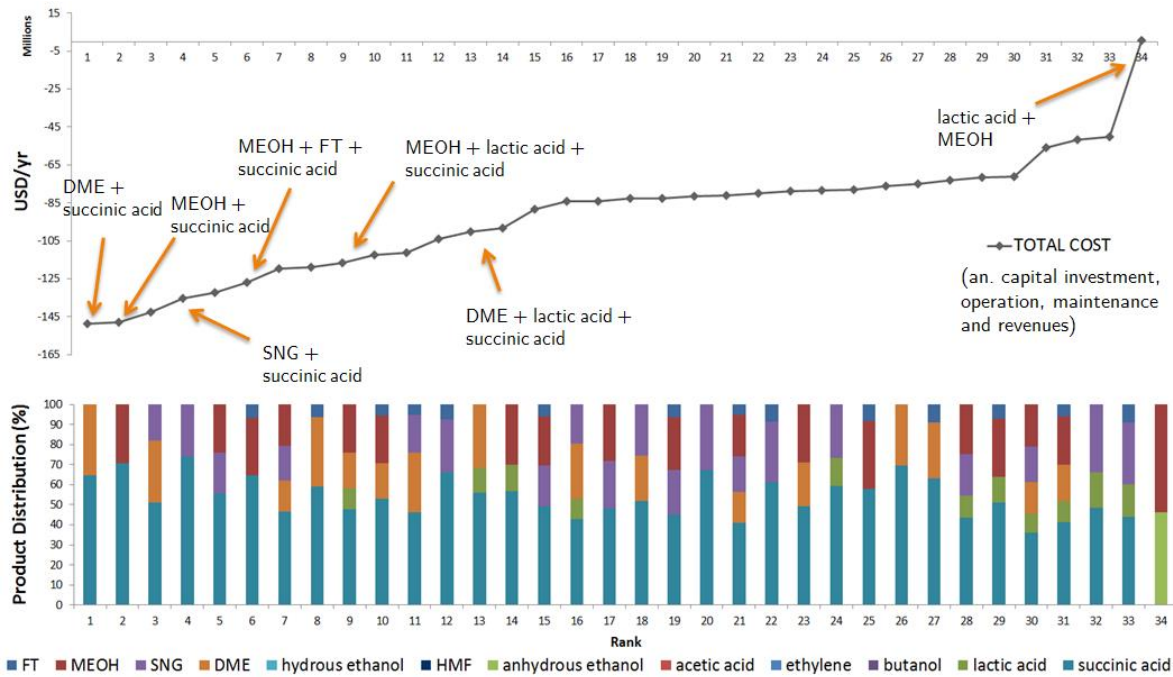


Figure 2.4: Ranking solutions - economic performance

Figure 2.6 shows the Pareto optimal front obtained after the solution of the energy integration optimization problem with integer cut constraints. Solutions containing succinic acid production dominate the Pareto front. Different configurations can be observed with different feedstock allocation ratios. Within this approach, a database of process configurations is obtained.

2.4.2 Biorefinery solutions using integer cut constraints (ICC) combined with epsilon constraint method

Using only ICC method, the solution space covers a high diversity of biorefinery configurations, but the solution space needs to be extended to cover a wider range of environmental objective simultaneously. Therefore, ICC method is combined with ϵ constraint method. The Pareto set and nearby solutions for 30 integer cuts and 30 subintervals of the CO₂ emissions are shown in Figure

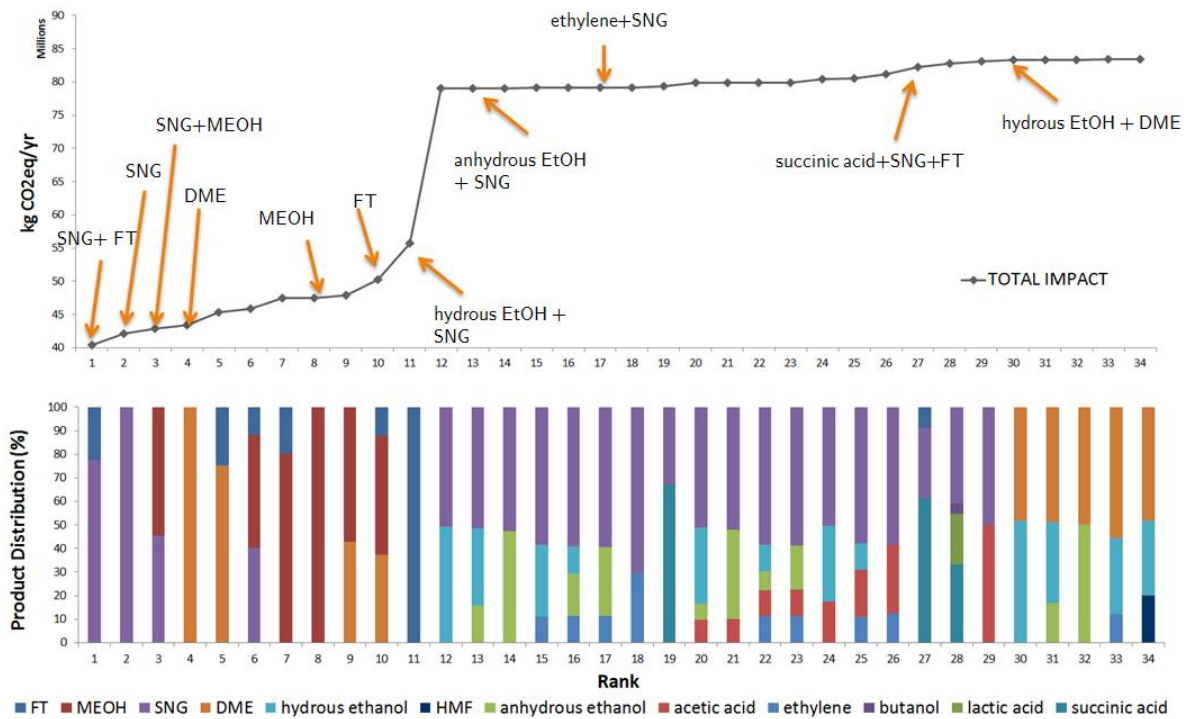


Figure 2.5: Ranking solutions - environmental performance

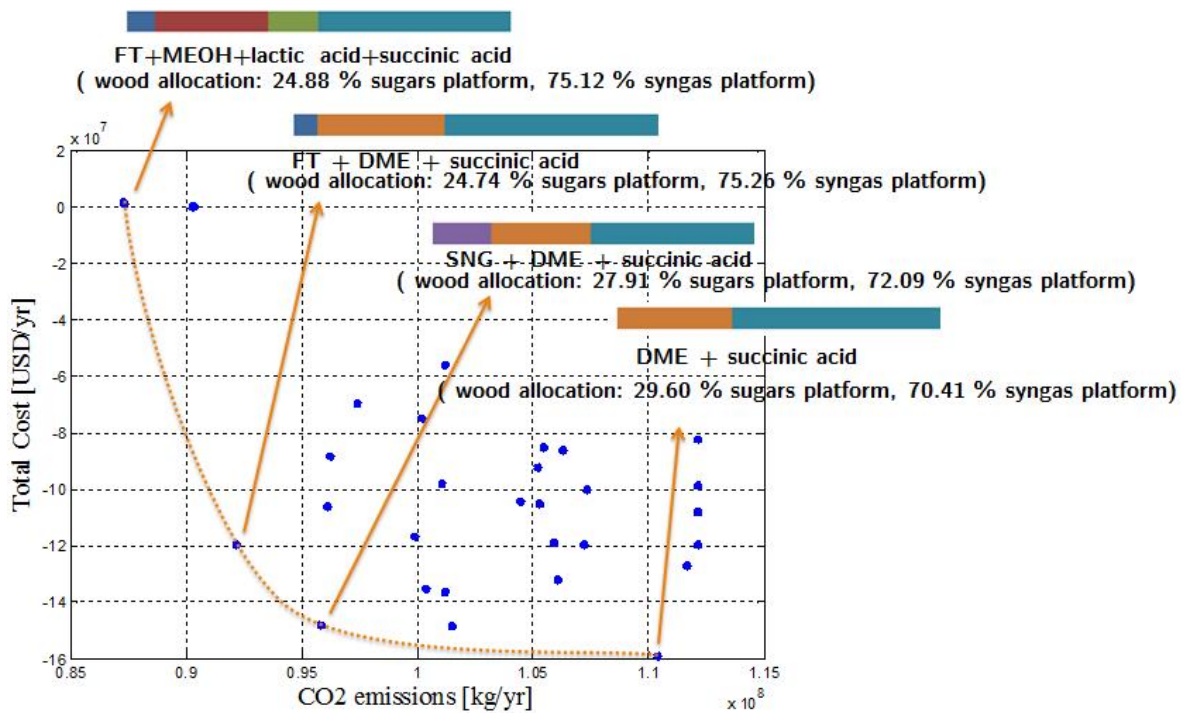


Figure 2.6: Pareto solutions using integer cut constraints (ICC)

2.7. Each iteration takes on average 5.8 CPU second on a single core computer which is higher than using the ICC method alone itself.

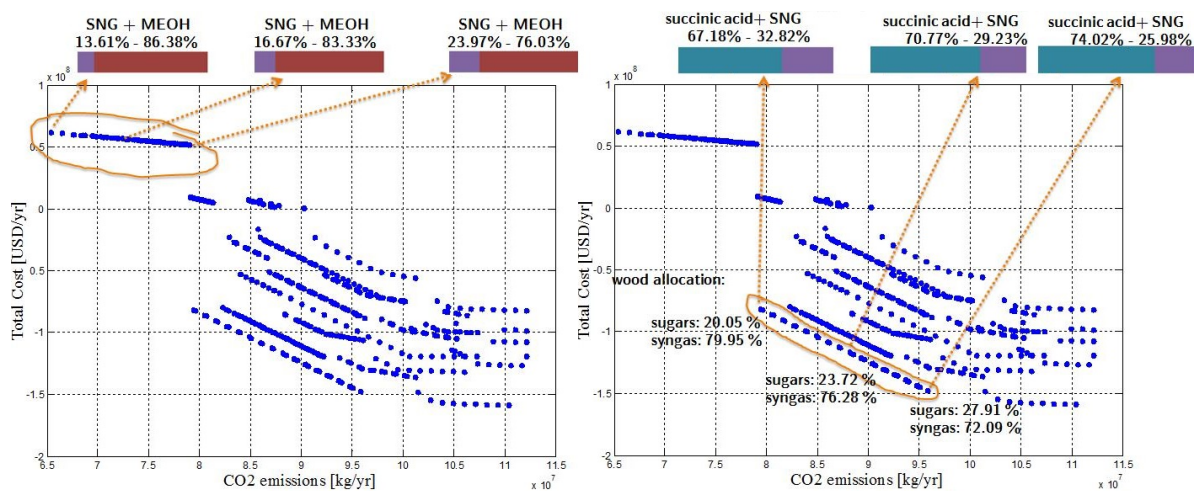


Figure 2.7: Pareto solutions with integer cut constraints (ICC) and epsilon constraint

2.4.3 Synergy analysis for bio-based products

Understanding the synergies between different conversion routes is important in order to quantify the energy integration improvement. Notably, the energy integration between thermochemical and biochemical conversion pathways results in a decrease in hot utility consumption, thus reducing the CO₂ emissions. Biochemical routes operate at low temperature thus external heat is needed to satisfy the heat demand of the system whereas thermochemical conversion routes operate at high temperatures and can provide the heat needed. In the cases where a part of the biomass feedstock is used to supply heat/energy by combustion as a process fuel, the carbon in the biomass is converted to carbon dioxide after combustion reaction. This decreases the carbon conversion efficiency to the products. Integration of syngas and sugar platforms brings the benefit of combined production of biofuels and biochemicals while the carbon in the biomass is not lost to carbon dioxide directly. The optimal integration between the energy conversion systems allows consuming minimum amount of resources by using this thermodynamics approach.

In order to highlight the benefit of integrated conversion pathways, a set of optimization problems are solved individually and limiting the superstructure to succinic acid, lactic acid and biofuels conversion pathways that were mostly occurring in the top solutions. As mentioned before, sugar platform shows big potential for high value chemicals. Succinic acid is a high-value chemical (Table 2.4), but its total environmental impact is higher compared to products of thermochemical conversion pathways such as SNG, DME and MEOH (Figure 2.8). Similarly, one can observe that thermochemical conversion products have higher total cost and lower emissions. For the scenarios where the integration between one thermochemical and one biochemical conversion pathway occurs, the objective function values remain between the individual scenarios in which only one

product is produced. Succinic acid is produced with high profit and high environmental impact while biofuels production is high at total cost with low environmental impact. Referring back to the results in Figure 2.7, combination of these two products is profitable with relatively low environmental impact when compared to only succinic acid production (Figure 2.8). For example, the amount of CO₂ avoided varies between 0.84 and 2.21 ton CO_{2eq}/h with respect to a purely biochemical pathway of succinic acid production. The energy balance is closed by combustion of a part of wood feedstock in a biomass boiler to produce biochemicals, and the depleted streams along the biofuels production process and a portion of the intermediate producer gas are sent to combustor (to prevent more CO₂ emissions). The same principle applies to the integrated production of lactic acid and biofuels.

Another important criteria is the reduction of CO₂ emissions using the biorefinery pathways for petroleum substitutes. When comparing the GHG emission savings according to results in Figure 2.8, it can be observed that higher emission savings can be obtained with biofuels than succinic acid production pathway since the final use of biofuels, i.e., combustion, releases biogenic carbon. For succinic acid production, lower GHG emissions target was not achieved. Integrating biochemical conversion pathway of these bio-based chemical with thermochemical conversion pathways gives a leverage to compete with their petroleum substitutes with their lower CO₂ emissions. Their substitutes and the corresponding emission values are given in Table Table B.1.

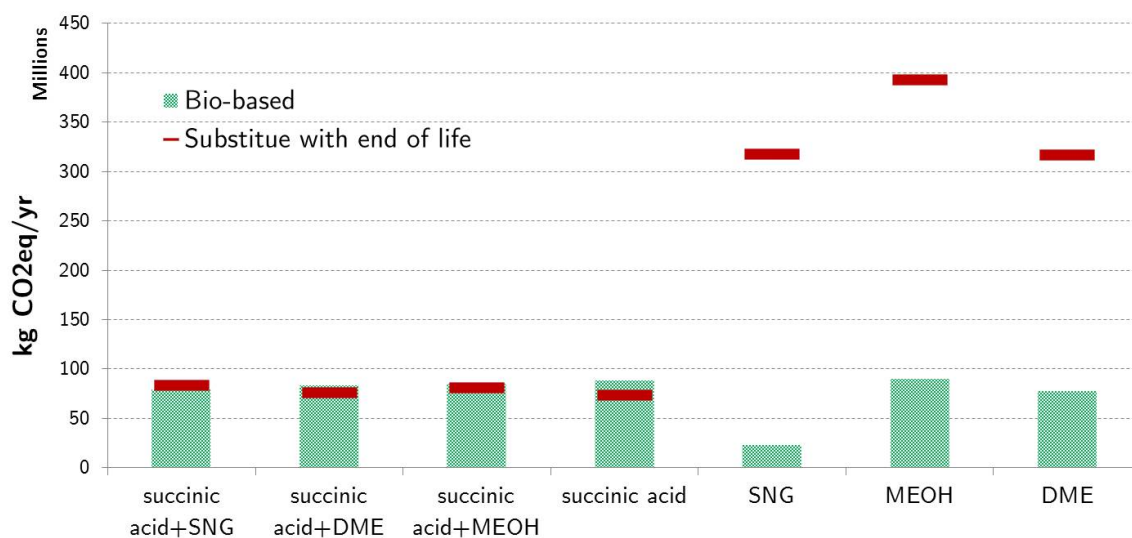


Figure 2.8: Comparison of GHG emissions of succinic acid and biofuels production pathways with their petroleum substitutes

Similarly, integration of lactic acid and SNG can be investigated. Figure 2.9 shows the grand composite curves for SNG production and minimum energy requirement of lactic acid production as well as GCC of integrated production of these two substances. In the integration case, biomass feedstock is allocated between lactic acid and SNG production with ratios of 45% and 55%, respectively.

Chapter 2. Assessment of integrated multi-product biorefineries

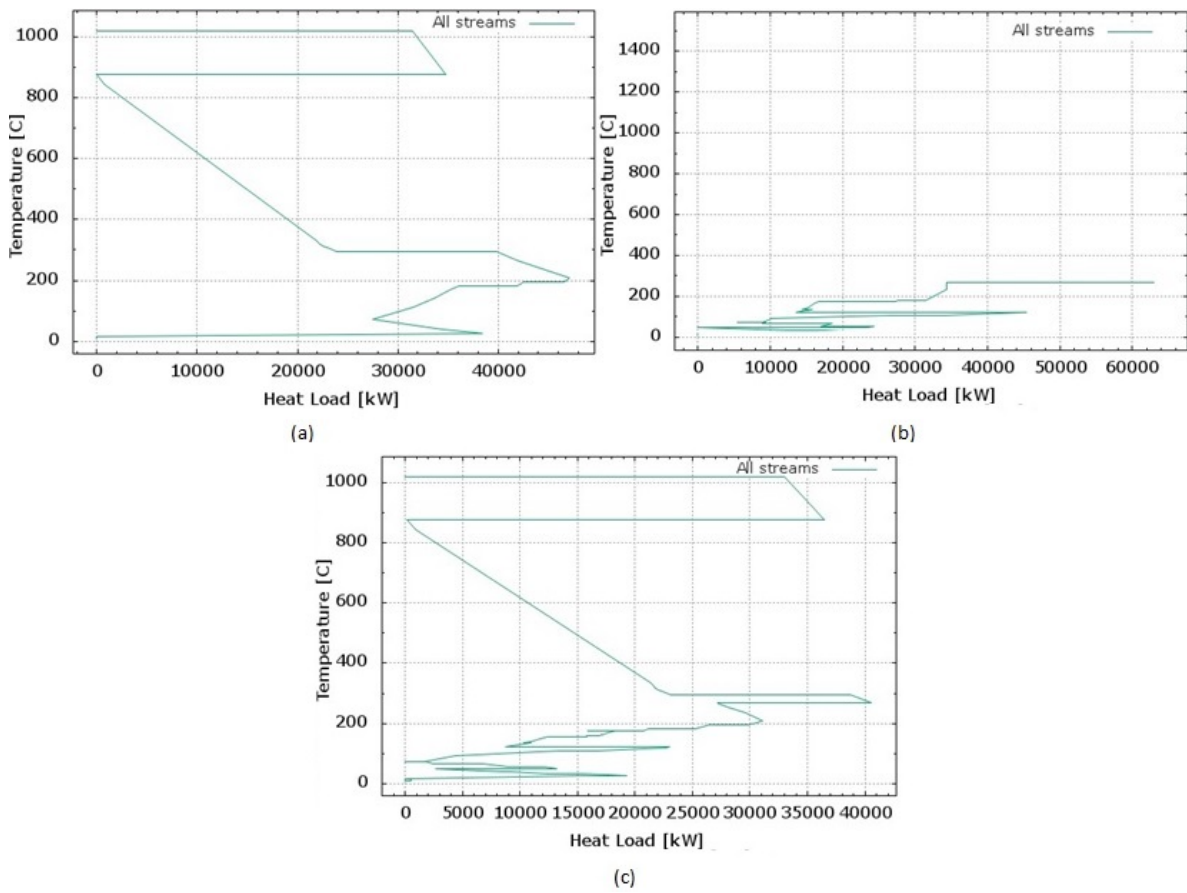


Figure 2.9: (a) GCC of SNG production, (b) MER of lactic acid production, (c) GCC of integrated SNG and lactic acid production

2.4.4 Power production - steam network integration

For the reasons of brevity, integrated lactic acid and SNG production result is chosen for further analysis. Combined heat and power (CHP) or cogeneration concerns the combined production of electricity and useful heat. The different cogeneration options are Rankine cycles, gas turbines, fuel cells, etc. The product of gasification unit can be converted into electricity using more efficient gas turbines, fuel cells or combined cycle technologies since it has a high chemical exergy. Based on the exergy analysis of the complete system, it is possible to recover the exergy lost in the heat exchange by generating mechanical power through a Rankine steam cycle. The energy expenses will be reduced due to the co-production of renewable electricity and selling of surplus electricity to the grid, as well as environmental impact benefits of the considered case study. Rankine cycles use the process and resource conversion units as heat source above the pinch point. High and/or low pressure steam is produced in the boilers or in the process, and it is expanded in steam turbines to produce mechanical power and condensed steam is used to supply heat to the process. A steam network model is integrated for the energy recovery in the superstructure with different steam production, condensation and bleeding levels which are characterized for each configuration. The steam network has the following characteristics as shown in Table 2.6.

Table 2.6: Process characteristics of steam cycle

Parameter	Value
Steam production pressure	80 bar
Steam superheat temperature	550 °C
Bleeding temperature (1)	150 °C
Bleeding temperature (2)	200 °C
Bleeding temperature (3)	20 °C
Condensation temperature	19 °C

Table 2.7 shows the power production by steam network integration. The renewable electricity produced via steam cycle is used inside the system thus reduces the energy cost and the environmental impact of the considered case study. The avoided CO₂ emissions are 2.6 times higher than the case without power production since 18% of the environmental impact is from electricity consumption for SNG and lactic acid production when electricity is imported from the grid.

Table 2.7: Mechanical power production via steam cycle integration

Integrated bio-chemical and thermochemical technology	Power production	Amount of power produced [MW]	Avoided CO ₂ emissions [kton CO ₂ /yr]
SNG + lactic acid	No	-	7.05
SNG + lactic acid	Yes	11.44	18.2

Figure 2.10 shows the integrated composite curve of steam network set-up via the biorefinery producing SNG and lactic acid.

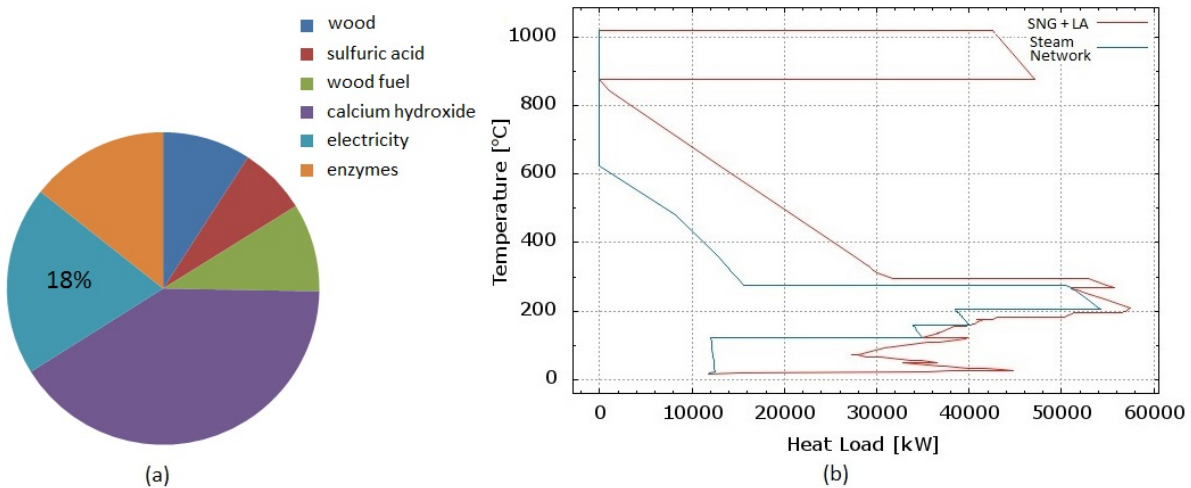


Figure 2.10: Benefit of CHP in lactic acid and SNG production (a) Impact contribution of resources, (b) Integrated composite curve of steam network and the biorefinery of SNG and lactic acid

2.5 Impact of integrated multi-product biorefinery on CO₂ balance

As the biomass is harvesting carbon from the atmosphere, the performance of a biorefinery can be studied on the basis of the amount of fossil CO₂ emission avoided per unit of atmospheric CO₂ converted by the photosynthesis. An example is a biorefinery which, in addition to the biochemical production of lactic acid from biomass, also produces thermochemically syngas together with CO₂ and electricity. Each bio-based product substitutes a fossil-based product. The waste heat of the gasification, as well as a part of the product gas are used to cover the heat and electricity demand of the model biorefinery. Considering the life cycle inventory of the fossil product, it is possible to calculate the fossil CO₂ emissions (fossil carbon) substituted by each unit of carbon in the bio-products or fuel. This value is indeed the amount of fossil CO₂ not emitted by unit of CO₂ captured by the photosynthesis as biogenic carbon. Table Appendix B.2 gives the fossil CO₂ emissions avoided per unit of carbon in different products. In the table, it can be seen that the bio-products have a higher substitution rate than the biofuels. Reference is taken as 100 kg of biogenic carbon entering the biorefinery as woody biomass. Via a biochemical conversion only, 26 kg of biogenic carbon in lactic acid is produced. It substitutes 93.65 kg of fossil carbon when considering the life cycle inventory of the conventional route as in Figure 2.11. The integrated biorefinery includes a synthetic natural gas production that supplies the heat needed for the lactic acid production and a steam cycle that cogenerates the electricity required for the biorefinery. The waste heat of the biorefinery can be used for district heating systems. A by-product of the biorefinery is biogenic CO₂ that is separated during the production. Without considering the waste heat valorisation, CO₂ capture and sequestration option is also implemented (only 30% of CO₂ is captured due to efficiency-cost penalty of membranes system [192]). Summing-up the substituted fossil carbon, 1 unit of biogenic carbon entering the biorefinery substitutes therefore 1.04 units of fossil carbon and the corresponding CO₂

2.5. Impact of integrated multi-product biorefinery on CO₂ balance

emissions (Figure 2.12).

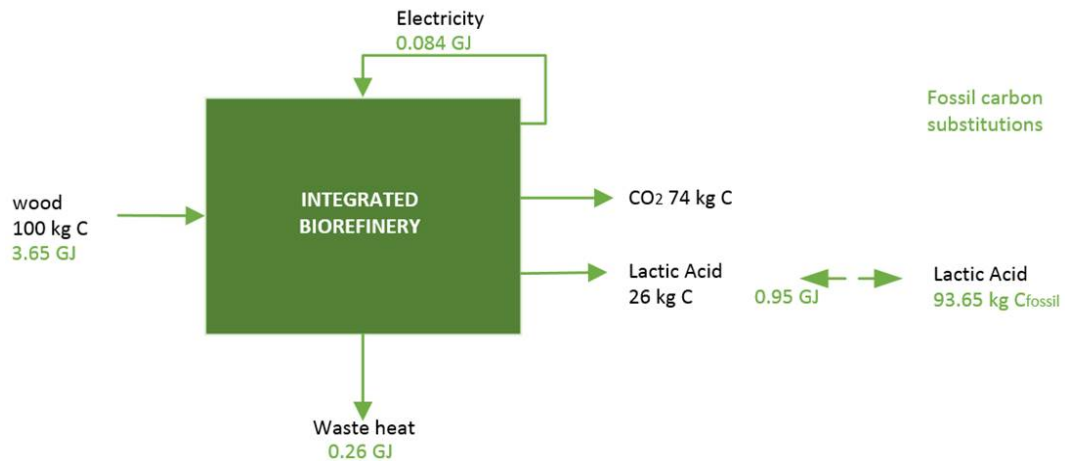


Figure 2.11: Biorefinery system replacing fossil lactic acid

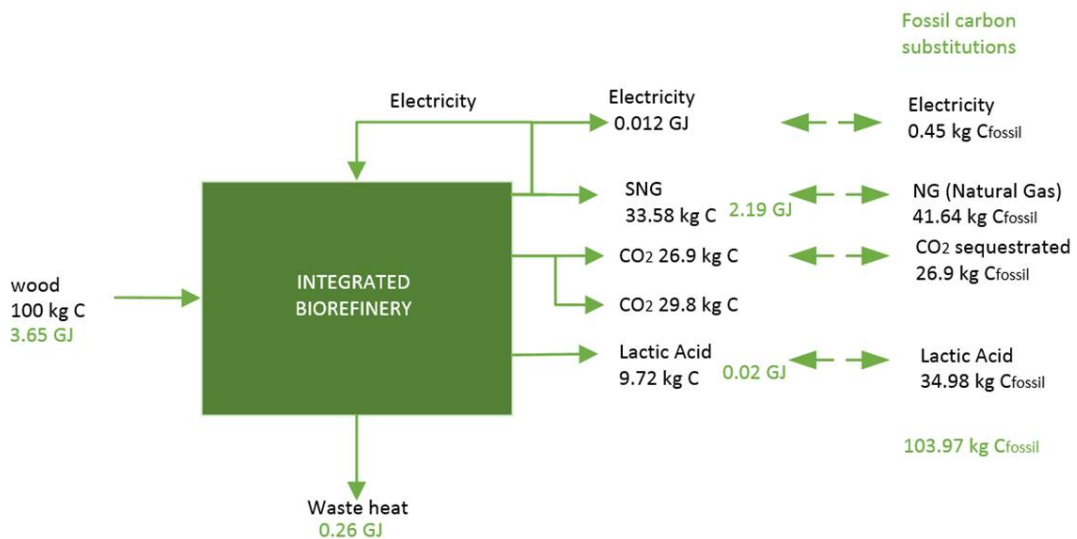


Figure 2.12: Biorefinery system replacing fossil lactic acid, SNG, electricity with CCS

In addition, if one considers that the synthetic natural gas of the biorefinery is used instead of natural gas in combined cycle with 60% efficiency and that the electricity produced is used in a heat pump with a COP of 4 to produce heat that substitutes the same fossil natural gas boiler, it can be shown that one unit of biogenic carbon entering the biorefinery would then substitute 1.73 units of fossil carbon.

This demonstrates that integrated approaches to biorefineries producing fuels and bio-products in a cascaded use of wood combined with CCS options have a higher potential for CO₂ mitigation and have therefore to be prioritized with respect to the production of individual bio-based products.

2.6 Conclusions

In this chapter, a systematic process design methodology is applied to a lignocellulosic biorefinery which utilizes the wood biomass to produce C5, C6 and lignin and syngas platforms of different bio-based fuels and chemicals. Thermo-environmental superstructure optimization is performed in order to increase energy conversion efficiency and minimize total cost and environmental impact of the biorefinery platform. Several process configurations are considered to analyze the potential for mass and energy exchange between the processes. Hybrid biochemical and thermochemical conversion pathways are also investigated. In this way, it is possible to highlight the advantages of integrating syngas and sugar platforms using a superstructure based approach.

The integer cut constraint method is applied to generate multiple solutions. The results, in terms of sets of candidate solutions considering different pathways were presented, distinguishing the results based on a minimum total cost optimization and a minimum environmental impact optimization. Using only ICC method, the solution space covers a high diversity of biorefinery configurations but the solution space needs to be extended to cover a wider range of environmental objective simultaneously. Therefore, ϵ -constraint is implemented coupled with ICC method. By this way, multi-objective optimization is implemented, using different objective functions such as economic and environmental criteria that are simultaneously considered to show the trade-offs between these conflicting objectives.

Technological challenges are identified and the synergies between these technologies are discovered. The results showed that the integration between biochemical and thermochemical conversion processes can avoid carbon dioxide emissions with respect to a purely thermochemical or purely biochemical pathway.

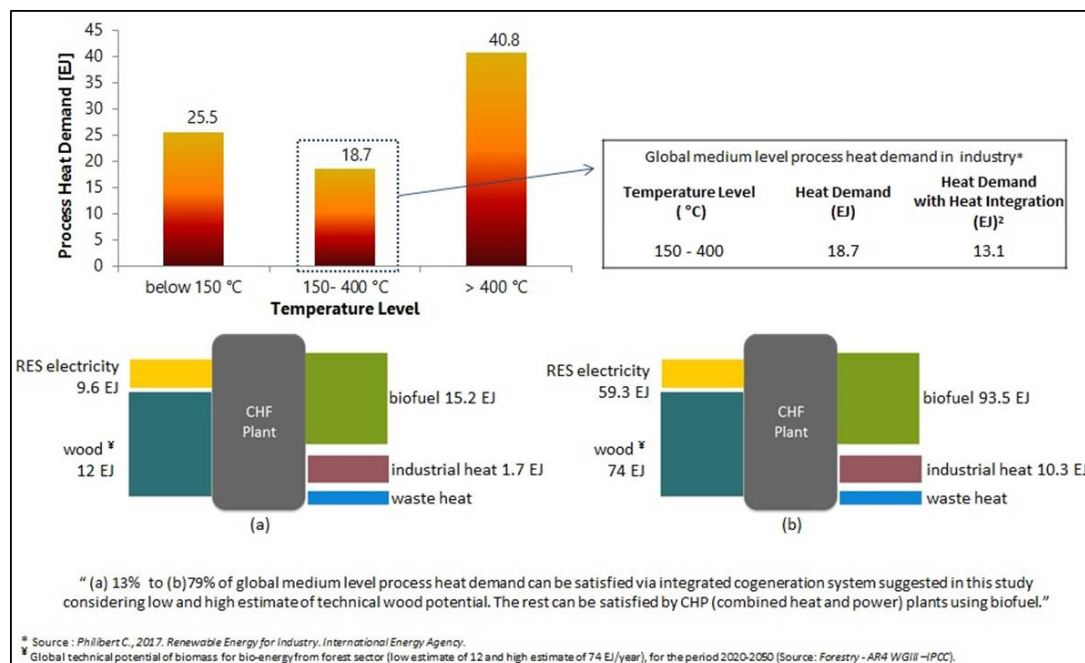
The integration of mechanical power production unit can be advantageous since the energy balance shows the potential to use the heat at high temperature for reducing the exergy losses from the integrated system and also reducing the energy cost at the same time.

The importance of efficiency of the carbon conversion in the biorefinery is shown with an illustrative example of a biorefinery where lactic acid, SNG, electricity is produced and by-product CO₂ is captured and sequestered. Summing-up the substituted fossil carbon, 1 unit of biogenic carbon entering this biorefinery substitutes therefore 1.04 units of fossil carbon. These solutions are important for engineers and decision-makers to understand the importance of overall efficiency in the design of biorefineries.

3 Synergies between biorefineries and energy system

Overview

- A cogeneration system (combined heat and fuel (CHF) plant) producing biofuels, heat and electricity is investigated.
- By-product CO₂ of biogenic origin is captured and sequestered (CCS) or seasonally stored.
- Stored CO₂ is used in co-electrolyser for storage of surplus renewable electricity thus boosting the biofuel production.
- Performance of CHF plants are compared with oil, natural gas and wood boilers.
- CHF plants mitigate fossil carbon emissions and may have negative heat price.



This chapter is extended version of Celebi et al. [193]

3.1 Introduction

Industrial heat demand constitutes two-thirds of industrial energy demand and one-fifth of global energy consumption, and is directly related to the most of the industrial CO₂ emissions as the majority of industrial heat is provided via fossil-fuel combustion [194]. Within the global industrial heat demand growth, the corresponding CO₂ emissions are estimated to account for a quarter of global emissions by 2040 [195]. In Europe, industries consume 25% of input energy for heat production, for which they use electricity and natural gas as their primary energy suppliers. Combined heat and power (CHP) plants are quite common to provide heat [196].

Since many industrial processes require high temperature heat, many renewable heat technologies are limited by temperature barrier. Solar collectors or geothermal sources can provide low temperature heat and are limited by geological location. Electricity can also be converted into heat via different technologies such as heat pumps that can provide low temperature heat for residential heating [197]. As a renewable energy source, biomass combustion systems are capable of providing high temperature process heat but they are responsible for a significant portion of the exergy losses in the overall system [198].

Biomass conversion via gasification may be the key to satisfy the heat demand at different temperature levels while enhancing the efficient use of limited biomass resources. The gasification process generates excess heat when producer gas is cooled down after the gasification stage. It is also possible to recover more surplus heat via extensive heat integration methods [199][192]. Excess heat from gasification can be used in many different ways: for electricity production via gas or steam turbine, for process integration with biochemical production process, for biomass drying, and for integration with an energy-intensive industrial site [200]. Different configurations provide different amounts of heat and exhibit different CO₂ emissions.

Damartzis and Zabaniotu [201] have reviewed the studies on the integrated design of biomass gasification processes to produce different biofuels by considering their energetic performance and CO₂ emissions. Caliandro et al. [114] and Sharma et al. [202] analyzed the potential of producing electricity using woody biomass in an integrated gasification and solid oxide fuel cell - gas turbine (SOFC-GT) hybrid system. Pihl et al. [203] showed a hybrid structure where existing combined cycle gas turbine (CCGT) and fluidized bed (FB) gasifier are combined with a steam cycle integration. Gassner et al. [192] proposed an integrated system in which woody biomass is converted to SNG (synthetic natural gas) and the excess heat is used to produce electricity considering different options for carbon capture and sequestration (CCS). Their work showed that in the presence of surplus electricity during summer, integration of an electrolysis unit results in higher economic profit for the conversion of wood into SNG.

Many studies considered the heat integration between a gasification plant within a pulp and paper mill [204, 205, 206, 207]. Some other studies focused on integrated biomass gasification systems with district heating system [208, 209]. Holmgren et al. [210] investigated the gasification systems connected to the district heating systems of industrial clusters, producing biofuels and considering

CCS. Werner et al. [196] performed an analysis to identify the potential of using cogeneration of biofuels and heat (CBH) in district heating in Europe.

A few studies considered the integration between gasification systems and the industrial clusters. Hackl and Harvey [211] replaced a natural gas boiler of a chemical cluster site in Sweden with a biomass gasification system. The concept showed that the cost and CO₂ emissions are improved when compared to stand-alone plants. Arvidsson et al. [212] integrated SNG production via different gasification systems into an industrial cluster. The benefit of excess heat integration into the clusters' heat demand was explained, but economics and emissions were not investigated. Johansson et al. [213] studied the integration of FT fuel via gasification pathway into an existing mineral oil refinery, and evaluated the performance in terms of economic and greenhouse gas emissions indicators.

CHP plants will no longer be attractive with the rapid energy transitions across Europe and the globe. Intermittent renewable power from wind and solar energy will shape future energy supply with their high shares. Therefore, surplus production of power will occur more often with increasing shares of variable renewable energy sources, that will increase energy storage requirements. Fuel storage systems and existing gas distribution networks are large and convenient facilities with proven and available technologies and it enables a seasonal storage of renewable energy [214].

Biomass is a source of carbon for seasonal storage of surplus renewable electricity and has a potential to mitigate fossil CO₂ from industry. Literature review showed that overall system integration between biomass gasification, carbon capture and sequestration (CCS) and power to gas (P2G) concepts is not widely investigated aiming to supply industrial heat. The goal of this paper is to assess the possible replacement of conventional (oil, natural gas, and wood) boilers with a combined heat and fuel (CHF) plant in which biomass gasification technologies are used to cogenerate industrial heat and variety of fuels (synthetic natural gas (SNG), Fischer-Tropsch (FT) crude, methanol (MEOH) and dimethyl ether (DME)) and CO₂ as a side product. Different scenarios are evaluated considering the CO₂ produced via this system is either released to atmosphere, sequestered, or stored and used in a co-electrolysis unit in which surplus renewable power is converted into more biofuel. Industrial heat prices are calculated assuming CO₂ reduction subsidies. A parametric sensitivity analysis is performed to investigate robustness of different scenarios to plant size, CO₂ tax and price of wood based on economics and potential CO₂ reduction. The heat market is dependent on multiple aspects such as primary energy supply, heat demands, heat carriers, prices of resources, plant investment and CO₂ tax. The current price of heat delivered from the conventional boilers is accounted as a basis for the calculation of breakeven CO₂ tax that should be imposed on conventional boiler heat.

3.2 Design methodology

The design methodology in this work is based upon the thermo-environmental optimization methodology explained in Section 2.2. For this study, a process flow superstructure of different biomass-to-fuels thermochemical conversion models is assembled. For each possible technology, separate energy-flow, energy-integration, economic and LCA (life cycle assessment) models are developed, as

outlined in Section 2.2.1. The thermo-environmental model consists of all these models and provides necessary information for impact assessment and energy demand profile to solve the energy integration optimization problem. The overall optimization problem is formulated as a Mixed-Integer Linear Programming (MILP) model and solved for minimizing the total cost.

3.3 Process description

3.3.1 Industrial heat demands by sector and quality

Different industrial sectors have different heat demands depending on their activities. The chemicals, food, minerals, pulp and paper and raw metals industries are the most heat demanding sectors [215]. Process heat can take up to 95% of total energy demand in some industrial sectors. Temperature quality for industrial heat demands is classified as high temperature ($\geq 400^{\circ}\text{C}$), medium temperature ($150\text{--}400^{\circ}\text{C}$) and low temperature ($\leq 150^{\circ}\text{C}$). Process operations such as melting, distillation, cracking, evaporation, and drying require heat at high and/or medium temperature, while low temperature heat is used for space heating and domestic hot water production. Food industry such as dairies and breweries, mainly requires low and medium temperature heat (pasteurization process around 80°C , drying process around 260°C) while pulp and paper industry requires medium temperature heat above 100°C for washing processes. Production of plastic materials have a temperature level of $180\text{--}290^{\circ}\text{C}$. High temperature heat demands mostly appear in chemicals, metals, and minerals production, reaching over 600°C for chemical industry while steel production has furnaces operating above 800°C and cement kilns operates around 1500°C [216]. Figure 3.1 shows the global process heating demand in industry by temperature level [8]. About 48% of global process heat demand is high temperature, 22% is medium temperature and 30% is low temperature [8]. In Europe, high temperature heat demand has a share of 43%, while medium and low temperature demand accounts for 27% and 30%, respectively [217].

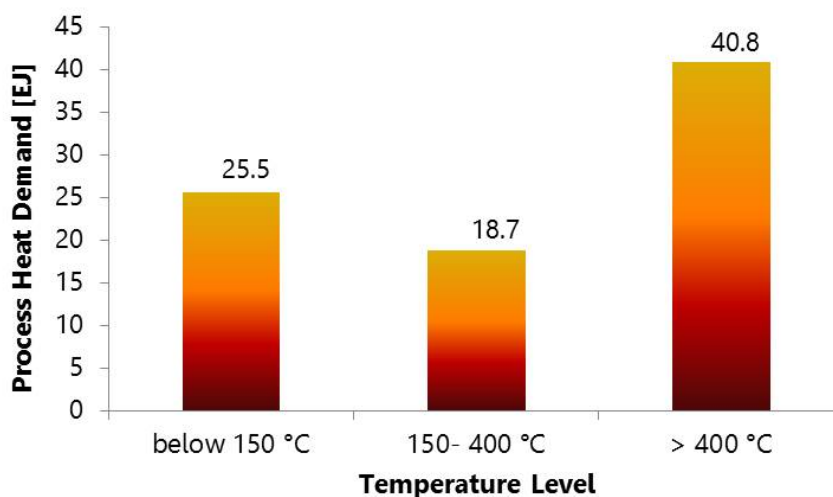


Figure 3.1: Global process heating demand in industry by temperature level in 2017[8]

The usability of the heat can be expressed by the temperature at which the heat is available. There is opportunity to integrate biomass gasification process with heat-demanding industrial processes at high and medium temperature levels. Low temperature heat demand is not considered in this study where heat pumps exhibit better performance.

3.3.2 Typical boilers in industry

Boilers use variety of fuels including natural gas, oil, coal and other resources such as biomass [218]. Heat transfer occurs via heat carriers such as flue gases, air and water. Steam is widely used in industry to convey heat energy for process operations due to its excellent heat transfer properties, price and safety. Without it, industrial sectors could not perform as they do today since they have a high use of steam boiler. Based on the flow of the medium, boilers can be categorized into different types, such as fire-tube or water-tube steam boilers. Fire-tube boilers are ideally used to provide large and constant amount of steam. Water-tube steam boilers are widely used where steam demand and pressure requirements are high. They can provide very high steam temperature up to 650°C. Fire-tube boilers have an economic advantage over water-tube boilers due to their relatively low cost [219]. In Europe, natural gas has the highest share (70%) to fuel the steam boilers and is followed by oil (15%), electricity (10%) and biomass (5%). In spite of the low use of biomass fired boilers in Europe, some countries such as Denmark favors the use of biomass boilers and according to one report [219], biomass-fired boilers are becoming more competitive.

To define the problem scale, boilers used in the industry can be grouped according to their sizes: very small to small 1–5 MW_{th}, small to medium, 5–25 MW_{th} and medium to large 25–50 MW_{th} [219]. According to the report from U.S. Office of Energy Efficiency and Renewable Energy, the average size of industrial boiler is around 10.5 MW_{th} [220]. The chosen boiler sizes for this study are presented in Table 3.1. Steam boilers fired by natural gas combining different sizes are chosen as a representative proxy for the European boiler population [219]. Fire-tube and packaged type of natural gas boilers operating at 15 bar are assumed to be the basis for this study, and the corresponding process model of the boiler is developed in the simulation environment. Other conventional boiler types such as wood and oil boilers are also studied in this study (Table 3.1). For the wood boiler model, air preheating is included where air inlet temperature to the wood boiler is assumed to be 25°C lower than the temperature level at which heat is provided. The corresponding investment costs are calculated by using the equipment cost correlations for industrial steam boilers [151] considering the boiler type, fuel, pressure and heat duty.

3.3.2.1 CO₂ tax on heating and process fuels

Switzerland has introduced CO₂ tax on the use of fossil fuels in heating and industrial process to promote more efficient use of fossil fuels and renewable energy sources. According to the working paper of Betz et al. [221], the initial CO₂ tax was 12 CHF/ton_{CO₂} in 2008, 60 CHF/ton_{CO₂} in 2016. It has increased over time reaching 96 CHF/ton_{CO₂} in 2018 with the current legislation. Maximum rate is put to 120 CHF/ton with the current legislation. This CO₂ levy corresponds to 0.215 CHF per kg of

Chapter 3. Synergies between biorefineries and energy system

Table 3.1: Selected characteristics of common natural-gas, oil and wood boilers, adapted from [219]

Capacity [MW_{th}]	Scale	Thermal Efficiency [%]			Investment [$\times 10^{-5}$, CHF] ¹		
		Natural Gas	Oil	Wood	Natural Gas	Oil	Wood
2.5	Very Small	91	92	85	2.23	1.90	8.94
7	Small	91	92	85	6.24	5.32	25.0
20	Medium	91	92	85	17.8	15.2	71.5
35	Large	91	92	85	31.2	26.6	125.2

¹ authors' own calculation.

natural gas (0.0164 CHF/kWh) additional to the bare price of natural gas.

3.3.2.2 Surplus electricity availability during summer

Aiming long term reduction in CO₂ emissions, the Swiss energy system is gradually transitioning into a system where the nuclear energy is ceased, and the dependency on fossil resources is cut down. The future energy scenario defined by the Swiss government in its Energy Strategy 2050 forecasts surplus electricity production during summer due to high penetration of renewable energy sources (RES) in the system. Around 4.9 TWh electricity has to be stored which corresponds to 7.7% of the annual production [222, 223, 224]. For Germany, energy surpluses up to 154 TWh per year are predicted until 2050. This corresponds to about 20% of the German gross electricity production in 2012 [225]. For the supply security, energy has to be balanced between periods with high renewable generation and low power demand and periods with low renewable generation and high demand [226].

Negative electricity prices have been allowed in the countries covered by the European Power Exchange (EPEX), i.e., France, Germany, Austria and Switzerland, in the countries covered by Nord Pool, i.e., Denmark, Estonia, Finland, Latvia, Lithuania, Norway, and Sweden, as well as in Belgium and the Netherlands [227]. Candra et al. [228] claims that the higher the share of stochastic RES, the more often the price will be 0 Euro/MWh. The electricity market should be adapted to cope with large share of renewables and put subsidies for the price of electricity when there is an excess production [229].

Due to the high share of fluctuating generation capacities (RES), electricity prices will become more volatile. Moreover, extremely high and extremely low prices will occur. Extreme prices are electricity prices equal to/below 0 EUR/MWh and those above 100 EUR/MWh. The anticipated ratio between the two extremes will create new opportunities for market newcomers and new technologies, e.g. storage systems. Severe extreme prices can be anticipated in Europe from 2026 onwards [230].

3.3.3 Process superstructure of biomass gasification pathways

The process modeling and simulations are performed using flowsheeting software Belsim VALI [161]. The lignocellulosic biomass resource used in the case study is the mixture of hardwood (57%) and softwood (43%) chips collected in Switzerland [34]. Characteristics of the woody biomass are shown

in Table 3.2.

Table 3.2: Characteristics of woody biomass

Proximate Analysis		Ultimate Analysis	
LHV_{Wood}	18.6 MJkg _{dry} ⁻¹	C	51.1 wt%
Humidity	50 wt%	H	5.8 wt%
Ash content	0.6 wt%	O	42.9 wt%
		N	0.2 wt%

Figure 3.2 shows the superstructure for the different configurations of combined heat and fuel plants. The main process conversion blocks are biomass pretreatment, gasification, syngas cleaning and processing, fuel synthesis and fuel upgrading. Depending on the synthesis reaction and the corresponding reactor technology, fuel upgrading consists of the production of different fuels such as SNG, FT fuels, MEOH and DME. Different technological options for each step are shown in Figure 3.2, and more details about the process operating conditions are provided in Table 3.3.

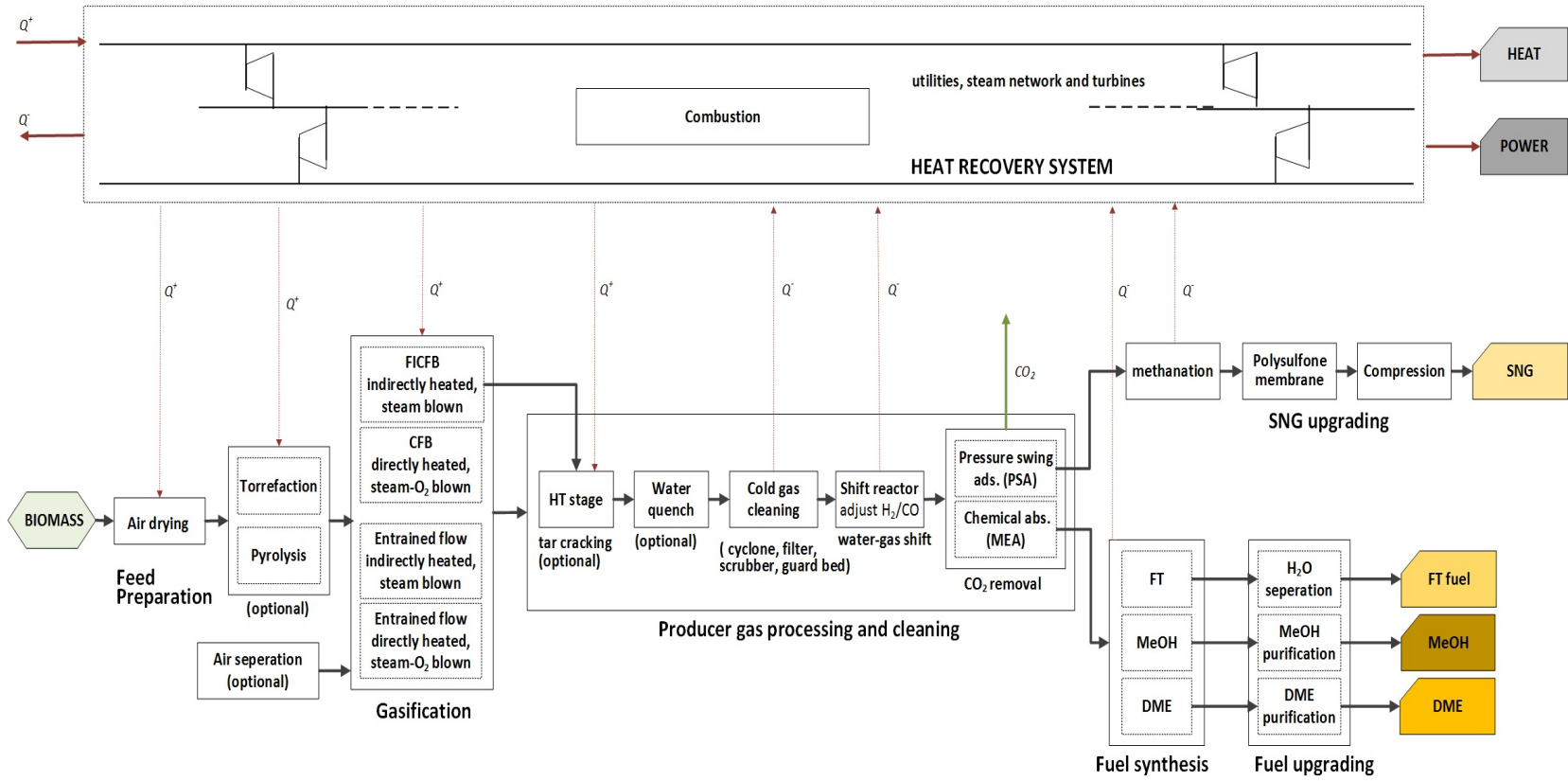


Figure 3.2: Superstructure of biofuels production plants (dashed lines show investigated alternatives for different process steps)

Biomass pretreatment step has air drying and optional pyrolysis unit which can operate in order to reduce the heat for gasification. Torrefaction, a different type of pyrolysis, mainly couples with entrained flow type gasifier to reduce the electricity consumption for grinding of biomass to fine particles. Different gasification technologies such as atmospheric or pressurized circulated fluidized bed (CFB) and entrained flow (EF) with indirectly heated, steam-blown and directly-heated, steam-O₂ blown options are considered for the production of producer gas (syngas). Depending on the gasification technology, producer gas has different H_2/CO ratios which will be further processed to synthesize biofuels. Air drying, pyrolysis/torrefaction and gasification are endothermic processes requiring heat supply. Before the fuel synthesis, impurities such as tar, metals and sulfur in the producer gas are removed by cold gas cleaning, filter, and sand beds. Then, to meet the requirement for optimal reactant stoichiometry for the fuel synthesis reactions, the gas composition is altered by optional water-gas shift reaction (WGS), and CO₂ removal/capture units. The technologies considered for CO₂ capture are chemical absorption with monoethanolamine (MEA) and pressure swing adsorption (PSA). The off-gases and the solid carbon along the processing steps, including, if necessary, some fraction of producer gas are burnt to satisfy the heat demand of the thermochemical conversion pathway. In the superstructure, power recovery expansion turbines are also included for all gas streams with a pressure of 25 bar. These can contribute to a reduction of the electricity consumption in the thermochemical conversion pathways. Steam network is optimized for each CHF plant configuration using header, draw-off and condensation pressures as decision variables.

Table 3.3: Characteristics of biofuels production plants

Section	Specification	SNG	FT	MEOH	DME
Drying	Technology		Air drying		
	Air inlet temperature [°C]		200		
	Wood outlet humidity [%]	20	10	30	25
Torrefaction	Temperature [°C]	-	250	-	-
Pyrolysis	Temperature [°C]	-	-	-	260
Gasification	Heating mode	Indirectly heated	Directly heated	Indirectly heated	Directly heated
	Gasification type	FICFB	EF	FICFB	CFB
	Temperature [°C]	850	1350	850	850
	Pressure [bar]	1	30	25	1
	Agent	Steam	Steam-O ₂	Steam	Steam-O ₂
	Steam preheat T [°C]	300	400	450	400
	Steam to biomass ratio	0.5	0.6	0.38	0.6
	Air separation	Technology	-	Cryogenic distillation	
	Energy consumption [kJ/kg O ₂]	-	1080	-	1080
Tar cracking	HTS temperature [°C]	-	1350	1350	950
	HTS heating mode	-	Directly heated	Directly heated	Directly heated
Water quench	Temperature [°C]	-	750	-	-
Gas cleaning	Filter temperature [°C]		150		
	Filter pressure drop [mbar]		100		
	Flash temperature [°C]		25		
Water gas shift	Temperature [°C]	200	300	313	443
CO ₂ removal	Technology	TSA & PSA		MEA ¹	
	Amount CO ₂ removed		95%		
Synthesis		Internally cooled	Multi-tubular,	Multi-stage	Slurry phase
	Technology	Fluidized bed reactor	Fixed bed reactor	Fixed bed reactor	reactor
	Catalyst	Ni/Al ₂ O ₃	Co/Zr/SiO ₂	Cu/ZnO/Al ₂ O ₃	ACZ & HZSM-5
	Temperature [°C]	320	220	315	277
	Pressure [bar]	5	25	85	50
Upgrading	Technology	Polysulfone membrane for H ₂ sep., compression	Private data	Flash, distillation (2x)	Flash, distillation (3x)
Fuel specifications		96 vol% 25°C, 50 bar	Liquid fuels 25°C, 1 bar	99.4 vol % 25°C, 1 bar	99.88 vol% 25°C, 1 bar
Steam network	Header pressures [bar]	70	115.4	56	110, 45
	Super-heating ΔT [°C]	274	200	200	250, 200
	Draw-off pressures [bar]	16.69, 6.02, 1.95	15, 8, 2.3	17, 6.5, 2.8	17, 6.3, 1.98
	Condensation pressure [bar]	0.03	0.07	0.02	0.07
Adapted source		[162]	[90]	[50]	[50]

¹ For MEA absorption, reboiler heat demand is fixed at 3.3MJ/kg CO₂ separated at 150°C, 20% of the heat duty is recoverable between 90°C to 40°C. Electricity consumption is fixed at 25 kJ/kg CO₂ [171].

3.3.4 Approach for scenario development

In order to assess the performance of different scenarios of the integrated biomass gasification systems with multiple products, system boundaries should be defined.

The biomass gasification system has three inputs:

1. biomass,
2. investment cost of the proposed plant design,
3. electricity which can have three difference sources: (a) electricity purchased from the grid, (b) renewable electricity produced in the system as a co-product, and (c) renewable electricity from the grid which is produced in excess amount during summer season (price of electricity = 0 CHF/kWh).

The system outputs are:

1. the heat cogenerated at a certain temperature level (assumed to be at 200 °C),
2. the cogenerated biofuel: stored and distributed renewable energy,
3. the renewable electricity produced in the system as the co-product,
4. CO₂ in one of the following forms: (a) CO₂ released to atmosphere, (b) CO₂ captured and sequestered, (c) CO₂ captured and stored in a pressurized tank to use in a co-electrolysis unit to produce more biofuel.

The process performance is measured by the cost of heat produced through the designed CHF system. The amount of heat is defined by the overall energy conversion efficiency and the quality of the process integration based on the selected energy conversion technologies. Four different CHF plant operation schemes are shown in Figure 3.3.

To determine the thermodynamic performances of the proposed designs, chemical and overall energy efficiency terms are defined as shown in equations 3.1 and 3.2, respectively:

$$\epsilon_{chem} = \frac{LHV_{Fuel} \cdot \dot{m}_{Fuel}}{LHV_{Wood} \cdot \dot{m}_{Wood}} \quad (3.1)$$

$$\epsilon_{tot} = \frac{LHV_{Fuel} \cdot \dot{m}_{Fuel} + \dot{E}^+ + \dot{Q}_{Heat}^+}{LHV_{Wood} \cdot \dot{m}_{Wood} + \dot{E}^-} \quad (3.2)$$

where LHV is the lower heating value per unit mass (MJ/kg), \dot{m} is the mass flow rate of the stream (kg/s), \dot{Q}_{Heat}^+ is the heat produced from the system (MW), and \dot{E}^- (and \dot{E}^+) represents electric power consumed (produced) in the system (MW).

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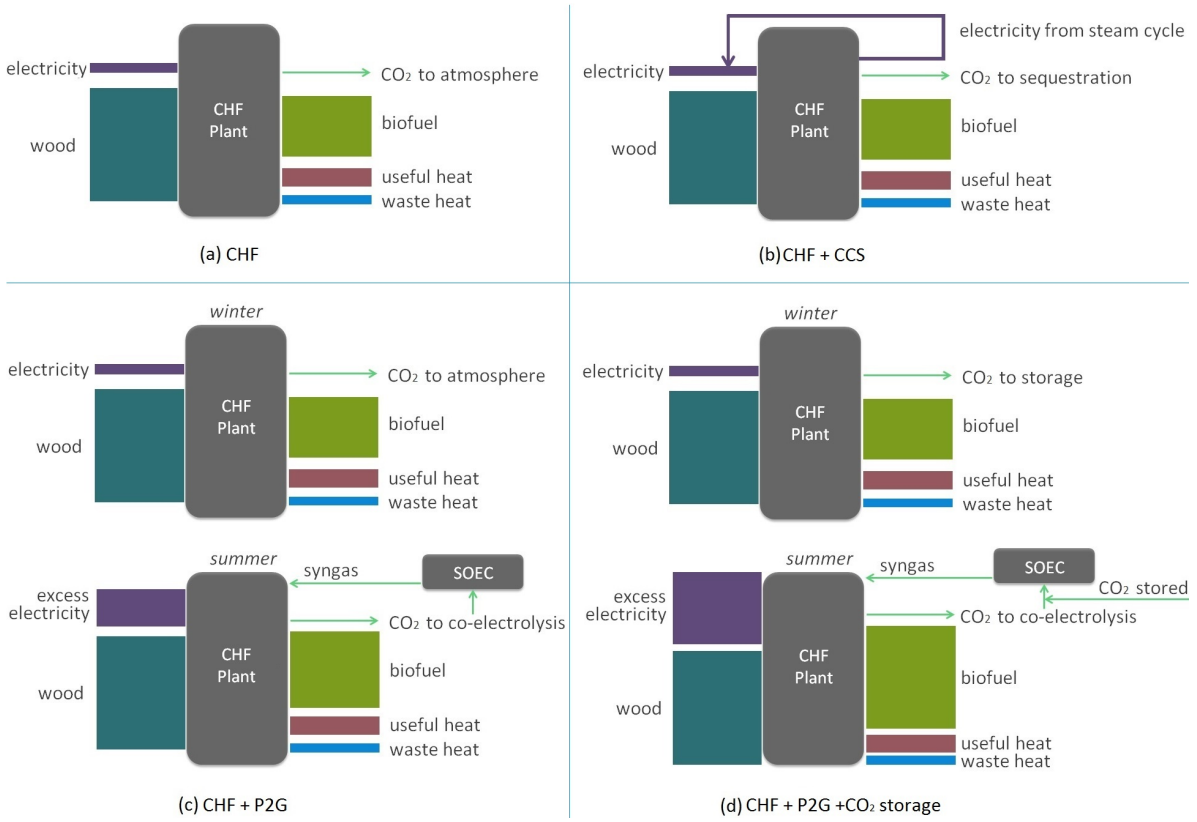


Figure 3.3: Conceptual CHF plant operation schemes: plot (a) - Case I (CHF), plot (b) - Case II (CHF+CCS), plot (c) - Case III (CHF+P2G), plot (d) - Case IV (CHF+P2G+CO₂ storage)

3.3.5 Cost of heat calculation

The calculation for cost of heat has the following elements: (1) investment cost of the proposed plant, (2) cost of wood, (3) operating cost, (4) revenues from biofuels and oxygen sell, and (5) costs related to CO₂.

$$c_{Heat} = \frac{c_{AI,Base} + c_{Wood,T} + c_{OP} - (c_{Fuel} + c_{CO_2}) + c_{CO_2}}{\dot{Q}_{Heat}} \quad (3.3)$$

$$c_{Wood,T} = (c_{Transport} + c_{Wood}) \cdot \dot{Q}_{Wood} \cdot h \quad [CHF/yr] \quad (3.4)$$

$$c_{OP} = c_R + c_L + c_M \quad [CHF/yr] \quad (3.5)$$

where $c_{AI,Base}$ is the annualized investment cost in CHF/yr, and it represents the overall investment cost for case I, where only CHF plant is considered. $c_{Wood,T}$ is the total cost of wood resource in CHF/yr, which has two elements namely, cost of transportation ($c_{Transport}$) and market price of wood (c_{Wood}). For more details on the calculation of transportation cost of wood, see Appendix C. c_{OP} is the operational cost that includes: (1) c_R - cost of resources consumed during the plant

operation, such as electricity purchased, water consumption and FAME consumption (only for SNG production) in CHF/yr, (2) c_L - labor costs in CHF/yr, and (3) c_M - annual operation and maintenance cost in CHF/yr. The maintenance cost of units is assumed to be 5% of the total investment cost per year. c_{Fuel} is the revenue generated by selling the biofuels in the market, and c_{O_2} is the revenue generated by selling the side product of co-electrolysis unit (i.e., oxygen) in the market. There are several elements related to costs of CO₂, as shown by following equations.

$$c_{CO_2} = c_{CO_2emissions,local} - c_{CO_2substitution} + c_{CO_2sequestration} + c_{CO_2storage} + c_{CO_2co-electrolysis} \quad (3.6)$$

$$c_{CO_2sequestration} = c_{CO_2inv,sequestration} + c_{CO_2op,sequestration} - c_{CO_2avoidance,sequestration} \quad (3.7)$$

$$c_{CO_2storage} = c_{CO_2inv,storage} + c_{CO_2op,storage} \quad (3.8)$$

$$c_{CO_2co-electrolysis} = c_{CO_2inv,co-electrolysis} \quad (3.9)$$

where (1) $c_{CO_2emissions,local}$ represents local CO₂ emissions tax due to the plant operation, (2) $c_{CO_2substitution}$ is tax benefit due to CO₂ avoided via substitution of fossil fuels by biofuels (local CO₂ tax is imposed on the fuels from fossil resources, both on fossil fuel production and use phase). For the substitution of biofuels with fossil fuels, it is assumed that 1 unit of SNG substitutes 1 unit of NG, 1 unit of FT fuels substitutes 1 unit of diesel fuel, and 1 unit of MEOH replaces same amount of fossil derived MEOH. The equivalent CO₂ emissions for the production and use phase of fossil substitutes are shown in see Table 3.5, (3) $c_{CO_2sequestration}$ is a premium for avoiding CO₂ emissions due to CO₂ sequestration, investment cost for compressing CO₂ to transport in the pipeline, related operating cost, (4) $c_{CO_2storage}$ is cost related to CO₂ storage with investment cost for a pressurized tank and operating cost of storing CO₂, and (5) $c_{CO_2co-electrolysis}$ is the investment cost of co-electrolysis unit. Further, operating cost of electrolysis unit includes cost of steam consumption which is included in the other operational cost (c_{OP}) of the overall system. The consumed electricity is assumed to be free as excess amount is produced during summer.

The economic performance indicators such as annual capital investment and the production costs are evaluated with the economic data depicted in Table 3.4.

The environmental impact of the each process design is assessed in terms of equivalent CO₂ emissions using the GWP100a impact category, which is Global Warming Potential impact assessment method for time-horizon of 100 years [238]. Related emission factors are gathered from the Ecoinvent® Life Cycle Inventory database version 3.4 [152] and presented in Table 3.5.

3.4 Process performance

Several scenarios have been proposed in order to assess the performance of the renewable CHF systems with regard to the conventional design. The functional unit in all these scenarios is the amount of heat provided. The study is parametrized by considering the type and size of plants, CO₂

Table 3.4: Assumptions for the economic performance evaluation

Parameter	Value	Source
CEPCI index (2017)	567.5	[231]
Biofuel plant yearly operation, h [h/year]	7884	
Electrolysis plant yearly operation [h/year]	2628	
Expected lifetime [years]	20	
Interest rate [%]	6	
Operators ¹	4 per shift ²	[162]
Salary [CHF/yr]	91070	[90]
Market price of wood [CHF/kg]	0.146	[232]
Market price of electricity [CHF/kWh]	0.0749	[233]
Market price of natural gas [CHF/kWh]	0.024	[234]
Market price of heating oil [CHF/kWh]	0.086	[235]
Market price of SNG [CHF/kWh]	0.056	[186]
Market price of FT fuels [CHF/kWh]	0.089	[236]
Market price of MEOH [CHF/kWh]	0.083	[189]
Market price of DME [CHF/kWh]	0.105	[237]

¹ Full time operation requires three shifts per day. One operator corresponds to 4.56 employees with a working time of 5 days per week and 48 weeks per year.

² Data is available for a plant size of 20 MW_{wood} . For different plant capacity, an exponent of 0.7 with respect to plant capacity is used.

Table 3.5: Emission factors from Ecoinvent® v3.4 [239]

Parameter	Value
Wood chips production [kg CO ₂ eq/kg dry]	0.037142
Electricity mix, CH [kg CO ₂ eq/kWh]	0.1176
Water [kg CO ₂ eq/kg]	0.0002
NG production and combustion, CH [kg CO ₂ eq/MWh]	241.7
Heating oil production and combustion, CH [kg CO ₂ eq/MWh]	311
Wood production and combustion ¹ , CH [kg CO ₂ eq/MWh]	11.8
Diesel production and combustion, CH [kg CO ₂ eq/MWh]	315
Methanol production and combustion, CH [kg CO ₂ eq/MWh]	318.9

¹ Ecoinvent® [239] has non-zero emissions in IPCC 2017 GWP indicator for the combustion of wood (3.67 kg CO₂eq/MWh).

tax and cost of wood for different biofuels production scenarios. For this, a comparative analysis is done by calculating the cost of heat and breakeven CO₂ tax values that would make the new system more profitable when compared to the conventional natural gas boiler and wood boiler. The approach of CHF systems is illustrated by different cases, and analysis results are presented in the following paragraphs.

3.4.1 Case 0 : Conventional natural gas and wood boilers for heat production

Conventional natural gas and wood boilers proposed in Table 3.1 are taken as basis for the calculations. Oil boiler is considered only for CO₂ reduction comparison. It is not considered in the breakeven CO₂ tax calculations due to highest heat price (Figure 3.4) and CO₂ emissions (Table 3.5).

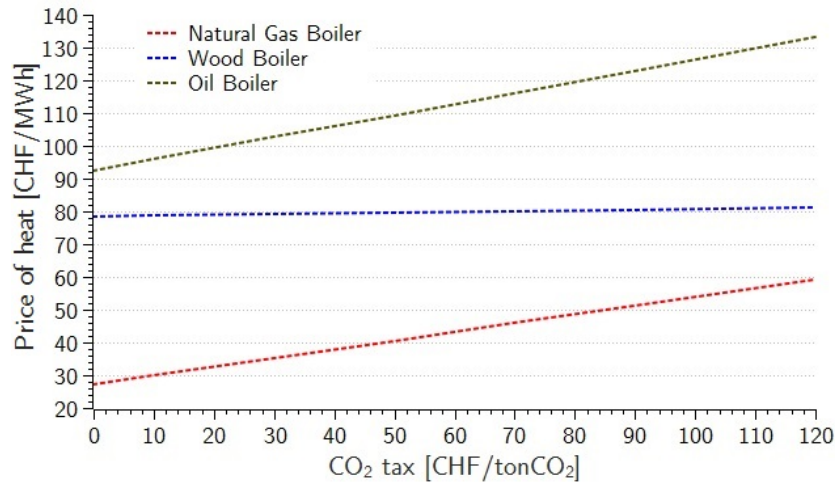


Figure 3.4: Case 0 - Conventional oil, natural gas and wood boilers

3.4.2 Case I : CHF plants

This cogeneration scenario is the base case, where heat and biofuels are coproduced and electricity is purchased from the current electricity grid. Different plant sizes of 2.5, 7, 20 and 35 MW heat (as proposed in Table 3.1) with one of the SNG, FT, MEOH and DME cogeneration options are chosen, and CO₂ is released to atmosphere assuming the corresponding emissions are carbon neutral (Figure 3.3). Figure 3.5 shows breakeven CO₂ tax for equal heat prices by natural gas and wood boilers, and CHF plant (heat and SNG; heat and FT; heat and MEOH; heat and DME).

As seen in Figure 3.5, for 20 MW heat and SNG plant, one needs to pay 62 CHF/tonCO₂ breakeven CO₂ tax for the conventional natural gas boiler to provide heat at 44 CHF/MWh. On the other hand, for a conventional wood boiler, the heat price would be 79 CHF/MWh. If we replace a conventional natural gas and wood boilers with the proposed CHF plant, it cogenerates 20 MW heat and 93 MW SNG (see Table Table D.1). With today's CO₂ tax of 96 CHF/tonCO₂ in Switzerland, the price of heat from CHF SNG plant with heat capacities of 7, 20 and 35 MW will be lower than traditional wood and natural gas boilers. With increase in plant size, heat is becoming cheaper for the same CO₂ tax. The reason is that the plant investment cost per unit production decreases with increase in the plant size. For large size of CHF SNG plants (20 and 35 MW), the heat prices are negative due to large production and sell of green fuel and corresponding benefits of CO₂ substitution for fossil CO₂ at higher CO₂ tax values. For different CHF plants, it can be observed that CHF FT configuration is the best choice and it is followed by CHF SNG, CHF MEOH and CHF DME plants. Table 3.6 highlights the overall process efficiency for all types of CHF plants. Due to different fuel synthesis processes

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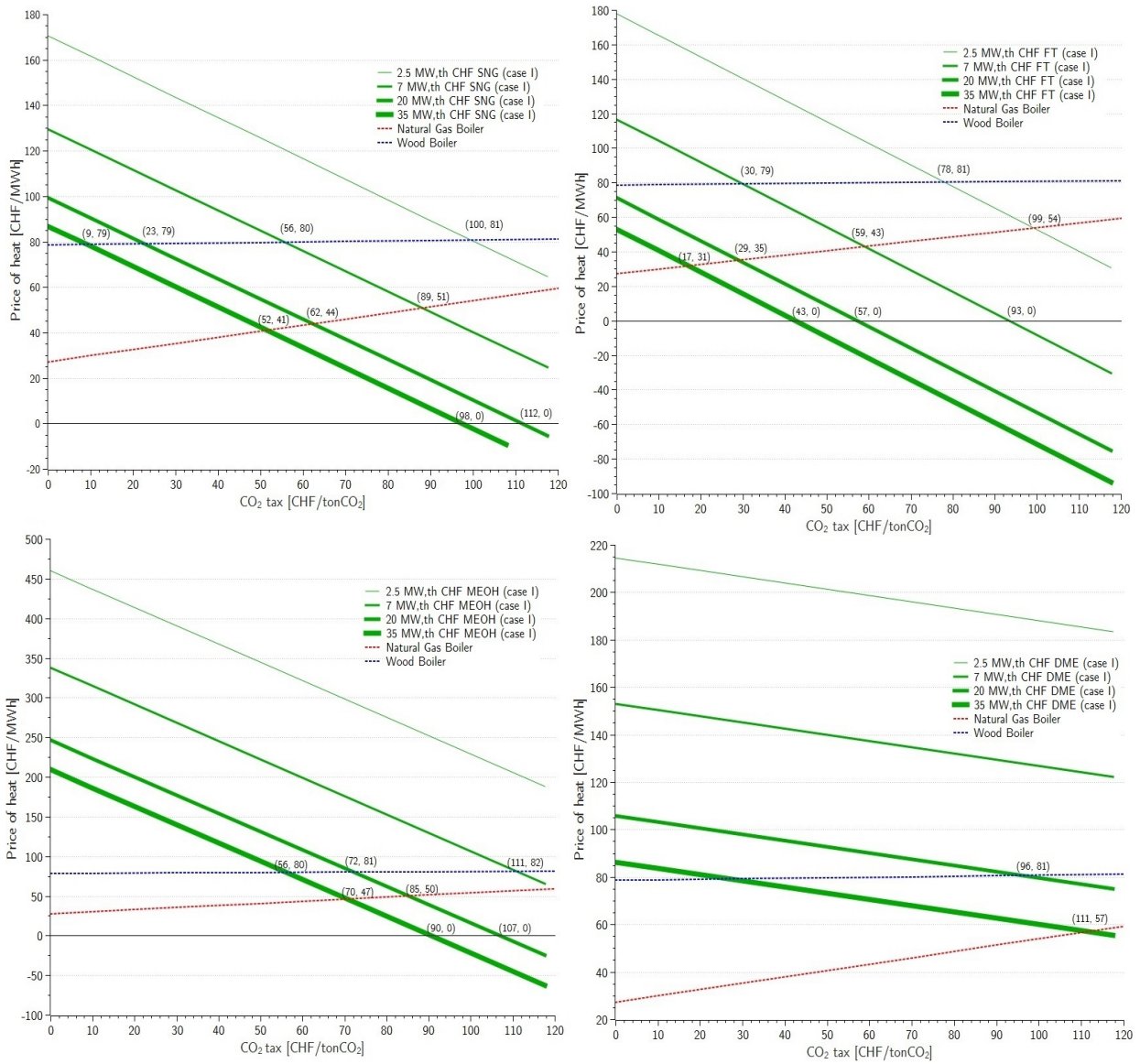


Figure 3.5: Case I: CHF (SNG, MEOH, FT and DME) with different plant sizes

and different gasification technology in the CHF systems, biomass input varies to provide same amount of heat. Therefore, amount of fuel cogenerated changes thus effecting the price of heat.

Table 3.6: Performance of different fuel (CHF SNG, FT, MEOH and DME) production scenarios in Case I with plant size of 2.5 MW heat production for the breakeven CO₂ tax values comparing to natural gas boiler

	Heat-SNG	Heat-FT	Heat-MEOH	Heat-DME
Wood [MW]	18.00	31.70	54.30	18.90
Biofuel [MW]	11.80	13.85	28.85	8.93
Net electricity [MW]	0.70	1.71	5.97	2.17
ϵ_{chem} [%]	63.10	43.68	53.12	47.24
ϵ_{tot} [%]	73.71	48.92	52.01	54.23
CO ₂ produced [ton/h]	2.29	1.45	6.64	2.13
Breakeven CO ₂ tax [CHF/tonCO ₂]	123	99	168	349

To determine the effect of variabilities in the market wood price, a sensitivity analysis is performed for some scenarios of 20 MW CHF plants with SNG, FT and MEOH production. The intersection points in Figure 3.5 where the heat prices of CHF plants are equal to the heat price from natural gas boiler are selected as basis. The market prices of wood are changed $\pm 20\%$ from the base market price of 0.146 CHF/kg. Figure 3.6 shows the corresponding CO₂ tax values which should be imposed on fossil CO₂ emissions of natural gas boiler to provide the heat at same price. When the wood price is higher, increased CO₂ tax will make equal heat prices from natural gas boiler and CHF plant. When the market price of wood drops, the heat price of the CHF plant will be same as heat price of natural gas boiler at lower CO₂ tax. It is determined from the Figure 3.6 that 20 MW CHF FT with lower wood price can provide heat for free with the same price of natural gas. The heat price from 20 MW CHF FT plant with the current wood price is 35 CHF/MWh (see Figure 3.5).

Figure 3.7(a) shows the integrated composite curve for CHF SNG plant of 2.5 MW heat and one can see that the proposed design is well heat integrated with a total efficiency of 73.71%. Case II is taking into account the long-term storage of captured biogenic CO₂ in the enhanced oil recovery sites. For transporting CO₂ to the storage sites, pipeline network is assumed to be in place for compressed CO₂ (200 bar, 25°C [240, 241]). Hence, captured CO₂ is compressed to 200 bar to meet the specifications of CO₂ transport pipeline. Before the injection, the compressed CO₂ is cooled down to 25°C and heat is recovered in the system [240]. As Figure 3.7(b) depicted, recovered heat can be used in a Rankine steam cycle to generate mechanical power. One can see the integrated composite curve of SNG, heat and electricity production configuration in Figure 3.7(c). For this specific system, overall efficiency reaches 75.48%. Furthermore, energy expenses are reduced due to the co-production of renewable electricity and use in the system. This will reduce the price of heat with a significant rate as well as environmental impact.

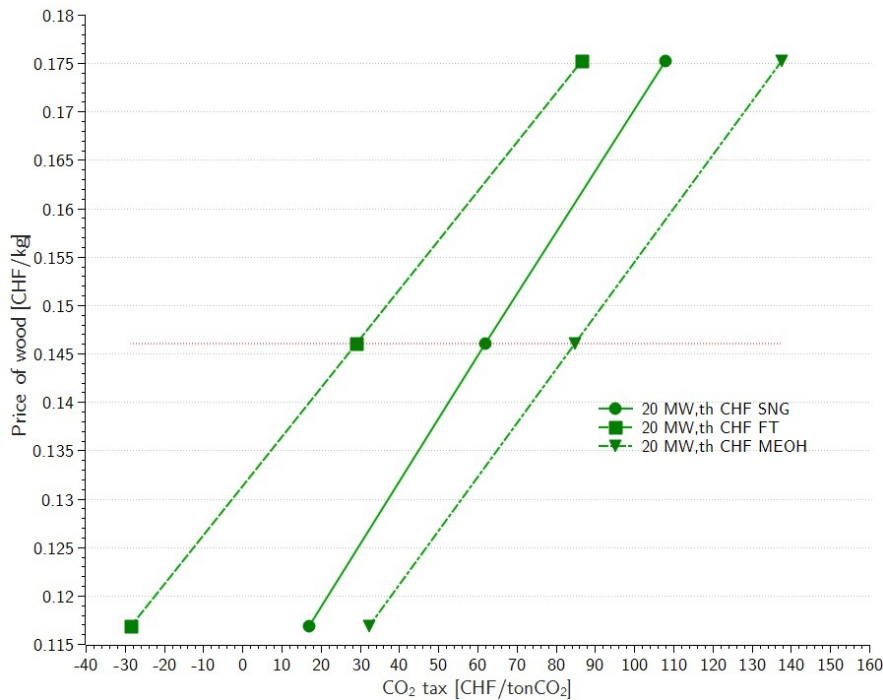


Figure 3.6: Sensitivity analysis with wood price

3.4.3 Case II: CHF plants with CO₂ capture and sequestration (CCS)

As mentioned above, CHF plant have CO₂ sequestration option in case II. Due to CO₂ tax on fossil carbon in Switzerland, the proposed scenario is assumed to have a premium for CO₂ sequestration. Figure 3.8 compares the case I and case II for CHF SNG plants of all sizes. As expected, the CHF systems with sequestration are performing better than CHF systems only. For 20 MW plant size, breakeven CO₂ tax for the conventional natural gas boiler is 47 CHF/tonCO₂ to provide heat at 40 CHF/MWh. While the CHF plants in Case I would produce more expensive heat than the natural gas boiler for the same CO₂ tax.

Figure 3.9 presents variations in heat price and breakeven CO₂ tax values for 2.5 MW next generation CHF plants (with SNG, FT, MEOH or DME biofuel production), natural gas boiler and traditional wood boiler. Comparing the CHF plants in Case I, the price of heat is reduced dramatically when CO₂ sequestration is considered. With a CO₂ tax of 96 CHF/tonCO₂ (Switzerland, 2018), very small size (2.5 MW) CHF SNG, FT and MEOH plants provide heat at prices lower than natural gas boilers. After CO₂ tax of 90 CHF/tonCO₂, CHF MEOH plant starts to perform better than CHF FT and SNG configurations. This is due to the large amount of wood used in the system thus producing more biofuel and replacing more fossil fuel. At the end, reduction in the heat price is proportional to the benefits from CO₂ sequestration and fossil carbon substitution. For bigger sizes, the heat would be free from the CHF plants with carbon capture and sequestration systems integrated. The cost build-up of different CHF scenarios, where heat price lines for biofuels production route intersects heat price line for natural gas boiler, is presented in the Figure 3.10.

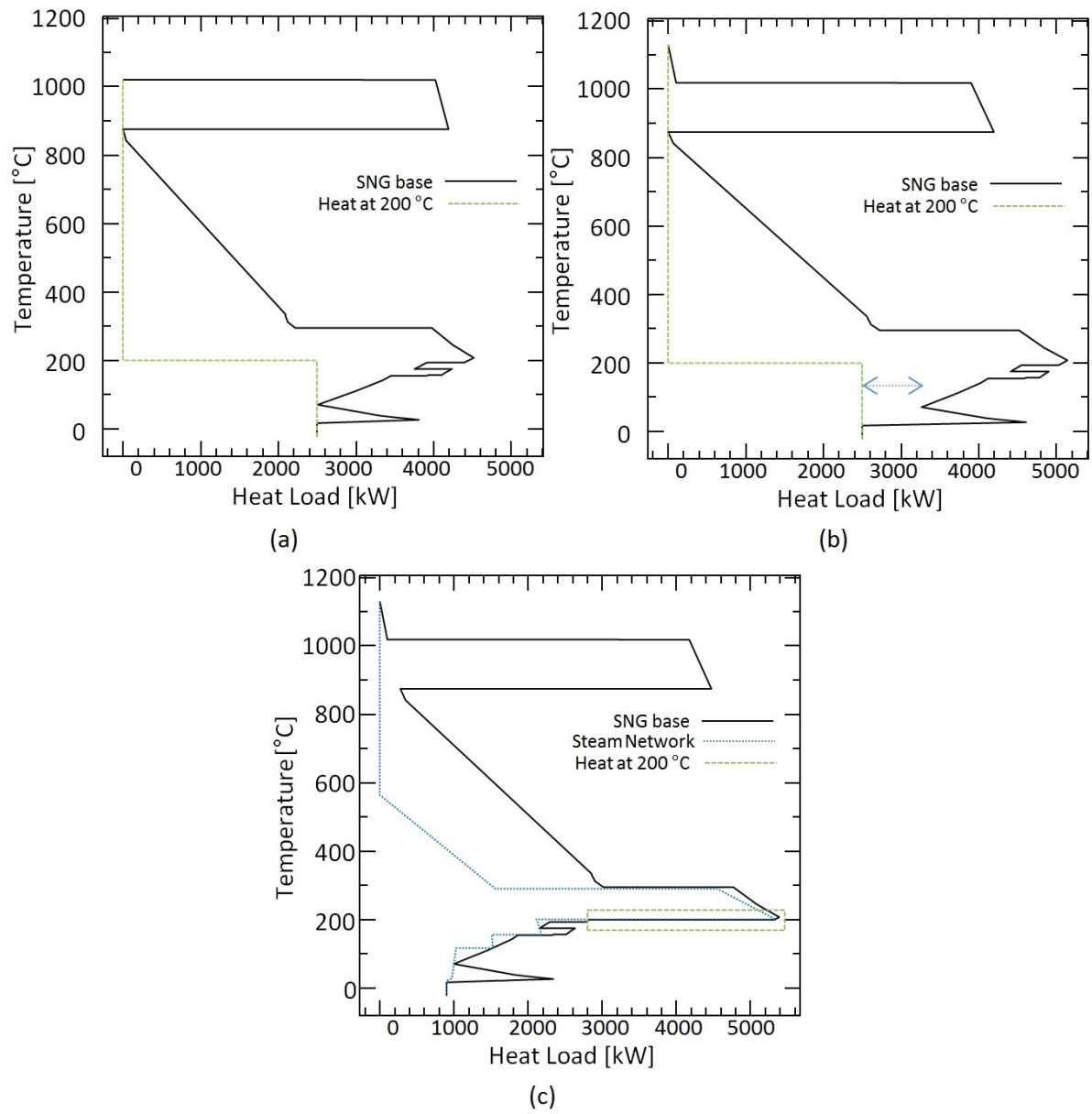


Figure 3.7: Integrated composite curves for Case I (Plot a) and Case II (Plots b and c) for CHF SNG plant with 2.5 MW size (Plot b represents Case II without electricity production)

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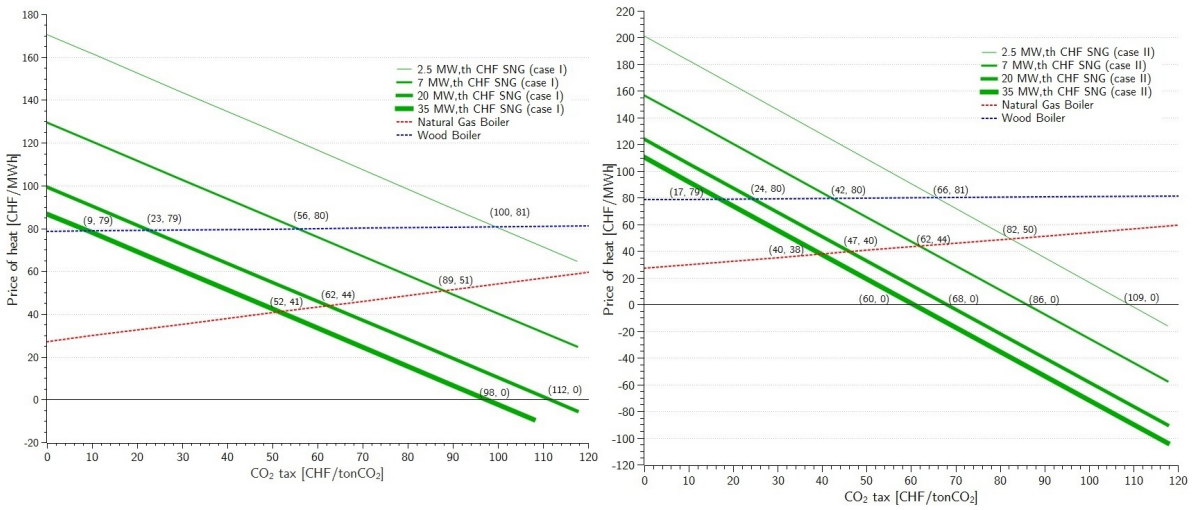


Figure 3.8: Comparison of Case I and Case II: CHF SNG with all plant sizes

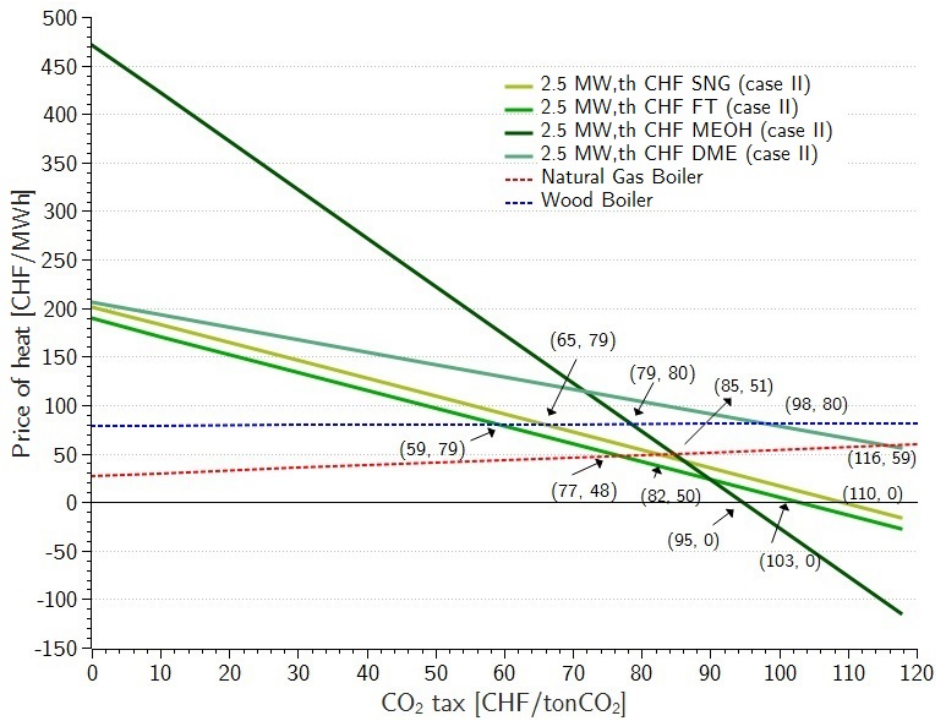


Figure 3.9: Case II: CHF SNG, FT, MEOH and DME systems of 2.5 MW size

Figure 3.11 shows the integrated composite curves for CHF SNG, FT, MEOH and DME plants for case II. Recovering heat from the cooling operation before transporting compressed CO₂ into the pipeline allows to produce renewable electricity through Rankine cycle. The produced electricity is used in the system, and the deficit in the electricity is covered by the grid electricity. Integration of steam cycle allow us to reduce the exergy losses from the system.

3.4. Process performance

Table 3.7: Performance of different processes (CHF SNG, FT, MEOH and DME) in Case II for plant size of 2.5 MW heat production

Process parameters	Heat-SNG	Heat-FT	Heat-MEOH	Heat-DME
Wood [MW]	18.00	31.70	54.30	18.90
Biofuel [MW]	11.80	13.85	28.85	8.93
Electricity consumed [MW]	1.42	1.80	6.32	2.33
Electricity produced [MW]	0.91	0.17	2.13	1.49
Net electricity [MW]	0.51	1.63	4.19	0.84
ϵ_{chem} [%]	63.10	43.68	50.65	45.13
ϵ_{tot} [%]	75.48	49.03	51.30	57.96
CO ₂ sequestrated [ton/h]	2.29	1.45	6.33	2.04
Breakeven CO ₂ tax [CHF/ton _{CO₂}]	82	77	85	116

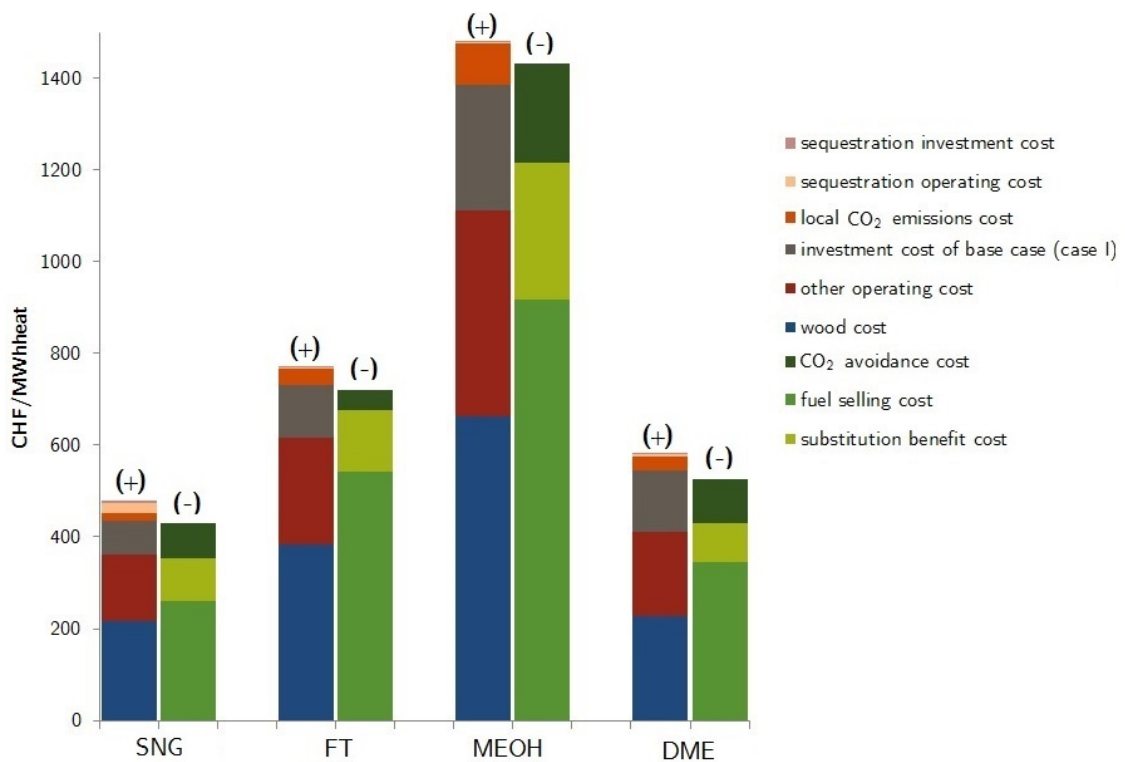


Figure 3.10: Heat cost build-up for CHF SNG, FT, MEOH and DME plants of 2.5 MW size in Case II (Positive sign represents the expenses, negative sign represents the incomes.)

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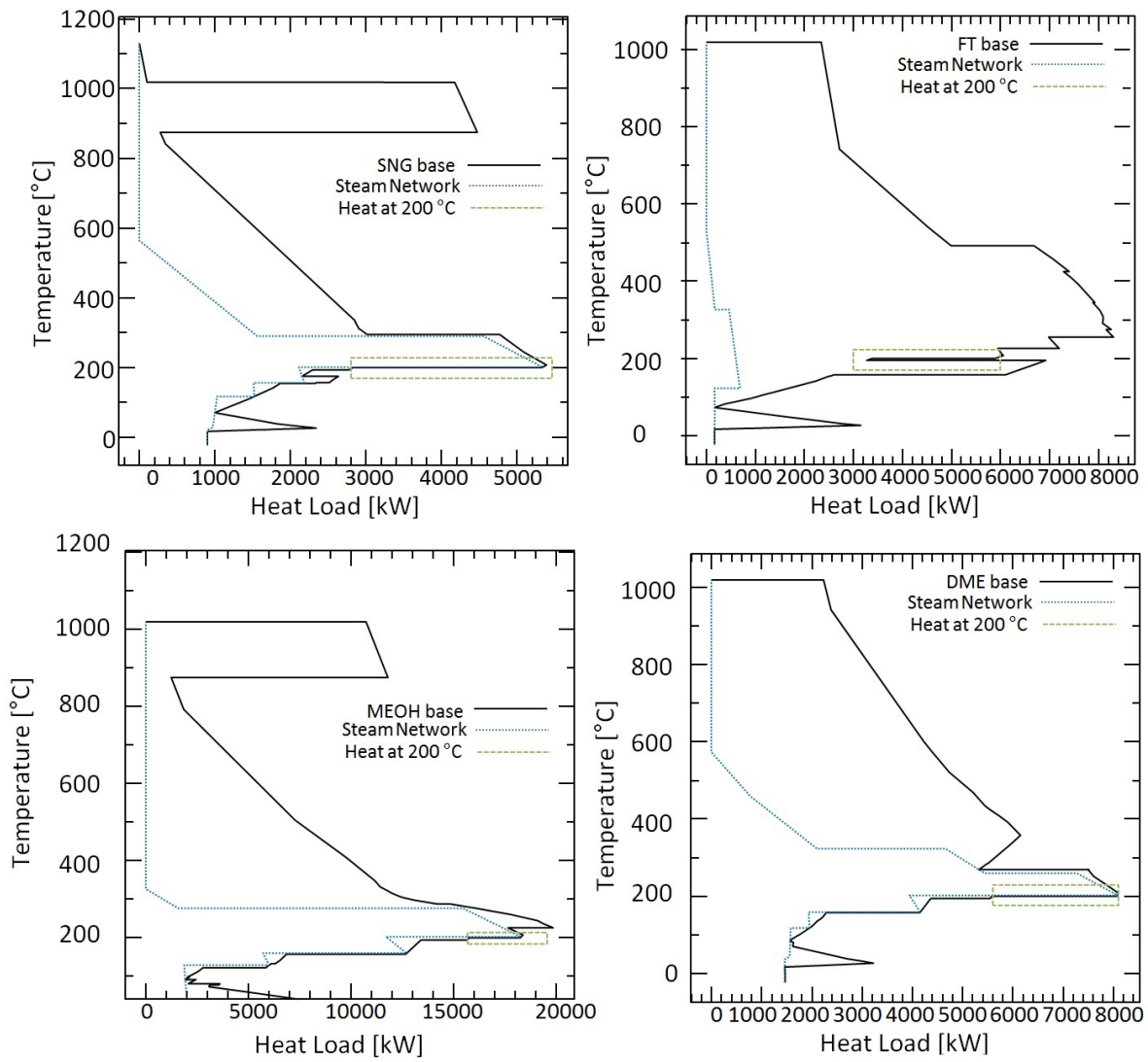


Figure 3.11: Integrated composite curves of CHF SNG, FT, MEOH and DME plants in Case II for 2.5 MW plant size

3.4.4 Case III and Case IV : CHF plants with Power-to-Gas (P2G) and CO₂ storage

As discussed earlier in section 3.3.2.2, new energy policy scenario (NEP) for the future Swiss energy system in 2050 forecasts surplus (or waste) electricity production during summer due to high penetration of solar photovoltaics (PV), wind and geothermal energy. Power-to-Gas systems can be used as a strong way to seasonally store electricity. Therefore, co-electrolysis unit is integrated to obtain maximum production of biofuels using excess electricity during 4 months of summer in both cases III and IV. Co-electrolysis unit uses CO₂ and steam inputs to produce a syngas with 75 vol% of hydrogen [242]. Produced syngas is then injected into the fuel synthesis reaction. Lifetime of a co-electrolyser is assumed to be 15 years with only 4 months operation in summer [114]. In Case III, CO₂ captured during 4 months of summer operation of CHF plant is sent to the co-electrolyser. In Case IV, CO₂ is captured and stored in a pressurized tank in liquid form at 25°C and 50 bar during the winter operation (8 months) of CHF plant, and the stored CO₂ is fed into the co-electrolyser together with the CO₂ captured during summer operation. The overall amount of electricity required for the integrated cogeneration system is available from the PV panels for zero cost with no resource emissions according to the scenario 2050 for Swiss Energy Transition [223]. In Figure 3.12, it can be seen that for a very small size of CHF SNG plant, integration of co-electrolysis unit lead to a great reduction in heat prices for both cases III and IV, having negative values for higher CO₂ tax. Figure 3.13 compares the heat cost build-up for 2.5 MW CHF SNG plants in all cases where heat price lines intersects heat price line for natural gas boiler.

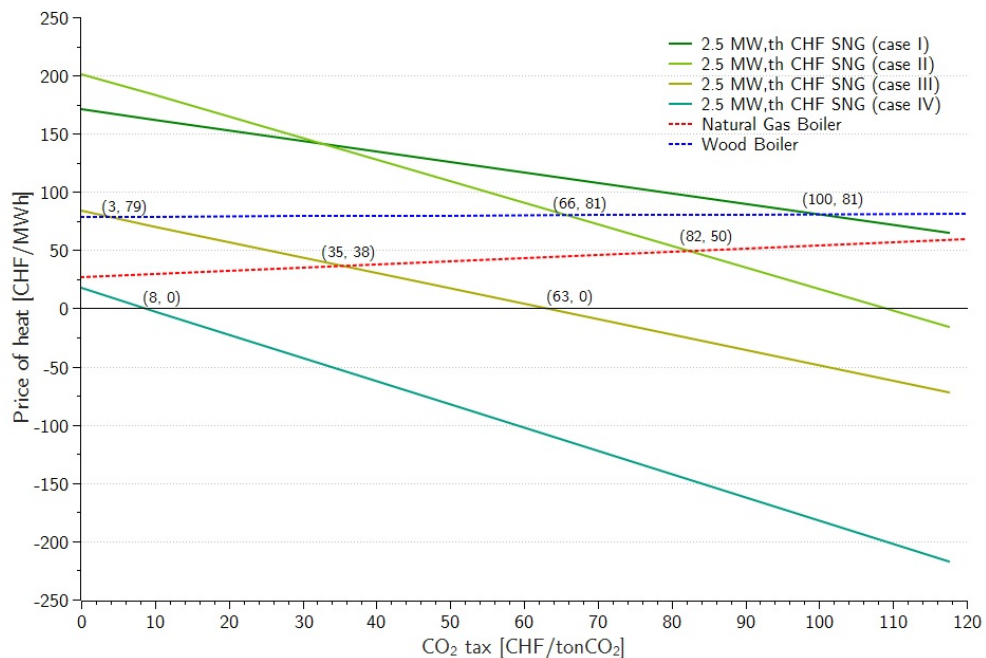


Figure 3.12: Case I, II, III, IV comparison for 2.5 MW CHF SNG plant

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Table 3.8: Performance of CHF SNG plant in Cases I, II, III and IV for plant size of 2.5 MW heat production

Process parameters	Case I	Case II	Case III-Summer	Case IV-Summer
Wood [MW]	18.0	18.0	18.0	18.0
Biofuel [MW]	11.8	11.8	23.54	44.61
Electricity consumed [MW]	0.70	1.42	15.78	43.20
Electricity produced [MW]	-	0.91	-	-
Net electricity [MW]	0.70	0.51	15.78	43.20
ϵ_{chem} [%]	63.10	63.10	130.8	247.81
ϵ_{tot} [%]	73.71	75.48	79.54	80.31
CO ₂ produced [ton/h]	2.29	-	-	-
CO ₂ sequestrated [ton/h]	-	2.29	-	-
CO ₂ to co-electrolysis [ton/h]	-	2.29	2.29	6.39

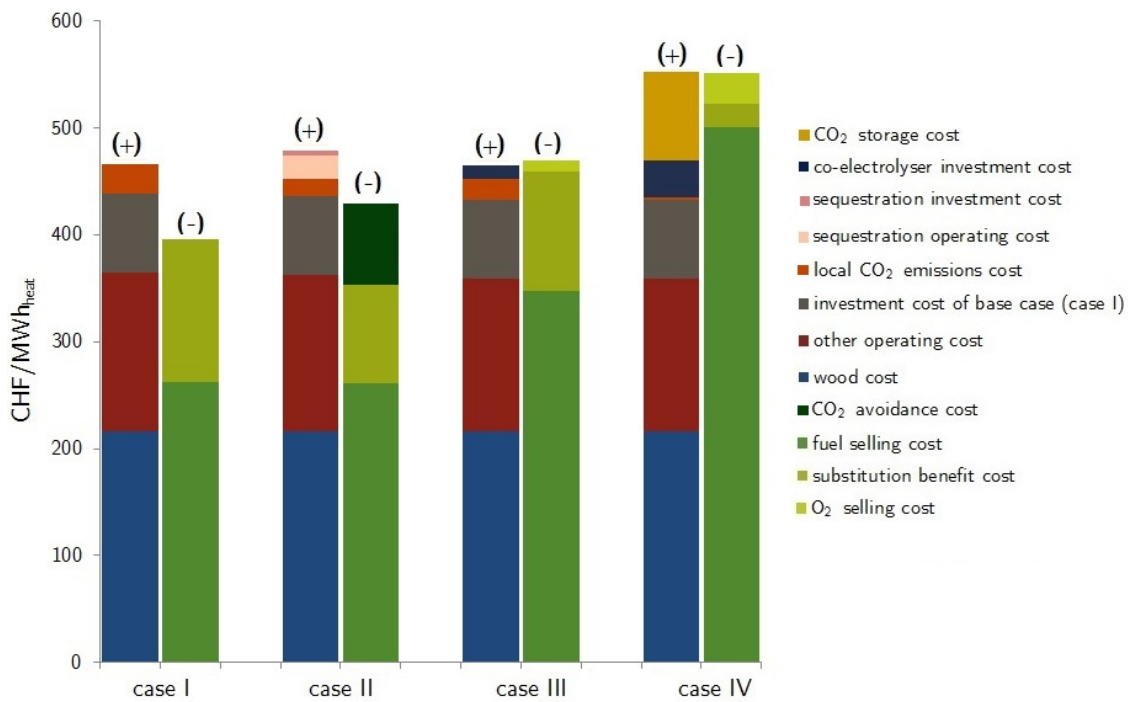


Figure 3.13: Heat cost build-up for CHF SNG plant of 2.5 MW size for all cases (Positive sign represents the expenses, negative sign represents the incomes.)

3.5 Conclusions

The ultimate goal for a sustainable development is the replacement of fossil based services with biomass based services. For the energy transition, CO₂ emissions have to be decreased, energy conversion efficiency has to be increased, and fossil resources have to be gradually replaced by renewable resources. Hence, the heat demand for industrial plants needs to be satisfied by renewable energy sources instead of using conventional natural gas boilers. This study proposes a new system approach for the design of cogeneration plants, which utilizes woody biomass as energy resource in the thermo-chemical conversion processes to produce heat at required temperatures for different industrial sectors while cogenerating biofuels. A by-product of the proposed CHF plant is biogenic CO₂ that is separated during the production. The CO₂ can be sold as a product, sequestered or used in power to fuel process for the long term storage of renewable intermittent electricity. In the future, electricity demand is expected to increase due to the addition of end-use devices such as heat pumps and electric mobility and with the increase in population. The future electricity system should be ensured for cost-effectiveness, security of supply and climatic impact. To achieve this, some measures including more renewable installations, efficiency improvements and additional electricity storage should be considered. With the penetration of renewable electricity, surplus electricity during summer period is forecasted in most studies. Seasonal storage of this renewable surplus electricity is possible with the conversion of electricity into fuel via the proposed CHF system in this study. The produced biofuel can be stored in tanks so that it can be used in combined cycle power plants to produce electricity at any time during the year.

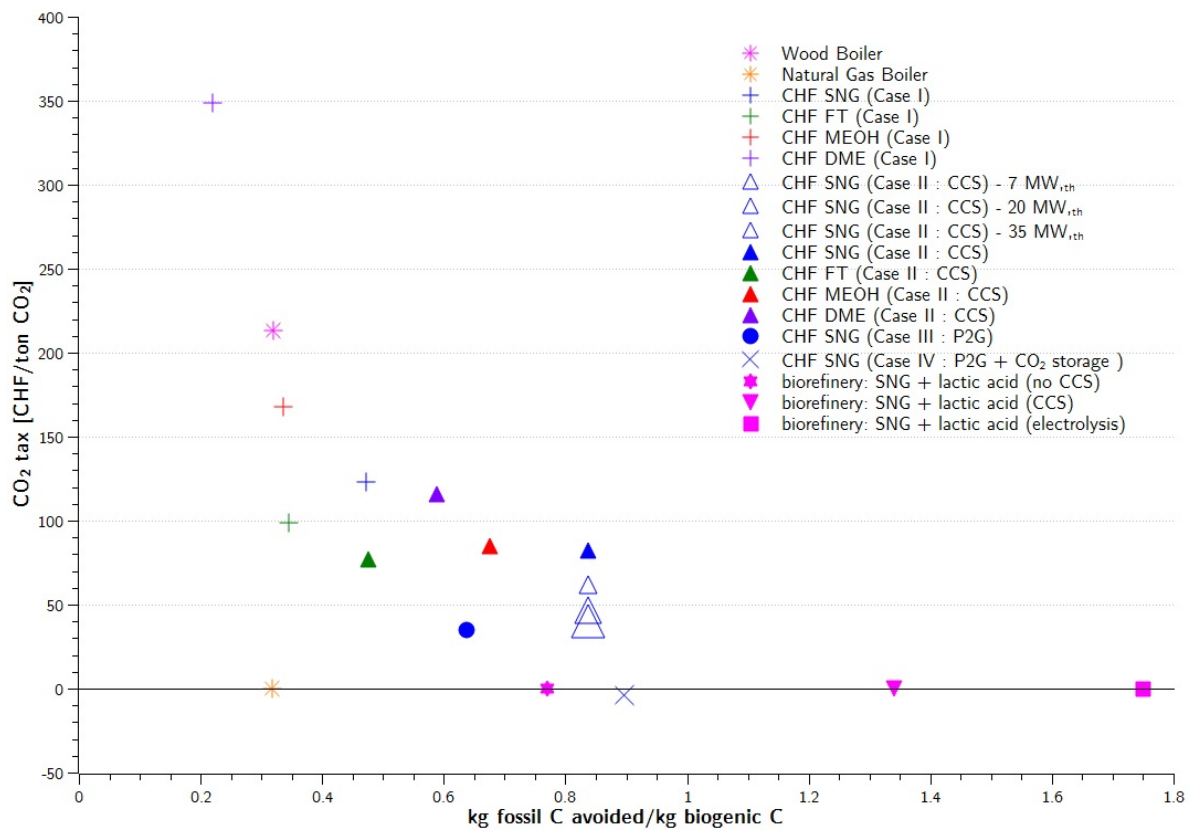
Based on life cycle inventory of the fossil product, it is possible to calculate the fossil carbon (CO₂ emissions) substituted by each unit of carbon in the bio-products or fuels. This value is indeed the amount of fossil CO₂ not emitted and replaced by CO₂ captured by the photosynthesis as biogenic carbon. As the biomass harvests carbon from the atmosphere, the performance of the proposed CHF systems can be studied on the basis of the amount of fossil CO₂ emission avoided per unit of atmospheric CO₂ converted by the photosynthesis. The oil boiler is taken as basis which has the highest fossil CO₂ emissions. First, it is considered that natural gas and wood boiler substitutes an oil boiler. Referring to Figure 3.14, 1 unit of carbon in the natural gas and wood avoids 0.31 and 0.32 units of fossil carbon emissions, respectively. To produce heat from wood boiler at the same price of natural gas boiler, one should put very high CO₂ tax on natural gas boiler (213 CHF/ton_{CO₂}).

Summing-up the substituted fossil carbon for CHF SNG plant in Case I, 1 unit of biogenic carbon entering the CHF system avoids 0.48 units of fossil carbon emissions. For 1 unit of CO₂ captured by the photosynthesis, the CHF SNG plant avoids therefore 1.5 times more CO₂ than the wood combustion. In addition, if one considers the CO₂ sequestration for CHF SNG plant (Case II), one unit of biogenic carbon entering the proposed CHF system would avoid 0.84 units of fossil carbon emissions. In this case, the wood used in the CHF plant is avoiding 2.63 times more fossil CO₂ emissions than the wood used in a boiler. Varying CHF SNG plant size between 2.5, 7, 20 and 35 MW heat duty, it is clear that bigger plant would provide heat at lower price. Similar to 2.5 MW CHF SNG

Chapter 3. Synergies between biorefineries and energy system

plant, CHF FT, MEOH and DME plants have large CO₂ savings when compared to the conventional boilers. For Case III, the co-electrolysis is used in addition to CHF SNG plant for the CO₂ captured during summer. In this case, 1 unit of biogenic carbon avoids 0.64 units of fossil carbon emissions. If co-electrolysis unit is also used for the CO₂ captured and stored during winter and CO₂ captured during summer, then the carbon saving ratio would be 0.9 while the heat price is negative.

Figure 3.14 also illustrates CO₂ avoidance for a multi-product biorefinery which produces SNG and lactic acid. In this case, bio-based SNG and lactic acid substitute natural gas for transportation and fossil-based lactic acid, respectively. With integration of CCS option into the system, biorefinery avoids 1.34 of fossil carbon emissions. CO₂ mitigation ratio improves to 1.75 when electrolysis is integrated as in previous scenarios, aiming to use seasonal renewable electricity for boosting biofuels production.



*The boiler size: 2.5 MW_{th}. Heat is substituted with the heat from the oil boiler.

**CO₂ tax represents the tax values when calculated heat price from the proposed CHF system is equal to the heat price from natural gas boiler.

***For the natural gas boiler, x axis is "kg fossil C avoided/kg C in natural gas (compared to oil boiler)".

Figure 3.14: Carbon savings comparison between technologies

The results demonstrate that integrated approaches such as heat and fuel cogeneration using wood, have a higher potential for CO₂ mitigation and therefore have to be prioritized with respect to combustion for heat supply. Imposing a carbon tax greatly penalizes conventional natural gas boilers

without CO₂ capture and favors biomass based processes. CHP plants will no longer be attractive with the rapid energy transitions across Europe and the globe. Intermittent renewable power from wind and solar energy will shape future energy supply with their high shares. The current research is searching solutions for long-term storage of electricity, and promising solutions are batteries, pump hydro storage, compressed air energy storage and power-to-X concepts. Hydrogen storage can be seen as an option for long-term storage however it has high costs, security issues and fuel cells have short lifetimes. Storage of biofuels is cheaper option and the environmental impact is also relatively small. Fuel storage systems are large and convenient facilities with proven and available technologies. Biomass cogeneration systems which cogenerates heat and fuel together, and uses co-electrolysers to boost biofuels production when electricity is surplus, provide a good solution for long-term electricity storage. In the way towards a sustainable future, providing heat for industrial processes via next generation cogeneration using biomass resource, appears to be a competitive transitional solution for mitigating climate change. Since the results are highly dependent on the market, uncertainties should be accounted for a more reliable analysis and more detailed technical study should be performed to establish this technology on a real large scale plant.

4 On the integration of catalytic reactions of sugar platform in biorefineries

Overview

- Techno-environmental optimization of the consolidated bioprocessing and catalytic upgrading of lignocellulosic biomass for the production of a bio-jet fuel blend and alpha olefins is performed aiming to minimize the operating cost of proposed process designs.
- Minimum energy requirement for both processes are identified by using pinch analysis approach. Energy balance is closed by different technologies: conventional natural and wood boilers as well as syngas platform technologies are considered to satisfy the heat demand.
- For the integrated platforms, minimum selling price and greenhouse gases emissions are calculated for the production of bio-jet fuel blend and alpha olefins and results are analyzed for each integration option for their economic and environmental competitiveness.

4.1 Introduction

The energy demand of the global transportation is projected to increase by about 30% from 2016 to 2040 (Figure 4.1). The aviation sector covers approximately 11% of transportation-related energy demands, and this could double or triple by 2050 [243]. This contributes 3% of the greenhouse gas emissions and is expected to increase up to 15% by 2050 [244]. Hence, the private and public sectors including IATA (trade associations) have set goals such as the carbon neutral growth of the aviation sector from 2020 and cutting 50% of net aviation CO₂ emissions (based on 2005 levels) by 2050 [92]. Hence, there is a niche market of alternative jet fuels to reduce the aircraft emissions.

The specifications and properties of aviation fuels are controlled by regulations, such as DEF STAN 91-91 in the United Kingdom and ASTM D1655 in the United States of America. Therefore, producing renewable jet fuel components such as Fischer-Tropsch synthesized paraffinic kerosene is subject to a certification process to be accepted with special allowance provided in ASTM D7566 and DEF STAN 91-91. Synthesized paraffinic kerosene is either blended with conventional jet fuel or used fully as jet fuel. The aromatic content of synthesized paraffinic kerosene produced via Fischer-Tropsch

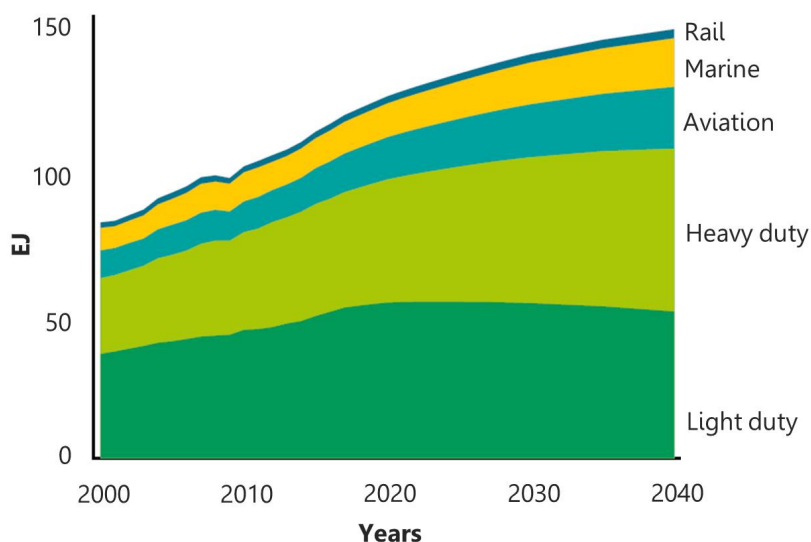


Figure 4.1: Transportation sector energy demand growth [245]

is typically low, often resulting in failure to satisfy conventional jet fuel standards [244]. Therefore, process technologies for the production of a renewable jet fuel blend containing aromatics is beneficial so that it can be blended into bio-based paraffinic kerosene.

Recent studies mainly focus on lab scale experiments and feasibility analysis to produce high yield of jet fuel range liquid hydrocarbons and their intermediates such as carboxylic acids [246, 247, 248]. There are only a few studies performing techno-economic analysis for the production of bio-jet fuel range fuels from levulinic acid platform [249, 250] and carboxylate salts platform [251] calculating minimum selling price and GHG emissions. Investigation of the scale-up potential of the experimental work done from lab to processes to integrate into biorefineries is lacking in the literature. Furthermore, measures such as process energy integration and integration with renewable energy sources need to be incorporated into thermo-environmental analysis to ensure energy efficiency and improved performance in terms of economic and environmental impact criteria.

In this study, a novel process design for the biochemical-catalytic production of jet fuel aromatics and cyclic hydrocarbons as well as linear alpha olefins/alkanes from lignocellulosic biomass is evaluated. The produced organic oil containing aromatics and cyclic hydrocarbons can be mixed with petroleum-derived kerosene for the aviation industry or can be blended into bio-based paraffinic kerosene to increase the content of aromatic compounds. This organic oil is a promising bio-jet fuel blend which has been tested to be compatible as a 10 vol% blend with Jet A-1 fuel in terms of specific energy and distillation properties [248].

Linear alpha olefins production technology in this study is producing 2-butene as the main product with 3 wt% of 1-butene production. More than 70% of the butenes produced worldwide are utilized as alkylate, polymer gasoline or blendstock for gasoline. Only about 14% of the produced butene is converted to specific chemicals [252]. Alpha olefins are used as generally co-monomers in the

manufacture of several products such as plasticizers and synthetic lubricants. The share of butene in the market is likely to increase with the increasing demand for rubber chemicals, as 1- and 2-butene can be used to make polybutylene (PB) [253].

Technology models have been developed combining biochemical conversion and chemical catalysis using experimental data. Modeling of lab-scale production allows for technical and economic analysis and optimization, as current estimates of energetic efficiencies and scale-up potential of novel conversion processes are missing. Production feasibility of bio-based products on a wide scale, as with their fossil fuel based counterparts, will be dependent on their energetic, sustainability, and economic potentials. Predicting the potential commercialization of a specific product is difficult since it can take years of development due to the availability of infrastructure, market demand and technologies available. Therefore, a systematic evaluation strategy is required. The extension of models from specific processes to whole value chains will allow for process- and system-level technical and sustainability assessments and optimization, as well as scalability assessment of the lab-scale process to the biorefinery level.

In this chapter, thermo-economic and environmental models are developed for the production of linear alpha olefins and liquid fuels (jet fuel blend) from lignocellulosic feedstock to analyze and compare the production costs, GHG equivalent emissions, and efficiency of the different conversion pathways. Furthermore, to contribute to the development and implementation of sustainable biorefineries, a systematic methodology that combines process modeling and optimization approaches is applied and a comparison of the pathways is then proposed. An energy-integration MILP optimization problem is solved to minimize the operating cost of the jet fuel blend and linear alpha olefins biorefinery. Waste lignin stream is valorized to provide process heat in different technologies such combustion and gasification aiming to increase the overall system efficiency. GHG emissions are evaluated considering life cycle assessment methodology where a comparison is made for the CO₂ equivalent emissions and minimum selling prices of the bio-based products produced from the proposed biorefinery design using the related values reported in the literature.

4.2 Methodology

The proposed thermo-environmental optimization methodology described in Section 2.2 is used in this work. Thermo-environmental models were developed by first defining the physical model with external flowsheeting software (Aspen PLUS) [160] along with the thermo-environmental optimization methodology explained in Section 2.2.

Property method

Unless otherwise stated, all of the models were modelled using the *NRTL-HOC* property method in Aspen PLUS [160] process flowsheeting simulation software. This is the physical property method selected in the National Renewable Energy Laboratory (NREL) [254] models for the production of hydrocarbon fuels. NRTL is a physical activity coefficient model for liquid phase fugacity calculations. The Hayden-O'Connell extension was used when dealing with non-ideal vapor phases that contain

polar or solvate compounds such as acetic acid.

4.3 Process description

4.3.1 Feedstock selection

A small biorefinery with an intake of 10000 tons dry beech wood per year was assumed for the assessment. The characteristics of the selected biomass are given in Table 4.1.

Table 4.1: Compositional analysis of biomass [255]

Moisture (%) ¹	5.7
Extractives (%) ¹	2.6
Weight fraction (wt%)²	
Glucan	37.1
Xylan	15.3
Arabinan	2.1
Galactan	2.2
Mannan	1.9
Klason lignin	22.8
Acid-soluble lignin	3.7

¹ dry biomass basis.

² wet biomass basis.

4.3.2 Biorefinery superstructure

The process models were developed using the experimental results of Shahab et al. [246] who detailed the steam explosion pretreatment and consolidated bioprocessing of biomass and those of Yeap et al. [248] on the catalytic upgrading of carboxylic acids. To connect these two studies and to ensure the process stream data has the same characteristics, some process modifications were implemented. A new design was developed for the purification of dilute carboxylic acids mixture. Simplified process model flowsheets for the production of linear alpha olefins (2-butene) and bio-oil (liquid fuel containing jet fuel blend compounds) are shown in Figure 4.2 and Figure 4.3, respectively.

The production of linear alpha olefins includes a 2-stage steam pretreatment of the biomass followed by Consolidated Bioprocessing (CBP). Consolidated bioprocessing offers a viable biochemical conversion pathway design, as high conversion rates are achieved while combining the hydrolysis and fermentation steps into one reactor, offering a low-cost configuration. This method of using a microbial consortium for conversion would likely open pathways via the production of carboxylic acids production platform to liquid fuels and commodity chemicals [255]. In this study, a broth of butyric acid (1 wt%) is obtained from the lignocellulosic biomass after steam explosion pretreatment and CBP. The pH was then adjusted by the addition of sodium hydroxide.

Carboxylic acids are good candidates as platform chemicals to synthesize value-added products. However, their low concentrations in the fermentation broth (here, 1 wt% butyric acid) requires

4.3. Process description

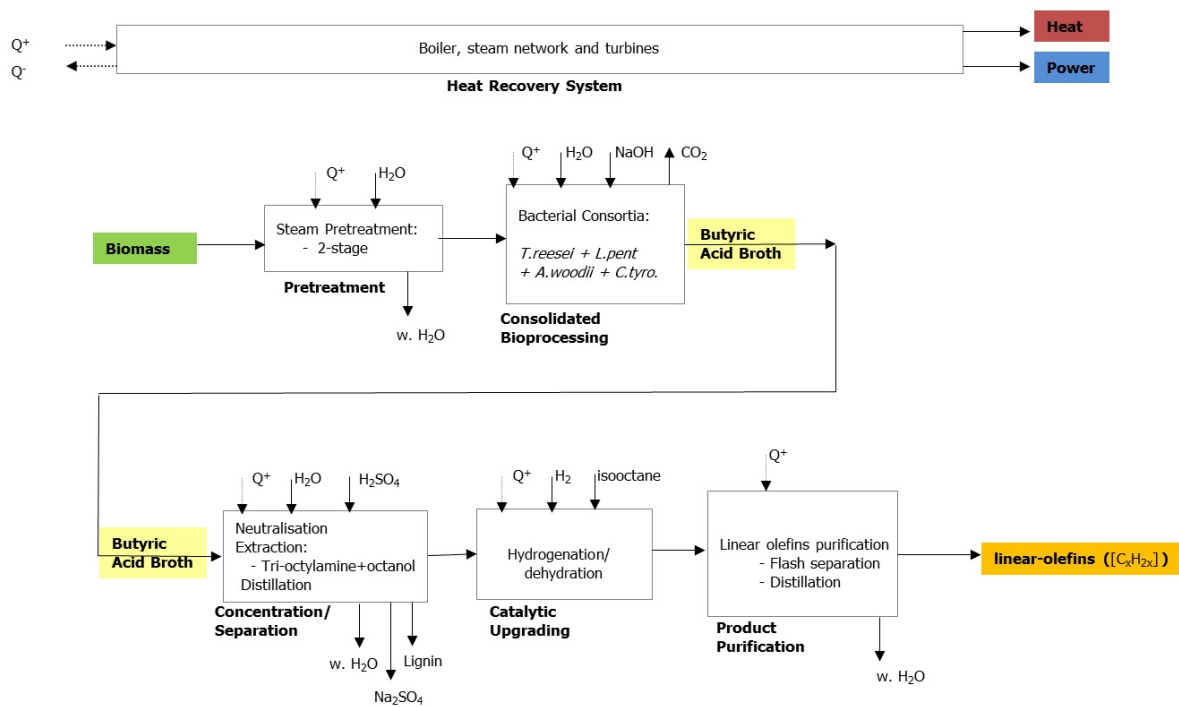


Figure 4.2: Process flowsheet of linear alpha-olefins production

further separation technologies to be used [256]. Furthermore, a dilute solution of carboxylic acids in water presents a separations challenge due to the similar volatilities of the acids and water, which could result in rectification columns with many stages operated at a high reflux ratio and thus high operating costs [257]. Therefore, cost-effective separation concepts should be investigated.

Reactive extraction is favorable and economically viable for the separation of carboxylic acids from water [258, 259]. To recover acids from aqueous solutions, hydrophobic extractants should be chosen. Using conventional solvents in the extraction, such as ketones and alcohols, is not efficient in recovering most of the carboxylic acids due to their low distribution coefficients [259, 247]. For the effective separation of carboxylic acids, reactive extraction processes with high molecular weight tertiary aliphatic amines has been widely studied in the literature [247, 260, 261]. In this process, the extractant in the organic phase reacts with the acid in aqueous phase to form an amine-acid complex. This reaction complex is then solubilized into the organic phase at ambient temperature [247]. This reactive extraction method was used by Yeap et al. [262] to experimentally purify butyric acid using Trioctylamine (TOA) as extractant.

Trioctylamine (TOA) has been commonly used with an organic diluent to reduce the high viscosity and control the density and corrosive property of the extractant [263]. Using a polar diluent such as 1-octanol increases the extractability of tertiary amines [247]. Therefore, TOA is used as extractant with 1-octanol diluent in this study.

The fermentation broth containing butyric acid was first mixed with sulfuric acid in a reacidification

Chapter 4. On the integration of catalytic reactions of sugar platform in biorefineries

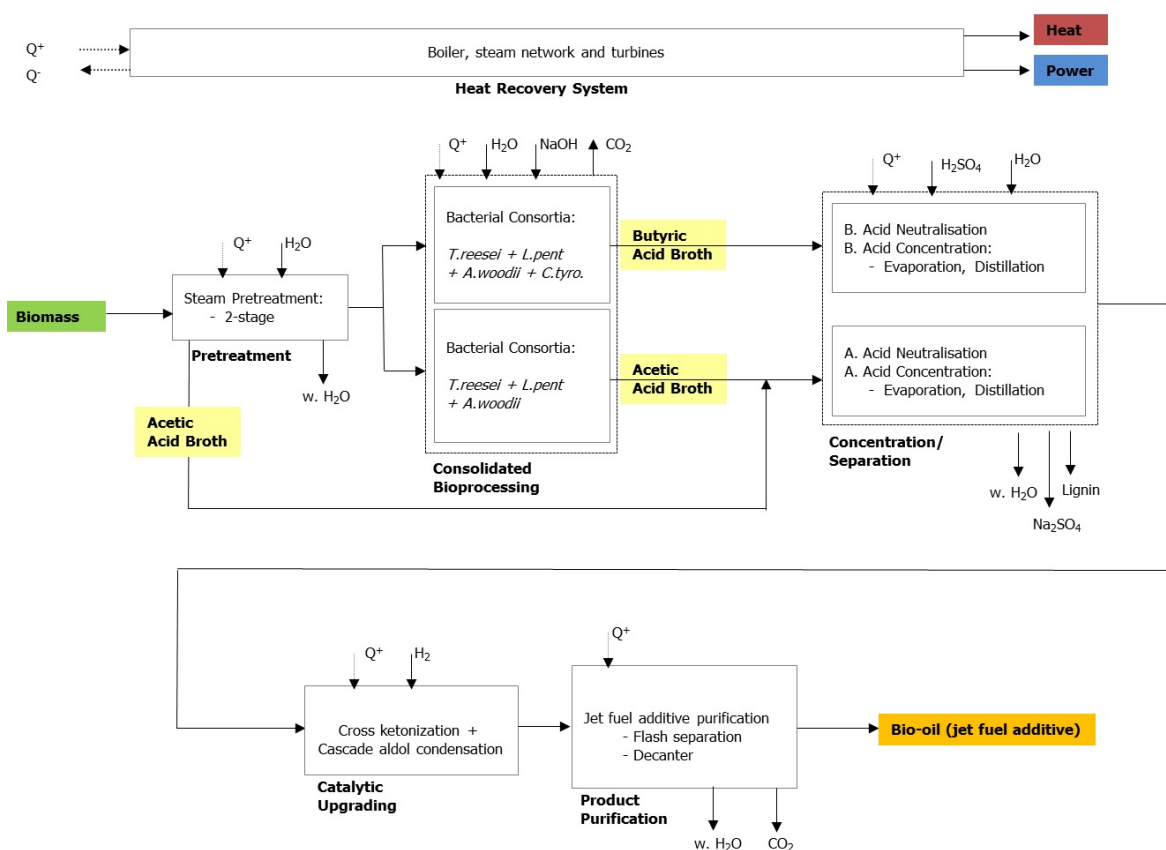


Figure 4.3: Process flowsheet of jet fuel blend production

unit and then extracted with TOA diluted in octanol to achieve an 75% extraction efficiency. Back-extraction is then necessary to reverse the reaction to regenerate the acid into the product phase [264]. Vacuum distillation is used for solvent recovery to obtain butyric acid with 96 wt% purity. Butyric acid is then recovered in the product phase and the extractant and diluent are recycled. The solvent recovery unit is followed by a hydrogenation/dehydration unit where butyric acid in iso-octane is converted into linear alpha olefins (80 wt% butenes, 19 wt% butanes) in a single step conversion via tandem hydrogenation/dehydration. Product purification is performed using flash separation and distillation units.

For the production of jet fuels, the process flowsheet similarly includes a 2-stage steam biomass pretreatment unit where acetic acid (1 wt%) is extracted from the filtrate. Two CBP units are then used to produce broths of butyric acid and acetic acid. The broth sent to the catalytic upgrading reactor requires 28 wt% and 12 wt% of acetic and butyric acid, respectively. The pH values of both broths are adjusted via the addition of sodium hydroxide. The acetic acid stream taken from the steam pretreatment is then mixed with the broth from the second CBP reactor. Sulfuric acid is then added to the butyric acid broth in the reacidification unit and a part of the water is removed by vacuum evaporation. The mixture is then sent to distillation columns where butyric acid is obtained with

4.3. Process description

40 wt% purity and with a final recovery yield of 82 wt%. The purification procedure is also applied to acetic acid broth. The concentrated broths are mixed and sent to a ketonization/cascade aldol condensation unit where the carboxylic acid mixture is converted into jet fuel blend compounds (liquid hydrocarbons (C5 - C15 compounds) and oxygenates (C3-C16 compounds)) in a single step. Product purification is then performed using flash separation and a decanter where the bio-oil containing the jet fuel blend compounds is separated. The yield is 16 wt% based on the total mass of carboxylic acids fed in. Table 4.2 and Table 4.3 summarize the characteristics of the process conversion pathways for linear alpha alkenes and jet fuel blends production, respectively.

Table 4.2: Characteristics of process conversion pathway for linear alpha olefins production

Section	Specification	Value	Ref.
Pretreatment <i>Stage 1</i>	Technology	2-stage steam explosion	[255]
	Temperature [°C]	180	
	Pressure [bar]	9	
<i>Stage 2</i>	Temperature [°C]	230	
	Pressure [bar]	28	
	Hemicellulose-xylose (pre-hydrolyzate)[wt%]	46	
Consolidated Bioprocessing (CBP)	Technology	butyric acid platform	[255]
	Temperature [°C]	30	
	Pressure [bar]	atmospheric	
	Fungal-bacterial consortia	<i>T.reesei</i> + <i>L.pent</i> + <i>A.woodii</i> + <i>C.tyro</i>	
	Solid loading [wt%]	3.86	
	NaOH addition [kg/ton dry wood]	97.6	
	pH	6.0	
	Butyric acid [kg/ton dry wood]	196.5	
	Acetic acid [kg/ton dry wood]	14.2	
Propionic acid [kg/ton dry wood]	4.06		
Butyric acid purification	Technology	Extraction, distillation	[262]
	Extraction Solvent	20 wt% Trioctylamine in Octanol	
	Solvent to broth ratio [wt%]	40	
	Extraction efficiency [%]	75	
	Distillation temperature [°C]	230	
Catalytic upgrading	Technology	Tandem hydrogenation/dehydration	[262]
	Reaction temperature [°C]	210	
	Reaction Pressure [bar]	5	
	Conditions	Flow reactor, H ₂ atmosphere	
	Loading in isooctane [wt%]	2	
	Catalyst	Cu/Si-Al	
Product purification	Technology	Flash separation + distillation	[262]
	Butene [kg/ton dry wood]	95.9	

The necessary input data for the calculations include the cost of wood feedstock and other raw materials (resource units), the efficiency and cost of each process conversion unit, the market condition for the products (prices for services), and the emission factors for the resource units to evaluate the life cycle impact cost by means of CO₂ equivalent GHG emissions. Operation impact of resource units are gathered from Ecoinvent database for the evaluation of the environmental

Chapter 4. On the integration of catalytic reactions of sugar platform in biorefineries

Table 4.3: Characteristics of process conversion pathway for bio-jet fuel blend production

Section	Specification	Value	Ref.
Pretreatment	Technology	2-stage steam explosion	[255]
<i>Stage 1</i>	Temperature [°C]	180	
	Pressure [bar]	9	
<i>Stage 2</i>	Temperature [°C]	230	
	Pressure [bar]	28	
	Hemicellulose-xylose (pre-hydrolyzate) [wt%]	46	
	Acetic acid (1 wt%) from filtrate [kg/ton dry wood]	19.2	
Consolidated Bioprocessing 1 (CBP)	Technology	Butyric acid platform	[255]
	Temperature [°C]	30	
	Pressure [bar]	atmospheric	
	Fungal-Bacterial Consortia	<i>T.reesei</i> + <i>L.pent</i> + <i>A.woodii</i> + <i>C.tyro</i>	
	Solid loading [wt%]	3.86	
	pH	6.0	
	Butyric acid [kg/ton dry wood]	95.8	
Consolidated Bioprocessing 2 (CBP)	Technology	Acetic acid platform	[255]
	Temperature [°C]	30	
	Pressure [bar]	atmospheric	
	Fungal-bacterial consortia	<i>T.reesei</i> + <i>L.pent</i> + <i>A.woodii</i>	
	Solid loading [wt%]	3.86	
	pH	6.0	
	Acetic acid [kg/ton dry wood]	189.5	
Butyric acid purification	Technology	vacuum evaporation, distillation	[248]
	Evaporator pressure [bar]	0.92	
	Distillation temperature [°C]	140	
	Butyric acid recovery [wt%]	83	
	Butyric acid purity [wt%]	40	
Acetic acid purification	Technology	vacuum evaporation, distillation	[248]
	Evaporator pressure [bar]	0.92	
	Distillation temperature [°C]	120	
	Acetic acid recovery [wt%]	82	
	Acetic acid purity [wt%]	40	
Catalytic upgrading	Technology	ketonization/cascade aldol condensation	[248]
	Reaction temperature [°C]	400	
	Reaction pressure [bar]	10	
	Reactor loading [wt% aqueous acetic/butyric acid]	28/12	
	Conditions	Flow reactor, H ₂ atmosphere	
	Catalyst	Cu/ZrO ₂	
	Oil yield [%]	16	
Product purification	Technology	Flash separation + decanter	[248]
	Bio-oil [kg/ton dry wood]	255	

objective and the values are presented in 4.4.

Table 4.4: Impact factors of resource units for the evaluation of environmental objective [239]

Parameter	Value
Wood chips production [kg CO ₂ eq/kg dry]	0.0372
Electricity mix, CH [kg CO ₂ eq/kWh]	0.1176
Water [kg CO ₂ eq/kg]	0.0002
Sulfuric acid [kg CO ₂ eq/kg]	0.1635
Caustic soda [kg CO ₂ eq/kg]	1.3707
TOA [kg CO ₂ eq/kg]	2.3827
Hydrogen [kg CO ₂ eq/kg]	2.165
Octane [kg CO ₂ eq/kg]	0.91
Octanol [kg CO ₂ eq/kg]	2.03
NG production and combustion, CH [kg CO ₂ eq/MWh]	241.7
Wood production and combustion, CH [kg CO ₂ eq/MWh]	11.8

The cost of wood must include the cost of transportation and the market price of wood. The logistics cost of wood increases as the size of plant increases and the transport distance is another criterion that depends on the location of the plant and availability of biomass supply; calculation details can be found in Chapter 3. The economic performance was evaluated by the capital investment and total production costs. The equipment costing was based on Aspen Plus Process Economic Analyzer [265]. Main economic parameters are provided in 4.5.

Table 4.5: Main economic parameters and assumptions

Parameter	Value	Source	Parameter	Value	Source
Economic assumptions			Market prices of resources		
CEPCI index (2017)	567.5	[231]	Wood [CHF/kg]	0.117	[266]
Yearly operation [h/year]	7884		Electricity [CHF/kWh]	0.0572	[193]
Interest rate [%]	4		Fresh water [CHF/kg]	0.0013	[193]
Plant lifetime	25		Sulfuric acid [CHF/kg]	0.066	[193]
Salary [CHF/yr]	91070	[138]	Caustic soda [CHF/kg]	0.1	[193]
Operators	8		TOA [CHF/kg]	1.786	[150]
Corporate income tax, CH [%]	19	[267]	Hydrogen [CHF/kg]	0.8	[268]
			Octane [CHF/kg]	1.9	[150]
			Octanol [CHF/kg]	1.3	[150]
			Natural gas [CHF/kWh]	0.024	[193]

4.4 Process performance

First, the minimum energy requirements (MER) for both processes were calculated by using pinch analysis. From Figure 4.4, one can see that hot utility requirements are 10.45 MW and 8.30 MW for the production of bio-jet fuel blend and olefins while cold utility requirements are 8.11 and 6.32 MW, respectively.

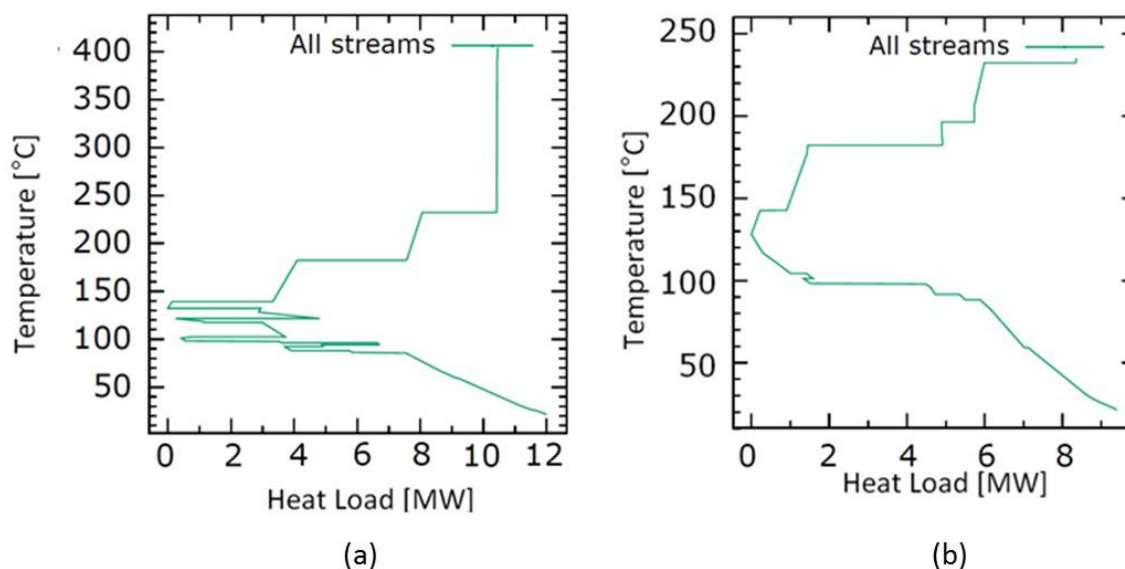


Figure 4.4: MER of (a) jet fuel blend and (b) linear alpha olefins production

Due to the fact that lowest temperature levels are above ambient, cooling towers using water can be used to cool the processes. The maximum temperature level that processes need heat in catalytic platform is at 400 °C where catalytic ketonization and cascade aldol condensation reactions occur to yield organic oil for aviation fuel blend. Differently from biological processes, catalytic conversions may require higher temperature level heat thus MER needs to be satisfied by using energy conversion units which can provide heat at upper medium or high temperature level. Figures 4.5 and 4.6 gives the overall system view for both pathways. Waste heat represents the energy lost via cooling water to cool down the process streams. The energy demand needs to be closed by a hot utility.

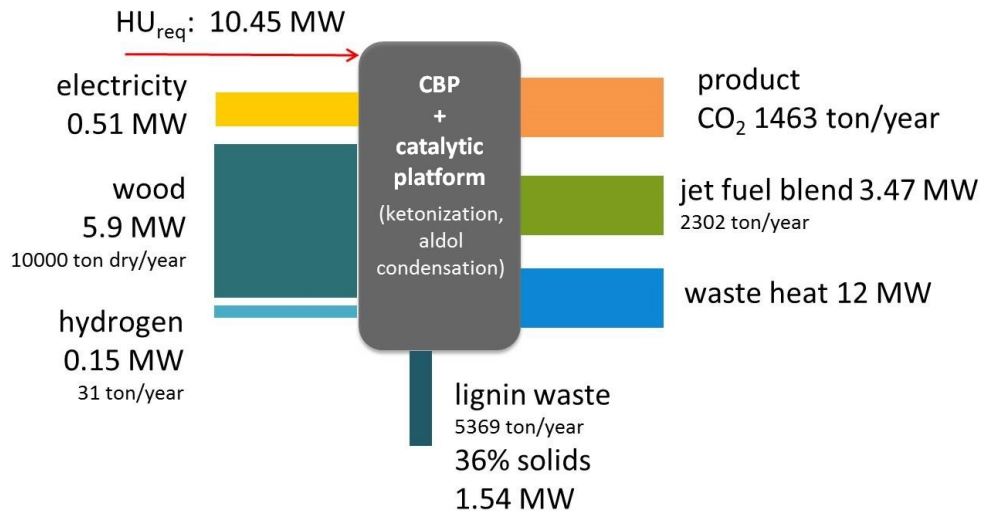


Figure 4.5: Overall plant mass and energy balance for jet fuel blend production

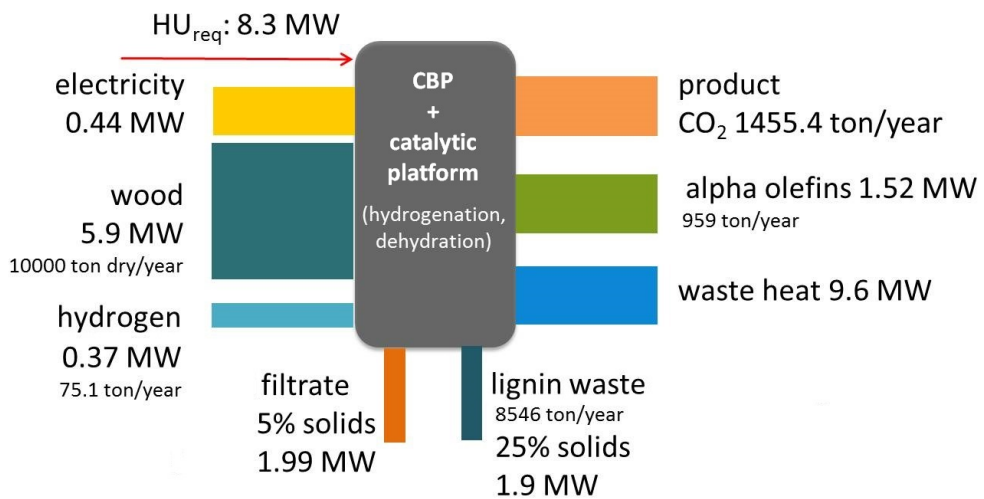


Figure 4.6: Overall plant mass and energy balance for linear alpha olefins production

4.4.1 Different scenarios for closing the energy balance of bio-jet fuel blend production process

Several system designs have been proposed to ensure a closed energy balance for catalytic pathways. Bio-jet fuel blend production is chosen to analyze the overall system performance in terms of economic and environmental impact. The functional unit in all these designs is the amount of heat provided to the catalytic platform. The approach for valorizing the process waste streams to satisfy the heat demand is illustrated by different cases, which are summarized in Figure 4.7.

Case I is implementing a conventional natural gas boiler to close the energy balance of both process designs. Thermo-environmental optimization (see Section 2.2) is solved for economic objective to minimize operating cost of the proposed systems. The minimum selling prices for the products are calculated based on the methodology proposed in Sen et al. [249], where the breakeven cost (sum of total production cost, investment cost, and income tax) is divided by annual production of the product. CO₂ equivalent emissions are calculated for both production pathways. Table 4.6 shows the main results of the thermo-environmental optimization problem for Case I where heat demand is satisfied by natural gas combustion. More detailed economic analysis can be found in appendix E.

Table 4.6: Economic analysis of production plants for Case I

Parameter	Value	Unit
Biomass available	10000	ton/year
linear alpha olefins production		
Yearly production	958.97	ton/year
Equipment cost	4.06	MillionCHF
Total capital cost	19.41	MillionCHF
Total production cost	9.62	MillionCHF/year
Breakeven point	1.71	years
Minimum selling price	9.91	CHF/kg
CO ₂ equivalent emissions	312.1	g CO ₂ eq/MJ
Bio-oil (jet fuel blend) production		
Yearly production	2302.13	ton/year
Equipment cost	4.29	MillionCHF
Total capital cost	20.53	MillionCHF
Total production cost	9.16	MillionCHF/year
Breakeven point	2.13	years
Minimum selling price	3.64	CHF/liter
CO ₂ equivalent emissions	237.5	g CO ₂ eq/MJ

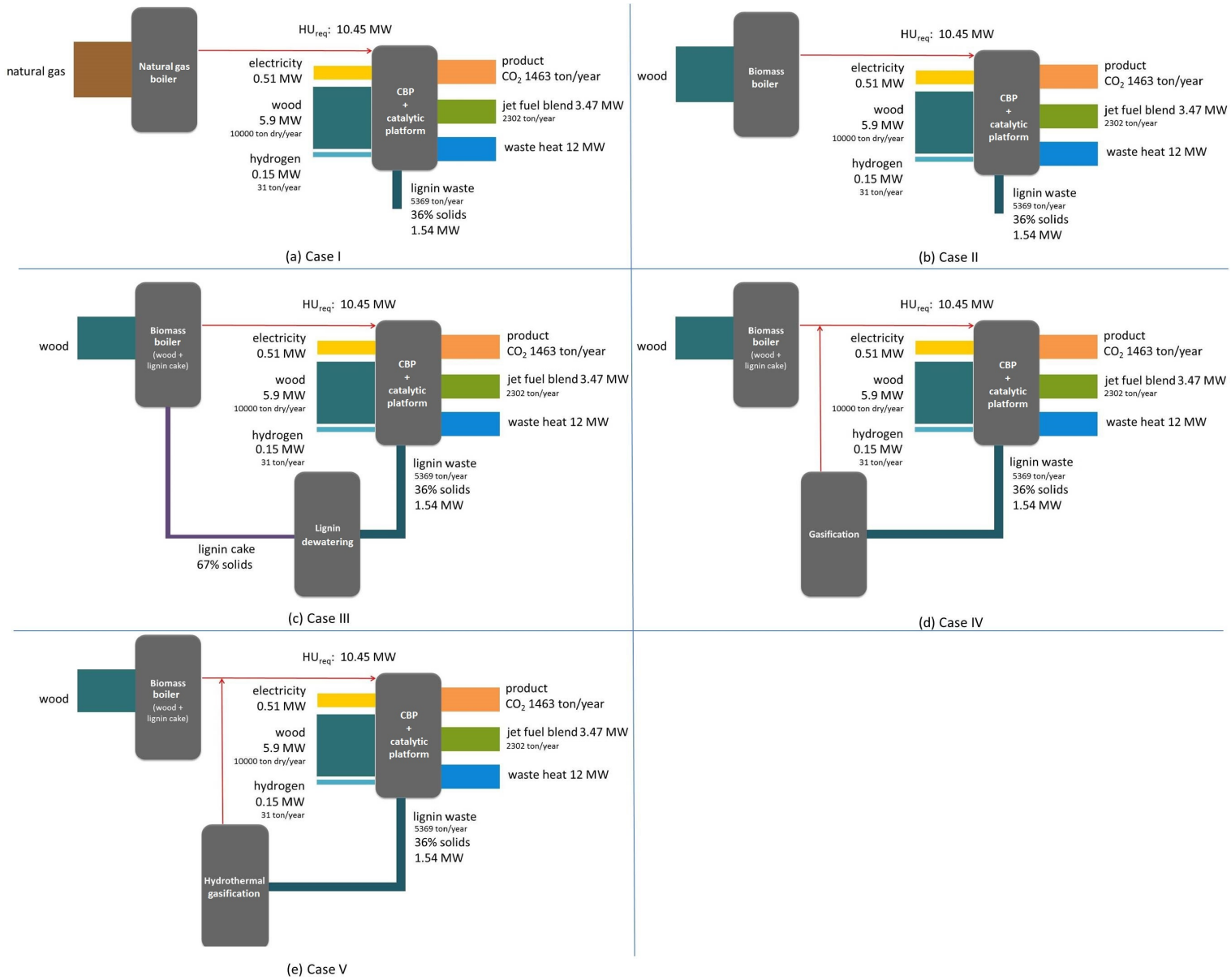


Figure 4.7: Different jet fuel blend production plant configurations with mass and energy balance

Case II is assessing the potential to replace natural gas boiler with a wood boiler where additional biomass resource is consumed for process heat production.

Case III suggest the first approach to valorize waste lignin. Literature studies show that valorization of waste streams enhances resource efficiency [269]. This waste stream contains 36% solids and 76% water. The presence of water reduces combustion efficiency if it is fed to the chambers directly. Therefore, dewatering the lignin will improve combustion characteristics of waste lignin stream. For that purpose, lignin cake is dried to 70% using rotary air dryer then co-fed to biomass combustion together with additional wood feedstock. Since, energy demand is large for the bio-jet fuel blend production, lignin valorization itself is not sufficient to close overall energy balance.

Case IV and V offers valorization the lignin in gasification pathways. As explained in Chapter 3, thermochemical conversion can provide heat at medium to high temperature heat due to their exothermic nature. Therefore, integration between syngas and catalytic platforms will result in reduced hot utility demand for the production of value-added products and corresponding CO₂ emissions. In this analysis, by producing syngas, the energy content of the waste stream is increased and syngas is sent to combustion process where the energy demand is partly satisfied. Case IV integrates gasification technology (CHF SNG plant Section 3.4.2) with air dryer to reduce the water content before entering the gasifier. Case V is adopting hydrothermal gasification to eliminate the drying step hence hydrothermal gasification can operate with wet lignocellulosic biomass. It is an alternative technology which produces methane rich syngas under supercritical water conditions [270, 55]. hydrothermal gasification model is adapted from Gassner et al. [271]. Similar to the previous Case III, wood combustion is assumed to be operating to provide the remaining heat demand for both Cases IV and V.

Table 4.7 and Figure 4.8 summarize the results of economic and environmental impact performance comparison for different jet fuel blend production plant configurations in the proposed cases. Comparing the fossil option in Case I (using natural gas combustion as hot utility) with renewable technologies in Cases II-V (using green combustion systems as hot utility), CO₂ emission reduction varies between 84% to 85%. Figure 4.9 demonstrates the build-up of GHG emissions for the proposed cases, showing that 60% of the environmental impact in Case I comes from the consumption of natural gas. Therefore, replacement of natural gas boilers with alternative renewable technologies leads to remarkably high emission reductions. With the integration of gasification technologies, further emission reductions are observed due to higher energy content of produced syngas.

Considering a scenario where the fossil kerosene in the market today is fully substituted with the renewable jet fuel produced in Cases II-V, 20-21% emission reductions can be achieved but the minimum selling price is approximately 3 times higher due to the consumption of wood resource to fuel the technologies used as hot utilities. Figure 4.10 shows that 65.3% to 71.5% of the operating cost is coming from the consumption of wood resource as a fuel. Comparing the minimum selling prices, designs with gasification options have relatively larger selling price due to their high investment cost as seen in Table 4.7. Gasifiers with bigger capacities may result in better economics therefore a sensitivity analysis is necessary to analyze the impact of larger production scales [34].

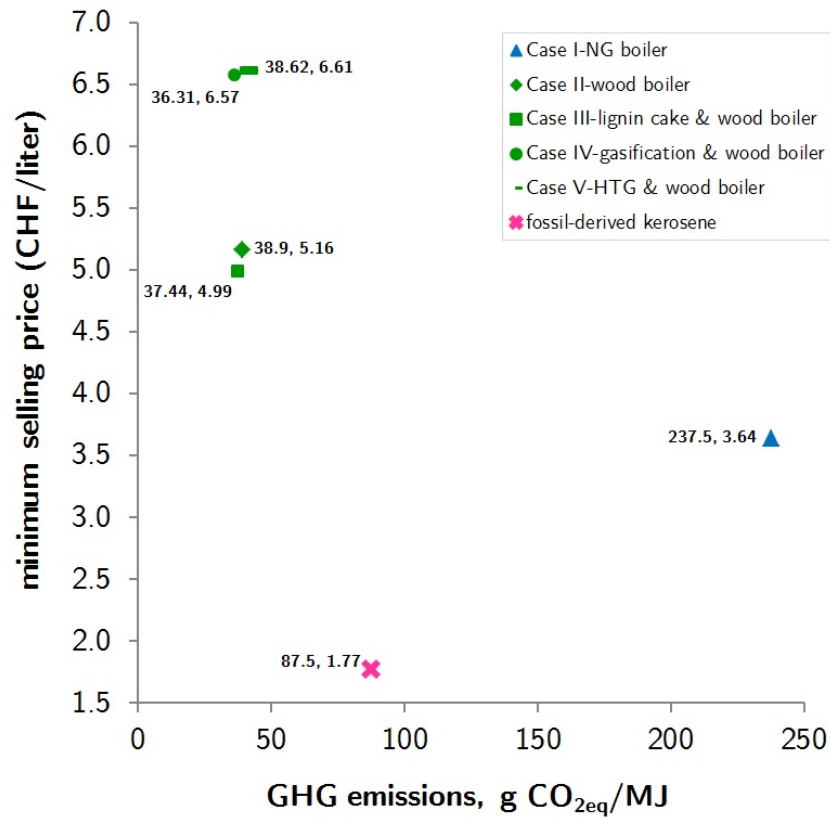


Figure 4.8: Performance of different jet fuel blend production plant configurations

Table 4.7: Detailed comparison of different system integration approaches

		Case I	Case II	Case III	Case IV	Case V
Parameter	Unit	Natural gas combustion	Wood combustion	Lignin cake combustion	Gasification + wood combustion	HT Gasification + wood combustion
TCI	millionCHF	20.53	30.68	30.62	54.48	50.46
C_{GR}	millionCHF	4.29	6.41	6.40	11.39	10.55
$C_{GR,sugars}$	%	43.1	17.0	17.9	10.4	11.9
$C_{GR,NGcomb.}$	%	56.9	-	-	-	-
$C_{GR,greencomb.}$	%	-	83.0	79.4	39.3	30.8
$C_{GR,technology}$	%	-	-	2.6	50.3	57.2
$C_{production}$	millionCHF/year	9.16	13.41	12.90	15.96	16.38
C_{op}	millionCHF/year	4.10	6.53	6.08	5.50	6.44
MSP	CHF/liter	3.64	5.16	4.99	6.57	6.61
GWP	g CO ₂ eq/MJ	237.5	38.90	37.44	36.31	38.62

Chapter 4. On the integration of catalytic reactions of sugar platform in biorefineries

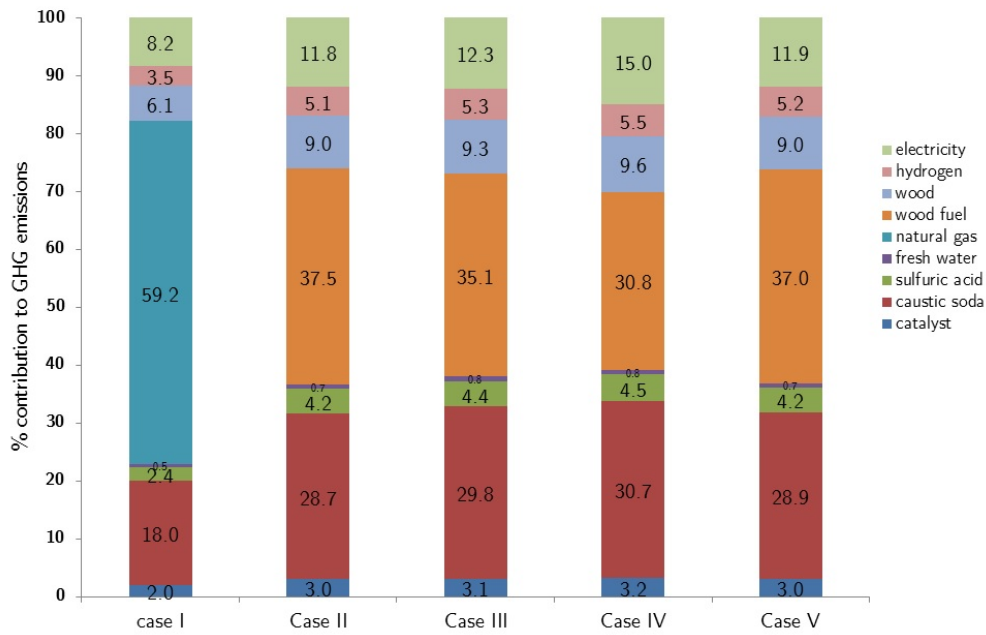


Figure 4.9: GHG emissions build-up for different process configurations

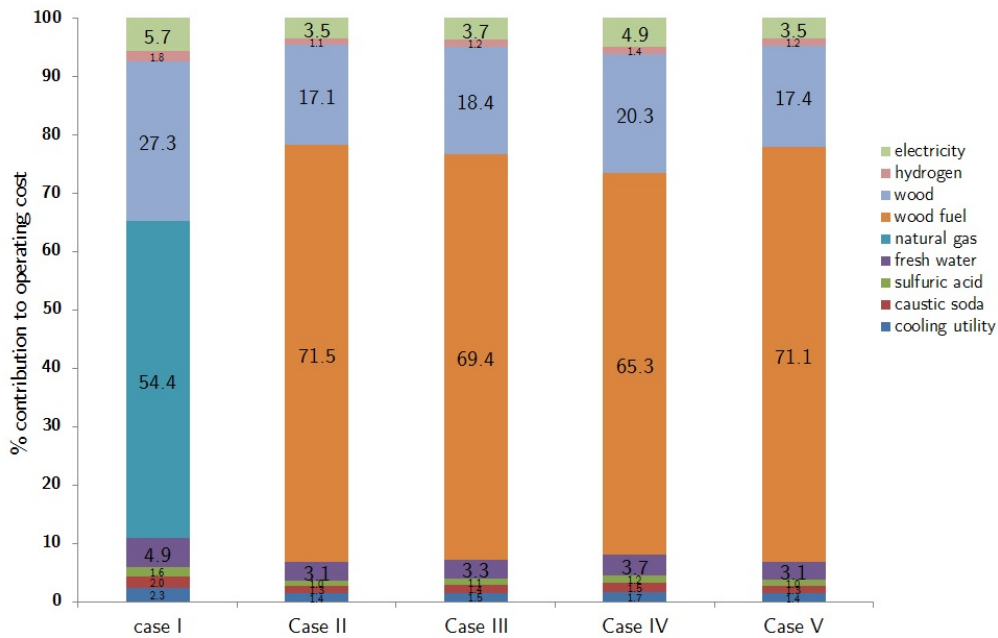


Figure 4.10: Operating cost build-up for different process configurations

Literature was then investigated to compare these results. Staples et al. [272] found that the attributional lifecycle GHG footprint of advanced fermentation of switchgrass to middle distillate (MD) fuels (including diesel and jet fuel) ranges from 11.7 to 89.8 g CO₂eq/MJ_{MD}. The GHG footprint for the proposed process designs (excluding Case I) for the jet fuel blend production in this study ranges between 36.31 to 38.90 g CO₂eq/MJ_{oil}. They also calculated the range for the minimum selling price of MD fuels from switchgrass between 1.09 and 6.30 USD/liter_{MD}. Proposed process designs (excluding Case I) for bio-oil (jet fuel blend) has minimum selling price of 4.99 to 6.61 CHF/liter.

4.5 Conclusions

Carbon-based chemicals and fuels such as alpha olefins and liquid jet fuels will still be needed in coming decades for a variety of industries, particularly the transportation and aviation industries. Lignocellulosic biomass is a reliable feedstock for producing these materials. In the proposed study, steam explosion-pretreated lignocellulosic biomass is converted into carboxylic acids through consolidated bioprocessing. The carboxylic acids can then be converted into an organic jet fuel blend containing aromatics and cycloalkenes with a carbon number range of C8-C16 via a single-step catalytic ketonization/aldol condensation. The carboxylic acid platform is also used to produce linear alpha olefins/alkanes via a catalytic tandem hydrogenation/dehydration in a single step. Alpha olefins can also be blended to jet fuel or can be used as building blocks for the production of bio-based commodity chemicals.

However, work has not yet been widely published to determine the feasibility or economic potential for such biorefineries combining biochemical conversion and chemical catalysis. Moreover, scale-up potential and feasibility studies are limited for many of these novel processes. Many of these concepts are still in the development stage, thus requiring the use of advanced process modeling and optimization techniques to make estimations.

To address the aforementioned lacks, a preliminary techno-economic modeling is performed in this chapter addressing the economic and environmental performance of these technologies. Minimum energy requirements are identified for the processes. Energy balanced is closed with conventional natural and wood boilers and gasification technologies.

The analysis illustrated that the minimum price of the product to run a small profitable biorefinery ranges from 4.99 to 6.61 CHF/liter. The current fossil-based kerosene price is 1.77 CHF/liter in Switzerland [273]. Proposed bio-jet fuel blend prices are well beyond the current market price, but on the same order of magnitude as other novel bio-based fuels. It is observed that integration between thermochemical and catalytic sugar platforms has the benefit of CO₂ reduction. If tax exemptions are applied as is currently done for imported biofuels fulfilling sustainability criteria, then competitive prices should be feasible.

Furthermore, process design is not optimal at this stage of research, therefore further process design improvements and optimization of operating conditions must be done to be able to create economic competitiveness.

Chapter 4. On the integration of catalytic reactions of sugar platform in biorefineries

The developed process chains represent an important step towards a renewable and sustainable production of specialty fuels (aviation, truck transport) and commodity chemicals, for example, olefins, which are among the most important compounds of the petrochemical industry. It is expected that a need for liquid fuels will persist for at least some decades. The biorefinery technology developed in this study has targeted this need by providing jet fuel blends, and thus bears the potential to close a gap in the supply of renewable energy.

Conclusions and perspectives

Overview

- Main results summary
- Recommendations and guidance
- Future perspectives

Main results summary

The requirement for sustainable development has prompted the researchers to explore solutions for better utilization of renewable energy resources in the future. Biomass is a promising renewable resource and it can be converted to multiple products and services including fuels, chemicals, heat and electricity via different conversion routes. Hence, replacement of fossil-based services with biomass-based services is critical to mitigate fossil CO₂ emissions, and process design of new and efficient energy conversion systems is necessary. With increasing climate change, the question arises as to which biomass conversion processes should be favored by the greatest overall efficiency.

This thesis empowers process integration in biorefineries with capabilities to address aspects of analysis such as different products, type of process equipment, type of process to integrate as degrees of freedom to screen and select. In this context, the thesis focus on proposing a combination of computational and thermodynamic tools that offer powerful support to design new biorefineries or upgrade existing ones.

The main findings and contributions are summarized below, followed by recommendations and future perspectives.

Chapter 1 - Context

Chapter 1 gives some background on process design of biorefineries and highlight the most promising biomass conversion technologies and products that have been identified. A state-of-the-art review is conducted on the process systems engineering tools for biorefinery design.

Chapter 2 - Assessment of integrated multi-product biorefineries

The goal of Chapter 2 is to make a comparison between technologies and to see if the process integration leading to multi-product biorefinery concept brings any additional benefit when compared to single product production.

Conclusions

To achieve this goal, systematic biorefinery design methodology is developed for thermo-environmental modeling, analysis and multi-objective optimization. This methodology allows identification of the most promising technologies and sizes of process units and comparison in terms of economic performance and environmental impact. Different performance targets are established to compare the alternative designs to increase the utilization of biogenic energy and understand the best combination of products and the synergies between them.

First, a database of thermo-environmental models is developed for different biomass conversion technologies and both sugar and syngas platforms are put in a superstructure considering multiple products (energy services, valuable chemicals, fuels). Thermo-environmental superstructure optimization problem is formulated as mixed integer linear programming (MILP) optimization problem. By applying pinch analysis internal heat exchange is maximized. The energetic synergy between the processing steps are exploited and trade-offs between multiple objectives are presented. Heat is generated due to the exothermic nature of the thermochemical conversion processes that operate at high temperatures. Excess heat from thermochemical pathways is valorized for biochemicals production and power generation. Integer cut constraints (ICC) algorithm is combined with epsilon-constraint method to create a multi-objective optimization (MOO) problem to systematically generate the list of competing options in a Pareto front considering economic performance and environmental targets. The ICC method allows different conversion pathways to be evaluated inside the superstructure and ordered according to their corresponding objective function values while epsilon constraint covered a wide range of environmental impact of the technologies. The portfolio of solutions are presented with the candidate technologies.

Results showed that economic competitiveness of the biorefineries is based on the production of high-value biochemicals together with comparably low-value biofuels. Sugar platform shows big potential for high value chemicals production (succinic acid, lactic acid, n-butanol) and higher GHG emission savings can be obtained with biofuels than chemicals. Also, valorization of C5 and lignin platforms is critical to be economically competitive. Integrating power production via steam network into biochemical or thermochemical conversion pathways is necessary to ensure self-sufficiency while contributing to lower CO₂ emissions. Co-production of SNG (Synthetic Natural Gas), lactic acid and electricity avoided 61% more CO₂ emissions when compared to the case without power generation. The analysis showed that great advantage of using biogenic chemicals and fuels is that the carbon cycle can be closed and thus fossil carbon emissions can be prevented. Using the life cycle data, the avoided fossil carbon emissions per carbon unit are calculated in the biogenic product. Bioproducts have a higher substitution rate than bioenergy services. However, co-production of biofuels, biochemicals and electricity together with the integration of CO₂ capture and storage (CCS) technologies yield in greater avoidance ratios. For the multi-product biorefinery of lactic acid, electricity and SNG production with CCS option, the replaced carbon ratio is 1.04 while this value is 0.94 for lactic acid production only.

Finally, the proposed design methodology can be applied to any small to large size biorefining plants. The computer-aided platform is expandable with flexible process models database and have

a plug-in approach.

Chapter 3 - Synergies between biorefineries and energy system

The aim of this chapter is to assess the performance of a combined heat and fuel production plant using biomass compared to conventional boilers under CO₂ emission and re-utilization constraints. It proposes a new system design of boilers, which utilizes woody biomass as energy resource in the thermo-chemical conversion processes to produce heat at required temperatures for different industrial sectors while cogenerating biofuels such as SNG, FT crude, DME and methanol. A by-product of the proposed combined heat and fuel (CHF) plant is biogenic CO₂ that is separated during the production. Different scenarios are evaluated considering the CO₂ produced via this system is either released, sequestered, or stored and used in a co-electrolysis unit in which surplus renewable electricity available during summer is converted into additional syngas. Storing liquid or gaseous fuels is an alternative option to expensive batteries to store excess renewable intermittent electricity.

Cost of heat is calculated considering different degrees of freedom such as carbon dioxide tax, operating cost, investment of the overall system, and profit from the fuel trade. A parametric analysis has been performed considering type and size of plants, CO₂ tax, and purchase and transportation costs of wood to compare the price of heat for the industrial sectors. Natural gas and wood boilers are used as the basis to calculate the breakeven CO₂ tax values for the same heat prices for the proposed CHF systems.

Summing-up the substituted fossil carbon for CHF SNG plant, 1 unit of biogenic carbon entering the cogeneration unit substitutes 0.48 units of fossil carbon and the corresponding CO₂ emissions from oil boiler. Per unit of CO₂ captured by the photosynthesis, the next generation SNG boiler substitutes therefore 50% more CO₂ than the wood combustion. If biogenic CO₂ sequestration is considered for SNG boiler (Case II), producing heat that substitutes the same fossil oil boiler, one unit of biogenic carbon entering the proposed cogeneration unit would then substitute 0.84 units of fossil carbon. In this case, the wood used in the next generation boiler is substituting 2.63 times more fossil CO₂ than the wood used in a boiler. Considering the cases (Case III and Case IV) where the co-electrolysis is used in addition to CHF SNG plant for the CO₂ captured, the heat price is negative while the system substitutes 0.64 and 0.9 units of fossil carbon from oil boiler, respectively.

Biomass cogeneration systems which cogenerates fuel and heat together and uses co-electrolysers to produce more biofuel when electricity is surplus as proposed in this study; provide a good solution for long-term electricity storage as it substitutes more CO₂ by the supply chain. The results of this study present a state-of-the-art renewable energy system as an alternative to conventional boilers.

Chapter 4 - On the integration of catalytic reactions of sugar platform in biorefineries

Chapter 4 presents economic and sustainability assessment of a novel process design for consolidated bioprocessing of biomass into carboxylic acids and catalytic upgrading into jet fuel aromatics and cyclic alkanes as well as linear alpha olefins. Thermo-environmental optimization methodology is

Conclusions

applied for minimization of operating cost of the proposed biorefinery designs. For each production pathway, minimum selling price (MSP) and GHG footprint in terms of CO₂ equivalent emissions are calculated. Catalytic reactions occur at medium temperature level hence the energy demand can be satisfied by process technologies such as combustion or gasification. Carboxylic acids platform processes C5 and C6 sugars while lignin is waste. Therefore, different options valorizing lignin for process heat demand are proposed to increase overall conversion efficiency. In different scenarios, energy balance is either closed with conventional natural gas or wood boilers or waste stream of lignin is combusted or converted into syngas through gasification. Comparing to producing heat from natural gas fired steam boilers, renewable technologies can reduce CO₂ emissions by 84% to 85% in a jet fuel blend production process. The biorefinery is small scale with 10000 dry ton of biomass per year. For different options of renewable hot utility, minimum selling price of bio-jet fuel blend is ranging from 4.99 to 6.61 CHF/liter. The proposed bio-jet fuel blend prices are higher than the current market price (1.77 CHF/liter), but in the same order of magnitude as other new bio-based fuels. GHG emissions are also comparable when considering other bio-based kerosene emissions.

Recommendations and guidance

Analogous to an oil refinery, a stand-alone biorefinery must look at coupling heat integration, fuel production, higher value co-product production as well as heat and electricity production. It is very important to see the fact that the biochemical conversion routes operate at respectively low temperatures and that they are endothermic. With the aim of sustainable biorefinery design, it is important to close the energy balance with renewable energy sources. The heat required by the biochemical conversion pathways should be satisfied by the heat generated thanks to the exothermic nature of thermochemical conversion (gasification) pathways. Therefore, biomass resource should be allocated to both gasification and biochemical-catalytic pathways in a way that the heat demand is satisfied, making profit with co-production of fuels, chemicals, heat and electricity with lower emissions than their fossil-substitutes.

Future perspectives

- **Uncertainty analysis:** Since the development of many promising biorefinery technologies are still at laboratory or pilot scale, incorporation of higher levels of process-inherent uncertainty is necessary. In these emerging technologies, design data are not very reliable and sometimes data is rarely available. Furthermore, researchers are forced on making assumptions based on heuristics to fill up the data gap when information is limited during the development of decision-making tools. Some sources of process-inherent uncertainty are flowrates, temperatures, pressures, stream quality. Furthermore, decision-making on the best production pathways in the biorefineries highly depends on the market prices of the products, availability and prices of raw materials, investment cost and plant operation, and all these are highly uncertain in nature. Therefore, stochastic multi-objective optimization method is necessary

to optimize the design and operating conditions of the integrated biorefinery superstructure for economic and environmental impact analysis.

- ***Simultaneous heat and mass integration:*** Biorefineries consume large amount of water especially in the distillation columns to separate dilute mixtures and wastewater treatment units are important to be considered in the context of biorefineries. Water optimization is an issue in biorefineries since the cost contribution of fresh water is very small and total cost optimization is unlikely to promote water conservation since economical benefit of reducing the freshwater consumption versus other utilities is currently still marginal at best. Mass integration is useful for wastewater minimization where the water and wastewater is optimally used by reuse, regeneration and recycling. A convenient simultaneous heat and mass integration strategy will address energetics, economic and environmental concerns.
- ***Expansion of biorefinery platform with new technologies:*** Biorefinery technologies are emerging in the area of energy systems design and integration of new technologies into the current biorefinery platform needs to be considered to extend the portfolio of biorefinery technologies. This also involves integration of other renewable energy sources (like solar/geothermal heat or renewable electricity) to increase the productivity of the bioresource.
- ***Supply chain and LCA:*** Since biomass is diluted and diversified in vast area, so supply chain optimization and economic viability study for different sizes of biorefineries is critical for investment planning. Robust scenarios for biomass logistics, seasonal availability are important to have a better assessment of biorefineries.



Appendix

A Energy-integration superstructure optimization - constraints

Heat balance of the temperature intervals

Section Section 1.2.2.1 gives an overview of the first and second law of thermodynamics and maximum heat recovery in the system. Detailed heat cascade formulation is explained in more detail in Marechal and Kalitventzeff [109]. Heat cascade constraints are shown in A.1-A.2. These constraints are necessary to calculate the minimum energy requirement.

$$\sum_{w \in \mathbf{W}} f^w \cdot \dot{Q}_k^w + \sum_{s \in \mathbf{S}} \dot{Q}_k^s + \dot{R}_{k+1} - \dot{R}_k = 0 \quad \forall k \in \mathbf{K} \quad (\text{A.1})$$

where

- w represents the units in the superstructure
- \mathbf{K} set of temperature intervals 1,2,3, ...,n_k
- \mathbf{S} set of process streams
- \dot{Q}_k^w [kW] reference heat release or demand of a utility technology w in the temperature interval k
- \dot{Q}_k^s [kW] heat release or demand of process stream s in the temperature interval k
- \dot{R}_k [kW] residual heat of temperature interval $k - 1$ that is cascaded to interval k

Thermodynamic Feasibility

The thermodynamic feasibility ensures a closed energy balance, as expressed in Equation A.2.

$$\dot{R}_k \geq 0, \quad \dot{R}_1 = 0, \quad \dot{R}_{n_k+1} = 0 \quad \forall k \in \mathbf{K} \quad (\text{A.2})$$

Energy Conversion Unit Selection

The maximum size of operation and existence of a unit w is given by Equation A.3.

$$f^{w,min} \cdot y^w \leq f^w \leq f^{w,max} \cdot y^w \quad \forall w \in \mathbf{W} \quad (\text{A.3})$$

where $f^{w,min}$ is the minimum size parameter of unit w , $f^{w,max}$ is the maximum size parameter of unit w , f^w is the multiplication factor of unit w and y^w represents the integer variable for use of unit w .

B Data for process design of biorefineries

B.1 Parameters and assumptions for environmental impact evaluation

Table B.1: Assumptions for the substitution and their equivalent emissions

Products	Substitutes used in the study	Value [kg CO ₂ eq/kg _{product}]
Hydrous ethanol	Petrol + operation	3.275
Anhydrous ethanol	Petrol + operation	4.678
Vanillin	Petr.derived phenol	3.869
Formic acid	Petr.-derived formic acid	2.49
Lactic acid	Petr.-derived lactic acid	3.813
n-butanol	Petr.-derived n-butanol	2.122
Succinic acid	Petr.-derived succinic acid	1.94
Acetic acid	Petr.-derived acetic acid	1.855
Acetone	Petr.-derived acetone	2.231
Xylitol	Beet sugar	0.66
Ethanol (95%)	Ethanol	3.094
Ethylene	Ethylene	1.399
FT fuel	Diesel + operation	4.424
SNG	NG + operation	3.242
MeOH	MeOH + operation	2.509
DME	Diesel (0.64 kg/kg DME) + operation	2.832
HMF (to FDCA)	Petr.-derived terephthalic acid	1.817

B.2 Fossil CO₂ emissions avoided for biorefinery products

Table B.2: Fossil CO₂ emissions avoided per unit of carbon in the bio-molecule (Source: Ecoinvent [152])

	$C_{\text{fossil avoided}}/C_{\text{biogenic}}$
Biochemicals	
Butanol	1.89
Acetone	1.98
Succinic acid	2.30
Lactic acid	3.60
Ethylene	1.45
HMF	1.40
Acetic acid	2.27
Formic acid	2.30
Biofuels	
SNG	1.24
DME	1.21
FT	1.20
Anhydrous ethanol	1.37
Ethanol (95%)	1.35
Methanol	1.54

C Transportation cost of wood resource

Logistics cost of wood increases as the size of heat supply increases and the transport distance is another criteria which depends on the location of the plant and availability of biomass supply. Steubing et al. [34], performed a study to analyze average biomass supply distances in Switzerland considering plant size, location and biomass availability scenarios. The plant location is chosen to be Bellinzona, Switzerland with longest transport distance. The function to calculate the average driving distance used in this study is taken from Peduzzi et al. [274].

$$d_{Average} = t_1 \dot{Q}_{Wood}^{t_2} \quad [\text{km}] \quad (\text{C.1})$$

Here, $d_{Average}$ is the average distance in km, \dot{Q}_{Wood} is the thermal plant capacity, calculated based on dry wood input in kW, and t_1, t_2 are the parameters calibrated for the case 'baseline scenario for Bellinzona, Switzerland' as shown in Table C.1. The cost of transportation is estimated by calculating the number of lorries required to transport the biomass satisfying the nominal plant capacity.

$$c_{Transport} = \frac{N_{Lorry} \cdot c_{Lorry}}{\dot{Q}_{Wood} \cdot h} \quad [\text{CHF/kWh}_{wood}] \quad (\text{C.2})$$

$$N_{Lorry} = \frac{m_{Wood}}{m_{Lorry}} \quad (\text{C.3})$$

$$m_{Wood} = \frac{\dot{Q}_{Wood} \cdot h}{LHV_{Wood} \cdot 1000} \quad [\text{ton/yr}] \quad (\text{C.4})$$

$$c_{Lorry} = \frac{d_{Average} \cdot e_{Lorry} \cdot c_{Diesel}}{LHV_{Diesel} \cdot \rho_{Diesel}} \quad [\text{CHF/lorry}] \quad (\text{C.5})$$

The transportation cost for each lorry ($m_{Lorry} = 10$ ton) is related to the total fuel consumption (e_{Lorry}), diesel market price (c_{Diesel}) and average distance covered ($d_{Average}$). The total fuel consumption of a lorry (e_{Lorry}) is calculated for the case where the fully-loaded lorry transports the biomass to the plant, unloads and returns to the biomass collection site empty to make another trip. All the parameters used in the wood transport cost model are presented in Table C.1.

Appendix C. Transportation cost of wood resource

Table C.1: Parameters used in wood transport cost model

Symbol	Parameter	Value	Unit	Source
t_1	in the calculation of $d_{Average}$	18.455	km/kW _{th}	[274]
t_2	in the calculation of $d_{Average}$	0.1776		[274]
e_{Full}	Fuel consumption (loaded lorry)	10.67	MJ/km	[274]
e_{Empty}	Fuel consumption (empty lorry)	8.37	MJ/km	[274]
e_{Lorry}	Total fuel consumption ($e_{Empty}+e_{Full}$)	18.99	MJ/km	[274]
LHV_{Diesel}	Lower heating value of diesel	42.791	MJ/kg	[274]
ρ_{Diesel}	Density of diesel	0.832	kg/l	[274]
c_{Diesel}	Diesel market price	1.71	CHF/l	[275]

D Results analysis for different scenarios

Table D.1: Performance of different fuel (SNG, FT, MEOH and DME) production scenarios in Case I heat production for the breakeven CO₂ tax values comparing to natural gas boiler

Plant size (heat output [MW])	SNG				FT			
	2.5	7	20	35	2.5	7	20	35
Wood [MW]	18.00	49.80	142.10	249.00	31.70	88.8	252.5	441.8
Biofuel [MW]	11.80	32.47	92.63	162.36	13.85	38.78	110.28	192.96
Net electricity [MW]	0.70	1.93	5.54	9.65	1.71	4.80	13.65	23.88
Breakeven CO ₂ tax [CHF/tonCO ₂]	123	89	62	52	99	59	29	17

Plant size (heat output [MW])	MEOH				DME			
	2.5	7	20	35	2.5	7	20	35
Wood [MW]	54.3	152.00	433.00	760.00	18.90	53.00	150.50	264.00
Biofuel [MW]	28.85	80.75	229.97	403.73	8.93	25.04	71.09	124.72
Net electricity [MW]	5.97	16.72	47.64	83.64	2.17	6.10	17.31	30.37
Breakeven CO ₂ tax [CHF/tonCO ₂]	168	119	85	70	349	237	149	111

Table D.2: Performance of SNG CHF plant in Case II for different sizes of heat production

Plant size (heat output [MW])	2.5	7	20	35
Wood [MW]	18.00	49.80	142.10	249.00
Biofuel [MW]	11.80	32.47	92.63	162.36
Net electricity [MW]	0.51	1.36	3.88	6.81
Breakeven CO ₂ tax [CHF/tonCO ₂]	82	62	47	40

E Economic analysis for catalytic platform pathways

Table E.1: Parameters and results for the capital investment cost calculations for the economic analysis for Case I

	Linear alpha olefins [MillionCHF]	Jet fuel blend [MillionCHF]
Equipment (E)	4.06	4.29
Installation (0.36 E)	1.46	1.54
Instrumentation and control (0.28 E)	1.14	1.20
Piping (0.32 E)	1.29	1.37
Electrical (0.2 E)	0.81	0.86
Building, process and aux., B (0.2 E)	0.81	0.86
Service facilities (0.6 E)	2.43	2.57
Land (0.04 E)	0.16	0.17
Direct costs (D)	12.17	12.87
Engineering & supervision (0.2 D)	2.43	2.57
Construction expense (0.15 D)	1.83	1.93
Contingency (0.1 D)	1.22	1.29
Indirect costs (I)	5.48	5.79
Fixed capital investment, F (D+I)	17.64	18.66
Working capital, W (0.1 F)	1.76	1.87
Total capital investment, TCI (F+W)	19.41	20.53

Appendix E. Economic analysis for catalytic platform pathways

Table E.2: Parameters and results for the total production cost calculations for the economic analysis for Case I

	Linear alpha olefins [MillionCHF/yr]	Jet fuel blend [MillionCHF/yr]
Raw material and utility cost (R)	4.67	4.10
Operation labor (L)	0.71	0.71
Direct supervisor labor, S (0.15 L)	0.11	0.11
Maintenance and repair, M (0.05 F)	0.88	0.93
Operating supplies (0.15 M)	0.13	0.14
Laboratory charges (0.1 L)	0.07	0.07
Direct production costs (DPC)	6.58	6.06
Depreciation (0.05 F)	0.88	0.93
Local taxes (0.01 F)	0.18	0.19
Insurance (0.01 F)	0.18	0.19
Fixed charges (FC)	1.24	1.31
Plant overhead, P (0.4 (L+S+M))	0.68	0.70
Manufacturing cost, MC (DPC +FC+P)	8.49	8.07
Admin. costs ((0.15 (L+S+M))	0.25	0.26
Distribution costs (0.02 TPC)	0.44	0.42
R&D (0.02 TPC)	0.44	0.42
General expenses, G	1.13	1.09
Total production cost (MC + G)	9.62	9.16

Bibliography

- [1] Intergovernmental Panel on Climate Change. *Global Warming of 1.5°C: An IPCC Special Report on the Impacts of Global Warming of 1.5°C Above Pre-industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty*. Intergovernmental Panel on Climate Change, 2018. URL <https://books.google.ch/books?id=RDsLvwEACAAJ>.
- [2] IEA Sankey Diagram, World Final Consumption (2016), . URL <https://www.iea.org/Sankey/#?c=World&s=Final%20consumption>.
- [3] IEA. Energy and climate change: World Energy Outlook Special Report. Technical report, International Energy Agency, Paris, France, 2015. URL <https://www.iea.org/publications/freepublications/publication/WEO2015SpecialReportonEnergyandClimateChange.pdf>.
- [4] IEA. The latest trends in energy and emissions in 2018. URL <https://www.iea.org/geco/emissions/>.
- [5] John M. Christensen. *Emissions Gap Report 2018*. UNEP DTU Partnership, 2018.
- [6] UN DESA. World population prospects, the 2017 Revision, Volume I: comprehensive tables. *New York United Nations Department of Economic & Social Affairs*, 2017.
- [7] International Energy Outlook 2017. Technical report, . URL [https://www.eia.gov/outlooks/ieo/pdf/0484\(2017\).pdf](https://www.eia.gov/outlooks/ieo/pdf/0484(2017).pdf).
- [8] Cédric Philibert. IEA INSIGHTS 2017 Renewable Energy for Industry. Technical report, 2017.
- [9] International Energy Agency. *CO2 Emissions from Fuel Combustion 2018*. 2018. doi: 10.1787/co2_fuel-2018-en. URL https://www.oecd-ilibrary.org/content/publication/co2_fuel-2018-en.
- [10] M. van der Hoeven, Y. Kobayashi, and R. Diercks. Technology roadmap: Energy and GHG reductions in the chemical industry via catalytic processes. *International Energy Agency: Paris*, page 56, 2013.
- [11] G. Yohe, R. Lasco, Qazi K. Ahmad, N. Arnell UK, S. Cohen, T. Janetos, R. Perez, K. Ebi, P. Romero Lankao, and E. Malone. Perspectives on Climate Change and Sustainability 3. *change*, 25(48):

Bibliography

49.

- [12] Iea. Combining Bioenergy with CCS: Reporting and Accounting for Negative Emissions under UNFCCC and the Kyoto Protocol. IEA Energy Papers 2011/16, OECD Publishing, December 2011. URL <https://ideas.repec.org/p/oec/ieaaaa/2011-16-en.html>.
- [13] C.J. Chen. *Physics of Solar Energy*. Wiley, 2011. ISBN 978-0-470-64780-6. URL <https://books.google.ch/books?id=U0d7DhnM0FMC>.
- [14] Exergy Analysis. In *Efficiency of Biomass Energy*, pages 37–90. John Wiley & Sons, Ltd, 2016. ISBN 978-1-119-11816-9. doi: 10.1002/9781119118169.ch2. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781119118169.ch2>.
- [15] Johan A. Martens, Annemie Bogaerts, Norbert De Kimpe, Pierre A. Jacobs, Guy B. Marin, Korneel Rabaey, Mark Saeys, and Sebastian Verhelst. The Chemical Route to a Carbon Dioxide Neutral World. *ChemSusChem*, 10(6):1039–1055, 2017. doi: 10.1002/cssc.201601051. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201601051>.
- [16] Edmund Henrich, Nicolaus Dahmen, Eckhard Dinjus, and Jörg Sauer. The Role of Biomass in a Future World without Fossil Fuels. *Chemie Ingenieur Technik*, 87(12):1667–1685, 2015. doi: 10.1002/cite.201500056. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/cite.201500056>.
- [17] OECD. *Meeting Policy Challenges for a Sustainable Bioeconomy*. OECD Publishing, 2018. ISBN 978-92-64-29234-5. URL <https://books.google.ch/books?id=JShWDwAAQBAJ>.
- [18] Sohrab Haghghi Mood, Amir Hossein Golfeshan, Meisam Tabatabaei, Gholamreza Salehi Jouzani, Gholam Hassan Najafi, Mehdi Gholami, and Mehdi Ardjmand. Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment. *Renewable and Sustainable Energy Reviews*, 27:77–93, November 2013. ISSN 1364-0321. doi: 10.1016/j.rser.2013.06.033. URL <http://www.sciencedirect.com/science/article/pii/S1364032113004103>.
- [19] Runsen Zhang, Shinichiro Fujimori, and Tatsuya Hanaoka. The contribution of transport policies to the mitigation potential and cost of 2\hspace0.167em°C and 1.5\hspace0.167em°C goals. *Environmental Research Letters*, 13(5):054008, April 2018. doi: 10.1088/1748-9326/aabb0d. URL <https://doi.org/10.1088%2F1748-9326%2Faabb0d>.
- [20] Ausilio Bauen, Inmaculada Gomez, Dave OudeNijeweme, Maria Paraschiv, and Inmaculada Gomez. *The Strategic Transport Research and Innovation Agenda (STRIA) Roadmap for Low-emission Alternative Energy for Transport*. Directorate-General for Research and Innovation (European Commission), 2016. URL <https://publications.europa.eu/en/publication-detail/-/publication/22bbaffc-00bb-11e8-b8f5-01aa75ed71a1>.
- [21] B Kamm and M Kamm. Biorefineries—multi product processes. *Advances in biochemical engineering/biotechnology*, 105(January):175–204, 2007. ISSN 0724-6145 (Print)\r0724-6145 (Linking). doi: 10.1007/10_2006_040.

- [22] A. Demirbas. *Biorefineries: For Biomass Upgrading Facilities*. Springer London, 2009. ISBN 978-1-84882-721-9.
- [23] E. Fahlén and E. O. Ahlgren. Assessment of integration of different biomass gasification alternatives in a district-heating system. *Energy*, 34(12):2184 – 2195, 2009. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2008.10.018>. URL <http://www.sciencedirect.com/science/article/pii/S0360544208002843>.
- [24] AntonisC Kokossis, Aidong Yang, Marinella Tsakalova, and Ta-Chen Lin. Systematic Screening of Multiple Processing Paths in Biorefineries. In *Integrated Biorefineries*, Green Chemistry and Chemical Engineering, pages 37–58. CRC Press, 2012. ISBN 978-1-4398-0346-2.
- [25] Jhuma Sadhukhan, Kok Siew Ng, and Elias Martinez Hernandez. Introduction. In *Biorefineries and Chemical Processes*, pages 1–41. John Wiley & Sons, Ltd, 2014. ISBN 978-1-118-69812-9. doi: 10.1002/9781118698129.ch1. URL <http://onlinelibrary.wiley.com/doi/10.1002/9781118698129.ch1/summary>.
- [26] Prodromos Daoutidis, Adam Kelloway, W. Alex Marvin, Srinivas Rangarajan, and Ana I. Torres. Process systems engineering for biorefineries: New research vistas. *Current Opinion in Chemical Engineering*, 2(4):442–447, 2013. doi: 10.1016/j.coche.2013.09.006. URL <http://dx.doi.org/10.1016/j.coche.2013.09.006>.
- [27] Zhihong Yuan, Bingzhen Chen, and Rafiqul Gani. Applications of process synthesis: Moving from conventional chemical processes towards biorefinery processes. *Computers & Chemical Engineering*, 49:217–229, 2013. ISSN 0098-1354. doi: <http://dx.doi.org/10.1016/j.compchemeng.2012.09.020>.
- [28] Mariano Martín and Ignacio E. Grossmann. On the Systematic Synthesis of Sustainable Biorefineries. *Industrial & Engineering Chemistry Research*, 52:3044–3064, March 2013. ISSN 0888-5885. doi: 10.1021/ie2030213.
- [29] Grégoire Léonard, Andreas Pfennig, Ayse Dilan Celebi, Shivom Sharma, and François Maréchal. Industrial Integration of Biotechnological Processes from Raw Material to Energy Integration: Study by Modeling Approach. In *Microbial Fuels: Technologies and Applications*, pages 493–510. 2017.
- [30] IEA. IEA Bioenergy Task 42 on Biorefineries: Co-production of fuels, chemicals, power and materials from biomass. Technical report, In: Minutes of the third Task meeting, Copenhagen, Denmark, 25–26 March 2007, 2008. URL <http://www.biorefinery.nl/ieabioenergy-task42/>.
- [31] Th Willke and K.-D. Vorlop. Industrial bioconversion of renewable resources as an alternative to conventional chemistry. *Applied Microbiology and Biotechnology*, 66(2):131–142, December 2004. ISSN 0175-7598, 1432-0614. doi: 10.1007/s00253-004-1733-0. URL <https://link.springer.com/article/10.1007/s00253-004-1733-0>.

Bibliography

- [32] Junaid Akhtar, Ani Idris, and Ramlan Abd. Aziz. Recent advances in production of succinic acid from lignocellulosic biomass. *Applied Microbiology and Biotechnology*, 98(3):987–1000, February 2014. ISSN 1432-0614. doi: 10.1007/s00253-013-5319-6. URL <https://doi.org/10.1007/s00253-013-5319-6>.
- [33] James Hettenhaus. Biomass Commercialization and Agriculture Residue Collection. In *Biorefineries-Industrial Processes and Products*, pages 316–344. John Wiley & Sons, Ltd, 2008. ISBN 978-3-527-61984-9. doi: 10.1002/9783527619849.ch14. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/9783527619849.ch14>.
- [34] Bernhard Steubing, Isabel Ballmer, Martin Gassner, Léda Gerber, Luca Pampuri, Sandro Bischof, Oliver Thees, and Rainer Zah. Identifying environmentally and economically optimal bioenergy plant sizes and locations: A spatial model of wood-based SNG value chains. *Renewable Energy*, 61:57 – 68, 2014. ISSN 0960-1481. doi: <https://doi.org/10.1016/j.renene.2012.08.018>. URL <http://www.sciencedirect.com/science/article/pii/S0960148112004880>.
- [35] Ruhan C. Uçar, Aslıhan Şengül, and Melih S. Celiktaş. 4 - Biorefineries for wheat bran: Sustainable utilization and market potential. In Charis M. Galanakis, editor, *Sustainable Recovery and Reutilization of Cereal Processing By-Products*, pages 87 – 124. Woodhead Publishing, 2018. ISBN 978-0-08-102162-0. doi: 10.1016/B978-0-08-102162-0.00004-6. URL <http://www.sciencedirect.com/science/article/pii/B9780081021620000046>.
- [36] R. Batsy Dieudonné, C. Solvason Charles, E. Sammons Norm, Chambost Virginie, DavidLbilhartz, R. Eden Mario, M. El-Halwagi Mahmoud, and R. Stuart Paul. Product Portfolio Selection and Process Design for the Forest Biorefinery. In *Integrated Biorefineries : Design, Analysis, and Optimization*, Green Chemistry and Chemical Engineering, pages 3–36. CRC Press, 2012. ISBN 978-1-4398-0346-2.
- [37] J.L. Wertz and O. Bédué. *Lignocellulosic Biorefineries*. EPFL Press, 2013. ISBN 978-2-940222-68-1. URL <https://books.google.ch/books?id=o84HnwEACAAJ>.
- [38] David Martin Alonso, Stephanie G. Wettstein, and James A. Dumesic. Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem. Soc. Rev.*, 41(24):8075–8098, 2012. doi: 10.1039/C2CS35188A. URL <http://dx.doi.org/10.1039/C2CS35188A>.
- [39] Arpan Das and Priyanka Ghosh. Solid State Fermentation – A Stimulating Process for Valorization of Lignocellulosic Feedstocks to Biofuel. In *Principles and Applications of Fermentation Technology*, pages 239–262. John Wiley & Sons, Ltd, 2018. ISBN 978-1-119-46038-1. doi: 10.1002/9781119460381.ch13. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781119460381.ch13>.
- [40] Chun-Yang Yin. Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel*, 90(3):1128 – 1132, 2011. ISSN 0016-2361. doi: <https://doi.org/10.1016/j.fuel.2010.11.031>. URL <http://www.sciencedirect.com/science/article/pii/S0016236110006460>.

- [41] Marina O. S. Dias, Tassia L. Junqueira, Carlos Eduardo V. Rossell, Rubens Maciel Filho, and Antonio Bonomi. Evaluation of process configurations for second generation integrated with first generation bioethanol production from sugarcane. *Fuel Processing Technology*, 109:84 – 89, 2013. ISSN 0378-3820. doi: <https://doi.org/10.1016/j.fuproc.2012.09.041>. URL <http://www.sciencedirect.com/science/article/pii/S0378382012003670>.
- [42] Peter McKendry. Energy production from biomass (part 1): overview of biomass. *Bioresource Technology*, 83(1):37 – 46, 2002. ISSN 0960-8524. doi: [https://doi.org/10.1016/S0960-8524\(01\)00118-3](https://doi.org/10.1016/S0960-8524(01)00118-3). URL <http://www.sciencedirect.com/science/article/pii/S0960852401001183>.
- [43] Ayhan Demirbaş and A. Hilal Demirbaş. Estimating the Calorific Values of Lignocellulosic Fuels. *Energy Exploration & Exploitation*, 22(2):135–143, 2004. doi: 10.1260/0144598041475198. URL <https://doi.org/10.1260/0144598041475198>.
- [44] ECN. Phyllis database for biomass and waste, 2012. URL <https://phyllis.nl>.
- [45] Carlo N. Hamelinck, Andre P. C. Faaij, Herman den Uil, and Harold Boerrigter. Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential. *Energy*, 29(11):1743–1771, September 2004.
- [46] C. Telmo, J. Lousada, and N. Moreira. Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood. *Bioresource Technology*, 101(11):3808 – 3815, 2010. ISSN 0960-8524. doi: <https://doi.org/10.1016/j.biortech.2010.01.021>. URL <http://www.sciencedirect.com/science/article/pii/S0960852410000787>.
- [47] Paul Tanger, John L Field, Courtney E Jahn, Morgan W Defoort, and Jan E Leach. Biomass for thermochemical conversion: targets and challenges. *Frontiers in plant science*, 4:218–218, July 2013. ISSN 1664-462X. doi: 10.3389/fpls.2013.00218. URL <https://www.ncbi.nlm.nih.gov/pubmed/23847629>.
- [48] J. Y. Zhu and X. J. Pan. Woody biomass pretreatment for cellulosic ethanol production: Technology and energy consumption evaluation. *Bioresource Technology*, 101(13):4992 – 5002, 2010. ISSN 0960-8524. doi: <https://doi.org/10.1016/j.biortech.2009.11.007>. URL <http://www.sciencedirect.com/science/article/pii/S0960852409015119>.
- [49] Prabir Basu. Chapter 5 - Pyrolysis. In Prabir Basu, editor, *Biomass Gasification, Pyrolysis and Torrefaction (Second Edition)*, pages 147 – 176. Academic Press, Boston, second edition edition, 2013. ISBN 978-0-12-396488-5. doi: 10.1016/B978-0-12-396488-5.00005-8. URL <http://www.sciencedirect.com/science/article/pii/B9780123964885000058>.
- [50] Laurence Tock, Martin Gassner, and François Maréchal. Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis. *Biomass and Bioenergy*, 34(12):1838 – 1854, 2010. ISSN 0961-9534. doi: <https://doi.org/10.1016/j.biombioe.2010.07.018>. URL <http://www.sciencedirect.com/science/article/pii/S0961953410002424>.

Bibliography

- [51] Thermochemical Conversion. In *Efficiency of Biomass Energy*, pages 153–202. John Wiley & Sons, Ltd, 2016. ISBN 978-1-119-11816-9. doi: 10.1002/9781119118169.ch5. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781119118169.ch5>.
- [52] Laurence Tock and François Maréchal. Co-production of hydrogen and electricity from lignocellulosic biomass: Process design and thermo-economic optimization. *Energy*, 45(1): 339 – 349, 2012. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2012.01.056>. URL <http://www.sciencedirect.com/science/article/pii/S0360544212000618>.
- [53] Yanna Liang, Tyler Kashdan, Christy Sterner, Lilli Dombrowski, Ingolf Petrick, Michael Kröger, and Rainer Höfer. Chapter 2 - Algal Biorefineries. In Ashok Pandey, Rainer Höfer, Mohammad Taherzadeh, K. Madhavan Nampoothiri, and Christian Larroche, editors, *Industrial Biorefineries & White Biotechnology*, pages 35 – 90. Elsevier, Amsterdam, 2015. ISBN 978-0-444-63453-5. doi: 10.1016/B978-0-444-63453-5.00002-1. URL <http://www.sciencedirect.com/science/article/pii/B9780444634535000021>.
- [54] Samuel Stucki, Frédéric Vogel, Christian Ludwig, Anca G. Haiduc, and Martin Brandenberger. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. *Energy Environ. Sci.*, 2(5):535–541, 2009. doi: 10.1039/B819874H. URL <http://dx.doi.org/10.1039/B819874H>.
- [55] Jeremy S. Luterbacher, Morgan Fröling, Frédéric Vogel, François Maréchal, and Jefferson W. Tester. Hydrothermal Gasification of Waste Biomass: Process Design and Life Cycle Assessment. *Environmental Science & Technology*, 43(5):1578–1583, 2009. doi: 10.1021/es801532f. URL <https://doi.org/10.1021/es801532f>.
- [56] Parveen Kumar, Parveen Kumar, Diane M Barrett, Diane M Barrett, Michael J Delwiche, Michael J Delwiche, Pieter Stroeve, and Pieter Stroeve. Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production. *Industrial and Engineering Chemistry (Analytical Edition)*, pages 3713–3729, 2009. doi: 10.1021/ie801542g.
- [57] P. Alvira, E. Tomás-Pejó, M. Ballesteros, and M. J. Negro. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology*, 101(13):4851–4861, 2010. ISSN 1873-2976 (Electronic)\n0960-8524 (Linking). doi: 10.1016/j.biortech.2009.11.093. URL <http://dx.doi.org/10.1016/j.biortech.2009.11.093>.
- [58] Venkatesh Chaturvedi and Pradeep Verma. An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products. *3 Biotech*, 3(5):415–431, October 2013. ISSN 2190-5738. doi: 10.1007/s13205-013-0167-8. URL <https://doi.org/10.1007/s13205-013-0167-8>.
- [59] Leonel Jorge Ribeiro Nunes, João Carlos De Oliveira Matias, and João Paulo Da Silva Catalão. Chapter 2 - Physical Pretreatment of Biomass. In Leonel Jorge Ribeiro Nunes, João Carlos De Oliveira Matias, and João Paulo Da Silva Catalão, editors, *Torrefaction of Biomass for*

- Energy Applications*, pages 45 – 88. Academic Press, 2018. ISBN 978-0-12-809462-4. doi: 10.1016/B978-0-12-809462-4.00002-X. URL <http://www.sciencedirect.com/science/article/pii/B978012809462400002X>.
- [60] M. Ståhl, K. Granström, J. Berghel, and R. Renström. Industrial processes for biomass drying and their effects on the quality properties of wood pellets. *Biomass and Bioenergy*, 27(6): 621 – 628, 2004. ISSN 0961-9534. doi: <https://doi.org/10.1016/j.biombioe.2003.08.019>. URL <http://www.sciencedirect.com/science/article/pii/S0961953404001047>.
- [61] Jonas Berghel and Roger Renström. Basic design criteria and corresponding results performance of a pilot-scale fluidized superheated atmospheric condition steam dryer. *Biomass and Bioenergy*, 23(2):103 – 112, 2002. ISSN 0961-9534. doi: [https://doi.org/10.1016/S0961-9534\(02\)00040-5](https://doi.org/10.1016/S0961-9534(02)00040-5). URL <http://www.sciencedirect.com/science/article/pii/S0961953402000405>.
- [62] Yi Zheng, Zhongli Pan, and Ruihong Zhang. Overview of biomass pretreatment for cellulosic ethanol production. *International Journal of Agricultural and Biological Engineering*, 2:51–68, 2009. ISSN 1934-6352.
- [63] J. A. Pérez, I. Ballesteros, M. Ballesteros, F. Sáez, M. J. Negro, and P. Manzanares. Optimizing Liquid Hot Water pretreatment conditions to enhance sugar recovery from wheat straw for fuel-ethanol production. *Fuel*, 87:3640–3647, 2008. ISSN 0016-2361. doi: <http://dx.doi.org/10.1016/j.fuel.2008.06.009>.
- [64] Venkatesh Balan, Bryan Bals, Shishir P S. Chundawat, Derek Marshall, and Bruce E Dale. Lignocellulosic Biomass Pretreatment Using AFEX. In Jonathan R. Mielenz, editor, *Biofuels*, volume 581 of *Methods in Molecular Biology*, pages 61–77. Humana Press, January 2009. ISBN 978-1-60761-213-1.
- [65] Yizhou Zheng, H. M. Lin, and George T. Tsao. Pretreatment for Cellulose Hydrolysis by Carbon Dioxide Explosion. *Biotechnology Progress*, 14:890–896, 1998. ISSN 1520-6033. doi: 10.1021/bp980087g.
- [66] E. Tomás-Pejó, P. Alvira, M. Ballesteros, and M. J. Negro. Chapter 7 - Pretreatment Technologies for Lignocellulose-to-Bioethanol Conversion. In Ashok Pandey, Christian Larroche, Steven C. Ricke, Claude-Gilles Dussap, and Edgard Gnansounou, editors, *Biofuels*, pages 149 – 176. Academic Press, Amsterdam, 2011. ISBN 978-0-12-385099-7. doi: 10.1016/B978-0-12-385099-7.00007-3. URL <http://www.sciencedirect.com/science/article/pii/B9780123850997000073>.
- [67] Badal C. Saha, Loren B. Iten, Michael A. Cotta, and Y. Victor Wu. Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol. *Process Biochemistry*, 40:3693–3700, 2005. ISSN 1359-5113. doi: <http://dx.doi.org/10.1016/j.procbio.2005.04.006>.
- [68] M. J. Taherzadeh and K. Karimi. Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review. *International Journal of Molecular Sciences*, 9:1621–51, September 2008. doi: 10.3390/ijms9091621.

Bibliography

- [69] Ye Sun and Jiayang Cheng. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*, 83:1–11, 2002. ISSN 0960-8524. doi: [http://dx.doi.org/10.1016/S0960-8524\(01\)00212-7](http://dx.doi.org/10.1016/S0960-8524(01)00212-7).
- [70] P Harmsen and W Huijgen. Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass. *Energy*, (September):1–49, 2010. ISSN 9789085857570. URL <http://www.ecn.nl/docs/library/report/2010/e10013.pdf>.
- [71] Carlos Martín, Helene B. Klinke, and Anne Belinda Thomsen. Wet oxidation as a pretreatment method for enhancing the enzymatic convertibility of sugarcane bagasse. *Enzyme and Microbial Technology*, 40:426–432, 2007. ISSN 0141-0229. doi: <http://dx.doi.org/10.1016/j.enzmictec.2006.07.015>.
- [72] Nahyun Park, Hye-Yun Kim, Bon-Wook Koo, Hwanmyeong Yeo, and In-Gyu Choi. Organosolv pretreatment with various catalysts for enhancing enzymatic hydrolysis of pitch pine (*Pinus rigida*). *Bioresource Technology*, 101:7046–7053, 2010. ISSN 0960-8524. doi: <http://dx.doi.org/10.1016/j.biortech.2010.04.020>.
- [73] Xuebing Zhao, Keke Cheng, and Dehua Liu. Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. *Applied Microbiology and Biotechnology*, 82(5):815–827, 2009. ISSN 0025300918831. doi: 10.1007/s00253-009-1883-1.
- [74] F. M. Gírio, C. Fonseca, F. Carvalheiro, L. C. Duarte, S. Marques, and R. Bogel-Lukasik. Hemicelluloses for fuel ethanol: A review. *Bioresource Technology*, 101:4775–4800, 2010. ISSN 0960-8524. doi: <http://dx.doi.org/10.1016/j.biortech.2010.01.088>.
- [75] Anantharam P. Dadi, Sasidhar Varanasi, and Constance A. Schall. Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step. *Biotechnology and Bioengineering*, 95:904–910, 2006. ISSN 1097-0290. doi: 10.1002/bit.21047.
- [76] Carmen Sánchez. Lignocellulosic residues: Biodegradation and bioconversion by fungi. *Biotechnology Advances*, 27(2):185 – 194, 2009. ISSN 0734-9750. doi: <https://doi.org/10.1016/j.biotechadv.2008.11.001>. URL <http://www.sciencedirect.com/science/article/pii/S0734975008001092>.
- [77] Sheldon J. B. Duff and William D. Murray. Bioconversion of forest products industry waste cellulose to fuel ethanol: A review. *Bioresource Technology*, 55:1–33, 1996. ISSN 0960-8524. doi: [http://dx.doi.org/10.1016/0960-8524\(95\)00122-0](http://dx.doi.org/10.1016/0960-8524(95)00122-0).
- [78] Ramesh Chander Kuhad, Rishi Gupta, Yogender Pal Khasa, Ajay Singh, and Y. H. Percival Zhang. Bioethanol production from pentose sugars: Current status and future prospects. *Renewable and Sustainable Energy Reviews*, 15:4950–4962, 2011. ISSN 1364-0321. doi: <http://dx.doi.org/10.1016/j.rser.2011.07.058>.
- [79] W. E. Mabee, P. N. McFarlane, and J. N. Saddler. Biomass availability for lignocellulosic

- ethanol production. *Biomass and Bioenergy*, 35:4519–4529, 2011. ISSN 0961-9534. doi: <http://dx.doi.org/10.1016/j.biombioe.2011.06.026>.
- [80] Ghasem D. Najafpour. CHAPTER 7 - Downstream Processing. In Ghasem D. Najafpour, editor, *Biochemical Engineering and Biotechnology*, pages 170 – 198. Elsevier, Amsterdam, 2007. ISBN 978-0-444-52845-2. doi: 10.1016/B978-044452845-2/50007-0. URL <http://www.sciencedirect.com/science/article/pii/B9780444528452500070>.
- [81] Joseph J. Bozell and Gene R. Petersen. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. *Green Chem.*, 12(4):539–554, 2010. doi: 10.1039/B922014C. URL <http://dx.doi.org/10.1039/B922014C>.
- [82] R. Taylor, L. Nattrass, G. Alberts, P. Robson, C. Chudziak, A. Bauen, I. M. Libelli, G. Lotti, M. Prussi, R. Nistri, D. Chiaramonti, A. M. López Contreras, H. L. Bos, G. Eggink, J. Springer, R. Bakker, and R. van Ree. From the Sugar Platform to biofuels and biochemicals : Final report for the European Commission Directorate-General Energy. Technical report, E4tech/RECORD/Wageningen UR, 2015. URL <http://library.wur.nl/WebQuery/wurpubs/492297>.
- [83] E4tech, nova-Institute, BTG, and DECHEMA. Roadmap for the Chemical Industry in Europe towards a Bioeconomy. Technical report, European Commission, 2019. URL <https://cordis.europa.eu/project/rcn/210288/factsheet/es>.
- [84] Sergey P. Verevkin, Vladimir N. Emel’yanenko, Elena N. Stepurko, Richardas V. Ralys, Dmitry H. Zaitsau, and Annegret Stark. Biomass-Derived Platform Chemicals: Thermodynamic Studies on the Conversion of 5-Hydroxymethylfurfural into Bulk Intermediates. *Industrial & Engineering Chemistry Research*, 48(22):10087–10093, November 2009. ISSN 0888-5885. doi: 10.1021/ie901012g. URL <https://doi.org/10.1021/ie901012g>.
- [85] Organic Compounds: Physical and Chemical Data, . URL http://www2.ucdsb.on.ca/tiss/stretton/database/organic_thermo.htm.
- [86] Björn Sandén and Karin Pettersson. *Systems Perspectives on Biorefineries 2014*. Chalmers University of Technology, 2014.
- [87] Michael Sauer, Danilo Porro, Diethard Mattanovich, and Paola Branduardi. Microbial production of organic acids: expanding the markets. *Trends in Biotechnology*, 26(2):100 – 108, 2008. ISSN 0167-7799. doi: <https://doi.org/10.1016/j.tibtech.2007.11.006>. URL <http://www.sciencedirect.com/science/article/pii/S0167779907003228>.
- [88] Tiago Lima de Albuquerque, Ivanildo José da Silva, Gorete Ribeiro de Macedo, and Maria Valderez Ponte Rocha. Biotechnological production of xylitol from lignocellulosic wastes: A review. *Process Biochemistry*, 49(11):1779 – 1789, 2014. ISSN 1359-5113. doi: <https://doi.org/10.1016/j.procbio.2014.07.010>. URL <http://www.sciencedirect.com/science/article/pii/S1359511314003961>.

Bibliography

- [89] Masoud Talebi Amiri. *Process design of 5-hydroxymethylfurfural (HMF) Process and integration in biorefineries, Master's Thesis*. PhD thesis, EPFL, Switzerland, 2014.
- [90] Emanuela Peduzzi. *Biomass To Liquids - Thermo-Economic Analysis and Multi-Objective Optimisation*. PhD thesis, EPFL, 2015.
- [91] Martin Gassner and François Maréchal. Thermo-economic optimisation of the polygeneration of synthetic natural gas (SNG), power and heat from lignocellulosic biomass by gasification and methanation. *Energy Environ. Sci.*, 5(2):5768–5789, 2012. doi: 10.1039/C1EE02867G. URL <http://dx.doi.org/10.1039/C1EE02867G>.
- [92] International Energy Agency. *Energy Technology Perspectives 2017*. 2017. doi: 10.1787/energy_tech-2017-en. URL https://www.oecd-ilibrary.org/content/publication/energy_tech-2017-en.
- [93] Standard Heats and Free Energies of Formation and Absolute Entropies of Organic Compounds, . URL <http://www.wiredchemist.com/chemistry/data/entropies-organic>.
- [94] Emma Aberg, Rana Adib, F. Appavou, A. Brown, B. Epp, F. Guerra, B. Kondev, H.E. Murdock, Scott Dwyer, E. Musolino, and J.L. Sawin. *REN21. 2018. Renewables 2018 Global Status Report*. Paris: REN21 Secretariat, 2018. ISBN 978-3-9818911-3-3.
- [95] Zhihong Yuan, Bingzhen Chen, Gürkan Sin, and Rafiqul Gani. State-of-the-art and progress in the optimization-based simultaneous design and control for chemical processes. *AIChE Journal*, 58(6):1640–1659, 2012. ISSN 1547-5905. doi: 10.1002/aic.13786. URL <http://dx.doi.org/10.1002/aic.13786>.
- [96] Matthew J. Metzger, Benjamin J. Glasser, Bilal Patel, Diane Hildebrandt, and David Glasser. Teaching process design through integrated process synthesis. *Chemical Engineering Education*, 46(4):260–270, 2012.
- [97] J. E. Hendry, D. F. Rudd, and J. D. Seader. Synthesis in the design of chemical processes. *AIChE Journal*, 19(1):1–15, 1973. ISSN 1547-5905. doi: 10.1002/aic.690190103. URL <http://dx.doi.org/10.1002/aic.690190103>.
- [98] V. Hlaváček. Synthesis in the design of chemical processes. *Computers & Chemical Engineering*, 2(1):67 – 75, 1978. ISSN 0098-1354. doi: [http://dx.doi.org/10.1016/0098-1354\(78\)80010-6](http://dx.doi.org/10.1016/0098-1354(78)80010-6). URL <http://www.sciencedirect.com/science/article/pii/0098135478800106>.
- [99] Naonori Nishida, George Stephanopoulos, and A. W. Westerberg. A review of process synthesis. *AIChE Journal*, 27(3):321–351, 1981. ISSN 1547-5905. doi: 10.1002/aic.690270302. URL <http://dx.doi.org/10.1002/aic.690270302>.
- [100] G Stephanopoulos. Synthesis of process flowsheets: an adventure in heuristic design or a utopia of mathematical programming? In *Foundations of Computer-Aided Chemical Process Design*, volume 2, page 439. Engineering Foundation New York, 1981.

- [101] P. Seferlis and M.C. Georgiadis. *The Integration of Process Design and Control*. Computer Aided Chemical Engineering. Elsevier Science, 2004. ISBN 978-0-08-047309-3. URL <https://books.google.ch/books?id=SkqDg-R9zU8C>.
- [102] J.M. Douglas. *Conceptual design of chemical processes*. McGraw-Hill chemical engineering series. McGraw-Hill, 1988. ISBN 978-0-07-017762-8. URL <https://books.google.ch/books?id=M6JTAAAAMAAJ>.
- [103] Bodo Linnhoff. Pinch analysis: a state-of-the-art overview: Techno-economic analysis. *Chemical engineering research & design*, 71(5):503–522, 1993.
- [104] IgnacioE. Grossmann, JoseAntonio Caballero, and Hector Yeomans. Mathematical programming approaches to the synthesis of chemical process systems. *Korean Journal of Chemical Engineering*, 16(4):407–426, 1999. ISSN 0256-1115. doi: 10.1007/BF02698263. URL <http://dx.doi.org/10.1007/BF02698263>.
- [105] CPLEX, . URL <https://ampl.com/products/solvers/solvers-we-sell/cplex/>.
- [106] Francisco Trespalacios and Ignacio E. Grossmann. Review of Mixed-Integer Nonlinear and Generalized Disjunctive Programming Methods. *Chemie Ingenieur Technik*, 86:991–1012, 2014. ISSN 1522-2640. doi: 10.1002/cite.201400037.
- [107] Ian C. Kemp. 2 - Key concepts of pinch analysis. In Ian C. Kemp, editor, *Pinch Analysis and Process Integration (Second Edition)*, pages 15 – 40. Butterworth-Heinemann, Oxford, second edition edition, 2007. ISBN 978-0-7506-8260-2. doi: 10.1016/B978-075068260-2.50007-9. URL <http://www.sciencedirect.com/science/article/pii/B9780750682602500079>.
- [108] T. Gundersen, IEA., and Trondheim SINTEF Energy Research. *A Process Integration PRIMER*. SINTEF Energy Research, 2000. URL <https://books.google.ch/books?id=KgqfXwAACAAJ>.
- [109] François Maréchal and Boris Kalitventzeff. Process integration: Selection of the optimal utility system. *Computers & Chemical Engineering*, 22:S149–S156, 1998. doi: 10.1016/S0098-1354(98)00049-0.
- [110] M. A. Duran and I. E. Grossmann. A mixed-integer nonlinear programming algorithm for process systems synthesis. *AIChE Journal*, 32(4):592–606, 1986. ISSN 1547-5905. doi: 10.1002/aic.690320408. URL <http://dx.doi.org/10.1002/aic.690320408>.
- [111] Léda Gerber, Martin Gassner, and François Maréchal. Systematic integration of LCA in process systems design: Application to combined fuel and electricity production from lignocellulosic biomass. *Computers & Chemical Engineering*, 35(7):1265 – 1280, 2011. ISSN 0098-1354. doi: <https://doi.org/10.1016/j.compchemeng.2010.11.012>. URL <http://www.sciencedirect.com/science/article/pii/S0098135410003595>.
- [112] Serina Ahlgren, Anna Björklund, Anna Ekman, Hanna Karlsson, Johanna Berlin, Pål Börjesson, Tomas Ekvall, Göran Finnveden, Matty Janssen, and Ingrid Strid. Review of methodological

Bibliography

- choices in LCA of biorefinery systems - key issues and recommendations. *Biofuels, Bioproducts and Biorefining*, 9(5):606–619, 2015. doi: 10.1002/bbb.1563. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/bbb.1563>.
- [113] Richard Turton. *Analysis, Synthesis, and Design of Chemical Processes*. Prentice Hall, Upper Saddle River, N.J, 3 edition, 2009. ISBN 978-0-13-512966-1.
- [114] Priscilla Caliendo, Laurence Tock, Adriano V. Ensinas, and François Marechal. Thermo-economic optimization of a Solid Oxide Fuel Cell – Gas turbine system fuelled with gasified lignocellulosic biomass. *Energy Conversion and Management*, 85:764 – 773, 2014. ISSN 0196-8904. doi: <https://doi.org/10.1016/j.enconman.2014.02.009>. URL <http://www.sciencedirect.com/science/article/pii/S0196890414001186>.
- [115] A. C. Kokossis, M. Tsakalova, and K. Pyrgakis. Design of integrated biorefineries. *Computers & Chemical Engineering*, 81:40 – 56, 2015. ISSN 0098-1354. doi: <https://doi.org/10.1016/j.compchemeng.2015.05.021>. URL <http://www.sciencedirect.com/science/article/pii/S0098135415002021>.
- [116] Edgard Gnansounou and Arnaud Dauriat. Techno-economic analysis of lignocellulosic ethanol: A review. *Bioresource Technology*, 101:4980–4991, 2010. ISSN 0960-8524. doi: <http://dx.doi.org/10.1016/j.biortech.2010.02.009>.
- [117] Martin Pfeffer, Walter Wukovits, Georg Beckmann, and Anton Friedl. Analysis and decrease of the energy demand of bioethanol-production by process integration. *Selected Papers from the 9th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction – PRES2006*, 27(16):2657–2664, November 2007. ISSN 1359-4311. doi: 10.1016/j.applthermaleng.2007.04.018. URL <http://www.sciencedirect.com/science/article/pii/S1359431107001780>.
- [118] Grace Pokoo-Aikins, Aubrey Heath, Ray A. Mentzer, M. Sam Mannan, William J. Rogers, and Mahmoud M. El-Halwagi. A multi-criteria approach to screening alternatives for converting sewage sludge to biodiesel. *Journal of Loss Prevention in the Process Industries*, 23:412–420, 2010. ISSN 0950-4230. doi: <http://dx.doi.org/10.1016/j.jlp.2010.01.005>.
- [119] Tanya Mohan and Mahmoud M. El-Halwagi. An algebraic targeting approach for effective utilization of biomass in combined heat and power systems through process integration. *Clean Technologies & Environmental Policy*, 9:13–25, 2007. ISSN 1618954X. doi: 10.1007/s10098-006-0051-x.
- [120] Robert Brunet, Gonzalo Guillén-Gosálbez, and Laureano Jiménez. Cleaner Design of Single-Product Biotechnological Facilities through the Integration of Process Simulation, Multi-objective Optimization, Life Cycle Assessment, and Principal Component Analysis. *Industrial & Engineering Chemistry Research*, 51(1):410–424, 2012. doi: 10.1021/ie2011577. URL <https://doi.org/10.1021/ie2011577>.

- [121] Norman Sammons Jr, Wei Yuan, Susilpa Bommareddy, Mario Eden, Burak Aksoy, and Harry Cullinan. A Systematic Approach to Determine Economic Potential and Environmental Impact of Biorefineries. In Jeżowski Jacek and Thullie Jan, editors, *Computer Aided Chemical Engineering*, volume Volume 26, pages 1135–1140. Elsevier, 2009. ISBN 1570-7946.
- [122] Denny Kok Sum Ng. Automated targeting for the synthesis of an integrated biorefinery. *Chemical Engineering Journal*, 162:67–74, 2010. ISSN 1385-8947. doi: <http://dx.doi.org/10.1016/j.cej.2010.04.061>.
- [123] José Ezequiel Santibañez-Aguilar, J. Betzabe González-Campos, José María Ponce-Ortega, Medardo Serna-González, and Mahmoud M. El-Halwagi. Optimal Planning of a Biomass Conversion System Considering Economic and Environmental Aspects. *Industrial & Engineering Chemistry Research*, 50(14):8558–8570, 2011. doi: 10.1021/ie102195g. URL <http://dx.doi.org/10.1021/ie102195g>.
- [124] Jiyong Kim, S. Murat Sen, and Christos T. Maravelias. An optimization-based assessment framework for biomass-to-fuel conversion strategies. *Energy Environ. Sci.*, 6(4):1093–1104, 2013. doi: 10.1039/C3EE24243A. URL <http://dx.doi.org/10.1039/C3EE24243A>.
- [125] Buping Bao, Denny K. S. Ng, Douglas H. S. Tay, Arturo Jiménez-Gutiérrez, and Mahmoud M. El-Halwagi. 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*, 35(8):1374 – 1383, 2011. ISSN 0098-1354. doi: <https://doi.org/10.1016/j.compchemeng.2011.04.013>. URL <http://www.sciencedirect.com/science/article/pii/S0098135411001475>.
- [126] Mariano Martín and Ignacio E. Grossmann. Superstructure optimization of Lignocellulosic Bioethanol plants. In S. Pierucci and G. Buzzi Ferraris, editors, *20th European Symposium on Computer Aided Process Engineering*, volume 28 of *Computer Aided Chemical Engineering*, pages 943 – 948. Elsevier, 2010. doi: 10.1016/S1570-7946(10)28158-0. URL <http://www.sciencedirect.com/science/article/pii/S1570794610281580>.
- [127] Maria-Ona Bertran, Rebecca Frauzem, Ana-Sofia Sanchez-Arcilla, Lei Zhang, John M. Woodley, and Rafiqul Gani. A generic methodology for processing route synthesis and design based on superstructure optimization. *Computers & Chemical Engineering*, 106:892 – 910, 2017. ISSN 0098-1354. doi: <https://doi.org/10.1016/j.compchemeng.2017.01.030>. URL <http://www.sciencedirect.com/science/article/pii/S0098135417300303>.
- [128] Pascual Eduardo Murillo-Alvarado, José María Ponce-Ortega, Medardo Serna-González, Agustín Jaime Castro-Montoya, and Mahmoud M. El-Halwagi. Optimization of Pathways for Biorefineries Involving the Selection of Feedstocks, Products, and Processing Steps. *Industrial & Engineering Chemistry Research*, 52:5177–5190, April 2013. ISSN 0888-5885. doi: 10.1021/ie303428v.

Bibliography

- [129] M. Alvarado-Morales, J. Terra, K. V. Gernaey, J. M. Woodley, and R. Gani. Biorefining: Computer aided tools for sustainable design and analysis of bioethanol production. *Chemical Engineering Research and Design*, 87(9):1171 – 1183, 2009. ISSN 0263-8762. doi: <https://doi.org/10.1016/j.cherd.2009.07.006>. URL <http://www.sciencedirect.com/science/article/pii/S0263876209001750>.
- [130] Lidija Čuček, Hon Loong Lam, Jiří J. Klemeš, Petar S. Varbanov, and Zdravko Kravanja. Synthesis of regional networks for the supply of energy and bioproducts. *Clean Technologies and Environmental Policy*, 12(6):635–645, December 2010. ISSN 1618-9558. doi: [10.1007/s10098-010-0312-6](https://doi.org/10.1007/s10098-010-0312-6). URL <https://doi.org/10.1007/s10098-010-0312-6>.
- [131] W. Alex Marvin, Lanny D. Schmidt, Saif Benjaafar, Douglas G. Tiffany, and Prodromos Daoutidis. Economic Optimization of a Lignocellulosic Biomass-to-Ethanol Supply Chain. *Chemical Engineering Science*, 67(1):68 – 79, 2012. ISSN 0009-2509. doi: <https://doi.org/10.1016/j.ces.2011.05.055>. URL <http://www.sciencedirect.com/science/article/pii/S0009250911003848>.
- [132] Daniel J. Garcia and Fengqi You. Multiobjective optimization of product and process networks: General modeling framework, efficient global optimization algorithm, and case studies on bioconversion. *AIChE Journal*, 61(2):530–554, 2015. doi: [10.1002/aic.14666](https://doi.org/10.1002/aic.14666). URL <https://aiche.onlinelibrary.wiley.com/doi/abs/10.1002/aic.14666>.
- [133] Fengqi You, Ling Tao, Diane J. Graziano, and Seth W. Snyder. Optimal design of sustainable cellulosic biofuel supply chains: Multiobjective optimization coupled with life cycle assessment and input–output analysis. *AIChE Journal*, 58(4):1157–1180, 2012. doi: [10.1002/aic.12637](https://doi.org/10.1002/aic.12637). URL <https://aiche.onlinelibrary.wiley.com/doi/abs/10.1002/aic.12637>.
- [134] Douglas H. S. Tay, Denny K. S. Ng, Norman E. Sammons, and Mario R. Eden. Fuzzy Optimization Approach for the Synthesis of a Sustainable Integrated Biorefinery. *Industrial & Engineering Chemistry Research*, 50(3):1652–1665, 2011. doi: [10.1021/ie1011239](https://doi.org/10.1021/ie1011239). URL <https://doi.org/10.1021/ie1011239>.
- [135] Richard C. Baliban, Josephine A. Elia, and Christodoulos A. Floudas. Biomass to liquid transportation fuels (BTL) systems: process synthesis and global optimization framework. *Energy & Environmental Science*, 6:267–287, 2013. ISSN 1754-5692. doi: [10.1039/C2EE23369J](https://doi.org/10.1039/C2EE23369J).
- [136] Adriano Viana Ensinas, Victor Codina Gironès, Juliana Queiroz Albarelli, François Maréchal, and Maria Aparecida Silva. Thermo-Economic Optimization of Integrated First and Second Generation Sugarcane Ethanol Plant. *CHEMICAL ENGINEERING TRANSACTIONS*, 35:523–528, 2013. doi: [10.3303/CET1335087](https://doi.org/10.3303/CET1335087).
- [137] Juliana Queiroz Albarelli, Sandro Onorati, Adriano Viana Ensinas, Priscilla Caliandro, Emanuela Peduzzi, and François Maréchal. Thermo-economic optimization of integrated ethanol and methanol production in the sugarcane industry. *CHEMICAL ENGINEERING TRANSACTIONS*, 2014.

- [138] Martin Gassner and François Maréchal. Methodology for the optimal thermo-economic, multi-objective design of thermochemical fuel production from biomass. *Computers and Chemical Engineering*, 33(3):769–781, 2009. ISSN 9780444531575. doi: 10.1016/j.compchemeng.2008.09.017.
- [139] Alexander M. Niziolek, Onur Onel, Josephine A. Elia, Richard C. Baliban, and Christodoulos A. Floudas. Coproduction of liquid transportation fuels and C₆-c₈ aromatics from biomass and natural gas. *AIChE Journal*, 61(3):831–856, 2015. doi: 10.1002/aic.14726. URL <https://aiche.onlinelibrary.wiley.com/doi/abs/10.1002/aic.14726>.
- [140] Alexis Duret, Claude Friedli, and François Maréchal. Process design of Synthetic Natural Gas (SNG) production using wood gasification. *Journal of Cleaner Production*, 13:1434–1446, 2005. ISSN 0959-6526. doi: <http://dx.doi.org/10.1016/j.jclepro.2005.04.009>.
- [141] Elvis Ahmetović, Mariano Martín, and Ignacio E. Grossmann. Optimization of Energy and Water Consumption in Corn-Based Ethanol Plants. *Industrial & Engineering Chemistry Research*, 49(17):7972–7982, 2010. doi: 10.1021/ie1000955. URL <https://doi.org/10.1021/ie1000955>.
- [142] Emre Gencer, Dharik Mallapragada, Mohit Tawarmalani, and Rakesh Agrawal. Synergistic Biomass and Natural Gas Conversion to Liquid Fuel with Reduced CO₂ Emissions. In Mario R. Eden, John D. Sirola, and Gavin P. Towler, editors, *Proceedings of the 8th International Conference on Foundations of Computer-Aided Process Design*, volume 34 of *Computer Aided Chemical Engineering*, pages 525 – 530. Elsevier, 2014. doi: 10.1016/B978-0-444-63433-7.50072-9. URL <http://www.sciencedirect.com/science/article/pii/B9780444634337500729>.
- [143] M. Gassner and F. Maréchal. Thermo-economic optimisation of the integration of electrolysis in synthetic natural gas production from wood. *Energy*, 33(2):189 – 198, 2008. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2007.09.010>. URL <http://www.sciencedirect.com/science/article/pii/S0360544207001764>.
- [144] Rakesh Agrawal, Navneet R. Singh, Fabio H. Ribeiro, and W. Nicholas Delgass. Sustainable fuel for the transportation sector. *Proceedings of the National Academy of Sciences*, 104(12):4828–4833, 2007. ISSN 0027-8424. doi: 10.1073/pnas.0609921104. URL <https://www.pnas.org/content/104/12/4828>.
- [145] Konstantinos A. Pyrgakis and Antonios C. Kokossis. A Total Site Synthesis approach for the selection, integration and planning of multiple-feedstock biorefineries. *Computers & Chemical Engineering*, 122:326 – 355, 2019. ISSN 0098-1354. doi: <https://doi.org/10.1016/j.compchemeng.2018.09.003>. URL <http://www.sciencedirect.com/science/article/pii/S0098135418309293>.
- [146] Qing Jin, Liangcheng Yang, Nicholas Poe, and Haibo Huang. Integrated processing of plant-derived waste to produce value-added products based on the biorefinery concept. *Trends in Food Science & Technology*, 74:119 – 131, 2018. ISSN 0924-2244. doi: <https://doi.org/10.1016/j>

Bibliography

- tifs.2018.02.014. URL <http://www.sciencedirect.com/science/article/pii/S0924224417305459>.
- [147] Lin Luo, Ester van der Voet, and Gjalt Huppes. Biorefining of lignocellulosic feedstock – Technical, economic and environmental considerations. *Bioresource Technology*, 101(13): 5023 – 5032, 2010. ISSN 0960-8524. doi: <https://doi.org/10.1016/j.biortech.2009.12.109>. URL <http://www.sciencedirect.com/science/article/pii/S0960852409018070>.
- [148] Merten Morales, Meric Ataman, Sara Badr, Sven Linster, Ioannis Kourlimpinis, Stavros Papadokostantakis, Vassily Hatzimanikatis, and Konrad Hungerbuhler. Sustainability Assessment of Succinic Acid Production Technologies from Biomass using Metabolic Engineering. *Energy & Environmental Science*, 2016. ISSN 1754-5692. doi: 10.1039/C6EE00634E.
- [149] Sampath Gunukula, Sharon J. W. Klein, Hemant P. Pendse, William J. DeSisto, and M. Clayton Wheeler. Techno-economic analysis of thermal deoxygenation based biorefineries for the coproduction of fuels and chemicals. *Applied Energy*, 214:16 – 23, 2018. ISSN 0306-2619. doi: <https://doi.org/10.1016/j.apenergy.2018.01.065>. URL <http://www.sciencedirect.com/science/article/pii/S030626191830076X>.
- [150] Ayse Dilan Celebi, Adriano Viana Ensinas, Shivom Sharma, and François Maréchal. Early-stage decision making approach for the selection of optimally integrated biorefinery processes. *Energy*, 137:908–916, October 2017. ISSN 0360-5442. doi: 10.1016/j.energy.2017.03.080. URL <http://www.sciencedirect.com/science/article/pii/S0360544217304565>.
- [151] G. D. Ulrich and P. T. Vasudevan. *Chemical Engineering Process Design and Economics: A Practical Guide*. CRC Press, 2 edition, 2003. ISBN 978-0-9708768-2-9.
- [152] Gregor Wernet, Christian Bauer, Bernhard Steubing, Jürgen Reinhard, Emilia Moreno-Ruiz, and Bo Weidema. The ecoinvent database version 3 (part I): overview and methodology. *The International Journal of Life Cycle Assessment*, 21:1218–1230, 2016. ISSN 1614-7502. doi: 10.1007/s11367-016-1087-8.
- [153] Samira Fazlollahi, Pierre Mandel, Gwenaëlle Becker, and Francois Maréchal. Methods for multi-objective investment and operating optimization of complex energy systems. *Energy*, 45(1):12–22, 2012. ISSN 0360-5442. doi: 10.1016/j.energy.2012.02.046. URL <http://dx.doi.org/10.1016/j.energy.2012.02.046>.
- [154] Y Y. Haimes, Leon Lasdon, and D A. Wismer. On a Bicriterion Formulation of the Problems of Integrated System Identification and System Optimization. *IEEE Transactions on Systems, Man, and Cybernetics - TSMC*, 1:296–297, 1971. doi: 10.1109/TSMC.1971.4308298.
- [155] Jung-Fa Tsai, Ming-Hua Lin, and Yi-Chung Hu. Finding multiple solutions to general integer linear programs. *European Journal of Operational Research*, 184(2):802 – 809, 2008. ISSN 0377-2217. doi: <http://dx.doi.org/10.1016/j.ejor.2006.11.024>. URL <http://www.sciencedirect.com/science/article/pii/S0377221706011611>.

- [156] N. V. Sahinidis, I. E. Grossmann, R. E. Fornari, and M. Chathrathi. Optimization model for long range planning in the chemical industry. *Computers & Chemical Engineering*, 13(9):1049 – 1063, 1989. ISSN 0098-1354. doi: [http://dx.doi.org/10.1016/0098-1354\(89\)87046-2](http://dx.doi.org/10.1016/0098-1354(89)87046-2). URL <http://www.sciencedirect.com/science/article/pii/0098135489870462>.
- [157] Stefano Maronese, Adriano V. Ensinas, Alberto Mian, Andrea Lazzaretto, and François Maréchal. Optimum Biorefinery Pathways Selection Using the Integer-Cuts Constraint Method Applied to a MILP Problem. *Industrial & Engineering Chemistry Research*, 54:7038–7046, July 2015. ISSN 0888-5885. doi: 10.1021/acs.iecr.5b01439.
- [158] Min-Jung Yoo, Lindsay Lessard, Maziar Kermani, Francois Marechal, Kv Gernaey, Jk Huusom, and R. Gani. OsmoseLua - An Integrated Approach to Energy Systems Integration with LCIA and GIS. In *Computer Aided Chemical Engineering*, volume 37, pages 587–592. Elsevier, 2015.
- [159] AMPL Optimization Inc., . URL <https://ampl.com/products/ampl/>.
- [160] ASPEN PLUS. Aspen Technology Inc., 2010. URL www.aspentech.com.
- [161] BELSIM VALI. Belsim S.A. URL www.belsim.com.
- [162] Martin Gassner and François Maréchal. Thermo-economic process model for thermochemical production of Synthetic Natural Gas (SNG) from lignocellulosic biomass. *Biomass and Bioenergy*, 33:1587–1604, 2009. doi: 10.1016/j.biombioe.2009.08.004.
- [163] I. A. Panagiotopoulos, R. P. Chandra, and J. N. Saddler. A two-stage pretreatment approach to maximise sugar yield and enhance reactive lignin recovery from poplar wood chips. *Bioresour. Technol.*, 130:570 – 577, 2013. ISSN 0960-8524. doi: <https://doi.org/10.1016/j.biortech.2012.12.093>. URL <http://www.sciencedirect.com/science/article/pii/S0960852412019517>.
- [164] Morales Merten. Wood2chem Project. URL https://www.rdb.ethz.ch/projects/project.php?proj_id=32132&int=0.
- [165] Merten Morales, Pierre Y. Dapsens, Isabella Giovinazzo, Julia Witte, Cecilia Mondelli, Stavros Papadokonstantakis, Konrad Hungerbühler, and Javier Pérez-Ramírez. Environmental and economic assessment of lactic acid production from glycerol using cascade bio- and chemocatalysis. *Energy Environ. Sci.*, 8(2):558–567, 2015. doi: 10.1039/C4EE03352C. URL <http://dx.doi.org/10.1039/C4EE03352C>.
- [166] Marios Batsos. *Study of potential bio-chemicals production from ethanol*. PhD thesis, 2014.
- [167] Maxence Fache, Bernard Boutevin, and Sylvain Caillol. Vanillin Production from Lignin and Its Use as a Renewable Chemical. *ACS Sustainable Chemistry & Engineering*, 4(1):35–46, January 2016. doi: 10.1021/acssuschemeng.5b01344. URL <http://dx.doi.org/10.1021/acssuschemeng.5b01344>.
- [168] F. G. Sales, C. A. M. Abreu, and Jafr Pereira. Catalytic wet-air oxidation of lignin in a three-phase

Bibliography

- reactor with aromatic aldehyde production. *Brazilian Journal of Chemical Engineering*, 21: 211–218, 2004.
- [169] Diego T. Santos, Boutros F. Sarrouh, Juan D. Rivaldi, Attilio Converti, and Silvio S. Silva. Use of sugarcane bagasse as biomaterial for cell immobilization for xylitol production. *Journal of Food Engineering*, 86(4):542–548, June 2008. ISSN 0260-8774. doi: 10.1016/j.jfoodeng.2007.11.004. URL <http://www.sciencedirect.com/science/article/pii/S0260877407005687>.
- [170] Anna Sophia Wallerand, Juliana Queiroz Albarelli, Adriano Viana Ensinas, Gianluca Ambrosetti, Alberto Mian, François Maréchal, and Ron Zevenhoven. Multi-objective Optimization of a Solar Assisted 1st and 2nd Generation Sugarcane Ethanol Production Plant, June 2014.
- [171] Stefan Heyne and Simon Harvey. Impact of choice of CO₂ separation technology on thermo-economic performance of Bio-SNG production processes. *International Journal of Energy Research*, 38(3):299–318, 2014. doi: 10.1002/er.3038. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/er.3038>.
- [172] Economic Indicators: CEPCI - Chemical Engineering, March 2015, 2015. URL <https://www.chemengonline.com/economic-indicators-cepci/?printmode=1>.
- [173] Bioethanol in Europe Overview and comparison of production processes Rapport 2gave0601. Technical report, SenterNovem GAVE programme, . URL www.senternovem.nl/gave.
- [174] Credit Suisse Average Foreign Exchange Rates as per end of december 2015, 2015. URL <https://www.credit-suisse.com/ch/en/unternehmen/unternehmen-unternehmer/kmugrossunternehmen/internationale-geschaefte/devisen.html>.
- [175] Nethaji J. Gallage and Birger Lindberg Møller. Vanillin–Bioconversion and Bioengineering of the Most Popular Plant Flavor and Its De Novo Biosynthesis in the Vanilla Orchid. *Molecular Plant*, 8(1):40 – 57, 2015. ISSN 1674-2052. doi: <https://doi.org/10.1016/j.molp.2014.11.008>. URL <http://www.sciencedirect.com/science/article/pii/S1674205214000094>.
- [176] Sergio da Cunha, G. P. Rangaiah, and Kus Hidajat. Retrofitting via Intensification: Application to Formic Acid Process. In Antonio Espuña, Moisès Graells, and Luis Puigjaner, editors, *27th European Symposium on Computer Aided Process Engineering*, volume 40 of *Computer Aided Chemical Engineering*, pages 1093 – 1098. Elsevier, 2017. doi: 10.1016/B978-0-444-63965-3.50184-7. URL <http://www.sciencedirect.com/science/article/pii/B9780444639653501847>.
- [177] Ephy Kouzi Eleni Karachaliou Evangelia Tsagaraki, Iakovos Deligiannis. Bio-based products and applications potential. May 2017. doi: 10.5281/zenodo.1434287. URL <https://zenodo.org/record/1434287#.XTcHI0dS9JQ>.
- [178] BIOREF-INTEG Deliverable 2 Total Identification and market analysis of most promising added-value products to be co-produced with the fuels. Technical report, Aston University,

2010. URL http://www.bioref-integ.eu/fileadmin/bioref-integ/user/documents/D2total_including_D2.1__D2.2__D2.3_.pdf.
- [179] Daniela Thrän, David Peetz, Kay Schaubach, Sofia Backéus, Luca Benedetti, Lena Bruce, Suani Coelho, Laura Craggs, Rocío Díaz-Chavez, Javier Farago Escobar, Jose Goldemberg, Ruben Guisson, Morten Tony Hansen, Jussi Heinimö, Bo Hektor, J Hess, Martin Junginger, Patrick Lamers, Thuy Mai-Moulin, and Michael Wild. *Global Wood Pellet Industry and Trade Study 2017*. January 2018.
- [180] Siti Noorain Mohamad Yousoff, 'Amirah Baharin, and Afnizanfaizal Abdullah. Differential Search Algorithm in Deep Neural Network for the Predictive Analysis of Xylitol Production in Escherichia Coli. In Mohamed Sultan Mohamed Ali, Herman Wahid, Nurul Adilla Mohd Subha, Shafishuhaza Sahlan, Mohd Amri Md. Yunus, and Ahmad Ridhwan Wahap, editors, *Modeling, Design and Simulation of Systems*, pages 53–67, Singapore, 2017. Springer Singapore. ISBN 978-981-10-6502-6.
- [181] International industrial energy prices, 2014. URL <https://www.gov.uk/government/statistical-data-sets/international-industrial-energy-prices>.
- [182] Debalina Sengupta. *Chemicals from Biomass: Integrating Bioprocesses into Chemical Production Complexes for Sustainable Development*. July 2012. ISBN 978-1-4398-7814-9. doi: 10.1201/b12341.
- [183] Juliana Allbarelli, Diego Santos, Adriano Ensinas, François Maréchal, and M. Angela Meireles. *Thermo-economic evaluation of enzymatic-based sugarcane biorefinery route by experimental design approach: Identifying and overcoming bottlenecks*, volume 34. January 2016.
- [184] Wenjing Fu. *Process Design and Evaluation for Chemicals Based on Renewable Resources*. PhD Thesis, Technical University of Denmark, Department of Chemical Engineering, 2012.
- [185] John A. Posada and Carlos A. Cardona. Propionic Acid Production from Raw Glycerol Using Commercial and Engineered Strains. *Industrial & Engineering Chemistry Research*, 51(5): 2354–2361, February 2012. ISSN 0888-5885. doi: 10.1021/ie201300d. URL <https://doi.org/10.1021/ie201300d>.
- [186] Pedro Haro, Filip Johnsson, and Henrik Thunman. Improved syngas processing for enhanced Bio-SNG production: A techno-economic assessment. *Energy*, 101:380 – 389, 2016. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2016.02.037>. URL <http://www.sciencedirect.com/science/article/pii/S0360544216300809>.
- [187] World Bank Commodities Price Data (The Pink Sheet) 2015. Text/HTML, 2018. URL <http://www.worldbank.org/commodities>.
- [188] Emanuela Peduzzi, Guillaume Boissonnet, Geert Haarlemmer, and François Maréchal. Thermo-economic analysis and multi-objective optimisation of lignocellulosic biomass

Bibliography

- conversion to Fischer–Tropsch fuels. *Sustainable Energy Fuels*, 2(5):1069–1084, 2018. doi: 10.1039/C7SE00468K. URL <http://dx.doi.org/10.1039/C7SE00468K>.
- [189] Methanol prices for north america, europe and asia, . URL <https://www.methanex.com/our-business/pricing>.
- [190] Change Intergovernmental Panel on Climate. *Climate Change 2013 – The Physical Science Basis: Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, 2014. ISBN 978-1-107-41532-4.
- [191] Ecoinvent Version 3.2 (2015) Database, 2015. URL <https://www.ecoinvent.org/>.
- [192] Martin Gassner. *Process Design Methodology for Thermochemical Production of Fuels from Biomass Application to the Production of Synthetic Natural Gas from Lignocellulosic Resources*. PhD thesis, École Polytechnique Fédérale de Lausanne, Switzerland, 2010. URL <http://infoscience.epfl.ch/record/147963>.
- [193] Ayse Dilan Celebi, Shivom Sharma, Adriano Viana Ensinas, and François Maréchal. Next generation cogeneration system for industry – Combined heat and fuel plant using biomass resources. *Chemical Engineering Science*, 204:59 – 75, 2019. ISSN 0009-2509. doi: <https://doi.org/10.1016/j.ces.2019.04.018>. URL <http://www.sciencedirect.com/science/article/pii/S0009250919303847>.
- [194] Energy Information Administration (U.S.) and Government Publications Office. *International Energy Outlook 2016: With Projections to 2040*. Government Printing Office, August 2016. ISBN 978-0-16-093333-2. Google-Books-ID: O6qH071W1PYC.
- [195] Elie Bellevrat. Commentary: Clean and efficient heat for industry, 2018. URL <https://www.iea.org/newsroom/news/2018/january/commentary-clean-and-efficient-heat-for-industry.html>.
- [196] Sven Werner. ECOHEATCOOL: European Heating and Cooling Market Study, Ecoheatcool Work Package 1. Technical report, Euroheat & Power, 2006. URL https://www.euroheat.org/wp-content/uploads/2016/02/Ecoheatcool_WP1_Web.pdf.
- [197] Tobias Naegler, Sonja Simon, Martin Klein, and Hans Christian Gils. Quantification of the European industrial heat demand by branch and temperature level. *International Journal of Energy Research*, 39(15):2019–2030, 2015. doi: 10.1002/er.3436. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/er.3436>.
- [198] Nico Woudstra and Teus van der Stelt. EXERGY ANALYSIS OF COMBUSTION SYSTEMS. *Proceedings of the International ECOS Conference, Copenhagen, Denmark*, page 8, 2003.
- [199] Andrea Egeskog, Julia Hansson, Göran Berndes, and Sven Werner. Co-generation of bio-fuels for transportation and heat for district heating systems—an assessment of the na-

- tional possibilities in the EU. *Energy Policy*, 37(12):5260 – 5272, 2009. ISSN 0301-4215. doi: <https://doi.org/10.1016/j.enpol.2009.07.071>. URL <http://www.sciencedirect.com/science/article/pii/S0301421509005679>.
- [200] Kristina Holmgren. *Integration Aspects of Biomass Gasification in Large Industrial or Regional Energy Systems - Consequences for Greenhouse Gas Emissions and Economic Performance*. PhD Thesis, CHALMERS UNIVERSITY OF TECHNOLOGY, Industrial Energy Systems and Technologies Department of Energy and Environment, 2015.
- [201] T. Damartzis and A. Zabaniotou. Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review. *Renewable and Sustainable Energy Reviews*, 15(1):366 – 378, 2011. ISSN 1364-0321. doi: <https://doi.org/10.1016/j.rser.2010.08.003>. URL <http://www.sciencedirect.com/science/article/pii/S1364032110002558>.
- [202] Shivom Sharma, Ayse Dilan Celebi, and François Maréchal. Robust multi-objective optimization of gasifier and solid oxide fuel cell plant for electricity production using wood. *Energy*, 137 (Supplement C):811–822, October 2017. ISSN 0360-5442. doi: 10.1016/j.energy.2017.04.146. URL <http://www.sciencedirect.com/science/article/pii/S0360544217307211>.
- [203] Erik Pihl, Stefan Heyne, Henrik Thunman, and Filip Johnsson. Highly efficient electricity generation from biomass by integration and hybridization with combined cycle gas turbine (CCGT) plants for natural gas. *Energy*, 35(10):4042 – 4052, 2010. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2010.06.008>. URL <http://www.sciencedirect.com/science/article/pii/S0360544210003221>.
- [204] Stefano Consonni, Ryan E. Katofsky, and Eric D. Larson. A gasification-based biorefinery for the pulp and paper industry. *Chemical Engineering Research and Design*, 87(9):1293 – 1317, 2009. ISSN 0263-8762. doi: <https://doi.org/10.1016/j.cherd.2009.07.017>. URL <http://www.sciencedirect.com/science/article/pii/S0263876209001804>.
- [205] J. Isaksson, K. Pettersson, M. Mahmoudkhani, A. Asblad, and T. Berntsson. Integration of biomass gasification with a Scandinavian mechanical pulp and paper mill - consequences for mass and energy balances and global CO₂ emissions. *Energy (Oxford)*, 44(1):420–428, 2012. ISSN 0360-5442. doi: 10.1016/j.energy.2012.06.013.
- [206] Elisabeth Wetterlund, Karin Pettersson, and Simon Harvey. Systems analysis of integrating biomass gasification with pulp and paper production – Effects on economic performance, CO₂ emissions and energy use. *Energy*, 36(2):932 – 941, 2011. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2010.12.017>. URL <http://www.sciencedirect.com/science/article/pii/S0360544210007073>.
- [207] E. Andersson and S. Harvey. Comparison of pulp-mill-integrated hydrogen production from gasified black liquor with stand-alone production from gasified biomass. *Energy*, 32(4): 399 – 405, 2007. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2006.06.021>. URL

Bibliography

- <http://www.sciencedirect.com/science/article/pii/S0360544206001575>.
- [208] Ilkka Hannula and Esa Kurkela. Liquid transportation fuels via large-scale fluidised-bed gasification of lignocellulosic biomass. Technical Report VTT Technology 91, VTT Technical Research Centre of Finland, 2013.
- [209] G. H. Huisman, G. L. M. A. Van Rens, H. De Lathouder, and R. L. Cornelissen. Cost estimation of biomass-to-fuel plants producing methanol, dimethylether or hydrogen. *Biomass and Bioenergy*, 35:S155 – S166, 2011. ISSN 0961-9534. doi: <https://doi.org/10.1016/j.biombioe.2011.04.038>. URL <http://www.sciencedirect.com/science/article/pii/S0961953411002406>.
- [210] Kristina M. Holmgren, Thore S. Berntsson, Eva Andersson, and Tomas Rydberg. Comparison of integration options for gasification-based biofuel production systems – Economic and greenhouse gas emission implications. *Energy*, 111:272 – 294, 2016. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2016.05.059>. URL <http://www.sciencedirect.com/science/article/pii/S0360544216306764>.
- [211] Roman Hackl and Simon Harvey. Opportunities for Process Integrated Biorefinery Concepts in the Chemical Cluster in Stenungsund. Technical report, CHALMERS UNIVERSITY OF TECHNOLOGY, Department of Energy and Environment, Division of Heat and Power Technology, 2010.
- [212] Maria Arvidsson, Stefan Heyne, Matteo Morandin, and Simon Harvey. Integration Opportunities for Substitute Natural Gas (SNG) Production in an Industrial Process Plant. In *Chemical Engineering Transactions*, volume 29, 2012. doi: 10.3303/CET1229056.
- [213] Daniella Johansson, Per-Åke Franck, Karin Pettersson, and Thore Berntsson. Comparative study of Fischer–Tropsch production and post-combustion CO₂ capture at an oil refinery: Economic evaluation and GHG (greenhouse gas emissions) balances. *Energy*, 59:387 – 401, 2013. ISSN 0360-5442. doi: <https://doi.org/10.1016/j.energy.2013.07.024>. URL <http://www.sciencedirect.com/science/article/pii/S0360544213006117>.
- [214] Hans-Werner Sinn. Buffering volatility: A study on the limits of Germany’s energy revolution. *European Economic Review*, 99:130 – 150, 2017. ISSN 0014-2921. doi: <https://doi.org/10.1016/j.eurocorev.2017.05.007>. URL <http://www.sciencedirect.com/science/article/pii/S0014292117300995>.
- [215] Ivan Daniel Kantor, Anna Sophia Wallerand, Maziar Kermani, Hür Ebuzer Bütün, Alessio Santecchia, Franz Wolf, Greta Martha Van Eetvelde, and François Maréchal. Thermal profile construction for energy-intensive industrial sectors. In *Proceedings of the 31st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, 2018.
- [216] Tobias Naegler, Sonja Simon, Martin Klein, and Hans Christian Gils. Quantification of the European industrial heat demand by branch and temperature level. *International Journal*

- of Energy Research*, 39(15):2019–2030. doi: 10.1002/er.3436. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/er.3436>.
- [217] S Werner. *The European Heat Market: Final Report*. Brussels: Euroheat and Power, 2006.
- [218] Nicolas Pardo Garcia, Konstaninos Vatopoulos, Anna Krook-Riekkola, Alicia Perez Lopez, and Lars Olsen. Best available technologies for the heat and cooling market in the European Union. Technical Report 978-92-79-25970-8 (ISBN), Publications Office of the European Union, Luxemburg, 2012. URL <http://urn.kb.se/resolve?urn=urn:nbn:se:ltu:diva-22355>.
- [219] Benjamin Köhler, Jörg Dengler, Arnulf Dinkel, Mauman Azam, Doreen Kalz, Paolo Bonato, Fleitern Tobias, Jan Steinbach, Mario Ragwitz, Marlene Arens, Ali Aydemir, Rainer Elsland, Clemens Frassine, Andrea Herbst, Simon Hirzel, Michael Krail, Matthias Reuter, Felipe Toro, Matthias Rehfeldt, and Martin Jakob. Mapping and analyses of the current and future (2020-2030) heating/cooling fuel deployment (fossil/renewables) Work package 2: Assessment of the technologies for the year 2012. Technical report, EUROPEAN COMMISSION DIRECTORATE-GENERAL FOR ENERGY, September 2016.
- [220] Inc. Energy and Environmental Analysis. Characterization of the U.S. Industrial/Commercial Boiler Population - Final Report. Technical report, Oak Ridge National Laboratory, 2005. URL <https://www.energy.gov/eere/amo/downloads/characterization-us-industrialcommercial-boiler-population-final-report-may-2005>.
- [221] Regina Betz, Thomas Leu, and Reto Schleiniger. Disentangling the effects of Swiss energy and climate policies. Technical report, Winterthur : ZHAW Zürcher Hochschule für Angewandte Wissenschaften, 2015. URL <https://digitalcollection.zhaw.ch/handle/11475/1009>.
- [222] calculator.energyscope.ch, . URL <http://calculator.energyscope.ch/>.
- [223] Víctor Codina Gironès, Emanuela Peduzzi, François Vuille, and François Maréchal. On the Assessment of the CO₂ Mitigation Potential of Woody Biomass. *Frontiers in Energy Research*, 5:37, 2018. ISSN 2296-598X. doi: 10.3389/fenrg.2017.00037. URL <https://www.frontiersin.org/article/10.3389/fenrg.2017.00037>.
- [224] Martin Densing, Stefan Hirschberg, and Hal Turton. Review of Swiss Electricity Scenarios 2050. Technical Report PSI Bericht Nr. 14-05, Paul Scherrer Institut (PSI), Villigen, Switzerland, 2014.
- [225] Martin Thema, Michael Sterner, Thorsten Lenck, and Philipp Götz. Necessity and Impact of Power-to-gas on Energy Transition in Germany. *Energy Procedia*, 99:392 – 400, 2016. ISSN 1876-6102. doi: <https://doi.org/10.1016/j.egypro.2016.10.129>. URL <http://www.sciencedirect.com/science/article/pii/S1876610216310906>.
- [226] M. Sterner. *Bioenergy and Renewable Power Methane In Integrated 100% Renewable Energy Systems: Limiting Global Warming By Transforming Energy Systems*. Erneuerbare Energien

Bibliography

- und Energieeffizienz - Renewable Energies and Energy Efficiency. Kassel University Press, 2009. ISBN 978-3-89958-799-9. URL https://books.google.ch/books?id=5Rzza2R8j_UC.
- [227] Martin Steurer, Ulrich Fahl, Alfred Voß, and Paul Deane. Chapter 15 - Curtailment: An Option for Cost-Efficient Integration of Variable Renewable Generation? In Manuel Welsch, Steve Pye, Dogan Keles, Aurélie Faure-Schuyer, Audrey Dobbins, Abhishek Shivakumar, Paul Deane, and Mark Howells, editors, *Europe's Energy Transition - Insights for Policy Making*, pages 97 – 104. Academic Press, 2017. ISBN 978-0-12-809806-6. doi: 10.1016/B978-0-12-809806-6.00015-8. URL <http://www.sciencedirect.com/science/article/pii/B9780128098066000158>.
- [228] Dodiak Ika Candra, Kilian Hartmann, and Michael Nelles. Economic Optimal Implementation of Virtual Power Plants in the German Power Market. *Energies*, 11(9), 2018. ISSN 1996-1073. doi: 10.3390/en11092365. URL <http://www.mdpi.com/1996-1073/11/9/2365>.
- [229] Michael Pollitt and Karim Anaya. Can current electricity markets cope with high share of renewables A comparison of approaches in Germany, the UK and the State of New York. *The Energy Journal*, 37, 2016. doi: 10.5547/01956574.37.SI2.mpol.
- [230] Carlos Perez-Linkenheil. Trends in the development of electricity prices – EU Energy Outlook 2050 - Energy BrainBlog. URL <https://blog.energybrainpool.com/en/trends-in-the-development-of-electricity-prices-eu-energy-outlook-2050/>.
- [231] CEPCI Updates: January 2018 (prelim.) and December 2017 (final) - Chemical Engineering. . URL <https://www.chemengonline.com/>.
- [232] La Foret (WaldSchweiz) 12/17 - marche suisse du bois de feu et du bois d'énergie. *ForêtSuisse*, 2017. URL https://www.foretsuisse.ch/fileadmin/user_upload/user_upload/Wald_und_Holz/Archiv/La_Foret/2017/La_Foret_12_72dpi.pdf.
- [233] D. G. Energy. Quarterly report on european electricity markets, Fourth Quarter of 2017. *Market Observatory for Energy*, 10(4):57–68, 2013.
- [234] Spot and futures market, . URL <http://www.swissgas.ch/>.
- [235] Mazout - L'indice de l'évolution des prix | Migrol SA, . URL <https://www.migrol.ch/fr/mazout/informations/indice-des-prix.aspx>.
- [236] Stamatis Kalligeros, Lars Waldheim, Kyriakos Maniatis, Ingvar Landalv, and Eric van den Heuvel. Building up the future, cost of biofuel. Technical report, Directorate-General for Mobility and Transport (European Commission), June 2018. URL <https://publications.europa.eu/en/publication-detail/-/publication/13e27082-67a2-11e8-ab9c-01aa75ed71a1/language-en>.
- [237] J. Mařík, P. Procházka, V. Hönig, and P. Zeman. Dimethyl ether as a renewable fuel for diesel engines. *Agronomy Research*, 15(5):2226–2235, 2017. doi: <https://doi.org/10.15159/AR.17.067>.
- [238] Thomas F. Stocker, Dahe Qin, Gian-Kasper Plattner, Melinda Tignor, Simon K. Allen, Judith

- Boschung, Alexander Nauels, Yu Xia, Vincent Bex, and Pauline M. Midgley. *IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.
- [239] Ecoinvent Version 3.4 (2017) Database, 2017. URL <https://www.ecoinvent.org/>.
- [240] Hailong Li, Jana P Jakobsen, Øivind Wilhelmsen, and Jinyue Yan. PVTxy properties of CO₂ mixtures relevant for CO₂ capture, transport and storage: Review of available experimental data and theoretical models. *Applied Energy*, 88(11):3567–3579, 2011. ISSN 03062619 (ISSN). doi: 10.1016/j.apenergy.2011.03.052. URL <http://urn.kb.se/resolve?urn=urn:nbn:se:mdh:diva-13347>.
- [241] Tihomir Lazic, Eni Oko, and Meihong Wang. Case study on CO₂ transport pipeline network design for Humber region in the UK. *Proceedings of the Institution of Mechanical Engineers, Part E: Journal of Process Mechanical Engineering*, 228(3):210–225, 2014. doi: 10.1177/0954408913500447. URL <https://doi.org/10.1177/0954408913500447>.
- [242] Ligang Wang, Mar Pérez-Fortes, Hossein Madi, Stefan Diethelm, Jan Van herle, and François Maréchal. Optimal design of solid-oxide electrolyzer based power-to-methane systems: A comprehensive comparison between steam electrolysis and co-electrolysis. *Applied Energy*, 211:1060 – 1079, 2018. ISSN 0306-2619. doi: <https://doi.org/10.1016/j.apenergy.2017.11.050>. URL <http://www.sciencedirect.com/science/article/pii/S0306261917316367>.
- [243] O. Edenhofer, R. Pichs-Madruga, Y. Sokona, K. Seyboth, S. Kadner, T. Zwickel, P. Eickemeier, G. Hansen, S. Schlömer, C. von Stechow, and others. *Renewable Energy Sources and Climate Change Mitigation: Special Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, 2011. ISBN 978-1-139-50559-8. URL <https://books.google.ch/books?id=AjP9sVg01zoC>.
- [244] Suandrie Cornel McLaren. *Evaluating a fast pyrolysis and hydrodeoxygenation process for the production of jet fuel and jet-fuel range aromatics*. Thesis, Stellenbosch : Stellenbosch University, December 2015. URL <https://scholar.sun.ac.za:443/handle/10019.1/98060>.
- [245] Exxon Mobil. 2018 Outlook for Energy: A view to 2040. Technical report, 2018.
- [246] Robert Lawrence Shahab. *Labor division in engineered cross-kingdom consortia: Consolidated bioprocessing of lignocellulosic biomass to carboxylic acids*. PhD thesis, 2019. URL <http://infoscience.epfl.ch/record/265280>.
- [247] H. G. Joglekar, Imran Rahman, Suresh Babu, B. D. Kulkarni, and Ajit Joshi. Comparative assessment of downstream processing options for lactic acid. *Separation and Purification Technology*, 52(1):1 – 17, 2006. ISSN 1383-5866. doi: <https://doi.org/10.1016/j.seppur.2006.03.015>. URL <http://www.sciencedirect.com/science/article/pii/S1383586606001080>.

Bibliography

- [248] Jher Hau Yeap. *Catalytic Upgrading of Biomass-Derived Carboxylic Acids to Fuels and Chemicals*. PhD thesis, École Polytechnique Fédérale de Lausanne, Switzerland, 2019. URL <http://infoscience.epfl.ch/record/264787>.
- [249] S. Murat Sen, Elif I. Gürbüz, Stephanie G. Wettstein, David Martin Alonso, James A. Dumesic, and Christos T. Maravelias. Production of butene oligomers as transportation fuels using butene for esterification of levulinic acid from lignocellulosic biomass: process synthesis and technoeconomic evaluation. *Green Chemistry*, 14(12):3289–3294, 2012. ISSN 1463-9262. doi: 10.1039/C2GC35881F. URL <http://dx.doi.org/10.1039/C2GC35881F>.
- [250] Jesse Q. Bond, Aniruddha A. Upadhye, Hakan Olcay, Geoffrey A. Tompsett, Jungho Jae, Rong Xing, David Martin Alonso, Dong Wang, Taiying Zhang, Rajeev Kumar, Andrew Foster, S. Murat Sen, Christos T. Maravelias, Robert Malina, Steven R. H. Barrett, Raul Lobo, Charles E. Wyman, James A. Dumesic, and George W. Huber. Production of renewable jet fuel range alkanes and commodity chemicals from integrated catalytic processing of biomass. *Energy Environ. Sci.*, 7(4):1500–1523, 2014. doi: 10.1039/C3EE43846E. URL <http://dx.doi.org/10.1039/C3EE43846E>.
- [251] Viet Pham, Mark Holtzapple, and Mahmoud El-Halwagi. Techno-economic analysis of biomass to fuel conversion via the MixAlco process. *Journal of Industrial Microbiology & Biotechnology*, 37(11):1157–1168, November 2010. ISSN 1476-5535. doi: 10.1007/s10295-010-0763-0. URL <https://doi.org/10.1007/s10295-010-0763-0>.
- [252] Fritz Obenaus, Wilhelm Droste, and Joachim Neumeister. Butenes. In *Ullmann's Encyclopedia of Industrial Chemistry*. American Cancer Society, 2011. ISBN 978-3-527-30673-2. doi: 10.1002/14356007.a04_483.pub2. URL https://onlinelibrary.wiley.com/doi/abs/10.1002/14356007.a04_483.pub2.
- [253] Alpha Olefins Market 6.38% CAGR Growth Report by 2021, 2017. URL <https://www.prnewswire.com/in/news-releases/alpha-olefins-market-638-cagr-growth-report-by-2021-649076683.html>.
- [254] Ryan E. Davis, Nicholas J. Grundl, Ling Tao, Mary J. Bidy, Eric C. Tan, Gregg T. Beckham, David Humbird, David Thompson, and Mohammad S. Roni. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update; Biochemical Deconstruction and Conversion of Biomass to Fuels and Products via Integrated Biorefinery Pathways. Technical report, National Renewable Energy Lab.(NREL), Golden, CO (United States), 2018.
- [255] Robert L. Shahab, Jeremy S. Luterbacher, Simone Brethauer, and Michael H. Studer. Consolidated bioprocessing of lignocellulosic biomass to lactic acid by a synthetic fungal-bacterial consortium. *Biotechnology and Bioengineering*, 115(5):1207–1215, 2018. doi: 10.1002/bit.26541. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/bit.26541>.
- [256] Ehsan Reyhanitash, Thomas Brouwer, Sascha R. A. Kersten, A. G. J. van der Ham, and Boelo

- Schuur. Liquid–liquid extraction-based process concepts for recovery of carboxylic acids from aqueous streams evaluated for dilute streams. *Chemical Engineering Research and Design*, 137:510 – 533, 2018. ISSN 0263-8762. doi: <https://doi.org/10.1016/j.cherd.2018.07.038>. URL <http://www.sciencedirect.com/science/article/pii/S0263876218303885>.
- [257] Ch Chilev, Farida Lamari, Moussa Dicko, and Evgeni Simeonov. Investigation of acetic acid dehydration by various methods. *Journal of Chemical Technology and Metallurgy*, 51:73–84, 2016.
- [258] Hasan Uslu. Reactive Extraction of Formic Acid by using Tri Octyl Amine (TOA). *Separation Science and Technology*, 44(8):1784–1798, 2009. doi: 10.1080/01496390902775893. URL <https://doi.org/10.1080/01496390902775893>.
- [259] Young-Si Jun, Yun Suk Huh, Won Hi Hong, and Yeon Ki Hong. Kinetics of the Extraction of Succinic Acid with Tri-n-octylamine in 1-Octanol Solution. *Biotechnology Progress*, 21(6): 1673–1679, 2005. doi: 10.1021/bp050083t. URL <https://onlinelibrary.wiley.com/doi/abs/10.1021/bp050083t>.
- [260] Shang Tian Yang, Scott A. White, and Sheng Tsiung Hsu. Extraction of carboxylic acids with tertiary and quaternary amines: effect of pH. *Industrial & Engineering Chemistry Research*, 30 (6):1335–1342, 1991. doi: 10.1021/ie00054a040. URL <https://doi.org/10.1021/ie00054a040>.
- [261] Bijan Choudhury, Aslam Basha, and Tyagarajan Swaminathan. Study of lactic acid extraction with higher molecular weight aliphatic amines. *Journal of Chemical Technology & Biotechnology*, 72(2):111–116, 1998. doi: 10.1002/(SICI)1097-4660(199806)72:2<111::AID-JCTB878>3.0.CO;2-O. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/%28SICI%291097-4660%28199806%2972%3A2%3C111%3A%3AAID-JCTB878%3E3.0.CO%3B2-O>.
- [262] Jher Hau Yeap, Florent Héroguel, Robert L. Shahab, Bartosz Rozmysłowicz, Michael H. Studer, and Jeremy S. Luterbacher. Selectivity Control during the Single-Step Conversion of Aliphatic Carboxylic Acids to Linear Olefins. *ACS Catalysis*, 8(11):10769–10773, 2018. doi: 10.1021/acscatal.8b03370. URL <https://doi.org/10.1021/acscatal.8b03370>.
- [263] Yun Suk Huh, Young-Si Jun, Yeon Ki Hong, Hyohak Song, Sang Yup Lee, and Won Hi Hong. Effective purification of succinic acid from fermentation broth produced by *Mannheimia succiniciproducens*. *Process Biochemistry*, 41(6):1461 – 1465, 2006. ISSN 1359-5113. doi: <https://doi.org/10.1016/j.procbio.2006.01.020>. URL <http://www.sciencedirect.com/science/article/pii/S1359511306000481>.
- [264] John A. Posada, Carlos A. Cardona, and Ramon Gonzalez. Analysis of the Production Process of Optically Pure d-Lactic Acid from Raw Glycerol Using Engineered *Escherichia coli* Strains. *Applied Biochemistry and Biotechnology*, 166(3):680–699, February 2012. ISSN 1559-0291. doi: 10.1007/s12010-011-9458-x. URL <https://doi.org/10.1007/s12010-011-9458-x>.
- [265] Aspen Process Economic Analyzer, . URL <https://www.aspentech.com/en/products/pages/>

Bibliography

aspen-process-economic-analyzer.

- [266] Stefano Moret, Emanuela Peduzzi, Léda Gerber, and François Maréchal. Integration of deep geothermal energy and woody biomass conversion pathways in urban systems. *Energy Conversion and Management*, 129:305 – 318, 2016. ISSN 0196-8904. doi: <https://doi.org/10.1016/j.enconman.2016.09.079>. URL <http://www.sciencedirect.com/science/article/pii/S0196890416308780>.
- [267] Tax rates in Switzerland - Business Environment - Nordea Trade Portal, 2018. URL <https://www.nordeatrade.com/en/explore-new-market/switzerland/taxes>.
- [268] Simbolotti, Giorgio. Hydrogen Production & Distribution. Technical report, IEA Energy Technology Systems Analysis Program (ETSAP), 2014. URL <https://webstore.iea.org/iea-energy-technology-essentials-hydrogen-production-distribution>.
- [269] Juliana Q. Albarelli, Alberto Mian, Diego T. Santos, Adriano V. Ensinas, François Maréchal, and M. Angela A. Meireles. Valorization of sugarcane biorefinery residues using supercritical water gasification: A case study and perspectives. *The Journal of Supercritical Fluids*, 96: 133 – 143, 2015. ISSN 0896-8446. doi: <https://doi.org/10.1016/j.supflu.2014.09.009>. URL <http://www.sciencedirect.com/science/article/pii/S0896844614002848>.
- [270] Maurice H. Waldner and Frédéric Vogel. Renewable Production of Methane from Woody Biomass by Catalytic Hydrothermal Gasification. *Industrial & Engineering Chemistry Research*, 44(13):4543–4551, 2005. doi: 10.1021/ie050161h. URL <https://doi.org/10.1021/ie050161h>.
- [271] Martin Gassner, Frédéric Vogel, Georges Heyen, and François Maréchal. Optimal process design for the polygeneration of SNG, power and heat by hydrothermal gasification of waste biomass: Thermo-economic process modelling and integration. *Energy Environ. Sci.*, 4(5): 1726–1741, 2011. doi: 10.1039/C0EE00629G. URL <http://dx.doi.org/10.1039/C0EE00629G>.
- [272] Mark D. Staples, Robert Malina, Hakan Olcay, Matthew N. Pearlson, James I. Hileman, Adam Boies, and Steven R. H. Barrett. Lifecycle greenhouse gas footprint and minimum selling price of renewable diesel and jet fuel from fermentation and advanced fermentation production technologies. *Energy Environ. Sci.*, 7(5):1545–1554, 2014. doi: 10.1039/C3EE43655A. URL <http://dx.doi.org/10.1039/C3EE43655A>.
- [273] Fuel Prices for AVGAS100ll & JET-A1, . URL <https://www.luganoairport.ch/en/business-partners-2/flight-ground-operations/fuel-prices/>.
- [274] Emanuela Peduzzi, Guillaume Boissonnet, Geert Haarlemmer, and François Maréchal. Process Integration of Lignocellulosic Biomass Pre-treatment in the Thermo-Chemical Production of F-T Fuels: Centralised Versus Decentralised Scenarios. *Chemical Engineering Transactions*, 35:553–558, 2013. doi: 0.3303/CET1335092.
- [275] Switzerland diesel prices, . URL https://www.globalpetrolprices.com/Switzerland/diesel_

prices/.

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EDUCATION

Ph.D. in Energy (2014 – 2019)

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Thesis Title: "Methodology for the identification of integrated biorefineries - A computer tool for decision making"

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Thesis Title: "Modeling and Optimization of a Diesel Hydroprocessing Plant: Theory and Industrial Applications"

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PROFESSIONAL EXPERIENCE

Ph.D. Research Fellow (2014 – Present)

Industrial Process and Energy Systems Engineering Group (IPESE), École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

- *Research:* Development of a methodology to optimally integrate bioprocessing process units together with co-generation options and other renewable energy sources in large scale industrial systems

- *Projects:*

(2014-2018) RENEwable Systems ENgineering (RENESENG), FP7 Marie Curie EU project

Research Title: "Methodology of the design of integrated industrial biorefinery concepts", providing a computer-aided tool for decision-makers to enable them decide between different biorefinery configurations which are economically and energetically viable with minimum environmental impact.

(2017-2019) NRP 70 Energy Turnaround, SNSF (Swiss National Science Foundation) Project

Sub-Project Title: "Sustainability evaluation of biorefinery systems for fuel and commodity chemical generation from plant residues", techno-economic modelling for energetic optimization of the consolidated bioprocessing of lignocellulosic biorefinery for fuel and chemical production, sustainability evaluation of the process chain from field to end-of-life of the product(s)

- *Teaching activities:* supervision of 2 master students, teaching assistant in "Energy Conversion" and "Advanced Energetics" courses

Research and Teaching Assistant (2012 – 2014)

Department of Chemical and Biological Engineering, Koç University, Istanbul, Turkey

- *Research:* Modeling of an industrial diesel hydroprocessing plant by the method of continuous lumping

- *Projects:*

(2012-2014) Real-Time Optimization of Diesel Hydroprocessing Plant, Kırıkkale Refinery, TUPRAS Petroleum Inc.

Building a model for simulation of input-output behavior of the reactors system by understanding the kinetics of the hydro-cracking and hydro-treating reactors in MATLAB environment

- *Teaching activities:* teaching assistant in "Process Dynamics and Control" and "Introduction to Chemical and Biological Engineering" courses

PUBLICATIONS

Journal articles

- A.D. Celebi, S. Sharma, A.V. Ensinas, F. Maréchal. Next generation cogeneration system for industry - combined heat and fuel plant using biomass resources. Chemical Engineering Science, (peer-reviewed), 2019
- A.D. Celebi, A.V. Ensinas, S. Sharma, F. Maréchal. Early-stage decision making approach for the selection of optimally integrated biorefinery processes. Energy, Volume 137, Pages 908-916, 2017
- S. Sharma, A.D. Celebi, F. Maréchal. Robust multi-objective optimization of gasifier and solid oxide fuel cell plant for electricity production using wood. Energy, Volume 137, Pages 811-822, 2017
- E. Aydın, A.D. Celebi, H. Sildir, Y. Arkun, U. Canan, M. Erdogan. Dynamic modeling of an industrial diesel hydroprocessing plant by the method of continuous lumping. Computers & Chemical Engineering, Volume 82, Pages 44-54, 2015

Conference papers

- M. Kermani, A.D. Celebi, A.S. Wallerand, A .V. Ensinas, I.D. Kantor, F. Maréchal. Techno- economic and environmental optimization of palm-based biorefineries in the Brazilian context. Computer Aided Chemical Engineering, 27th European Symposium on Computer Aided Process Engineering. Elsevier, Pages 2611-2616, 2017
- A.D. Celebi, A.V. Ensinas, S. Sharma, F. Maréchal. Early-stage decision making approach for the selection of optimally integrated biorefinery processes. Proceedings of ECOS 2016, Portorož, Slovenia, 2016
- S. Sharma, A.D. Celebi, E. Peduzzi, A.V. Ensinas, F. Maréchal. Multi-objective optimization of solid oxide fuel cell-gas turbine hybrid cycle and uncertainty Analysis. Proceedings of ECOS 2016, Portorož, Slovenia, 2016
- M. Kermani, A.D. Celebi, A .V. Ensinas, F. Maréchal, Process integration potential between biodiesel production from palm oil and 2nd generation bioethanol production from empty fruit bunches (EFBs) in Brazilian context: Thermo-economic and environmental evaluation, 6^o Congresso da Rede Brasileira de Tecnologia de Biodiesel, 9^o Congresso Brasileiro de Plantas Oleaginosas, Óleos, Gorduras e Biodiesel, Natal, Brazil, 2016

Book chapter

- G. Léonard, A. Pfennig, A.D. Celebi, S. Sharma, F. Maréchal. Industrial Integration of Biotechnological Processes from Raw Material to Energy Integration: Study by Modeling Approach. Microbial Fuels: Technologies and Applications, Taylor and Francis, Pages 493-510, 2017

Patent

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SKILLS

- **Languages:** Turkish (native), English (proficient-C1), French (intermediate-B1) German (beginner-A2)
- **Programming:** MATLAB, Lua, AMPL, JAVA
- **Technical Software:** Aspen Plus, Belsim VALI, CAPE-OPEN, gPROMS, ChemCAD, COMSOL

HONORS & AWARDS

- Koç University, Vehbi Koç Fellowship (Full merit scholarship for master study), 2012-2014
- Hacettepe University, Excellent thesis award due to 1st rank in "Project Competition of Engineering Faculty", with project "Recovery of Lithium from Calcined Boron Tailings", 2012
- Hacettepe University, Cemal Pamuk Students of Honor Award, Department of Chemical Engineering, Awarded with scholarship for excellent academic performance, due to top ranking in consecutive two years, 2010-2011

EXTRACURRICULAR ACTIVITIES

TURQUIA 1912 – Turkish Students Association in Switzerland

- Vice President (2018-2019), Secretary (2017-2018)
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