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Optimum biorefinery pathways selection using MILP with Integer-Cuts constraint method

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Abstract

The object of the thesis is to develop a methodology to evaluate and rank different technologies for biorefineries, in particular biorefineries which convert wooden biomass into valuable products. The goal is to developed a robust and effective method to be applied to the Wood2CHem OSMOSE Platform, a computer aided tool developed by Master and PhD. Students of LENI (EPFL) and designed to perform process design and analysis of integrated energy systems.

The method consists in the application of Integer-Cuts constraint together with a balanced set of constraints that boost the speed of the solver thus keeping the problem MILP. This is a key issue for such a work: the challenge is to set up a linear model, simple but accurate and capable to give useful informations in detecting the most promising pathways and products for lignocellulosic biorefineries.

Such is a preliminary analysis of different biorefinery concepts, carried out in order to allow decision makers to evaluate which is the best use of wood under a given set of boundary conditions (economics, technology) and constraints (wood availability).

Finally, the methodology developed is applied in a case study in which the best employment of wood in Switzerland is evaluated according to a small pilot scale (20 MW biomass input) and a big commercial sized plant (200 MW biomass input).

Sommario

L'obbiettivo di questo lavoro é quello di sviluppare una metodologia per valutare e ordinare una serie di processi di conversione di biomassa legnosa in prodotti energetici o biomateriali. Il fine ultimo iluppare un metodo robusto ed efficiente che possa essere applicato alla piattaforma OSMOSE Wood2CHem, un software sviluppato da studenti di Master e Dottorati presso il LENI (EPFL) e concepito per permettere l'analisi e la sintesi di sistemi energetici integrati.

Il metodo sviluppato consiste nell'applicazione dell'Integer-Cut constraint insieme ad una serie ponderata di ulteriori vincoli, il tutto volto al raggiungimento delle soluzioni richieste nel minore tempo possibile mantenendo il problema lineare (MILP). Questo é il problema chiave per il progetto: la sfida di costruire un modello lineare che tuttavia sia rappresentativo della realt modo tale da fornire informazioni sui prodotti e processi di conversione pi promettenti.

Questa 'analisi preliminare dei diversi concetti di bioraffineria, il fine proporre una visione globale dei diversi processi di conversione, ordinati secondo le condizioni al contorno, in modo da permettere al progettista di valutare l'impiego ottimale della biomassa legnosa in base alle condizioni al contorno stabilite (che possono essere di tipo economico o tecnologico) o ai vincoli di disponibilit risorse.

Infine, per validare l'efficacia del metodo sviluppato, esso ato applicato ad un caso di studio volto a valutare il migliore uso della biomassa legnosa in Svizzera in due scale diverse (impianto dimostrativo da 20 MW e impianto commerciale da 200 MW).

Acknowledgement

I would like to express my gratitude to Professor Andrea Lazzaretto, my research supervisors, for his support and critiques through this work. His kind willingness has been very much appreciate.

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I would also like to extend my thanks to Atish and Priscilla, always ready to help and share their knowledge with students - even if the time is scarce for everyone.

Finally, I wish to thank my parents for their support and encouragement throughout my study. I could not make it without you.

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Nomenclature

η_{ref}	Reference electrical efficiency
η_{sol}	Efficiency of the constraint
$^{+}$	Material or energy stream entering the system
$^{-}$	Material or energy stream leaving the system
C	Cost
c	Specific cost
$d_{average}$	Average transportation distance
E	Energy
e	Specific energy
f	Multiplication factor
f_{max}	Maximum value for the multiplication factor
f_{min}	Minimum value for the multiplication factor
IC	Investment cost
N_s	Number of the subsystems (units) in the superstructure of the model
n_{rank}	Position of the solution in the rank
n_{sol}	Number of solution
OC	Operating cost
P	Power
TC	Total cost
y	Unit use
BtT	Biomass-to-liquid
c	Specific cost
CFB	Circulate Fluidized Bed (gasifier

DME Dimethyl ether

EF Entrained Flow (gasifier)

FICFB Fast Internal Circulating Fluidized Bed (gasifier)

FT Fisher Tropsh fuel

ICC Integer-Cut Constraint

MI(N)LP Mixed Integer (non) Linear Programming

SNG Synthetic natural gas

Chapter 1

Introduction

This work is part of the Wood2CHem project, a cooperation between the ETH Zurich and the EPF Lausanne fostered by Swiss National Research Programme "Resource Wood" (NRP 66) [17]. The aim is to establish basic scientific knowledge and practical methods for increasing the availability of wood as a resource and expanding its use in Switzerland [18]. The goal of this project is to gather the experience and the studies developed by students and researchers from EPFL and ETHZ in a computer aided platform to analyse various biorefinery concepts

The object of this work is to develop a methodology to find not only the best biorefinery design but also to generate systematically a full rank of promising models for converting wood into marketable products and energy services under a given set of constraints (e.g. available technology, market prices).

In order to achieve such objective, a methodology is proposed to screen all the solutions and obtain a rank of feasible biorefinery design. The combinations are ordered according to the objective function, thus allowing the decision maker to choose among a variety of different designs. This is the crucial aspect of biorefineries: the uncertainty of the best application for the raw materials is due to the large, increasing, variety of products that can be obtained and therefore other criteria can be applied in evaluating the pathways.

The idea of developing a method to create a list of pathways is due to the fact that biomass conversion technologies are still young and the bio-based product market is still in a developing phase. Consequently, both technological and economic uncertainty could mean that the optimal pathway for biorefinery is not the best. The extension of the analysis of technologies including sub-optimal solutions could help the decision maker to focus towards more reliable – although less efficient – technologies. It can also happen that several pathways are remarkably close (in term of objective function) so much so that the difference is negligible and therefore other criteria can be applied in choosing the most suitable technology (market request or market prevision, utility available, subsidies).

Moreover, another task of this project is to create a light and fast tool to quickly evaluate different pathways without resort to complex methods (such as multi objective optimization). At this level of research, the aim is not to provide a full integrated analysis but to compare and evaluate in a general way different processes with multiple output. The detailed process flow design and analysis will be conducted in a following step, after the pre-analysis performed with this tool. Elaborate a simple and light model with a robust problem statement is challenging: the call for a robust problem imposed to go for MILP and the need for retrieving results in a brief time lead to computational issue that were overtaken through to a rigorous approach.

In conclusion, the novelty of the work relies on the development of a quick and robust methodology to rank pathways and adapt it to the Wood2CHem Optimization Platform. The chosen method is Integer-Cuts Constraint, a simple but effective approach. Anyway, the application of the Integer-Cut is not enough to achieve the objective of having a fast tool, thus further analysis and constraint turned out to be necessary to fulfill all the objectives. Finally, the Platform is applied to a case study, performed according to the Swiss economic condition and wood availability to evaluate the effectiveness of the methodology developed.

Chapter 2

The Biorefinery concept

Abstract

In this chapter the concept of biorefinery is presented with an overview of the main features and potentialities of the technologies that can be used in a biorefinery. Indeed, the idea of biorefinery is the result of the systematic application of process integration, the essential methodology which allows to exploit the resources given with the best yield. After a brief presentation of the biorefinery classification, the main biorefinery concepts are analysed focusing especially on wooden biomass biorefinery, the most promising platform. Finally, in the state-of-the-art Section, the most outstanding example of biorefinery are described.

2.1 Introduction

The steady increasing global energy demand is creating great issues in term of availability of resources and environmental sustainability. In order to face this challenge, around the world several steps have been taken to move towards a more sustainable economy. In recent years we have seen the first steps into the transition towards a Bio-based Economy. In order to move from a fossil-based economy to a bio-based one, a key role will be played by the biomass in the near future. The main drivers of this change are [9]:

- The need to go for a totally sustainable economy (environmentally, socially and economically)
- The global issue of climate change due to greenhouse gases;
- The need to diversify the resources, reducing the fossil-fuel dependency, both for economical matters (few countries own most of the world's resources);
- The anticipation that fossil fuels (used for both energy production and in chemical industry) will peak in the near future and prices will increase;

- The desire to stimulate the rural economy in order to reinvest in the home market.

The systematically application of process integration methods, pinch analysis and Life Cycle Assessment paved the road to a new definition of process industry, developing a new concept of process industry highly integrated in order to reach the best achievable efficiency.

In this framework of rising concern on the environment, depletion of fossil resources and rising cost of energy, the concept of biorefinery impose as a possible answer to the challenge. Biomass, similar to oil, has a complex composition and it is made of a wide range of heterogeneous components. In petrochemical industry, crude oil is initially separate into simple to handle and well chemically defined products [1]. This is the same principle of biorefineries, as shown in Figure 2.1.

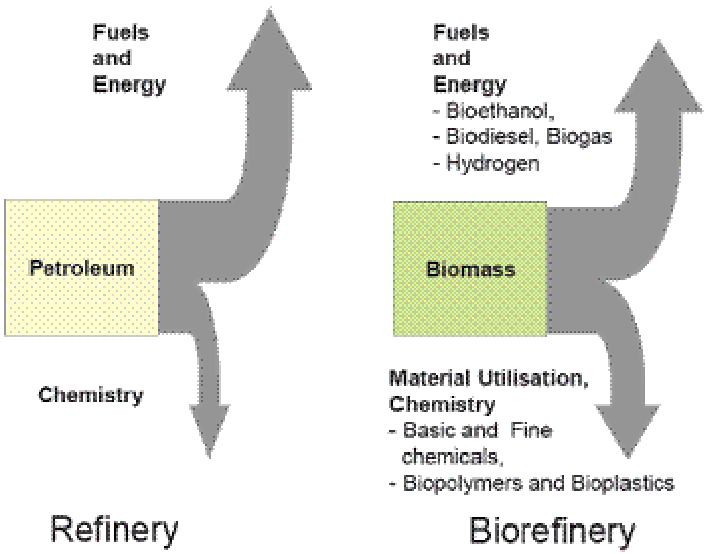


Figure 2.1: Comparison between oil refinery and biorefineries [1].

The importance of biorefineries was recognized by the International Energy Agency (IEA) which issued a specific Task (Task42) [2] in order to gather the necessary knowledge and actively promote information exchange on all features of biorefinery. Task42 carries on the work started in 1992 with the biomass conversion Task VII [19] and gather the work developed in other related IEA Bioenergy Tasks [20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30].

2.2 Definition of Biorefinery

The International Energy Agency Bioenergy Task42 proposed the following definition of biorefinery [2]: *"Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)".*

This definition clearly defines the object. First, it states that the main driver that leads to the concept of biorefinery is the call for sustainability, in its broader meaning. A biorefinery should be designed to be sustainable along the whole chain, therefore all the possible implications and impacts must be taken into account: competition between food and energy crops, impact on water use, change in land use, soil stock and long term fertility, net balance of greenhouse gas emissions and impact on biodiversity are issues that must not be neglected [2].

Secondly a biorefinery can use all kind of biomass as an input, including energy crops (coming from short rotation forestry or agriculture), forest residues, organic residues (both plant and animal derived) and even aquatic biomass (such as algae, micro-algae and sea weed).

Finally a plant (which can be a concept, a facility or even a cluster of facilities) must be capable of converting the biomass in a wide range of valuable products and energy to be classified as a biorefinery, as imaginatively shown in Figure 2.2. This is the key issue for a biorefinery: the pursuit of simultaneously production of different kind of services is the best way to maximize the efficiency in biomass conversion, minimize the waste and minimize the raw material requirements.

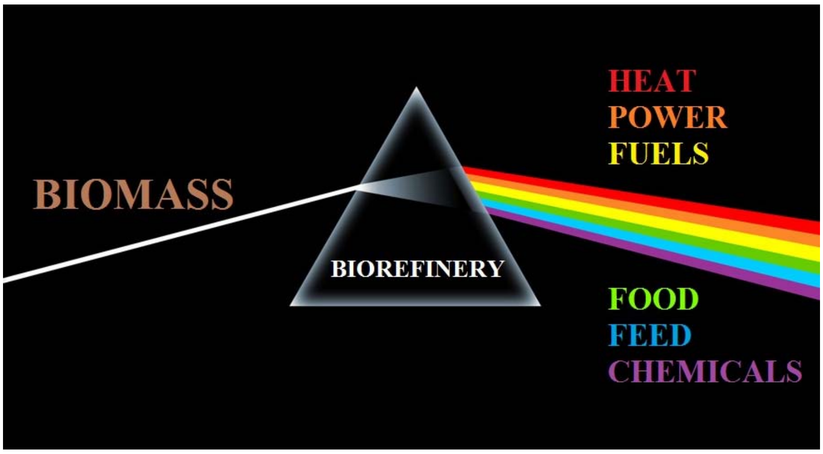


Figure 2.2: Biorefinery should sustainably produce a spectrum of marketable products and services [2].

Nevertheless, biorefinery is not a brand new concept. The production of bio-based chemicals is a long standing discipline which dates back to the very beginning of the industrial era. The industrial conversion of renewable sources started at the beginning of the 18th century but, after the Second World War, the great availability of cheap oil caused the decline of bio-based industry. For instance, in 1941 Henry Ford produced a car made of 100% bio-synthetic material (70% cellulose, 20% soy meal, 10% formaldehyde resin) [1]. Another explanatory example is the production of nylon-6,6: the original process was based on furfural, a bio-based chemical coming from lignocellulosic biomass (see also Section 2.4.3). The bio-furfural production stopped in 1961 because it turned out to be not economically sustainable if compared to the oil-based chemicals, as a consequence of the low crude oil price.

Nowadays, the recent climb in oil price and the awareness that oil is a finite resource is persuading decision makers, stakeholders and governments to look for new resources to fulfill the demand. Moreover, the call for sustainability and the great concern about global worming and climate changes are making biorefineries and bio-based products more and more attractive. Despite the great effort made to steer towards a biomass based economy, there are still a lot of issues and challenges that slow down the transition.

2.3 Classification of Biorefineries

IEA Task 42 also focused on the classification of biorefineries. The most relevant features that characterize and described a system of this kind are [2]:

1. **Platforms**, the intermediate products or vectors which are able to link different systems and processes (e.g. intermediates such as C5-C6, syngas, pyrolytic liquid).

2. **Products**, the final valuable output. It can divided into two sub category:

   2.1. *energy products* (biofuels, power, heat);

   2.2. *material products* (chemicals, building blocks, food, feed).

3. **Feedstock**, the input of the system. Feedstock can be grouped as follow:

   3.1. *energy crops* from agriculture (e.g. starch crops, short rotation forestry);

   3.2. *residual biomass* coming from either agriculture (e.g. straw, cattle manure) or forestry (e.g. bark) or industry (e.g. used cooking oils, waste stream from biomass processing).

4. **Conversion processes**, the technology used to convert the biomass. For what concern the processes, four main group can be identified:

   4.1. *biochemical route* (e.g. fermentation, enzymatic conversion);

   4.2. *thermochemical route* (e.g. gasification, pyrolysis, combustion);

   4.3. *chemical route* (e.g. acid hydrolysis, synthesis, esterification);

   4.4. *mechanical route* (e.g. fractionation, pressing, milling).

Consequently, biorefineries are classified quoting *platform*, *product*, *feedstock* and *processes* (if necessary). For instance, a typical classification of biorefinery can be:

- C6 sugar platform biorefinery for bioethanol and animal feed from starch crops;
- Syngas platform biorefinery for FT-diesel and phenols from straw;
- C6-C5 sugar and syngas platform biorefinery for bioethanol, FT-diesel and furfural from saw mill residues.

Another way to classify biorefineries, based only on the feedstock, is proposed by Kamm et al. [1]:

- **Lignocellulosic Feedstock Biorefinery (LFB)** which use "nature-dry" raw material, for example cellulose-containing biomass and waste;
- **Whole Crop Biorefinery** which uses raw material such as cereals or maize;
- **Green Biorefinery** which use "nature-wet" biomass such as green grass, alfalfa, clover, or immature cereals [31, 4];

This broader classification will be used in Section 2.4 to group different kinds of concepts of biorefinery into few main groups.

Figure 2.3 depicts an overview of the complexity of all the possible links between platforms, products, feedstock and processes. As new technologies are developed and new processes are defined, the scheme is addressed to get more and more complicated. Therefore if the aim is to investigate which is the best biorefinery design for a given amount of biomass or to find the most efficient conversion pathways to fulfill a set of needs, a scientific approach is needed to investigate and compare different paths. Such work focuses on the developing of a method to compare all the possible processes to convert wooden biomass into valuable products. Then, despite this project deals only with a specific type of biorefinery, it will soon be clear that even addressing the attention to only one feedstock, the complexity of the processes available is really wide.

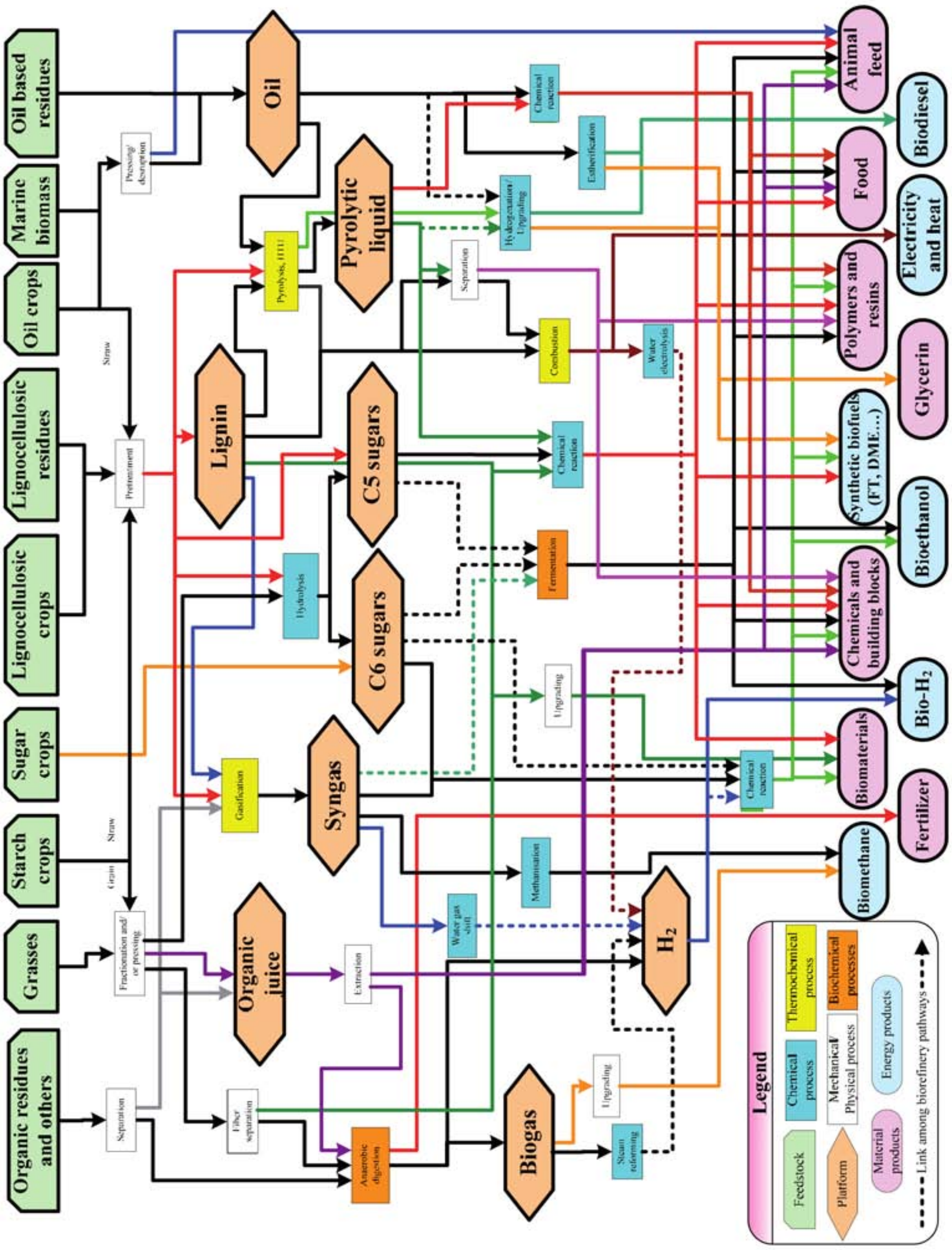


Figure 2.3: Overview of the possible link between platform, products, feedstock and processes [3].

2.4 Biorefinery system design: most promising Bio-Based products and Processes

Since biomass has a complex composition, the first step to be taken is to separate the raw material into main groups of substances. The processing and treatment of biomass leads to a whole palette of products, as shown in Figure 2.4.

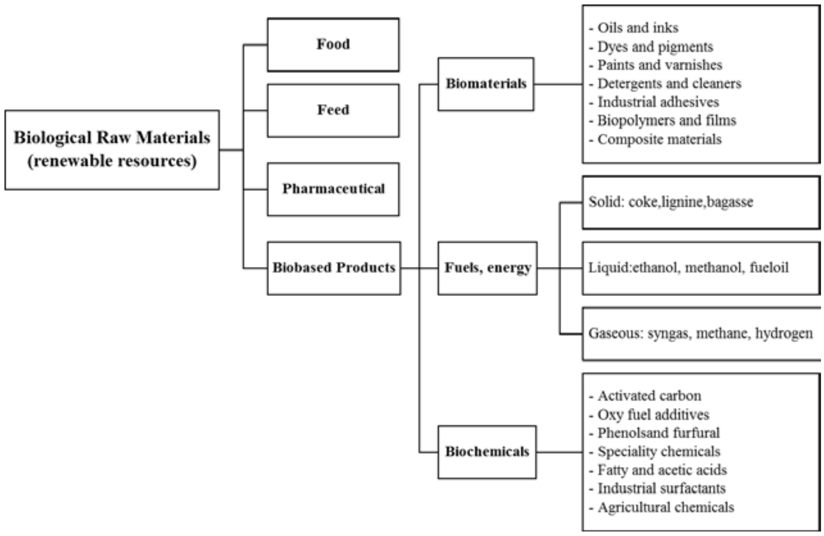


Figure 2.4: Classification of products based on biological raw material [4].

Biomass is processed and modified to obtain other products called precursors which are at the base for the chemical products. Biomass is composed by carbohydrates (up to 75% [1]) so the first problem is how to efficiently access to carbohydrates to subsequently convert them into chemical bulk.

Biotechnology has a great role in biorefineries: the integration between biotechnological, chemical and thermochemical methods should be managed according to the physical and chemical conversion tree of the biomass (Figure 2.5).

Finally, another interesting by-product from biorefineries could be electricity and heat. In both cases, the eventually positive output power is the result of an energy recovery inside the main process. Indeed, the power production is not the key issue for a biorefinery, but it can substantially help in improving the overall efficiency and the cost-effectiveness of the system. The technologies available to convert biomass into energy are already well-known and well-established; however, the great issue is how to integrate these technologies inside the new concept of biorefinery. Moreover, another problem is whether it is more efficient - or cost-effective - to use biomass for chemical production or for energy production. Such work tries to solve the problem by proposing a methodology applied to a computer platform in order to obtain a list of possible designs for a biorefinery, according to the objective function stated.

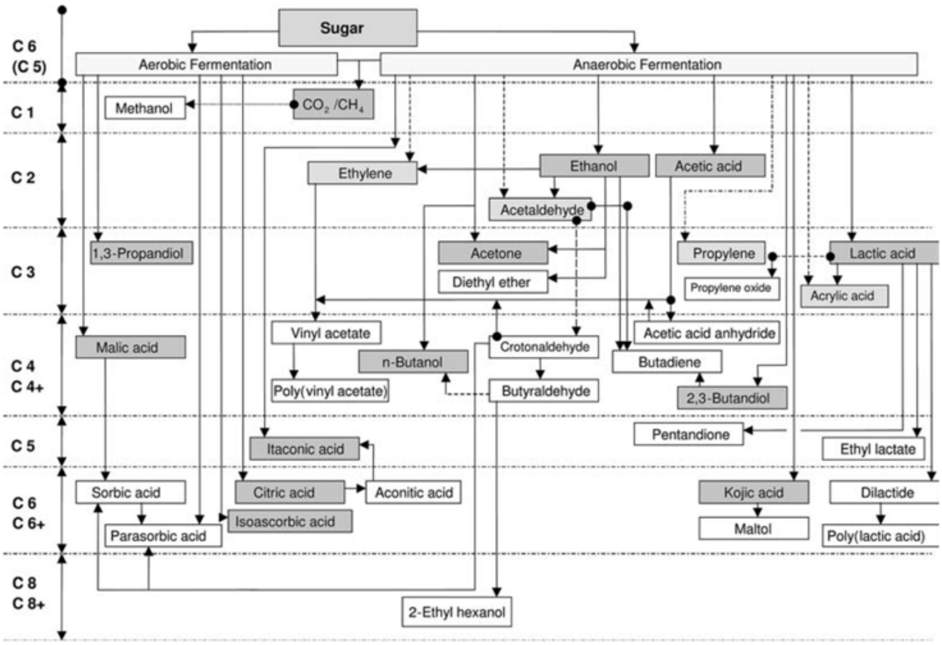


Figure 2.5: Biotechnological sugar based product family tree [1].

The variety of processes and products is really wide, as it can be seen in Figure 2.6; thus a systematic approach is needed to select the most promising.

Focusing on the most promising bio-products, the US Department of Energy [5, 8] identified a group of chemicals derived from biomass that can represent the building blocks of a new bio-based economy (see Table 2.1). Also the International Energy Agency, tried to analyse the economic potential of co-production of biofuels and chemicals, assessing commercial and near-market products [2, 9].

Building Blocks
1,4 succinic, fumaric and malic acids
2,5 furan dicarboxylic acid
3 hydroxy propionic acid aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol
arabinitol

Table 2.1: Twelve promising building block chemicals that can be produce from sugar via biological or chemical conversion [5].

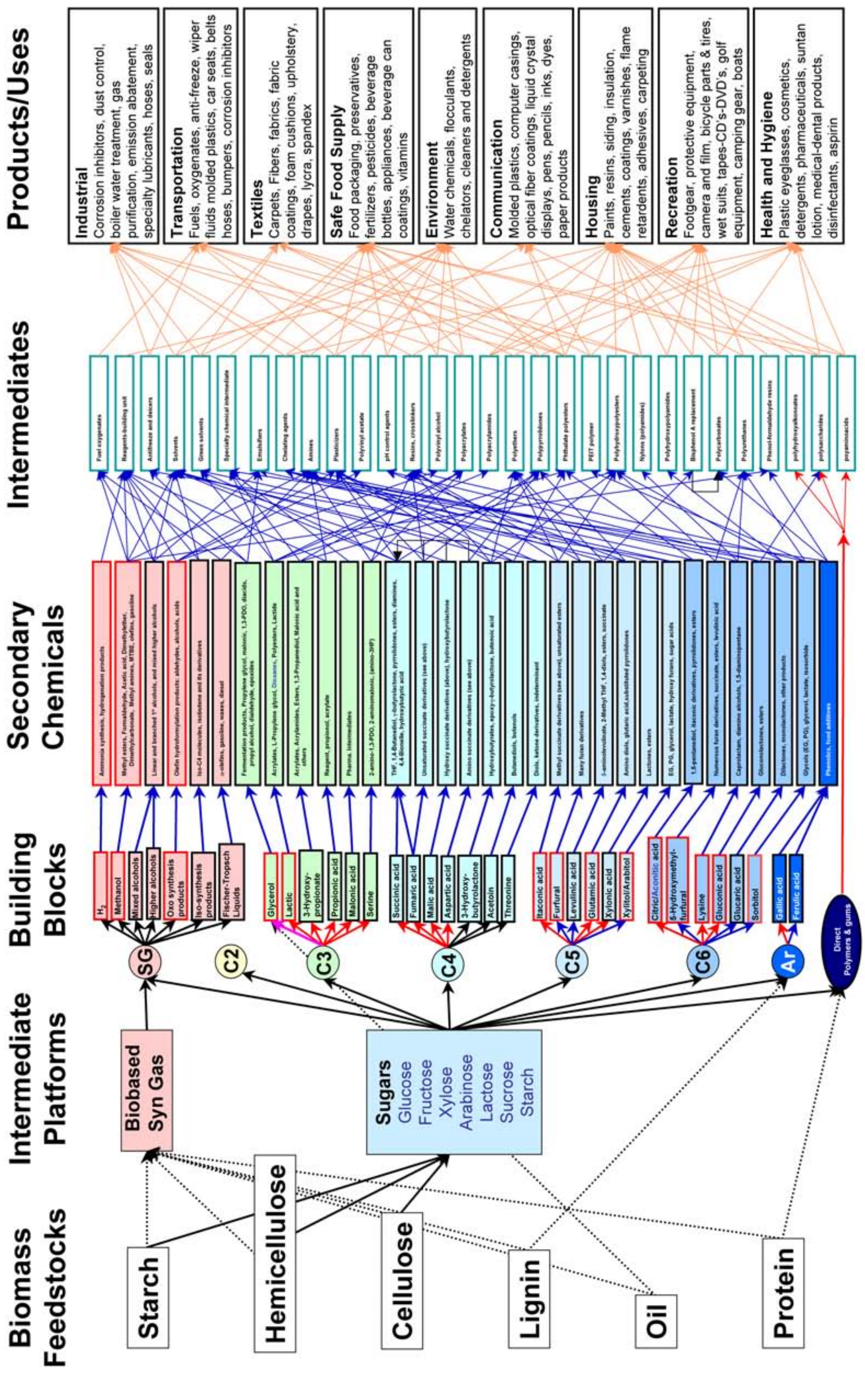


Figure 2.6: Detailed bio-based products flow-chart [5].

2.4.1 Whole-crop Biorefinery

The Whole-crop Biorefinery (WCB) uses cereals (such as rye, wheat, triticale, maize) as input feedstock [1]. The first pretreatment is the separation of straw from corn: straw is mostly a lignocellulosic material, and therefore can be treated as feedstock for LFB (see Paragraph 2.4.3) while corn can be further processed by fermentation of sugar (to produce ethanol) or converted into bioplastic (through extrusion and plasticization) and binders (through extrusion) [4].

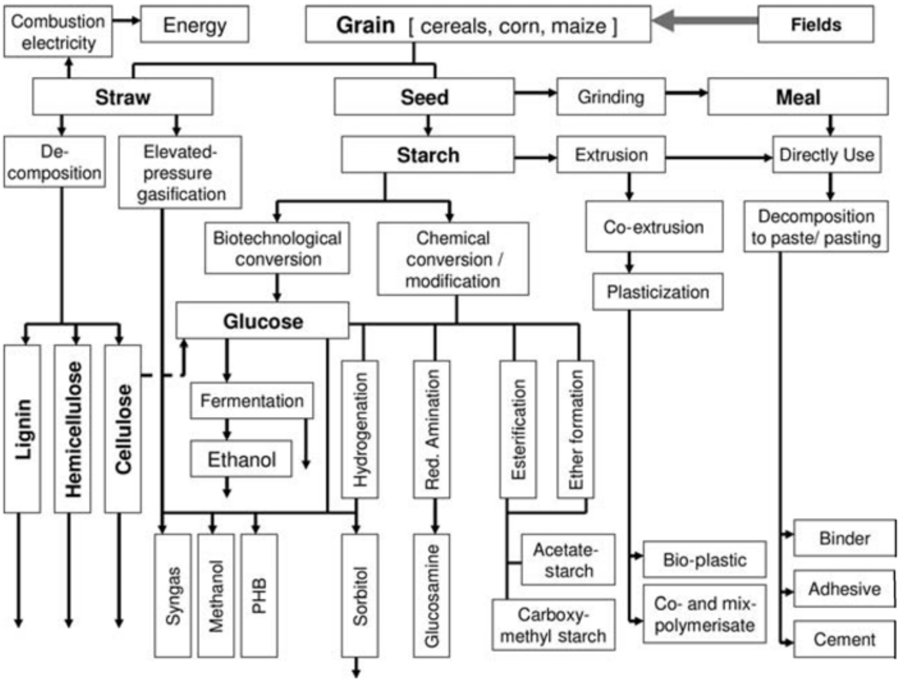


Figure 2.7: General scheme of a whole-crop Biorefinery [1, 4].

2.4.2 Green Biorefinery

A Green Biorefinery is a multi-product facility that deals with a great variety of green biomass such as grass (from cultivations or permanent grass land) and green crops (i.e. lucerne, clover and immature cereals from intensive cultivations) [1]. The first step in processing green feedstock is fractionation, in order to separate a fiber-rich press cake from a nutrient-rich green juice. From these two main streams, biotechnological and chemical technologies can be used to obtain a broad variety of products. The press cake contains not only cellulose and starch, but also dyes, pigments and other organic compounds. The cellulose can be further separate and used in lignocellulosic feedstock biorefineries, while the remaining can be used in the production of feed pellets and chemicals (such as levulinic acid) or in gasification process for the synthesis of biofuels. The other stream, the green juice, contains proteins, amino acids, organic acids and consequently the obtainable products are lactic acid, amino acids, ethanol and proteins [1].

In addition, green biorefinery can exploit also the residues of the input biomass: biogas production coupled with combined heat and power generation boost the efficiency and the economic performances of such class of biorefineries. The great advantages of green biorefineries are the high yield per hectare and possibility of a perfect coupling with agricultural production, in order to achieve low prices for the raw materials.

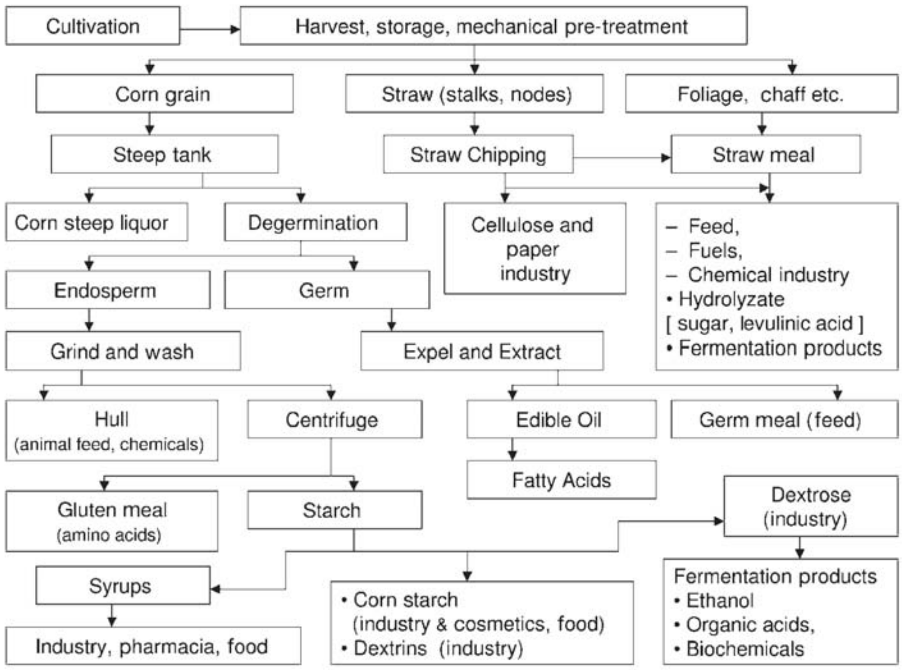


Figure 2.8: General scheme of a Green Biorefinery [1, 4].

2.4.3 Lignocellulosic Feedstock Biorefinery

In this Section an overview of the potential processes and products of a lignocellulosic biorefinery are presented. Lignocellulosic Feedstock Biorefinery (LFB) is currently the most promising biorefinery concept: on one side the input biomass is largely available (straw, reed, grass, wood, paper-waste) and does not conflict with the food industry. On the other side, the conversion pathways can lead to a staggering number of final products.

The main components of lignocellulosic biomass are: hemicellulose/polylose (a sugar polymers of phentose), cellulose (a glucose polymer) and lignin (a polymer of phenol) [1].

One of the most promising product from hemicellulose is furfural and hydroxymethylfurfural (HMF). Furfural is a member of the Furanic class and it is produced from the dehydration of C5 sugar such as xylose and arabinose [9]. Furfural is a building block for nylon 6, and, as recalled in Section 2.2, nylon-6,6 production was based on furfural. The hydrolysis of cellulose into simple sugars (glucose) can be carried out via biological processing or chemical processing [32] in order to obtain useful products such as ethanol, acetic acid, acetone, butanol, succinic acid [9]. For what concern the last component of lignocellulosic biomass, lignin, it has limited use: currently the most widespread use is direct combustion but the potential of lignin is really high and not yet exploited and it could lead to create monoaromatic hydrocarbons [32] thus improving the efficiency and the economic performance of LFB.

An overview of the pathways and the potential products of LFB is shown in Figure 2.9.

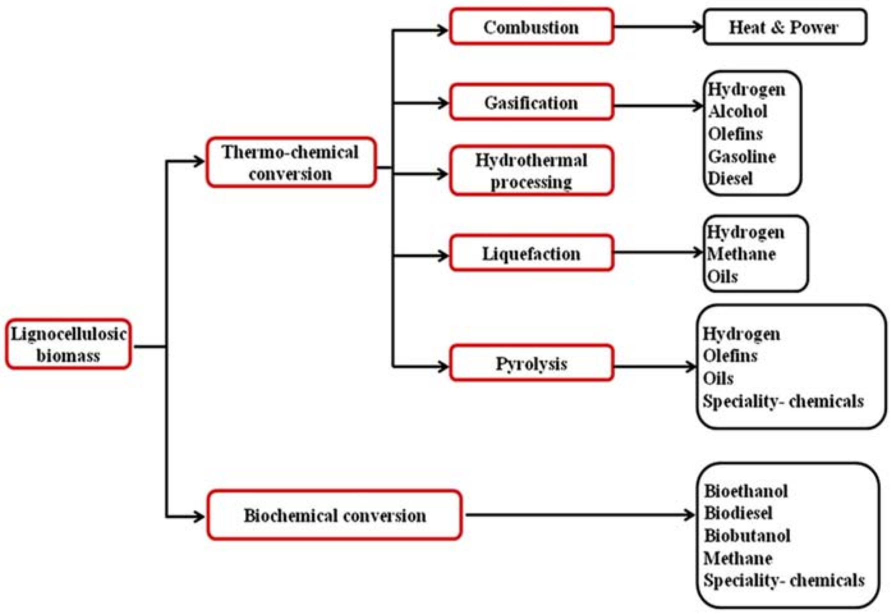


Figure 2.9: Processing tree of lignocellulosic biomass [6].

A more detailed analysis of the literature about lignocellulosic biorefineries, leads to the diagram in Figure 2.12: it is clear that the main conversion route is the thermochemical one, and the most effective technology is gasification. Syngas can be used for the synthesis of a wide variety of chemicals and fuels [5, 7], as it can be seen in Figure 2.10.

Other pretreatment involve physico-chemical processes (such as steam explosion, ammonia fiber explosion, microwave chemical pretreatment) or chemical processes (acid or alkaline pretreatments) [6]. For what concerns the biochemical way, the most widespread processes are fermentation and enzymatic transformation [33], however there are still big issues because in many cases there are no natural enzymes able to split the raw material into basic monomers. For all the processes, the key issue is decomposing the raw material into simple blocks to proceed with further processing, as it can be seen in Figure 2.11.

Moreover, to achieve the same products, many routes can be followed, as depicted in Figure 2.12: the complexity in biorefinery design is higher than in traditional oil industry [34] thus new tools and approaches are needed to analyse and develop new concepts of integrated biorefinery.

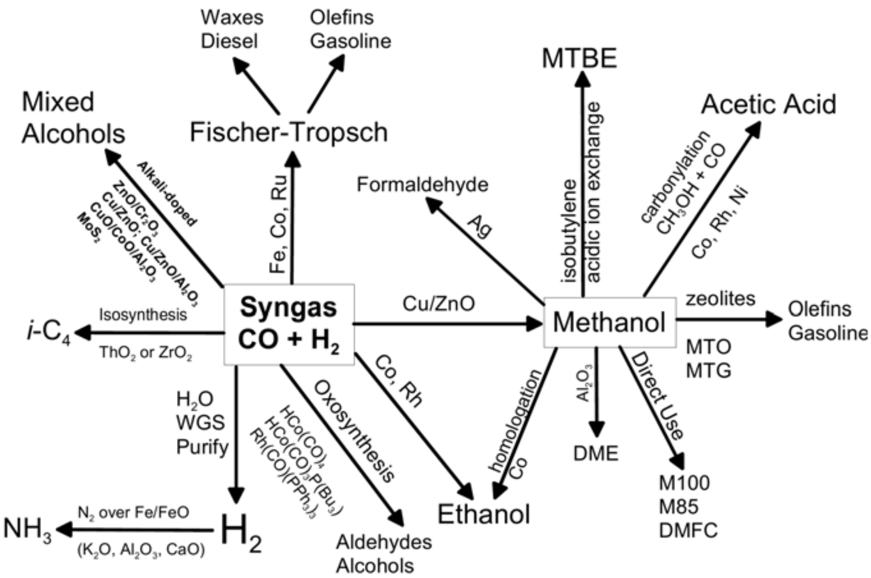


Figure 2.10: Diagram of the syngas conversion processes analysed by [7].

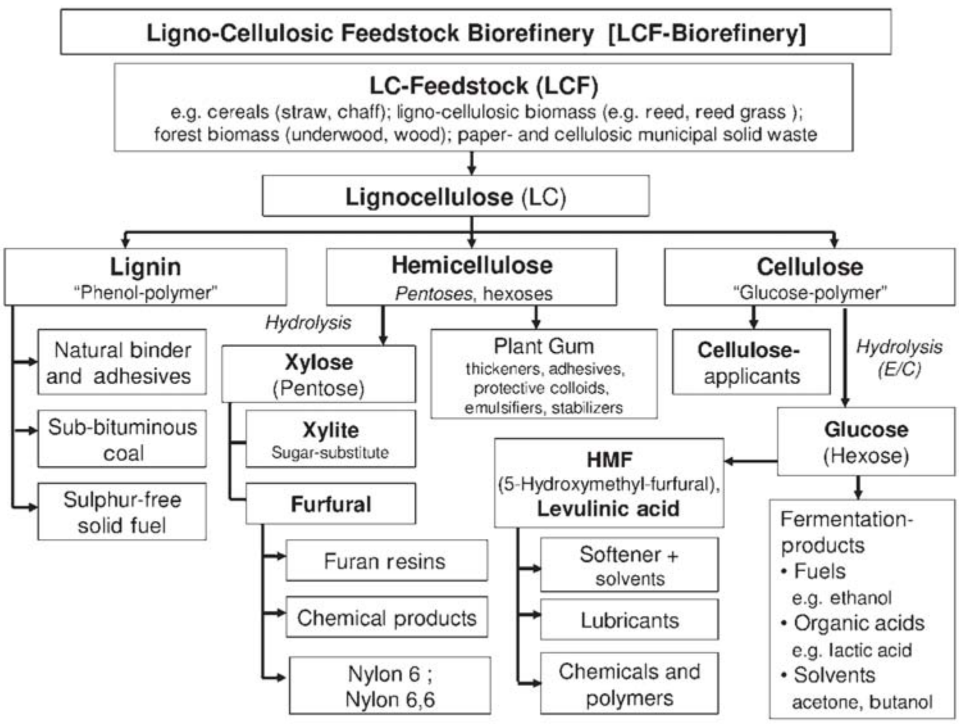


Figure 2.11: General scheme of a LCF Biorefinery [1, 4].

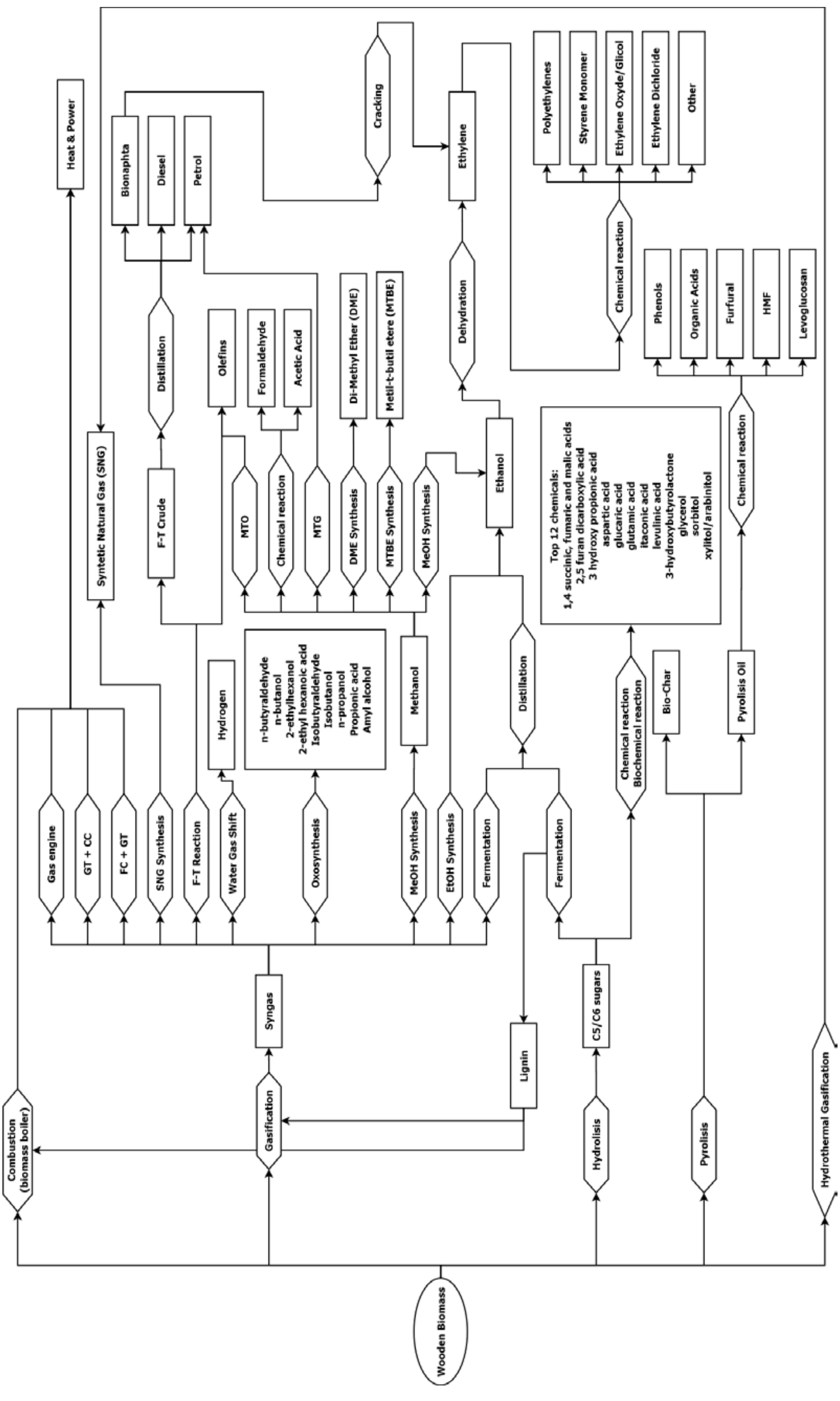


Figure 2.12: Diagram of the possible pathways and processes for a Lignocellulosic Biorefinery [7, 5, 8, 9, 10].

2.5 State-of-the art: operating biorefineries

In this Section some examples of already operating biorefineries are presented. Since the definition of biorefinery given in Section 2.2 is really broad, it is easy to understand that even a simple facility can be classified as a biorefinery when it has multiple outputs. In this perspective, a traditional bioethanol plant could be a biorefinery if it produces and sells cattle feed (DDGS) as a by-product (see Section 2.5). Other really basic biorefinery design are biogas plant like the one presented in Section 2.5, where electricity and fertilizer are produced. Indeed, part of the currently operating biorefineries are just upgrading of existing industrial structures towards better process integration (another example can be a paper production plant upgraded with a CHP section explained in Section 2.5).

Starting from these elementary examples, an overview of existing platforms is therefore presented with their most remarkable features, with special focus on biorefineries that use lignocellulosic feedstock as an input. All the following examples come from the report of the Interational Energy Agency Task 42 Biorefinery [2] in which the most outstanding examples of biorefineries are gathered.

C6 sugar biorefinery for bioethanol and animal feed from sugar and starch crops

The CropEnergies Group owns the largest European bioethanol plant (with an annual capacity of 360.000 m^3 of bioethanol) settled in Zeitz (Germany). It can process up to 700.000 tonnes of grain and sugar syrups and up to 1.000.000 tonnes of sugar beet per year.

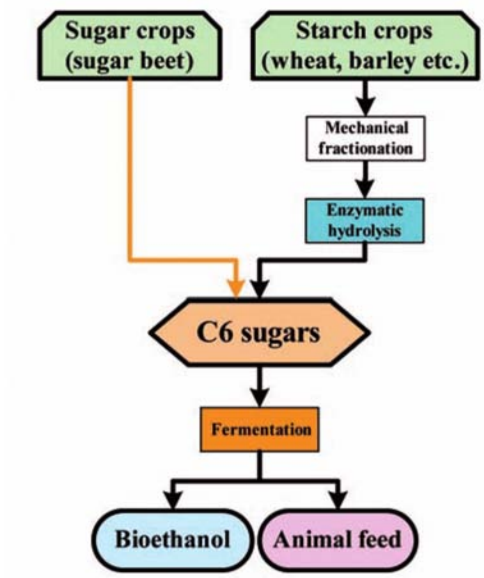


Figure 2.13: Scheme of the bioethanol plant of Zeitz [2].

Bioethanol is produced from cereals like wheat, barley, triticale or maize as well as sugar syrups. The by-products of the plant are: energy (produced via an high efficient CHP section) which not only can supply the plant's need but also is sold to the grid and a high protein and fat content animal feed (DDGS: Distillers' Dried Grains with Solubles), which is sold under the brand name ProtiGrain®, suitable for all types of livestock and pet food.

C6 sugars and biogas biorefinery for bioethanol, animal feed, fertilizer, electricity and heat from starch crops and organic residues

The canadian Highmark Renewables developed a concept of biorefinery coupling two processes. As it is shown in Figure 2.14, the bioethanol production works in symbiosis with the cattle breeding and the digestion plant: the main process converts grain (wheat) into ethanol while the residual products (the DDGS) is fed to cattle to a nearby feed-lot. Cattle manure and slaughtering residues are collected and used in an anaerobic digester to generate biogas which is sent to the co-generation section. The CHP plant provides steam, heat and electricity for the bioethanol process and for the digestion and the surplus of power is sold to the grid. Finally, the by-product of the anaerobic digestion is sold as a fertilizer and it returns to the land, thus closing the circle.

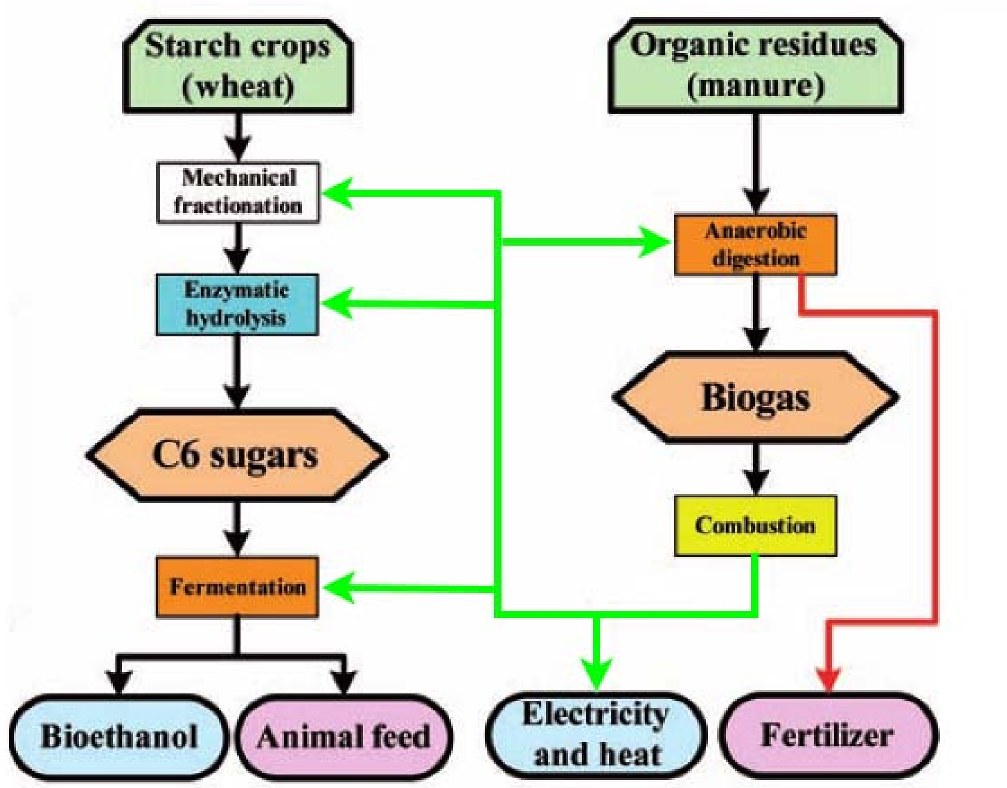


Figure 2.14: Scheme of the Integrated BioRefinery™[2].

The core of the facility is the power section, (see Figure 2.15) the essential link between the ethanol production and the biogas plant. This facility is a clear example of integration between two independent processes, in the perspective of achieving the most cost-effective production of ethanol. The net yearly output of the biorefinery is 40 million litres of bioethanol, 10.000 tonnes of fertilizer and 8760 MWh of electricity delivered to the grid [2].

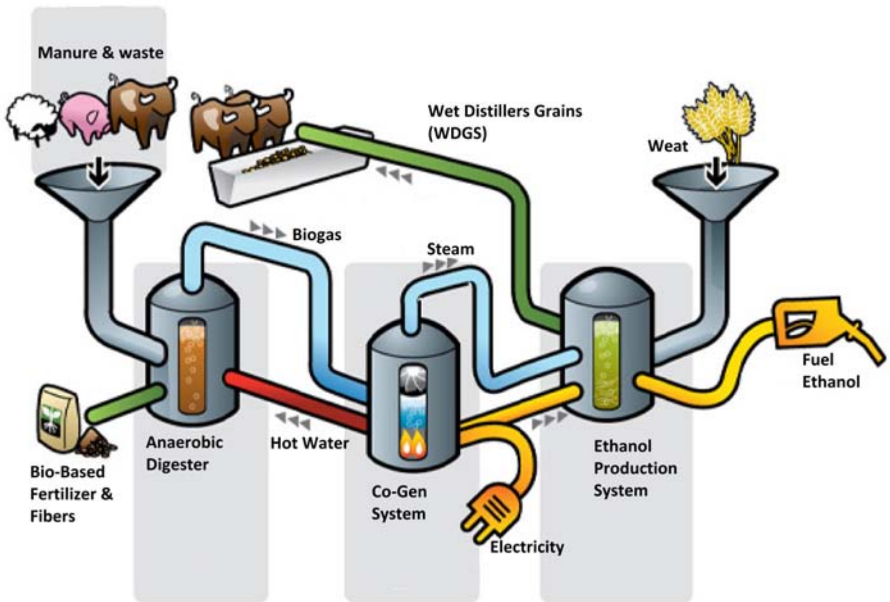


Figure 2.15: Overview of the Integrated BioRefinery™, Alberta (Canada).

Lignin biorefinery for biomaterials, electricity and heat from lignocellulosic crops or residues

Zellstoff Stendal is one of the largest producer of virgin fibre on Europe, with an annual output of 640.000 tonnes of pulp [35].

The plant consists in a main line, in which the feedstock (softwood, small logs and sawmill chips) is treated and decomposed, and a co-generative unit which produces electricity and heat with a global efficiency of 70%. The power section burns lignin coming from the pulp process in a steam boiler, feeding the largest bioenergy turbine in Europe (100 MWe [2]). Consequently, this kind of biorefinery has biomaterials (paper) and bioenergy as outputs.

It is clear that this plant was not designed to be a biorefinery, and the cogenerative section was settled up in order to improve the overall plant efficiency. This could be the first step towards a bio-based economy: first upgrade existing plants (the way pursued nowadays) and then move to newly designed facilities.

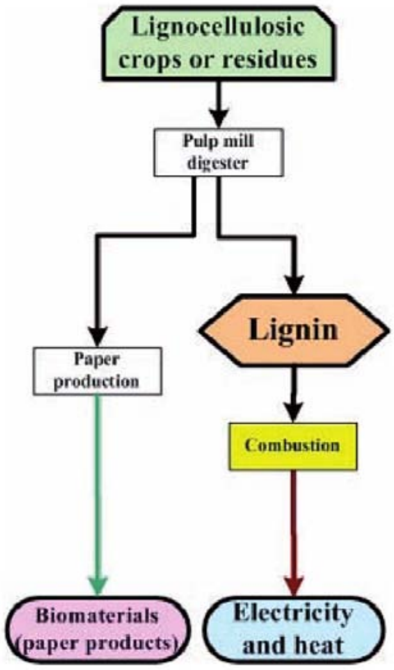


Figure 2.16: Scheme of the Zellstoff Stendal GmbH plant [2].

C6/C5 sugars and lignin biorefinery for bioethanol, animal feed, electricity and heat from lignocellulosic residues

The Integrated Biomass Utilization System (IBUS) owned by Inbicom is built close to the Asnæs Power Station, in a sort of mutual symbiosis with the existing power station, located in Kalundborg (Denmark), where energy and by-products are exchanged. Actually this facility itself it is not a biorefinery, but enlarging the boundary of the system and considering also the CHP plant located nearby (and connected with the facility) it becomes a biorefinery.

Waste steam from the power station is sent to the biorefinery to be used in the conversion of straw into cellulosic ethanol. One of the by-product of the refinery is a lignin powder that it is burnt in the power plants boiler without additional treatment in order to replace part of the coal. Moreover, the lignin could also be pelletised and used as solid fuel elsewhere.

This energy exchange increases the efficiency and shrinks the carbon footprint of both plant, allowing high electrical efficiency to the biomass, efficiency that would be impossible to reach in a biomass-only power station. Pentose sugars are not necessarily fermentation to ethanol but all liquid streams are combined to give a sugar (hemicelluloses) and mineral rich product, which can be used as cattle feed.

The technology was originally developed to convert straw into bioethanol, animal feed and solid biofuel, but it can be adapted to other types of biomass such as corn stover, grasses, bagasse, household waste, etc. Presently the plant has a capacity of 100 tonnes of straw per day and an overall output of 4300 tonnes of ethanol per year.

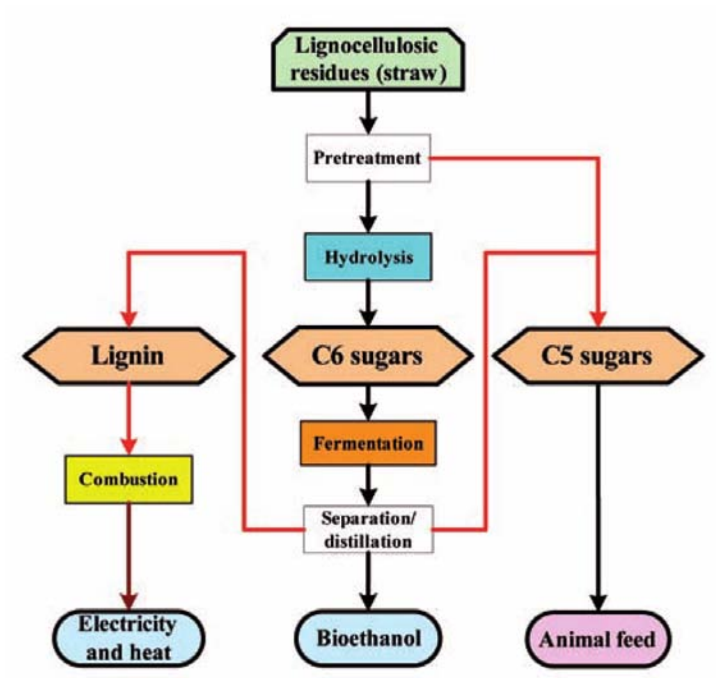


Figure 2.17: Scheme of the IBUS plant [2].

Syngas platform biorefinery for fuels and chemicals from imported lignocellulosic biomass. C5/C6 sugar, lignin and protein platform biorefinery for feed, chemicals and fuels from biofuel process residues

The Port of Rotterdam is the fourth world biggest harbour. The Rotterdam Climate Initiative, together with the Municipality of Rotterdam and the Port Authority, is developing an ambitious project which aim at reducing the carbon footprint of the whole port area by 50% (compared with 1990).

The challenge is to create an European Bio-Hub in which imported densified biomass is processed in the port facilities to get high value products that could be exported both in Europe and world wide. Currently, the state-of-the-art of the programme is still demonstration, but the objective is to set-up an integrated feedstock demonstration plant which comprehends:

- a 10 MWth entrained-flow gasification system for the co-production of base chemicals, biofuels (Biomass-to-Liquid) and power;
- food and biofuels production from residues, valorization facilities co-producing: proteins, amino-acids, chemicals, bioethanol and biogas (used in CHP plant).

The feedstock used are either imported energy crops (such as soy, rape, palm, sugar cane) but also lignocellulosic biomass (densified raw biomass, intermediates and agroresidues).

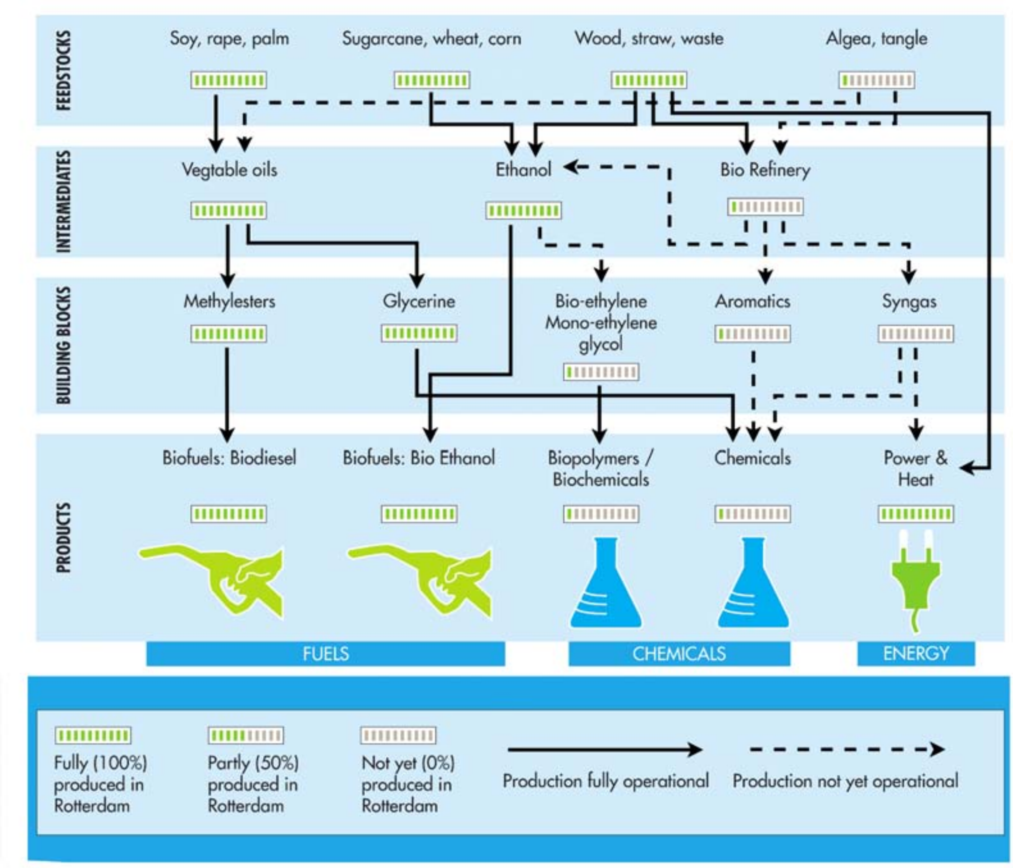


Figure 2.18: Scheme of the European Bio-Hub Rotterdam (the Netherlands) [11].

2.6 Conclusions

Sustainable economical growth needs a safe and reliable source of raw materials. Today's petroleum-based economy is neither sustainable (because fossil fuels are limited) nor eco-friendly. But while the energy industry can rely on different resources (e.g. wind, hydro, sun, biomass) the chemical and material industry is strictly connected with the oil industry. Further development are expected but currently biorefineries are the most promising answer to the issue. Nevertheless there are numerous technological issues that must be faced and solved in order to smooth the way towards a bio-based economy. To sum up the complexity connected to the future development of biorefineries, the Biorefinery Task 42 concludes its work proposing an

Strenght	**Weakness**
• Adding value to the use of biomass • Maximizing biomass conversion efficiency, minimizing raw material requirements • Production of a spectrum of bio-based products (food, feed, materials, chemicals) and bioenergy (fuels, power and/or heat) feeding the full Bio-based Economy • Strong Knowledge Infra Structure available to tackle both non-technical and technical issues potentially hindering the deployment trajectory • Biorefinery is not new, it builds on agriculture, food, and forestry industries	• Broad undefined and unclassified area • Involvement of stakeholders of different market sectors (agro, energy, chemical) • Most promising biorefinery processes/concepts not clear • Most promising biomass value chains, including current/future market volumes/prices, not clear • Studying and concept development instead of real market implementation • Variability of quality and energy density of biomass
Opportunities	**Threats**
• Biorefineries can make a significant contribution to sustainable development • Challenging national, European and global policy goals, international focus on sustainable use of biomass for the production of bioenergy • International consensus on the fact that the biomass availability is limited so that the raw materials should be used as efficiently as possible (e.g. development of multi-purpose biorefineries a in framework of scarce raw materials and energy) • International development of a portfolio of biorefinery concepts, including composing technical processes • Strengthening of the economic position of various market sectors (e.g. agriculture, forestry, chemical and energy)	• Fast implementation of other renewable energy technologies feeding the market requests • Bio-based products and bioenergy are assessed to a higher standard than traditional products (no level playing field) • Availability and contractibility of raw materials (e.g. climate change, policies, logistics) • High investment capital for pilot and demo initiatives difficult to find, and existing industrial infrastructure is not depreciated yet • Changing governmental policies • Questioning of food/feed/fuels (land use competition) and sustainability of biomass production • Goals of end users often focused upon single product

Table 2.2: SWOT analysis on biorefineries [2, 9].

interesting table of Strength, Weakness, Opportunities and Treats (SWOT analysis) [2, 9].

Table 2.2 display really well the complexity of the issues connected to the concept of biorefinery. The most important from an engineering point of view is the analysis and the synthesis of new biorefinery concepts, which requires new synergies between different disciplines (process engineering, chemistry, biology, economy) but also new methods and approaches. As shown in Figure 2.3, the complexity of the matter must be taken into account in building the models. In the current work, a methodology is proposed and applied to a tool whose goal is to confront and synthesize new concepts of biorefinery. The challenge is to find a systematic scientific procedure to analyse different concepts of biorefinery and develop new design.

Biorefineries have the great chance of being a crucial contribute in steering towards a sustainable economy, being the pillars of a new concept of economy. According to [1], biorefineries will play a determinant role, as they are at the base of the future bio-based economy. However, besides the massive potential, the weakness of biorefineries must not be underestimated: the biorefinery approach is a necessity to meet the biofuel European policy but the current allocation of subsidies takes into account only biofuels and electricity. Therefore, to fully support the development of biorefineries, it will be necessary to adjust the economic support including chemicals and other bio-based products.

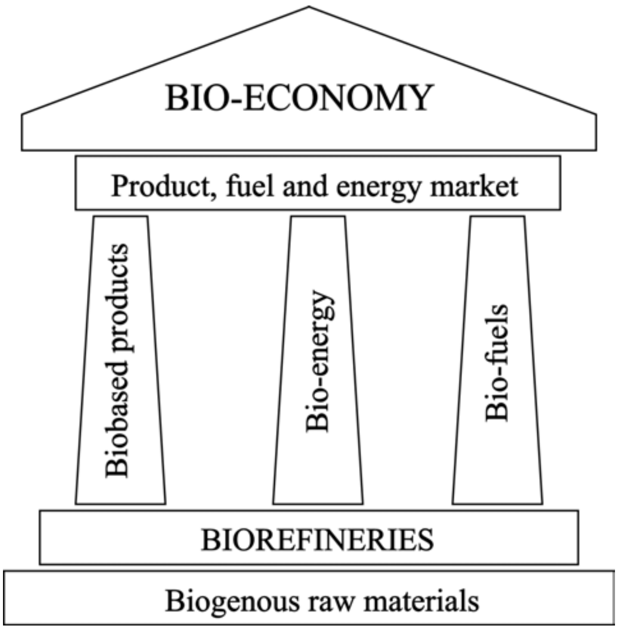


Figure 2.19: Pillar model of future economy based on biorefineries [1].

Bioefineries can improve the economy of rural area being new field of investment. In the long term period, re-investing money in a regional contest enhance the import/export balance: exploiting domestic resources helps to become energy self-sufficient and keep the assets inside the homeland, enhancing the economy of rural area. Unluckily, full chain is not yet market competitive because of the relatively cheap fossil fuels. Moreover, investment capitals for pilot plant are hard to be found, thus slowing the development of a practical know-how.

In order not to waste this huge potential, a strong cooperation between different players (government, industry, agriculture and energy sector) must be fostered and put into effect by a common vision and setting up roadmaps.

As it was discussed through this chapter, a staggering number of variables and players are involved in the development of biorefineries. The challenge is to steer towards a sustainable economy: thank to biorefineries, bio-based products, energy and fuels can be produced in a economically, socially and environmentally sustainable manner. This will lead to the development of new competence, creating new job opportunities and opening new markets.

Chapter 3

OSMOSE: a multi-purpose optimization platform

Abstract

In the following chapter the OSMOSE Platform is described. OSMOSE is a MatLab code developed by Master and PhD. students of LENI, that allows to deal and elaborate models created with different software. Then OSMOSE in the Wood2CHem mode is illustrated, focusing on how to create a superstructure and models of biomass conversion processes. This procedure is the general methodology used to build models for the Platform.

3.1 Introduction

OSMOSE is an acronym for "OptimiSation Multi-Objectifs de Systemes Energetiques integres" (Multi-Objective OptimiZation of integrated Energy Systems) and it was created as a tool for the design and the analysis of integrated energy systems [36]. The goal of the OSMOSE Platform is to allow the integration of flow-sheeting tools, process integration and costing tools to realise the study of integrated energy conversion systems. The code is based on MatLab but it can deal with other software software (like Belsim, Easy, Moo, Aspen, GLPK, AMPL) thus boosting the potential of a simple MatLab code [37]. Among other features, OSMOSE has a complete suite of computation and results analysis tools (such as optimization, sensitivity analysis, pareto curve analysis) [38]. Indeed the major goal of OSMOSE is to allow the integration of different models and to organise the process design methods using process integration techniques and multi-objective thermo-economic optimisation techniques [38].

3.2 Features of the OSMOSE Platform

The OSMOSE Platform has several features and therefore can be used in different ways. OSMOSE is able to deal with other flow-sheeting software (such as Aspen or Belsim Vali) and perform a broad variety of analysis like pinch analysis, life cycle assessment, sensitivity analysis, thermo-economic analysis, mono and multi-objective optimization. Three main uses of OSMOSE can be identified:

1. OSMOSE can manage models created with other software and use the results coming from those models to perform post-analysis such as pinch analysis. For instance, OSMOSE can extract values of temperature, pressure and mass flow of each stream to build the composite curves or perform thermo-economic analysis extracting the thermodynamic data of the streams and the costs;

2. OSMOSE can also directly deal with the flow-sheeting software and perform sensitivity analysis or optimization (mono and multi-objective), in which the decision variables are stated by the user. In this mode, OSMOSE can gather models of components, utilities or energy systems to create complex energy system superstructures;

3. OSMOSE can separate a complex energy system into several units and perform energy or economic analysis of part of a system.

In order to handle the above mentioned problems, general elements are used to set up the desired structure in OSMOSE: units (which represent components or sub-systems of any kind modelled with different software), streams (mass, energy or costs) and tags (sets of data that can be declared by the users and then used as input data instead of similar data of the single model). The general structure and rationale of OSMOSE is presented in Figure 3.1.

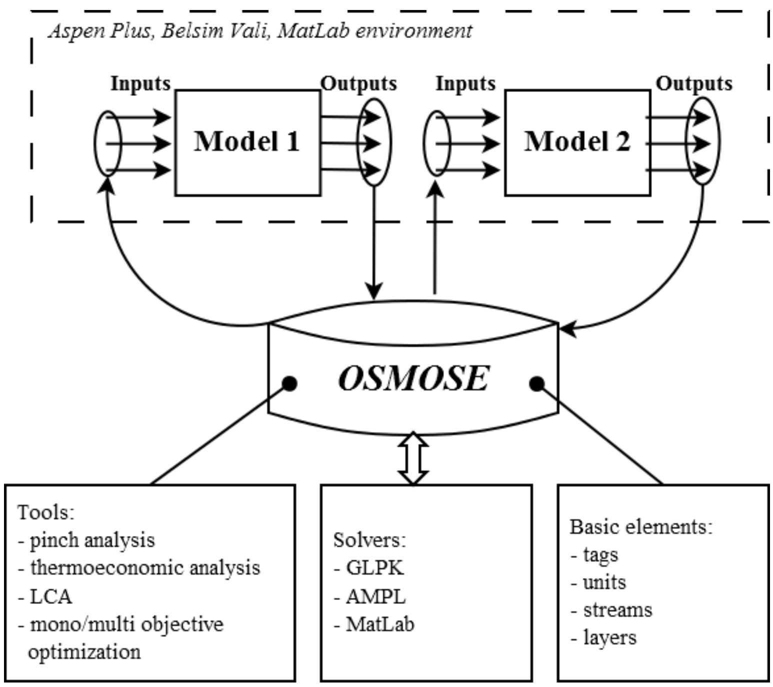


Figure 3.1: Organization of the OSMOSE Platform.

The core is made by the technology model, which is composed by units, streams and tags (see Section 3.3 for more details). Beside that, OSMOSE has a pre-compute phase (pre-Energy Integration, in which the costs are calculated to update the model) and a post-compute phase (post-Energy Integration). The latter is needed in case of multi objective optimization because, since the optimization model is MILP, a recalculation of the cost according to the real cost function is required.

For what concerns the generic model in OSMOSE, Figure 3.2 shows the features that can be included in each model: besides internal parameters (for instance thermodynamic data for the streams), each model can be characterized by streams, environmental impact (needed to perform LCA) and economics parameters (necessary to perform an economic analysis).

As an example, there are a considerable wide number of products that can be derived from lignocellulose feedstock, each of them can be obtained from numerous alternative pathways. Thus, to determine an optimal mix of products and a biorefinery process structure, several possible process configurations have to be evaluated and compared. This can be done by using an approach based on process integration and mathematical multi-objective optimization or it can be done following a simpler approach: if the aim is to have a straight forward model, easy to be solved in a short time, a simplified linear model that can be solved avoiding the MOO is the answer. OSMOSE allows to handle both kind of problems.

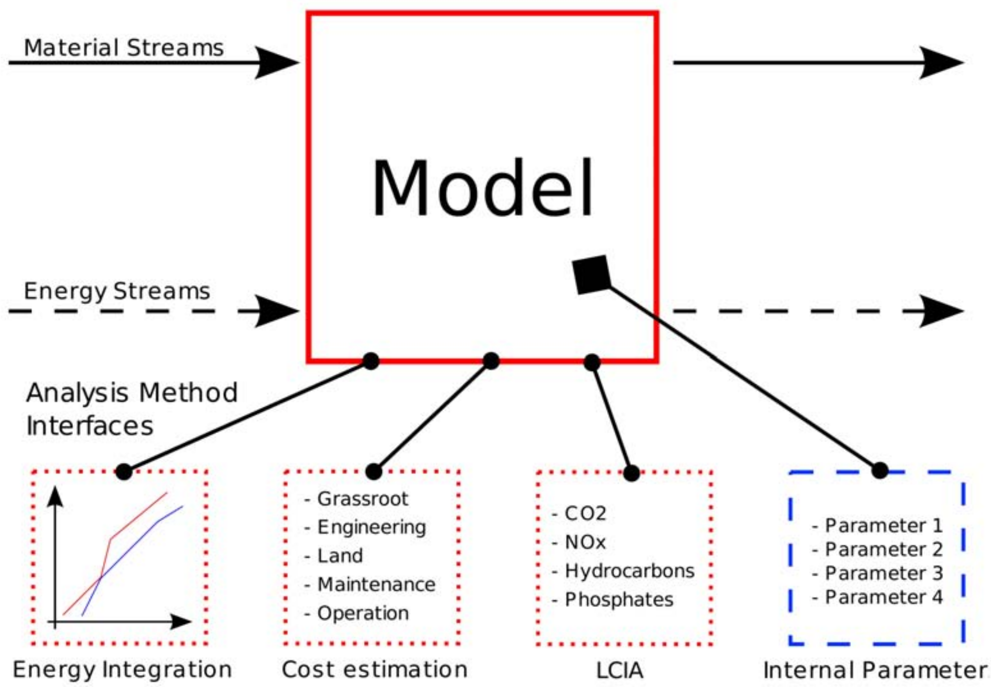


Figure 3.2: General scheme a model in OSMOSE.

3.3 Using OSMOSE in the Wood2CHem mode

In this section the basic concept of the use of OSMOSE in the Wood2CHem mode is explained. Initially, the first draft of the Platform was developed by a master student, Atish Jaientilal [39].

Wood2CHem is a framework Platform created inside OSMOSE, which has the purpose of performing multi-scale process design to synthesize conversion chains of wood, especially lignocellulose feedstock, into marketable products. It is currently being developed in a partnership between the Safety and Environmental Technology (S&ET) group in Eidgenössische Technische Hochschule Zürich (ETHZ) and the Industrial Energy Systems Laboratory (LENI) of École Polytechnique Fédérale de Lausanne (EPFL). The purpose of this project is to create a decision support Platform by using process modelling, multi-objective optimization and process integration techniques. Moreover, it allows the systematic generation and comparison of wood conversion chains.

The Wood2CHem project is organized in three main work packages [39]:

1. development of a wood conversion process models database. The models database will be used as building blocks for the Platform;

2. development of the process modelling methodology to systematically assess the required environomic (that combines thermochemical conversion, economic assessment and environmental assessment) models of the building blocks of wood conversion chains;

3. study of the process system engineering methods to systematically generate wood conversion chains.

This work is part of the third work package, as it addresses its attention in developing the proper methodology to evaluate different pathways and order them in a rank. Moreover, since the objective is to have a light and fast tool to analyse different technologies, the problem is simplified and all the models are treated as simple black boxes.

The Wood2CHem Platform is a specific condition of use of OSMOSE which allows to evaluate different processes that convert biomass into valuable products (heat, power, fuels). In particular, the Wood2CHem Platform exploit a specific feature of OSMOSE which is the capability of gather various models and generate complex structures. In this specific case, the processes considered are technologies for integrated biorefineries, as it was previously explained in Section 2.2 when dealing with the concept of biorefinery.

In Figure 3.3 is presented a general scheme of a superstructure created with OSMOSE in the Wood2CHem Platform. The highlighted key features that characterise the superstructure are:

- **Tags**
- **Units**;
- **Layers**;
- **Streams**.

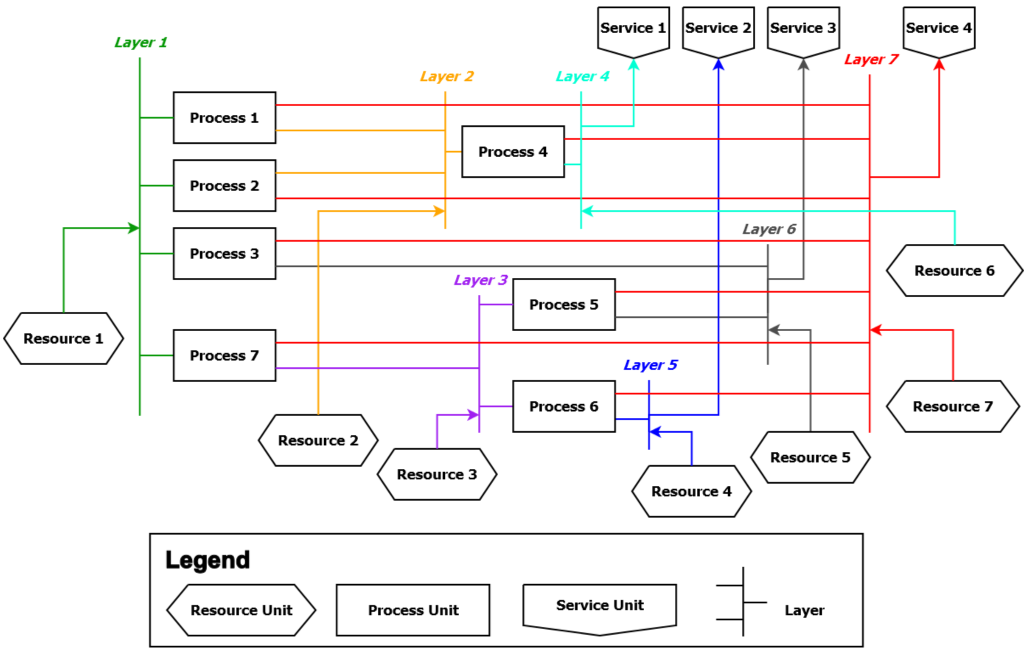


Figure 3.3: General scheme of a superstructure built with the Wood2CHem OSMOSE Platform.

These elements are the basic bricks needed to create and run a model that can be plugged into the Platform. Such structures are part of the OSMOSE package and can be linked together to create the desired superstructure. In the next paragraphs, a brief focus on the features of each structure is performed in order to make clear the basis of the tool used throughout the current work.

Tags

The tags are the basic structure in which the data are saved to be recalled in any part of the model, simply by calling the TagName. Consequently, a tag is a basic structure to organize data.

```
%% Tags definition
nc=nc+1;
technology.Tags(nc).TagName = {'investment'};
% identifier for the parameter, unique name in the model
technology.Tags(nc).DisplayName = {'Investment Money'};
% used to display the name of the parameter
technology.Tags(nc).Description = {'Tag used as example'};
% defines more details about the tag/parameter
technology.Tags(nc).Status = {'CST'};
% status of the parameter: CST = fixed, OFF = calculated
technology.Tags(nc).DefaultValue = 100;
% value of the parameter before computation
technology.Tags(nc).Unit = {'Euro'};
% measurment unit of the parameter
technology.Tags(nc).isVIT = 1;
% indicated is the parameter is a Very Important Tag
```

Table 3.1: Example of tags in OSMOSE

Units

The units are the core of the models created in OSMOSE. The units can have two different features:

- `process`, which means that the unit has a fixed size;
- `utility`, which means that the unit can be scaled linearly multiplying each stream and tags of the unit by the multiplication factor (see Section 4.3).

The Wood2CHem Platform is therefore composed by several units, each one of a specific type:

- **Process units**, i.e. unit in which there is the conversion of one or more input streams into multiple output streams. It represents a conversion technology.
- **Resource unit**, i.e. unit that can provide mass or energy streams to the model. For example, the resource unit "wood" is the model of the wood supply while the resource unit "electricity" is the model of the grid that can provide power to the system;
- **Service unit**, i.e. output unit that collects the products from the process units.

There are several combinations of type of units in the Wood2CHem Platform: for example, if the resource unit "wood" is set to process, it is equal to impose a fixed amount of wood entering the system. In this case the Platform can work input-pushed: stated the overall amount of biomass available, the best pathways and amount of products can be evaluated. On the contrary, if the aim is to fulfill a specific request of products, the service

```
%% Units
% Reference capacity of MeOH unit: 20 MW
nu = 0;
nu = nu+1;
technology.EI.Units(nu).Type = {'utility'}; % Process or Utility
technology.EI.Units(nu).TagName = {'meoh'};
technology.EI.Units(nu).DisplayName = {'methanol utility'};
technology.EI.Units(nu).AddToProblem = 1;
technology.EI.Units(nu).Parent = {'@groups.meoh'};
technology.EI.Units(nu).ITY = {'0'};
technology.EI.Units(nu).Fmin = {'0'}; % min mult
technology.EI.Units(nu).Fmax = {'@services.f_max'}; % max mult
technology.EI.Units(nu).Cost1 = {'0'}; % fixed operating cost
technology.EI.Units(nu).Cost2 = {'@meoh_TOPC'}; % linear op. cost
technology.EI.Units(nu).Cinv1 = {'0'}; % fixed investment cost
technology.EI.Units(nu).Cinv2 = {'@meoh_TGRC'}; % linear inv. cost
technology.EI.Units(nu).Power1 = {'0'}; % fixed power requirement
technology.EI.Units(nu).Power2 = {'0'}; % linear power requirement
```

Table 3.2: Example of Unit in OSMOSE

units can be set to "process" while the resource units are switched to utility and let the Platform select the best pathways and evaluate whether it is more convenient to produce the desired services with biomass or simply buy the necessary goods on the market. This means to run the Platform in the reverse direction, output-pulled.

Streams

The elements that connect units and layers are the streams. Two different kind of streams can be declared:

- Energy streams (see Table 3.3);
- Mass streams (see Table 3.4).

Actually there is a third, hidden stream which is the cost stream. It is automatically included inside the unit definition seen in the paragraph above thus a specific statement is useless.

```
% Mass Streams
ns=ns+1;
technology.EI.Streams(ns).Short = {'type','layer_tagname',...
'unit_tagname','stream_tagname','in_or_out','value'};
```

Table 3.3: Example of mass stream in OSMOSE

```
% Energy Stream
ns=ns+1;
technology.EI.Streams(ns).Short = {'type','unit_tagname',...
'stream_tagname','Tin','Hin','Tout','Hout','deltaT'};
```

Table 3.4: Example of energy stream in OSMOSE

Layers

The layers are simply nodes in which mass and energy balance is performed. There are three main kind of layer:

- **mass balance**, in which the mass balance is performed;
- **cost layer**, that collects all the cost streams and computes the overall investment and operative cost;
- **heat cascade**, in which the energy balance is done, in case of pinch analysis.

3.4 Creating models for the Wood2CHem Platform

Once specified the feature of the Platform, the methodology to create the models to be plugged into the superstructure must be explained. Even if each model inside the Platform is simple a black box, the synthesis of the model of the Platform do not exclude a detailed pre-analysis of the model that will be included.

The steps that must be taken to create a Platform model are:

1. create the flow-sheet model of the process or of the plant and optimize it. In case literature data are available, instead of creating the whole model, a correct analysis of the literature model is necessary. For instance, in the current work all the models were taken from literature, proving how this procedure can easily be integrated with an accurate literary review;

2. set the boundary of the system and analyse the cross-boundary flows. This is a preliminary task that must be fulfilled according to the following step;

3. extract the useful data. For example, from Figure 3.4, if the aim is to build a simple input/output model, the useful data are the frontier interactions (costs, amount of input wood and amount of products). As it can be seen, the fumes stream is considered to be inside the boundary of the system an therefore ignored. However, if the aim is

to perform a more detailed analysis of the process, it can be decompose into several parts and each one analysed separately;

4. create the black box model putting the reference value of cost, input and output streams as tag of the model.

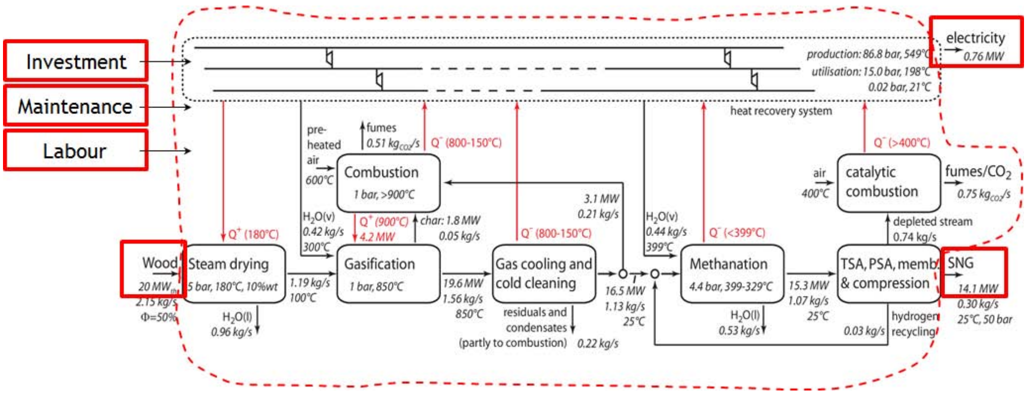


Figure 3.4: Analysis and extraction of data from a process flow diagram [12].

With this simple procedure a great variety of processes can be simplified and plugged inside the Platform easily. The last step is to link the streams to the corresponding layer. This prove how flexible and easily upgraded the Platform is. The choice of having many basic black box models is due to the pursuit of a simple and agile tool. This fact obviously reduces the accuracy but boosts the speed in solving the model. Since this level of research is a pre-analysis of conversion pathways, having a robust simple model quick to be solved is a more urgent issue. The detailed modelling and optimization is left to a following step.

3.5 Conclusions

In this brief introduction, the key features of OSMOSE are presented. The software has a huge potential to analyse energy system and, in particular, the application of OSMOSE to the Wood2CHem Platform was illustrated, focusing on the key aspects of the structure of the Platform. The role of OSMOSE in such a work is used to set up superstructures of biomass conversion processes. The goal is to find a methodology to be applied to the OSMOSE Wood2CHem Platform that can generate a full rank of conversion pathways. The final object is to evaluate and compare different processes and pathways and there fore detect the best exploitation of wood, according to the boundary conditions.

Consequently, the methodology must be first of all developed and therefore adapted to the feature of the OSMOSE Wood2CHem Platform, thus requiring a strong skill in OSMOSE programming. This is challenge from the computational point of view and required to deeply dive into OSMOSE MatLab programming. The development of the methodology and its application is discussed in the next chapters.

Chapter 4

A methodology to select and rank conversion pathways for bioenergy sources

Abstract

The effectiveness of the platform is based on the methodology used. After a general definition of the problem, the equations and constraints used in the Platform to obtain an ordered set of pathways, the focus has been set on the Integer-Cuts constraint method, which turns out to be the most efficient condition to select and rank multiple pathways. However, the use of Integer-Cut leads to some computational issues. Given the non-heuristic nature of the problem, a set of tests was necessary to figure out how the solver behaves under each constraint and consequently to find the best set of conditions to achieve the result in a fast, efficient way.

4.1 Introduction

As a new field of research, biorefineries present some peculiar aspects. First of all, most of the conversion technologies are still in a research and development stage. This condition makes the economics of biorefineries really uncertain, because of the scarcity of experience about this kind of plant and the production costs are still high.

Secondly, biomass, although a renewable source, has a small energy density. The economy of scale tends to go for big sized plant in order to reduce the specific cost of the output but the harvesting of biomass becomes more expensive (both in term of energy and money) as the biomass source is far from the plant, as pointed out in the works of [14] and [40]. For these reasons, computer aided tools are used to search the best way to convert biomass into valuable products with the higher yield and the minimum cost.

In order to select and compare different pathways, [41] and [42] used a fuzzy methodology applied to a linear problem; another approach is automated targeting followed by [43]. From the computation side, several researches focused on solving MILP [44], which is the most common typology of engineer problem [45]. In the work of [46] a logic-cut approach to process network selection is followed while [47] proposed a disjunctive programming in order to decompose the problem of finding the best pathways into two sub-problems. Also [48] focused on the evaluation of different alternatives of conversion routes inside the same process (i.e. biofuels production from wooden biomass or sugar crops). Process synthesis techniques are used by [49] and [50] to generate and evaluate alternatives among biorefinery conversion processes using pinch analysis and water assessment.

The method proposed by [51] is original as it involves the decomposition of each mass flow into the basic components to find the best pathways to produce fuels. In that work, the integer-cuts method were used to generate more solutions with different objective functions (yield, payback period) to be compared.

For what concerns the generation of multiple solutions, [52] proposed three different algorithms: the one-tree algorithm (a modification of the standard branch-and-bound algorithm), a MIP heuristics algorithm and the third one that generalizes the previous approaches.

The peculiarity of this research is not only to explore and evaluate different technologies for biorefineries but also to rank them according to their total cost using the Integer-Cuts methodology. This enlarges the view on the synthesis of biorefinery and allows to choose among a wider variety of solutions. But while finding the optimum of a MINL or MIL problem can be handled by current solver, a new methodology to generate a full rank of solutions that make sense is required. This is the most challenging task and the key issue of the present work. In order to obtain the rank the integer cuts methodology is most suitable according to the MIL problem definition.

For example, if a certain amount of wood is available, several routes to convert it into valuable bioenergy services can be followed. For instance, the biomass con be converted into syngas and the syngas can be burnt in a gas turbine and therefore produce heat and electricity. Otherwise, another option is to synthesize methanol from the syngas, as it can be seen in Figure 4.1.

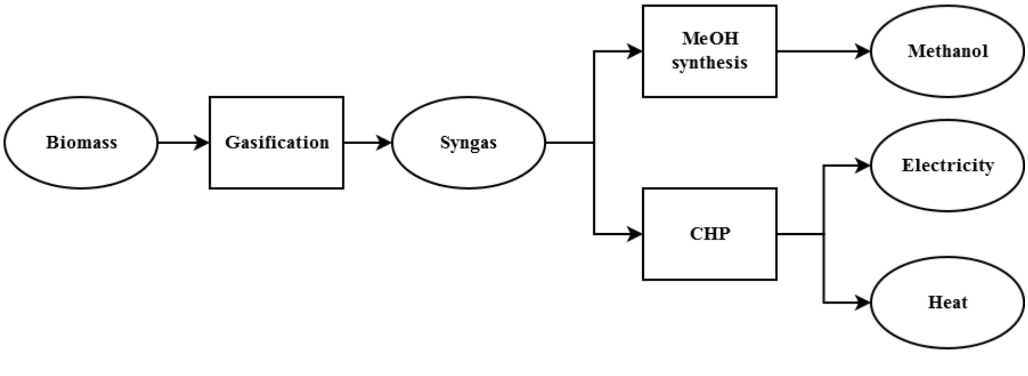


Figure 4.1: A simple example of choosing the best conversion pathways for wooden biomass.

Another intermediate option is to sent part of the syngas to the methanol synthesis and part to the combined heat and power section to fulfill the thermal and electrical needs of the plant. Comparing these options leads to choose the best exploitation of wood. Indeed, creating a rank of the possible alternatives can help in the decision process because if two pathways are close one to the other in term of objective function, other criteria con be applied to choose the most suitable pathway. The order in the rank is influenced by numerous factors: investment cost, cost of the necessary supplies needed by the plant (for instance heat, electricity) and, obviously, the value of the products obtained by the plant. If the number of processes to evaluate is small, the problem is simple to handle but if the complexity of the superstructure and the interaction between processes increases, a systematic approach must be followed. The aim of this Section is to present and validate a method to systematically analyse different pathways inside a superstructure and create and ordered list of technology according to the objective function. This requires to define an objective function which will be the comparison parameters in creating the rank. A similar problem of detecting pathways was covered by the works of [53] and [54].

4.2 General classification of the problem

In this section a simple and general approach to classify the problem [55] is presented. Basically, the steps needed in building a model are:

1. Choose dependent and independent variables;
2. Define the equation of the model (i.e. maps of the component, mass and energy balance, thermodynamic properties of the fluids).

For what concerns the variables, they could be of different kinds:

- Real, used to describe a state or a size of a component;
- Integer binary, mostly used as a mathematical index to account the presence of a unit in the system;
- Integer natural, mostly used to account for the presence of multiple units of the same kind.

In the problem in analysis, an example of an integer variable is the parameter used to set the existence of a unit, which can be 1 if the unit is activated or 0 in case it is not. An example of a real variable is the size, which can range inside the minimum and maximum allowed size.

The number of dependent and independent variables states the size and the accuracy of the model. Increasing the number of independent variables increases not only the accuracy of the model but also its complexity. In the problem in analysis there are only two sets of variables (unit use and multiplication factor): since the aim is to sort different technologies, the only information needed are whether that technology is used (information provided by the variable unit use) and the size of the technology (which is related to the mult). For instance, while knowing the temperature of the methanol is useless, the amount of methanol produced is a way more important data. Since the essential goal is to know which is the best conversion pathways and how much products can be extracted from a given amount of input biomass, the model used inside the platform can simply be "black box".

Obviously this approach presents important simplifications: each model used in the platform comes from studies and analysis available in literature (one example among other is the work of [15] and [56]). These models were studied and optimized separately, and it is clear that the single model's optimum could not correspond to the system optimum. However, this is another simplification used in order to keep the problem straight forward and easy to be solved. The aim of this level of research is not to find how to integrate different processes but which processes could be coupled, which are the most effective, according to the boundary conditions, while the process design analysis and detailed modelling is left for a second stage.

4.3 MILP problem statement

In this Section the equation of the model will be presented. In the platform several objective functions can be stated (operating cost, total cost, total cost with impacts). Both during the test (see Section 4.5) and the run of the platform (see Section 5), the objective function selected is to minimize the total cost (TC), sum of operating cost (OC) and investment cost (IC):

$$\text{minimize} \quad TC = \sum_{s=1}^{N_s}(OC_s + IC_s) \tag{4.1}$$

Where:

$$OC_s = Cost_{1,s} \cdot y_s + Cost_{2,s} \cdot f_s \tag{4.2}$$

$$IC_s = Cinv_{1,s} \cdot y_s + Cinv_{2,s} \cdot f_s \tag{4.3}$$

Subject to:

- Energy conversion Technology Selection:

$$f_{min,s} \cdot y_s \leq f_s \leq f_{min,s} \cdot y_s \tag{4.4}$$

- Mass/Energy Balance at Layers

$$\sum_{s=1}^{N_{s,l}} f_s e_s^+ + \sum_{s=1}^{N_{s,l}} f_s e_s^- = 0 \tag{4.5}$$

The variables of the problem are the integer unit use $y_s \in \{0, 1\}$ and the real multiplication factor $f_s \in \Re$ so in this optimization problem, only size and existence of the unit are the variables, thus it is a mixed-integer problem. Moreover, the structure of the cost function is linear, so the whole optimization problem belongs to the MILP class. Linear cost hypothesis keeps the problem simple and easy to be handled by the solver. However, it is a simplification, as it is possible to linearise cost functions only in a certain range, by keeping a good accuracy.

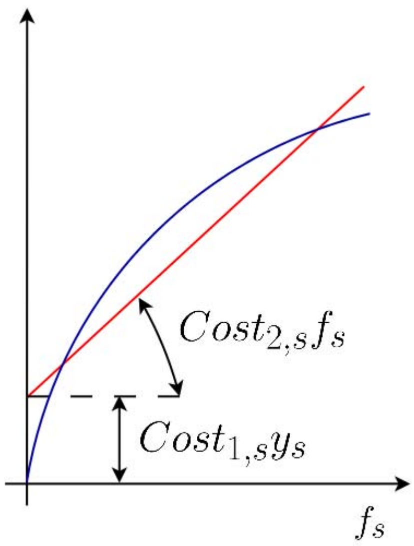


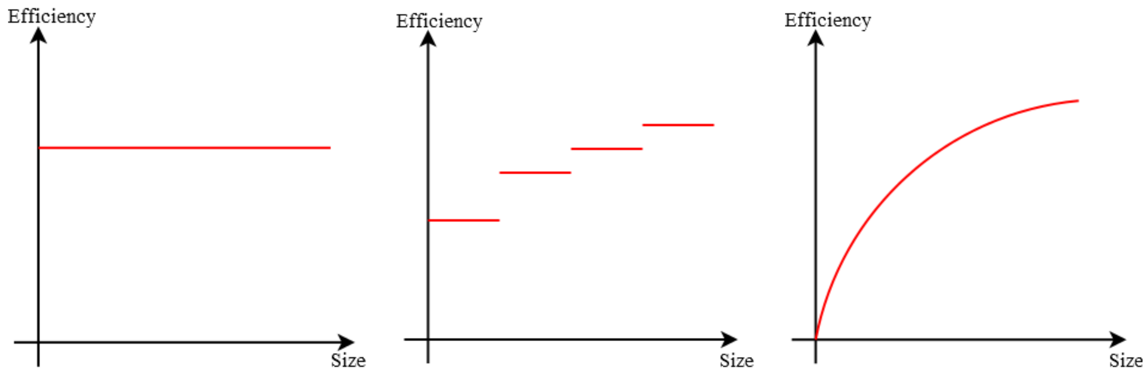
Figure 4.2: Linear regression of the real cost function in a neighbourhood of the size in analysis.

Nevertheless, among all the ways in which a real cost function can be linearised, the choice was addressed firstly to interpolate the exponential cost function $y = ax^b$ given two sets of point (size and investment cost) then to find the linear regression in a neighbourhood of the size of the plant in analysis, thus finding the $y = mx + q$ function (Figure 4.2).

Another aspect that must be pointed out in the cost function is that the value of $Cost_{2,s}$ could be positive (as for resource units, which represent a cost) or negative (as for service units, because the output is a revenue). Consequently, striving for being more precise, the actual objective function not only deals with the total production cost (considering operating and investment) but also takes into account the revenue generated by selling the products. This is due to the fact that the platform is dealing with multi-product processes: in order to state which is the best one according to the economics, the revenue must be considered. For instance, a plant with a poor conversion efficiency of biomass into fuels, but with a valuable by-product (electricity, for example), is preferred to an highly efficient process which produces high amount of fuel requiring electricity. In the end, the real objective function is total cost minus incomes, so if it is negative there is a positive revenue from the plant. On the other hand, if it is positive, the break even price of the input biomass can be calculated from the objective function value in order to evaluate the gap between market price and break even price.

For what concerns the constraint of the problem, the existence of subsystem (4.5) states that the size of the unit must be between the limit size stated by the user. The balance at each layer sets the conservation of mass and energy in the model. $N_{s,l}$ is the number of subsystem (also called units) connected to layer l, e_s^+ is the value of the reference stream leaving subsystem s while e_s^- is the reference value of the stream entering unit s. Consequently, as each stream is multiplied by the unit mult, the connection between different units is guaranteed by the layers.

Concerning the equation that characterizes each unit, it must be pointed out that the map of the component is assumed to be constant. This is a simplification from an engineering point of view. However, it is necessary to keep the size of the problem within manageable dimensions.



(a) Constant map (b) Piecewise map (c) Non-linear map

Figure 4.3: Comparison between different method of describing an efficiency map.

A more sophisticated approach could use piecewise map for each component (see Figure 4.3), but in that case the number of integer variables increases because a new integer variable must be stated for each interval of the piecewise efficiency curve, thus increasing the complexity of the problem. For instance, if each unit in the example test of Section 4.5 has piecewise map with 4 steps, the number of integer needed to describe the units jumps from 4 to 16. Practically, it is like multiplying the number of unit in parallel, forcing the solver to switch from an unit to another according to the size. This simplification can be used in case of chemical processes (i.e. reactor vessels, distillation columns) without loosing accuracy while, in case of engines (i.e. gas turbines, reciprocating engines, steam turbines), this can be a strong simplification if the range of size is wide.

4.4 Generation of multiple pathways with Integer Cut constraint

Once the superstructure is set using layers, the following issue is to find a methodology to generate an ordered set of solutions. Presently, the solvers used at LENI (AMPL, GLPK) can find the optimum pathway in a superstructure but they are not able to investigate the overall space, finding also the sub-optimal solutions.

If a rank of the most performing pathways is obtained (according to the objective function stated), then it is possible to analyse and choose among the sub-optimal conversion pathways that suit most to the case in analysis or the available resources and utilities. For instance, the optimum solution could involve the employment of a not-well-established technology, whereas a sub-optimal solution, although less performing, could be easily exploited using mature processes or even already available utilities.

In this way, the platform gains flexibility: it can be used either to find the best use for a certain amount of biomass according to the objective and the boundary constraints (biomass availability, prices, etc), or to find the possible pathways to obtain a set of specific products and services.

Therefore, a constraint is needed to allow the solver to look for other solutions besides the optimum [57]. Literature presents numerous example of methodology to analyse process networks. For instance [46] proposed the use logic-cuts, but without being able to state an algorithm to automatically generate them. The integer cut constraint [58] is an interesting approach because it acts on the integer variables thus allowing to generate multiple solutions [13].

One of the most promising methodology to retrieve multiple solutions is applying Integer-Cuts constraints. While it is rather easy to confront two consecutive solutions, it is more challenging to make the solver avoid replicating an already found solution. If the aim is to look for all the possible solutions and to put them into order, then a constraint is needed to compare the current solution with all the previously obtained ones.

There are substantially two ways of imposing an Integer-Cuts constraint useful to the platform: the first constraint presented is an original solution, the second one is taken from [59].

The first way of stating the constraint is this:

$$\sum_{j=1}^{k-1} \left\lceil \frac{\sum_{s=1}^{N_s} |y_s^k - y_s^{k-j}|}{N_s} \right\rceil \geq k - 1 \tag{4.6}$$

With:

- k is the index of the current solution;
- $j \in \{1, .., k-1\}$ is the index used to make the comparison with the past $k-1$ solutions;
- N_s is the number of subsystems (units) in the superstructure;
- $s \in \{1, .., N_s\}$ is the index of the subsystem;
- $y_s^k \in \{0, 1\}$ is the integer variable "unit use" of unit s in solution k (where 1: active, 0: inactive). y_s^k is an item of the vector $Y^k = [y_1^k, y_2^k, .., y_{N_s}^k]$, which is the unit use vector of solution k.

The constraint is verified when the current solution $Y^k = [y_1^k, y_2^k, .., y_{N_s}^k]$ is a brand new combination. The logic step of the equation can be summarized as follows:

1. the term $|y_s^k - y_s^{k-j}|$ compares the unit use of unit s at the current k-th solution with the unit use in the $k-j$ solution. The result is either 0, if there is no change in the unit use, or 1 if the unit use changes;

2. $\sum_{s=1}^{N_s} |y_s^k - y_s^{k-j}| \in \{0, 1, .., N_s\}$ gives as a result an integer between 0 (which means that in the current solution the solver is analysing an already found solution) and N_s (which means that all the unit use have changed status);

3. Dividing by the total number of the units in the superstructure is just a mathematical trick to get a number less or equal to one in order to apply the operator ceiling $\frac{\sum_{s=1}^{N_s} |y_s^k - y_s^{k-j}|}{N_s} \leq 1$;

4. $\left\lceil \frac{\sum_{s=1}^{N_s} |y_s^k - y_s^{k-j}|}{N_s} \right\rceil \in \{0, 1\}$ the operator ceiling gives as an output an integer which is 1, if at least one unit use has changed status, or 0 if no changes occurred in the unit use in the k-th solution;

5. Finally, the parameter that gives the constraints is obtained by summing up all the changes occurred in the unit status in the past solutions. The constraint must be grater equal than the number of the already found solution minus 1. The inequality is stated in this way because it is useless to confront the current solution with itself (so $k-1$ confronts are necessary).

Consequently, whenever the constraint assumes value greater than the number of the current solution minus 1, it means that the solver is analysing a brand new solution. Otherwise, the constraint is not verified and the solution ignored. The great advantage of this formula is that it is a unique constraint that can deal with all the past solutions simultaneously. Besides this good point, it must not be forget that with this new constraint the problem is no more MIL but MINL. This is due to the use of the function ceiling, which is non-linear, as it can be see in Figure 4.4.

In order to keep the problem linear, a different statement of the constraint is necessary. The main concern in keeping the problem MIL is because non-linear solvers are still in a development stage, thus linear problems are more robust and easy to be solved. The integer-cuts methodology proposed by [58] and used by [13] and [59] was analysed in order to be applied to the problem. In [13] the attention is addressed to find multiple heat exchangers networks with the optimal configuration while in [59] the object of the study is a multi-period energy system optimization with several technologies.

As in the case in analysis, in [59] the aim was to find multiple solutions of a mixed integer linear problem. The approach followed was to change the

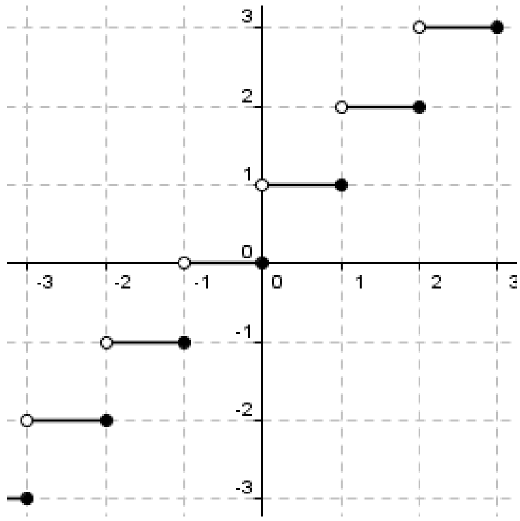


Figure 4.4: The ceiling function is clearly non-linear.

problem definition at each iteration, in order to explore all the solutions. The rationale of the constraint is presented in the algorithm of Figure 4.5.

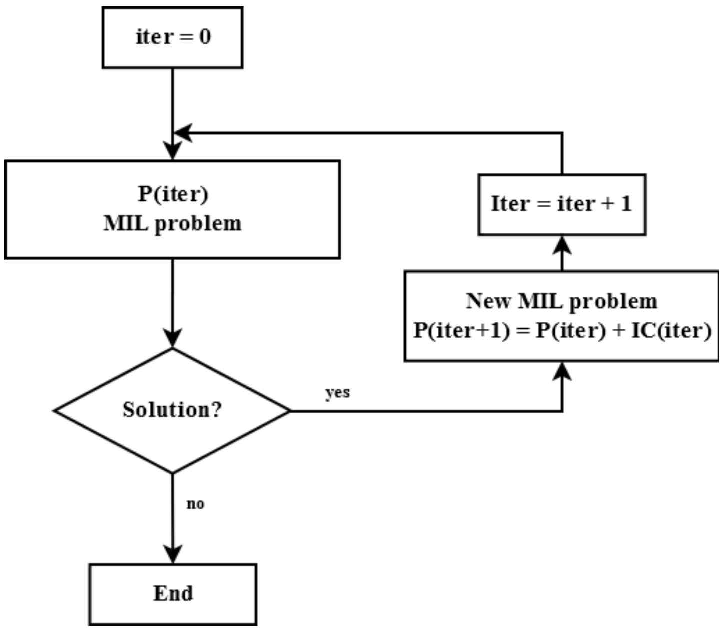


Figure 4.5: Algorithm for multiple solution generation [13].

After the first solution is found, the initial problem is updated adding a new Integer-Cut constraint, consequently a new problem is defined and solved. The Integer-Cut prevents from replicating the already found solution. The Integer-Cut used to avoid repeating the solution is stated as follows [59]:

$$\sum_{s=1}^{N_s} \left(2y_s^k - 1\right) y_s \leq \left(\sum_{s=1}^{N_s} y_s^k\right) - 1 \qquad \forall\, k = 1, ..., n_{sol} \tag{4.7}$$

With N_s is the number of subsystem in the model, y_s^k is the unit use of subsystem s at the k-th iteration and y_s is the unit use of the current iteration. This constraint must be added at each run, consequently the problem definition changes at each iteration and the number of constraints increases linearly. The term $2y_s^k - 1$ can have the following values:

$$2y_s^k - 1 = \begin{cases} 1 & \text{if } y_s^k = 1, \\ -1 & \text{if } y_s^k = 0, \end{cases}$$

Consequently:

$$\left(2y_s^k - 1\right) y_s = \begin{cases} 0 & \text{if } y_s^k = 0 \wedge y_s = 0, \\ 0 & \text{if } y_s^k = 1 \wedge y_s = 0, \\ 1 & \text{if } y_s^k = 1 \wedge y_s = 1, \\ -1 & \text{if } y_s^k = 0 \wedge y_s = 0, \end{cases}$$

If the unit use changes, $\left(2y_s^k - 1\right) y_s \leq 0$ because the value could be either zero or -1. If there are no changes in the unit use, $\left(2y_s^k - 1\right) y_s \geq 0$ because the value could be either zero or 1. Finally, if there is at least one unit use change in the current solution $\sum_{s=1}^{N_s} \left(2y_s^k - 1\right) y_s = \left(\sum_{s=1}^{N_s} y_s^k\right) - 1$. If there are multiple units that change their y_s the constraint is verified being the left term lower than the right. In case there are no units changes, since:

$$\sum_{s=1}^{N_s} \left(2y_s^k - 1\right) y_s = \{0, 1, ..., N_s\} \tag{4.8}$$

and

$$\left(\sum_{s=1}^{N_s} y_s^k\right) = \{-1, 0, ..., N_s - 1\} \tag{4.9}$$

if the current solution is a copy of the k-th solution:

$$\sum_{s=1}^{N_s} \left(2y_s^k - 1\right) y_s > \left(\sum_{s=1}^{N_s} y_s^k\right) \tag{4.10}$$

and the constraint is not verified.

The two approaches proposed in equation (4.6) and (4.7) present positive and negative aspects. The great advantage of equation (4.6) is that the problem does not change from one iteration to another. On the other hand, the use of ceiling function makes the constraint non-linear, which could be a problem. The constraint proposed in [59] is linear and is proved to be effective with no downsides. The characteristic that must be pointed out is that the constraint (4.7) needs to be stated $k - 1$ times, so there is a linear increase of the number of constraints, as a new constraint must be stated after each new solution. However, this is not a big issue, as in AMPL it is rather easy to state indexed equations. Consequently, the best Integer-Cuts method which can be applied to the problem is (4.7). For what concerns the computational side, beside the application of the Integer-Cuts, a new set parameter must be created inside the code to store the old solutions. The AMPL syntax of the constraint is reported in the Appendix 6.

4.5 Preliminary test of the Platform

After presenting the constraint and the equation of the model, the next step is testing the platform with different sets of constraint. The aim at this stage of research is to find the best trade off between computation time (expressed in terms of runs needed for retrieving the solutions) and quality of the solutions found by the platform. The tests were performed with a simplified version of the platform (see Figure 4.6) and with simplified economic parameters; however, it could be an interesting example and show a rank of technologies of the same kind.

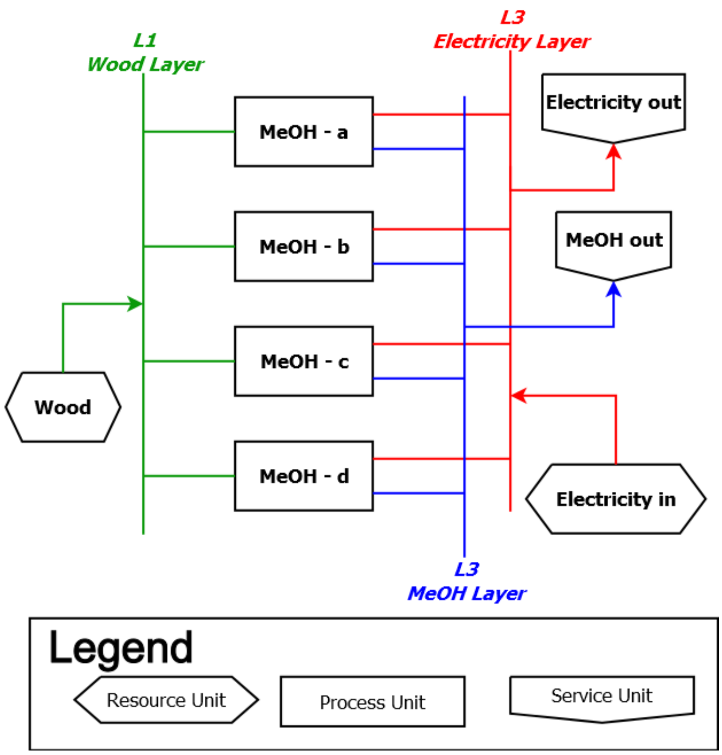


Figure 4.6: Scheme of the process considered in testing the Platform

In these tests, only methanol process was taken into account. The detailed presentation of these models is done in Section 5.2.2. The input data necessary for running the platform are presented in Table 4.1 and the economics parameters used in the tests are summarized in Table 4.2.

At this stage of test of the platform, it is not compulsory to be faithful to reality because the aim is not to focus on the results themselves, but to analyse the way in which the results are retrieved and to discuss their quality.

Parameter	MeOH-a	MeOH-b	MeOH-c	MeOH-d
Fuel Output [kW/MW]	570	570	318	318
Net electricity [kW/MW]	-85	-59	-18	35
Economic performance of 20 MW biomass plant				
Investment [M€]	27	28	15	15

Table 4.1: Parameters and economic performance of the methanol models used in the Test [15]

Parameter	Value	Unit	Source
Electricity	0.212	USD/kWh	[60]
Methanol	0.111	USD/kWh	[61]
Wood	0.05	USD/kWh	[62]

Table 4.2: Economic parameters used in the tests

For what concerns the quality of the solutions, they can be classified in the following categories:

- **Simple solution** i.e. solution that involves only one technology;

- **Complex solution** i.e. solution that involves two or more processes of different kind working in parallel, for instance MeOH-b and MeOH-d. The first uses the electricity output of the latter;

- **Fake solution** i.e. solution in which the size of the plant is too small or even zero. The most outstanding example of fake solution is the combination of unit use $y_s = 1$ and unit mult $f_s = 0$, as it will be explained further;

- **Meaningless solution** i.e. solution in which two or more processes of the same kind work in parallel, for instance MeOH-a and MeOH-b. A plant that couples these two technologies that have the same input and outputs is useless because its complexity is increased with no remarkable advantages. Another example of meaningless solutions is when two plants of different kind (for instance MeOH-a and MeOH-d) are coupled but with a small amount of electricity consumed or produced. This is a meaningless solution as well because it represents another working condition of the plant with MeOH-a and MeOH-d different from the optimal one, in which the two plants are perfectly coupled (for instance, MeOH-d produces all the electricity needed by MeOH-a).

Consequently, the analysis of the solutions retrieved from the platform will be done accordingly to fore-mentioned considerations. The biomass input used to run the test is 200 MW.

Test 1 - Base case

The base case (test 1) is obtained by running the platform with no additional constraints, except the Integer-Cuts. This means that $f_{min} = 0$ for all the units, no limits are imposed for the sum of the integer and no epsilon constraint is stated.

In this case, the most remarkable issue is that a lot of combination have unit mult $f_s = 0$ while unit use $y_s = 1$ and consequently there is the replication of many solutions with the same objective function. This happens because the integer cuts acts only on the integer, while the mult is a result of the optimization. So the solver is exploring all the combinations of unit use but, due to the fact that the multiplication factor can be zero, several combinations, although different, are just the same solution. The solver finds a new combination of units turning on an unit which was previously off, but, since the objective function is minimize the total cost, the optimum solution is to keep the mass flow of that unit zero (and so that is why the unit mult is zero). Consequently, the platform explores all the combinations of unit use and unit mult that give the same objective function before "jumping" to a new solution, thus taking a lot of runs between a solution and another, even for a very simple model with a small number of units.

A filtering of the outputs of the platform is therefore needed to get only the real solution purged by the fake ones (a fake solution is a combination in which there is $f_s = 0$ and $y_s = 1$) and the meaningless ones. The process flow of the solution filtering and cleaning can be summarised in these steps:

1. filter the output checking for fake solutions, which means:
   1.1. calculate the product $f_s y_s$. If it is zero, force the unit use to be zero;
   1.2. check if any solution has $f_s = f_{s,min}$;
2. clean the results using the equation (4.6). This step is needed because the step number one modified the combination of unit use thus is needed another check to discard the already found solutions;
3. check for meaningless solutions, which means:
   3.1. check if $f_s < f_{min,size}$ (discard solutions with uneconomic size);
   3.2. check if the current solution is made by coupling processes of the same kind.

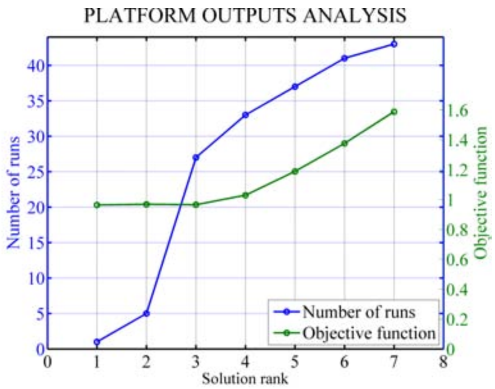
First the unit use must be changed according to the mult of the unit, secondly the solution must be compared with all the previous ones. In order to do this comparison, the formula (4.6) is really helpful as it is a unique equation that allow to compare the current solution with the old ones. An additional condition that can be imposed is to check if the objective function is different from the value of the previous solution, in order to eventually eliminate duplicated solutions.

The result of testing the platform with this condition are shown in Figure 4.7: the evolution of the solution retrieving and the gap between the objective function between each solution. The solutions retrieved in the base case are shown in Table 4.3.

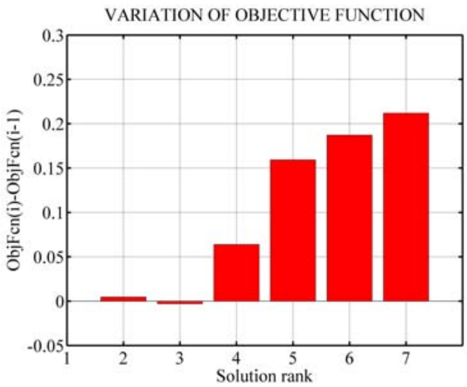
Rank	**Test**
	1
1	d+E_{out}
2	b+E_{in}
3	b+d
4	a+d
5	a+E_{in}
6	c+d
7	c+E_{in}

Table 4.3: Solutions found in Test 1 - Base case.

Looking at the figure 2b), it is interesting to point out that the second solution is found after 5 runs and the third is obtained after 27 runs, although it has a smaller objective function compared with the second solution. This is probably due to the fact that the solver, exploring the solution space, find first the local minimum of the second solution and the, moving towards the border of the solution space, it finds another local minimum, smaller than the solution found before. This is a weakness of the structure of the problem and prove that the problem definition is not so robust.



(a) Runs and objective function - Test 1



(b) Variation of objective function - Test 1

Figure 4.7: Results from test 1 - Base case.

As a base case, the assumption made is that all the solutions found are the real solutions of the problem. Nonetheless, even if in this test was assumed that there is no solution missing, an index of the performance of the method can be introduced:

$$\eta_{sol} = \frac{n_{sol}}{n_{run}} \quad (4.11)$$

This index is simply the number of solutions retrieved per run while the reciprocal is the number of run taken to obtain a solution. The higher the efficiency of the method in analysis is, the closer η_{sol} is to 1. Obviously the ideal method should be able to find all the solutions with 100% efficiency.

A summary table of the base case test is given in Table 4.4:

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	**Cost1**	ε **cstr**	$\sum y_s$ **cstr**
1	44	7	0	16%	0	0	0	none	none

Table 4.4: Summary of test 1 - Base case

Test 2

Once tried the base case, the second step is to improve the robustness of the problem and to speed up the retrieving of solutions. Improving the robustness of the problem is compulsory to get an ordered set of solutions while accelerating the speed is necessary when dealing with structure with a lot of units. In the current example there are 8 units and the Platform took 44 runs in the base case to get the results. Increasing the number of units in the model, the number of possible combinations increases exponentially, thus a faster way to get the solutions is necessary.

In order to force the solver to avoid the combination $f_s = 0$ and $y_s = 1$, a possible solution is to set:

$$F_{min,s} > 0 \qquad \forall\, s \in N_s \tag{4.12}$$

With a minimum allowed size greater than zero for all the units (processes, resources and services), the combination $f_s = 0$ and $y_s = 1$ can no longer exist. On the other hand, limiting the size of an utility affects the solutions. In effect, after the optimal solution, the solver now will look for combination of the optimal set of utilities adding other utilities but whit the minimum mult allowed before finding a brand new solution. So instead of having fake solutions in which $f_s = 0$ and $y_s = 1$ now there will be fake solutions in which $y_s = 1$ and $f_s = f_{min,s}$.

The defect in this method is that if a really small $f_{min,s}$ is stated, a solution can consist of an utility with a really small size (which is economically a nonsense) while if a big $f_{min,s}$ affects the size of the resources (could happened that a small amount of electricity is needed in a good solution). A filtering of the result is still needed, but the criteria is different: the filtering must be updated in order to verify if there is an unit with $y_s = f_{min,s}$ and, in case, eliminate that solution.

Additionally, another constraint to trick the solver was added. As stated in the definition of the problem, the objective function is to minimize the total cost.

$$\text{minimize} \quad TC = \sum_{s=1}^{N_s} (OC_s + IC_s) \tag{4.13}$$

Where:

$$OC_s = Cost_{1,s} \cdot y_s + Cost_{2,s} \cdot f_s \tag{4.14}$$

$$IC_s = Cinv_{1,s} \cdot y_s + Cinv_{2,s} \cdot f_s \tag{4.15}$$

Subject to:

$$f_{min,s} \cdot y_s \leq f_s \leq f_{min,s} \cdot y_s \tag{4.16}$$

Since the operating cost are calculated as shown in formula 4.14, setting a $Cost_{1,s} > 0$ will force the solver to skip the solution with minimum size. This because if the units is activated with the $f_s = f_{min,s}$ the solver has a positive cost while the products are negligible. The effects on the objective function of these fake costs are limited and the effect on the final result is irrelevant.

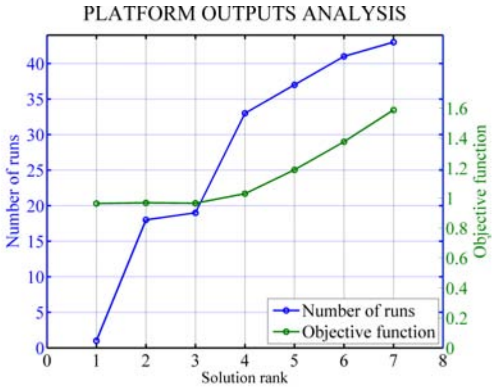
After those considerations, the next tests were done with increasing value of both the global $f_{min,s}$ and the $Cost_{1,s}$ to see how the magnitude of these fake cost affects the problem. The expected effect is that increasing the $f_{min,s}$ the objective function should be forced to grow steadily thus giving robustness to the problem. The test 2 consists in a sensitivity analysis on $f_{min,s}$ and the $Cost_{1,s}$:

- **Test 2a)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-6}$;
- **Test 2b)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-5}$;
- **Test 2c)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-4}$;

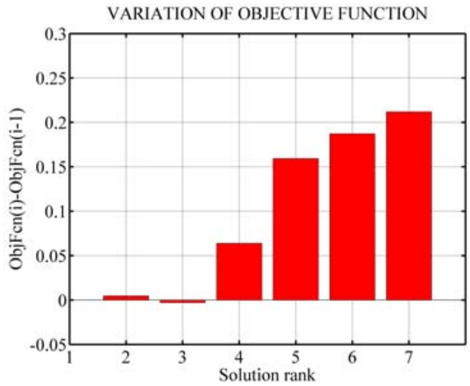
As shown in the graphs of Figure 4.8, it appears that this method does not really add up. In case 2a) the second solution is found after 18 runs (in the base case the second solution needed 5 runs), the third is found after 19 runs (while in the base case it took 27 runs). For what concerns the other solutions, they are found after the same number of runs. As in the base case, it happens that the third solution found has a lower objective function than the second solution for case 2a) while increasing the $f_{min,s}$ and $Cost_{1,s}$ the solution are perfectly ordered.

In cases 2b) and 2c) the solutions are finally ordered according to the objective function and the number of run taken to get each solution is the same of the base case, except for the solution number 7 in case 2c), which is found after 44 runs instead of 43. The table below shows the comparison between the different solutions retrieved.

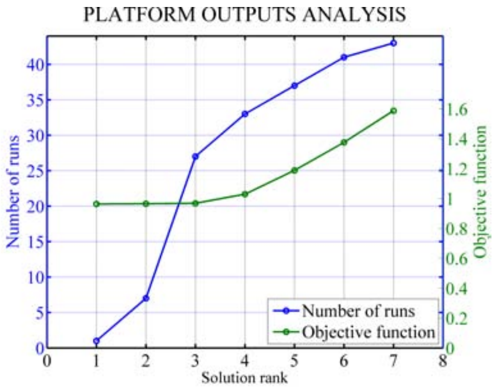
Actually, the effect of $f_{min,s} > 0$ is not so relevant: in all cases, the overall number of iterations needed to achieve the result is 44, so there is no gain in speed. However, the most important fact to be pointed out is that a too small value of $f_{min,s}$ and $Cost_{1,s}$ cause the problem to be not very robust as happens in the base case. This lead to have, for instance, that the solution number 3 in case 2a) has a smaller objective function if compared to solution number 2 while increasing the value of $f_{min,s}$ and $Cost_{1,s}$ this issue is avoided and the results are ordered in a rank. In conclusion, setting $f_{min,s} > 0$ and $Cost_{1,s} > 0$ has irrelevant effect on the computational speed



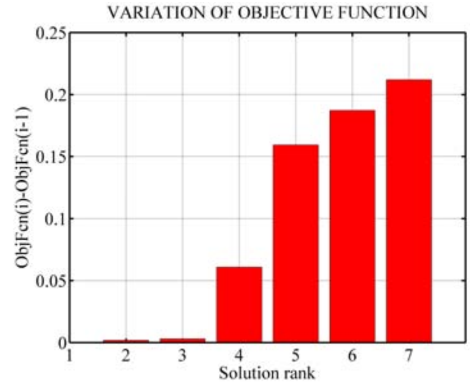
(a) Runs and objective function - Test 2a



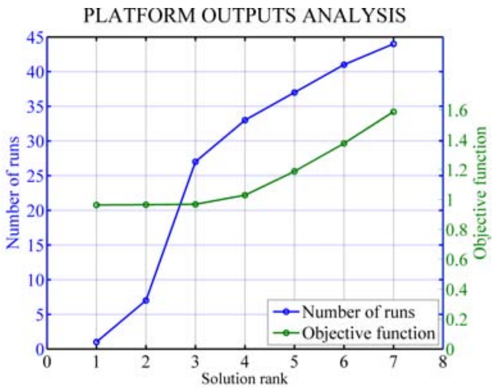
(b) Variation of objective function - Test 2a



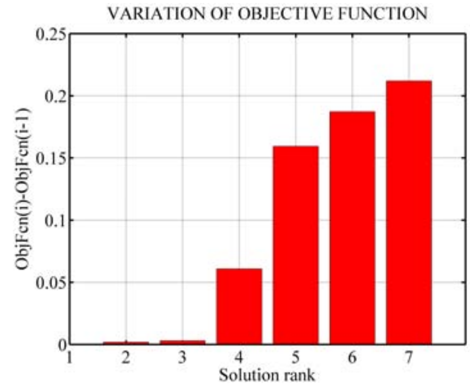
(c) Runs and objective function - Test 2b



(d) Variation of objective function - Test 2b



(e) Runs and objective function - Test 2c



(f) Variation of objective function - Test 2c

Figure 4.8: Results from test 2.

Rank	**Test**		
	2a	**2b**	**2c**
1	d+E_{out}	d+E_{out}	d+E_{out}
2	b+E_{in}	b+d	b+d
3	b+d	b+E_{in}	b+E_{in}
4	a+d	a+d	a+d
5	a+E_{in}	a+E_{in}	a+E_{in}
6	c+d	c+d	c+d
7	c+E_{in}	c+E_{in}	c+E_{in}

Table 4.5: Results after the cleaning in Test 2

but helps in adding robustness to the problem and obtain an ordered rank of solutions.

The summary of this test is reported in Table 4.6.

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	**Cost1**	ε **cstr**	$\sum y_s$ **cstr**
2a	44	7	0	16%	10^{-6}	10^{-6}	10^{-6}	none	none
2b	44	7	0	16%	10^{-5}	10^{-5}	10^{-5}	none	none
2c	44	7	0	16%	10^{-4}	10^{-4}	10^{-4}	none	none

Table 4.6: Summary of Test 2

Test 3

Since the major concerns is to speed up the retrieving of results, other constraints can be added to limit the size of the problem. Limiting the size of the problem can be helpful to avoid to screen all the possible combinations, especially when the number of variable in the model increases. In order to reduce the size of the problem and help the solver to converge faster, other constraints can be stated. A limit in the number of processes involved in the plant reduces the number of combinations thus reducing the size of the problem. A constraint of this kind can be stated as follows:

$$\sum_{s=1}^{N_s} y_s \leq N_p \tag{4.17}$$

N_p must be chosen accordingly. The constraint acts on all the integer variables of the problem, so even this constraint could be grouped into the Integer-Cuts class. Both versions of the constraint were implemented in the platform, the corresponding syntax in AMPL can be found in Appendix 6.

A more refined version of this constraint could be implemented if there are several technologies of the same kind. For instance, in order to use only one process per technology, a limit can be imposed stating the maximum number of units with the same output working in parallel.

$$\sum_{s}^{N_{s,t}} y_s \leq N_t \qquad \forall\, t \in T \tag{4.18}$$

Where T is the set of available technologies, N_t is the maximum number of processes of type t allowed to work in parallel.

So the constraint sum of integer (4.17) can be added on the maximum number of units that can be activated. In this simplified model of the platform there are 4 process units (MeOH-a, MeOH-b, MeOH-c, MeOH-d), 2 resource units (wood, electricity in) and 2 service units (methanol and electricity out), so the maximum value of the sum of the unit use is 8.

If the number of resource and service units is fixed, the number of process units that can work in parallel can be decided. Moreover, since it not smart to have both unit electricity in and out activated (because it is useless), the unit that must be always active are three: wood (resource), electricity (resource or service) and methanol (service), while the sum of the integer of all the other units can be managed and stated as a variable in the constrain.

The general expression of the constraint, applied to the problem is the following:

$$\sum_{s=1}^{N_s} y_s \leq 3 + N_p = 2 + N_{max,p} \tag{4.19}$$

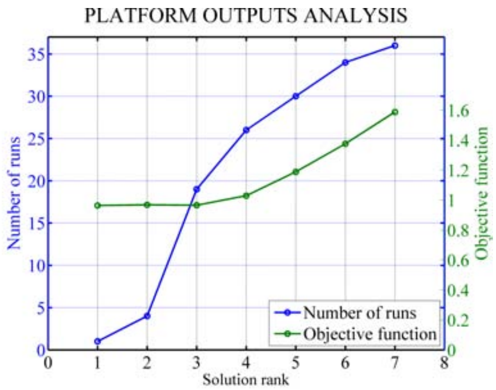
With N_p is the number of processes that work in parallel when at least one of electricity unit (resource or service) is activated and $N_{max,p}$ is the maximum number of processes that are allowed to work in parallel. In order to test the effects of this new constrain, three cases were analysed:

- **Test 3a)** $\sum y_s \leq 6$ (up to three/four processes in parallel);
- **Test 3b)** $\sum y_s \leq 5$ (up to two/three processes in parallel);
- **Test 3c)** $\sum y_s \leq 4$ (up to one/two processes in parallel);

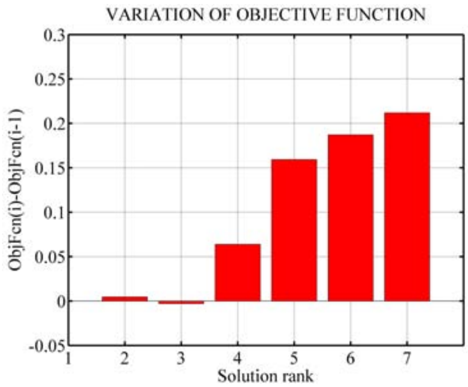
The results after the cleaning of the outputs are shown in the graphs of Figure 4.9.

Limiting the sum of unit use immediately turns out to be really effective for what concerns the obtaining of the solutions. In case 3a) and 3b) the same solutions of the base case are retrieved in 37 and 23 runs. The tighten the constraint is, the faster the platform is. However, on the other hand, a strict constraint causes the loss of some solutions: for instance, in case 3c) the constraint is so strict that 5 solution are found in five runs: 100% solution efficiency is achieved but there are two solutions missing, as it can be clearly seen in Table 4.7:

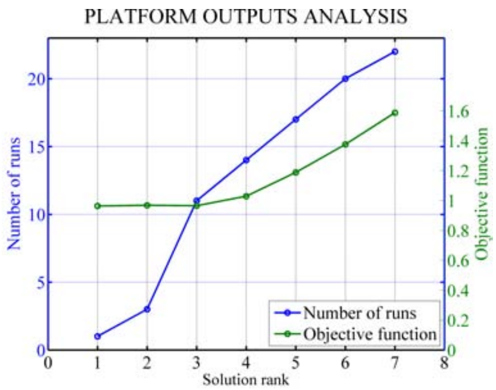
In conclusion, stating a maximum sum of the unit use is effective and helps reducing the number of iterations but the maximum number of units must be chosen accordingly to avoid loosing solutions. The summary of the test performed is in Table 4.8.



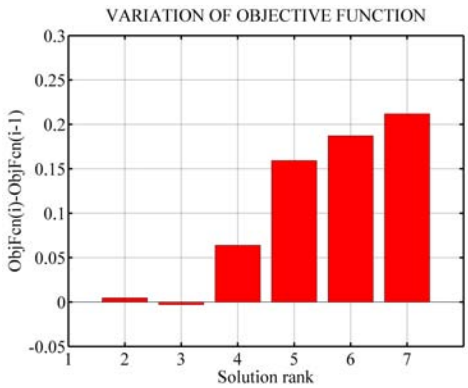
(a) Runs and objective function - Test 3a



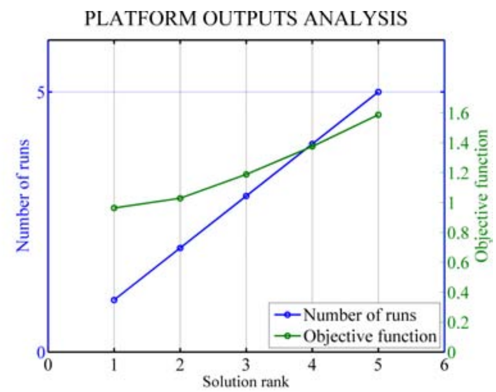
(b) Variation of objective function - Test 3a



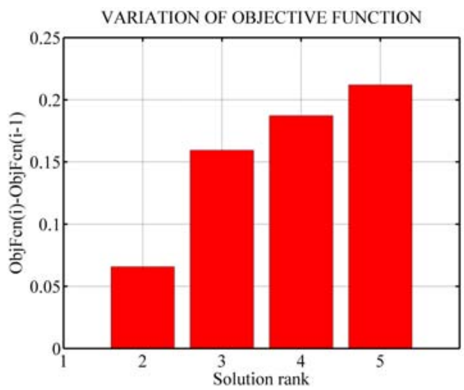
(c) Runs and objective function - Test 3b



(d) Variation of objective function - Test 3b



(e) Runs and objective function - Test 3c



(f) Variation of objective function - Test 3c

Figure 4.9: Results from test 3.

Rank	**Test**		
	3a	**3b**	**3c**
1	d+E_{out}	d+E_{out}	d+E_{out}
2	b+E_{in}	b+E_{in}	a+d
3	b+d	b+d	a+E_{in}
4	a+d	a+d	c+d
5	a+E_{in}	a+E_{in}	c+E_{in}
6	c+d	c+d	
7	c+E_{in}	c+E_{in}	

Table 4.7: Results after the cleaning in Test 3

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	**Cost1**	ε **cstr**	$\sum y_s$ **cstr**
3a	37	7	0	19%	0	0	0	none	6
3b	23	7	0	30%	0	0	0	none	5
3c	5	5	2	100%	0	0	0	none	4

Table 4.8: Summary of Test 3

Test 4

Another constraint that can be applied to the Platform in order to speed up the searching of solutions is the epsilon constraint, proposed and applied by [59]. This constraint forces the objective function to increase at each iteration, thus forcing the solver to jump from a local minimum to another. The rationale of the constraint can be summarized in the following formula:

$$F_k(x) > F_{k-1}(x) \tag{4.20}$$

Where the k is the index of the current iteration and $F_k(x)$ is the objective function at the k-th iteration. Since it not possible to state a constraint of this kind in AMPL, it must be rewritten according to AMPL syntax, with the inequality expressed as "greater equal":

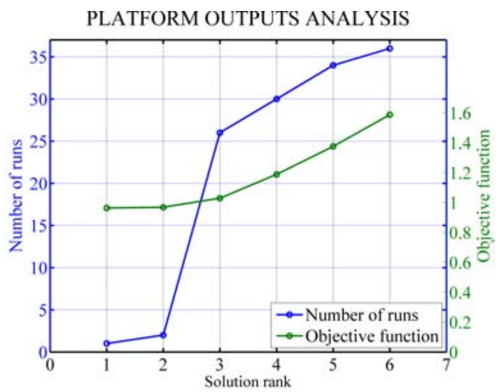
$$F_k(x) \geq F_{k-1}(x) + \varepsilon \tag{4.21}$$

This constraint forces the objective function to increase at each run, thus exploring the solution space by cutting it with parallel planes. The AMPL syntax of the constraint is reported in the Appendix 6. The value of the epsilon has a great influence in retrieving the results: a really small value can slow down the results while a big value can accelerate the exploring of the solution space but with the risk of missing solutions with difference between the objective function smaller than the epsilon.

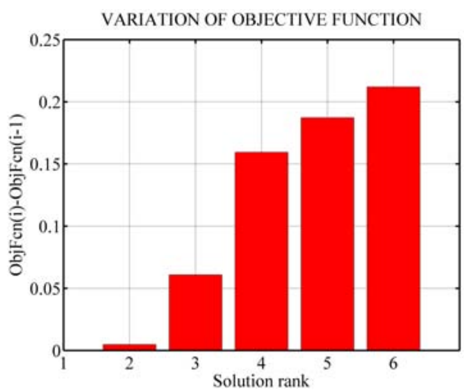
In order to test the effect of the epsilon constraint applied to the platform, a sensitivity analysis of epsilon is performed:

- **Test 4)** $\varepsilon = 0.001\%$;
- **Test 4a)** $\varepsilon = 0.001\%$;
- **Test 4b)** $\varepsilon = 0.01\%$;
- **Test 4c)** $\varepsilon = 0.1\%$;
- **Test 4d)** $\varepsilon = 0.5\%$;
- **Test 4e)** $\varepsilon = 1\%$;

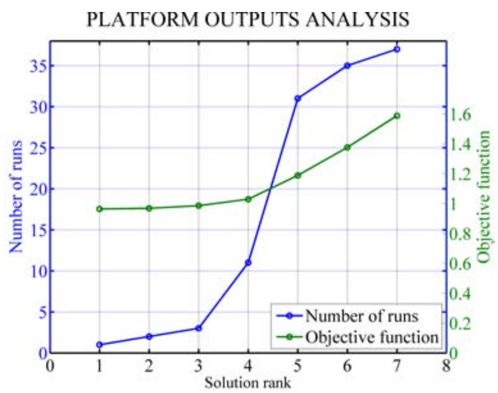
The test 4 is carried out without other constraints while in the test from 4a) to 4e) $f_{min,MeOH} = 1$ in order to avoid solutions in which the methanol units have a too small size. Setting a minimum size for the process units is necessary because of the nature of the epsilon constraint: the solver tries to minimize the objective function but the constraint set a value of the minimum value of the objective function. Consequently is like giving already the solution of the function (because the minimum value is imposed) and the solver tries to find the combination of unit use and mult that gives exactly the $F_{k-1}(x) + \varepsilon$ instead of jumping from a local minimum to another.



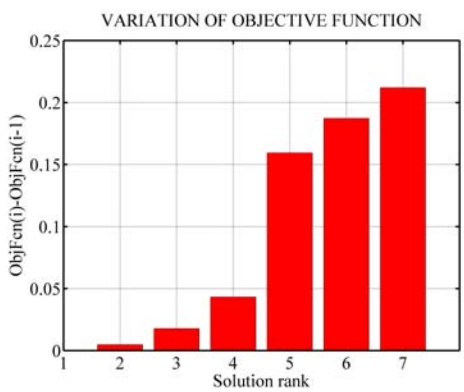
(a) Runs and objective function - Test 4



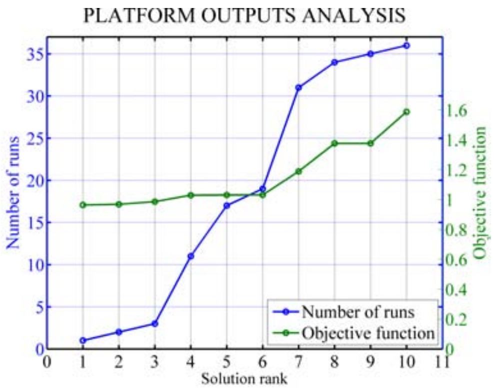
(b) Variation of objective function - Test 4



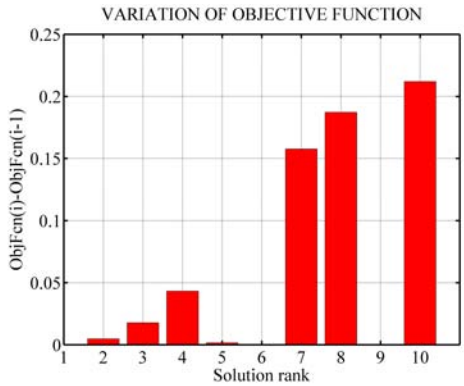
(c) Runs and objective function - Test 4a



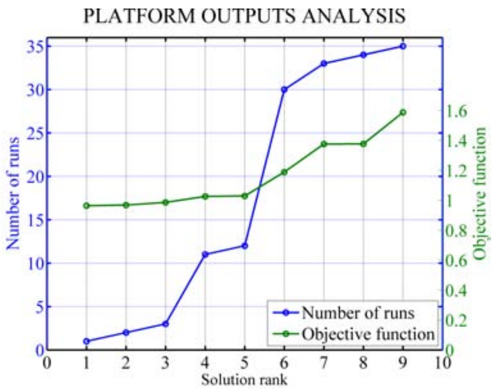
(d) Variation of objective function Test 4a



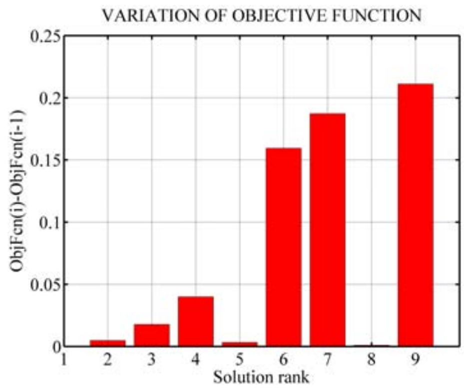
(e) Runs and objective function - Test 4b



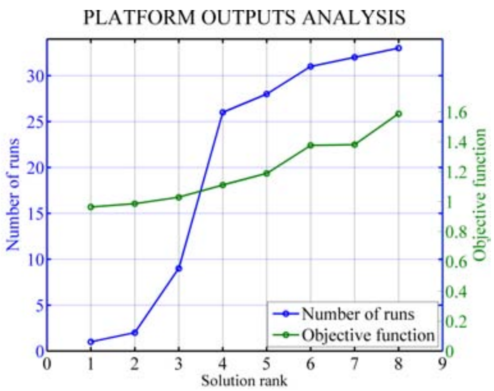
(f) Variation of objective function - Test 4b



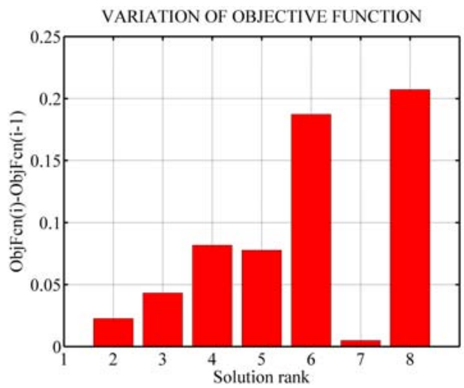
(g) Runs and objective function - Test 4c



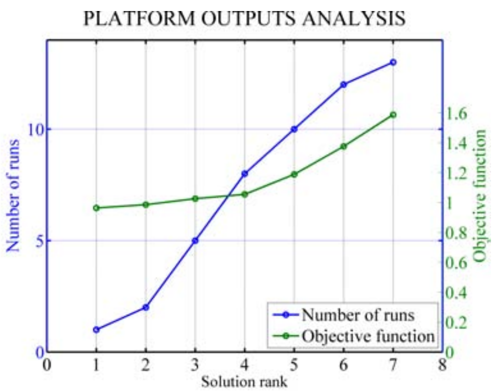
(h) Variation of objective function - Test 4c



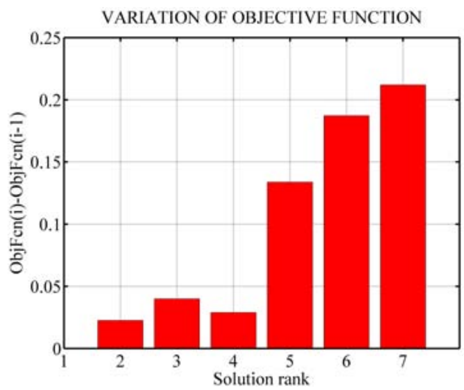
(i) Runs and objective function - Test 4d



(j) Variation of objective function - Test 4d



(k) Runs and objective function - Test 4e



(l) Variation of objective function - Test 4e

Figure 4.9: Results from test 4.

The most remarkable results, after the cleaning, is that the number of solutions obtained is greater than the tests previously done. This wider variety of solution is a direct consequence of using the epsilon constraint, as it appears in Table 4.9.

Rank	**Test**					
	4	**4a**	**4b**	**4c**	**4d**	**4e**
1	d+E_{out}	d+E_{out}	d+E_{out}	d+E_{out}	d+E_{out}	d+E_{out}
2	b+E_{in}	b+E_{in}	b+E_{in}	b+E_{in}	a+d+E_{out}	a+d+E_{out}
3	a+d	a+d+E_{out}	a+d+E_{out}	a+d+E_{out}	a+d	c+d+E_{out}
4	a+E_{in}	a+d	a+d	c+d+E_{out}	c+d+E_{out}	a+d
5	c+d	a+E_{in}	c+d+E_{out}	a+d	a+E_{in}	a+E_{in}
6	c+E_{in}	c+d	a+d+E_{in}	a+E_{in}	a+c+E_{in}	c+d
7		c+E_{in}	a+E_{in}	a+c+E_{in}	c+d	c+E_{in}
8			c+d	c+d	c+E_{in}	
9			c+d+E_{in}	c+d+E_{in}		
10			c+E_{in}	c+E_{in}		

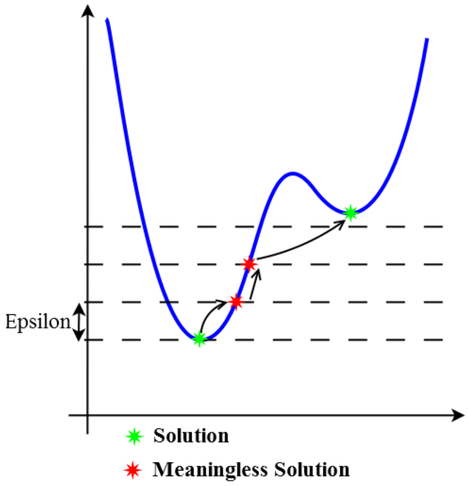
Table 4.9: Results after the cleaning in Test 4.

Not all the solutions found in this test really have meaning. For instance, coupling two processes that produce methanol and consume electricity (like c+d+E_{in} or c+d+E_{out}) is a nonsense because the real solution is coupling the two plant on order that the surplus electricity coming from one process is used in the second one. Unluckily this nonsense cannot be detected by the cleaning, it is necessary to carefully read the results and eventually discard the solutions that do not make sense (meaningless solutions, highlighted in red in Table 4.9).

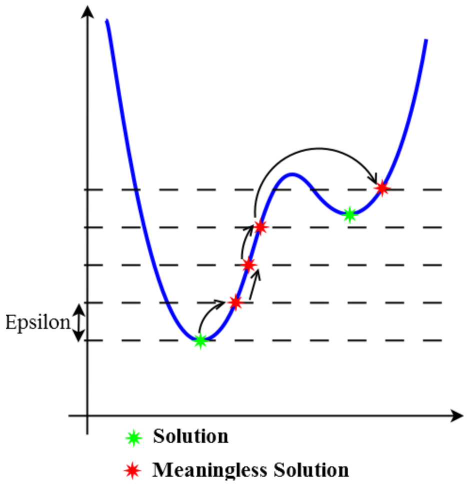
Using the epsilon constraint leads to some solutions missing. Obviously, the greater the epsilon is, the higher loss of solution will be. However, even with a really small epsilon (0.001%) there is one solution missing if compared to the base case. On the other hand, the use of epsilon constraint allows to explore in more detail the solution space, speeding up the retrieving of results and giving a full rank of possible solutions and combinations of processes and sizes. This could be both an add up in a decision process (because there are more combinations to choose among, and they are all ordered) and a downside (because increasing the dimension of the problem increases also the number of solution retrieved with this method, thus creating a huge number of results to be read and analysed).

The most important result that must be pointed out in using epsilon constraint is the unpredictable behaviour of this constraint. As it can be seen in Figure 4.10, the ideal behaviour of the constraint is jumping from a solution to another, even if it takes some meaningless solutions in the middle. This can happen only if there are no combinations of variables that can give exactly $F_k(x) = F_{k-1}(x) + \varepsilon$. Otherwise, if the value of epsilon is too small, the solver miss the solution because it is forced to look for combination with the imposed objective function. One way to avoid this issue could be to set a really small epsilon, but, as it can be seen in Table

4.10, even a low value for epsilon do not prevent from loosing solutions.



(a) Optimal behaviour



(b) Missing solution

Figure 4.10: Behaviour of epsilon constraint.

Test	n_{run}	n_{sol}	n_{missed}	η_{sol}	$f_{min,MeOH}$	$f_{min,s}$	Cost1	ε cstr	$\sum y_s$ cstr
4	37	6	1	16%	0	0	0	0.001%	none
4a	38	6	1	16%	1	0	0	0.001%	none
4b	36	6	1	17%	1	0	0	0.01%	none
4c	35	6	1	17%	1	0	0	0.10%	none
4d	33	5	2	15%	1	0	0	0.50%	none
4e	13	5	2	38%	1	0	0	1.00%	none

Table 4.10: Summary of Test 4

Test 5

Starting from the results of the previous tests, combinations of constraint can be performed in order to find the best set of constraints that allow to get a rank of good solution with the smallest number of iterations. The term "rank of good solutions" means that the rank must contain all the local minimums. The new tests are done combining the different constraints. First the epsilon constraint is combined with the sum of the unit use. The following cases are analysed:

- **Test 5a)** $\sum y_s \leq 5$ and $\varepsilon = 0.01\%$;
- **Test 5b)** $\sum y_s \leq 5$ and $\varepsilon = 0.05\%$;
- **Test 5c)** $\sum y_s \leq 5$ and $\varepsilon = 0.1\%$;
- **Test 5d)** $\sum y_s \leq 5$ and $\varepsilon = 0.5\%$;

- **Test 5e)** $\sum y_s \leq 5$ and $\varepsilon = 1\%$;

The maximum sum of integer is assumed to be 5 because in the previous test done it turned out to be the best trade off between effectiveness of the constraint and quality of the results. The graphical representation of the output after the result cleaning can be found in Figure 4.10.

Rank	**Test**				
	5a	**5b**	**5c**	**5d**	**5e**
1	d+E_{out}	d+E_{out}	d+E_{out}	d+E_{out}	d+E_{out}
2	b+E_{in}	b+E_{in}	b+E_{in}	a+d+E_{out}	a+d+E_{out}
3	a+d+E_{out}	a+d+E_{out}	a+d+E_{out}	c+d+E_{out}	c+d+E_{out}
4	c+d+E_{out}	c+d+E_{out}	c+d+E_{out}	a+d	a+d
5	a+d	a+d	a+d	a+E_{in}	a+E_{in}
6	a+d+E_{in}	a+d+E_{in}	a+d+E_{in}	c+d	c+d
7	a+E_{in}	a+E_{in}	a+E_{in}	c+E_{in}	c+E_{in}
8	c+d	c+d	c+d		
9	c+E_{in}	c+E_{in}	c+E_{in}		

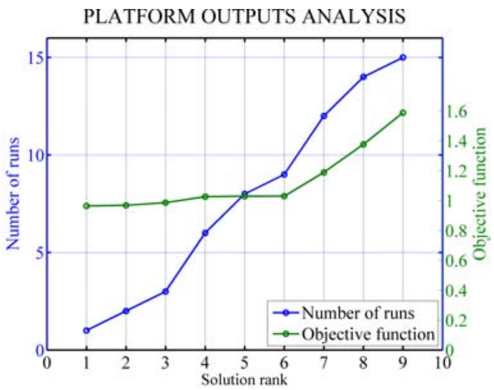
Table 4.11: Results after the cleaning in Test 5.

In cases a), b) and c) 6 solution are retrieved in 15 runs but there is one solution missing if compared to the base case plus 3 meaningless solutions that are not detected and discarded by the cleaning (in red in Table 4.11). In cases d) and e) the number of solutions are 5 and 4 . As already found in the previous tests performed, a small value of epsilon is necessary to screen the solution space, thus it is not enough for finding all the solutions.

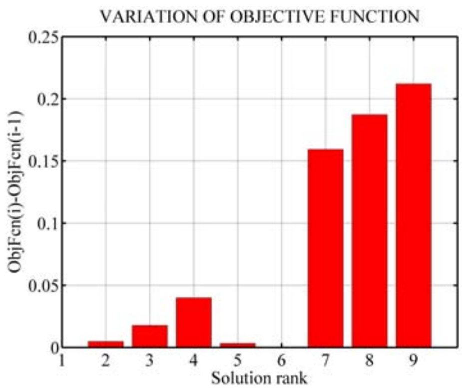
The combination of epsilon constraint and sum of the unit is not really efficient, as we can see in table 4.12. Moreover, there is the problem of missed solutions and meaningless solutions, as pointed out in the test 4. As it can be seen in Table 4.11, not all the meaningless solutions can be detected by the cleaning: for instance it is clear that a+d+E_{in} does not make any sense but it can't be discarded automatically. This is a consequence of the use of epsilon constraint: it creates combinations that are not solutions but simply other working conditions of complex solutions. Again, epsilon constraint turned out to be not reliable.

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	**Cost1**	ε **cstr**	$\sum y_s$ **cstr**
5a	15	6	1	40%	1	0	0	0.01%	5
5b	15	6	1	40%	1	0	0	0.05%	5
5c	15	6	1	40%	1	0	0	0.10%	5
5d	13	5	2	38%	1	0	0	0.50%	5
5e	13	4	3	31%	1	0	0	1%	5

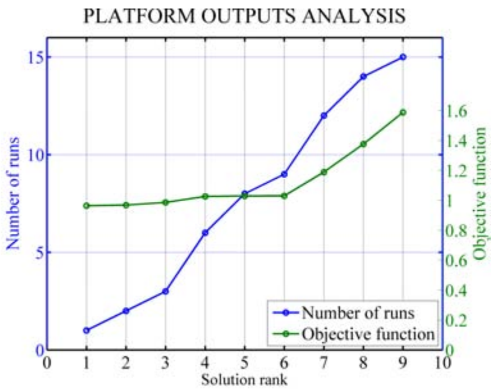
Table 4.12: Summary of Test 5.



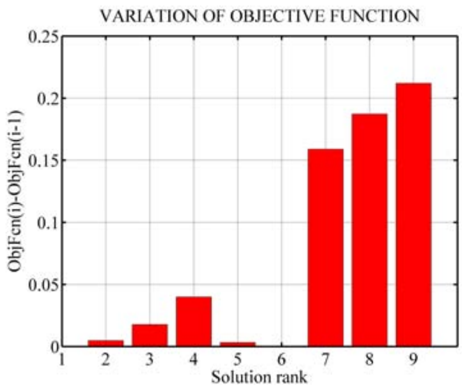
(a) Runs and objective function - Test 5a



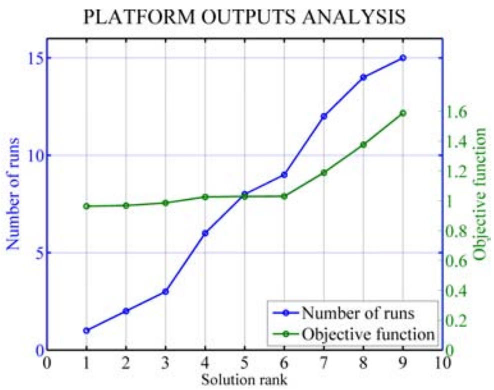
(b) Variation of objective function - Test 5a



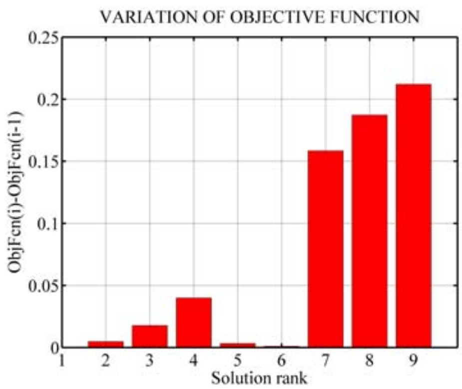
(c) Runs and objectivefunction - Test 5b



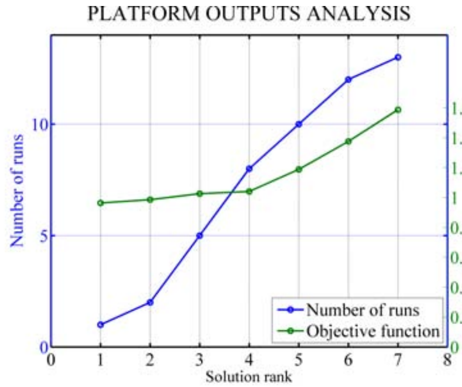
(d) Variation of objective function - Test 5b



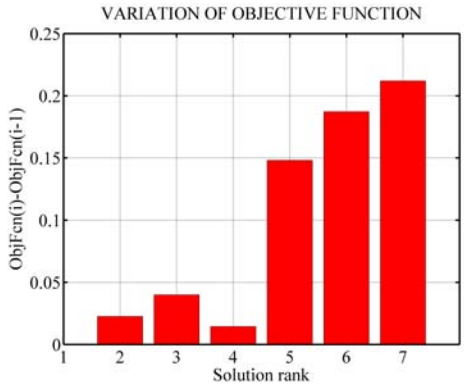
(e) Runs and objectivefunction - Test 5c



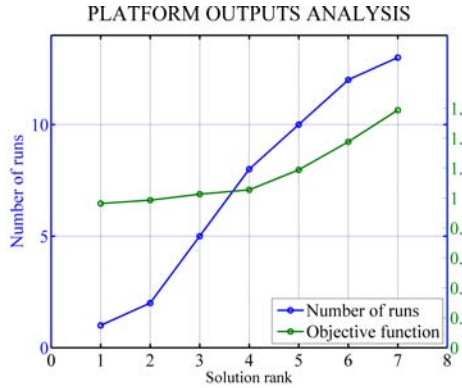
(f) Variation of objectivefunction - Test 5c



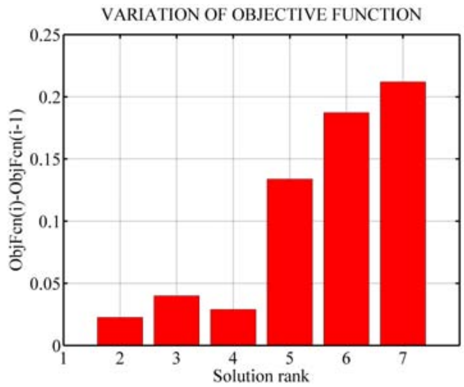
(g) Runs and objective function - Test 5d



(h) Variation of objective function - Test 5d



(i) Variation of objective function - Test 5e



(j) Variation of objective function - Test 5e

Figure 4.10: Results from test 5.

Test 6

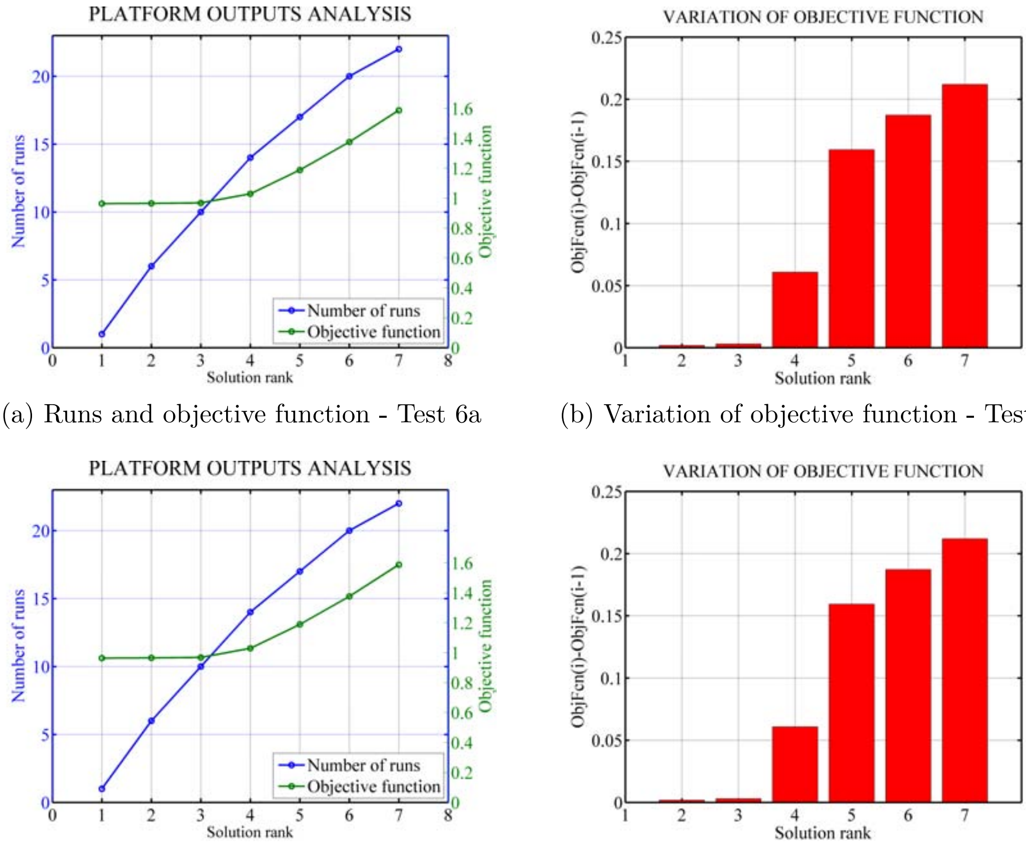
A new set of constraint to be tested is the combination $f_{min,s} > 0$ and limit on the sum of unit use. This set were tested in two different cases:

- **Test 6a)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-5}$ and $\sum y_s \leq 5$;
- **Test 6b)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-4}$ and $\sum y_s \leq 5$;

The plots of the output after the cleaning is in Figure 4.11 while the list of combination can be seen in Table 4.13.

Rank	Test	
	6a	**6b**
1	d+E_{out}	d+E_{out}
2	b+d	b+d
3	b+E_{in}	b+E_{in}
4	a+d	a+d
5	a+E_{in}	a+E_{in}
6	c+d	c+d
7	c+E_{in}	c+E_{in}

Table 4.13: Results after the cleaning in Test 6.



(a) Runs and objective function - Test 6a

(b) Variation of objective function - Test 6a

(c) Runs and objective function - Test 6b

(d) Variation of objective function - Test 6b

Figure 4.11: Results from Test 6.

In both cases, 7 solution were found after 23 run, the effect of setting $f_{min,MeOH} > 0$ do not affect the results, which are exactly the same that were found in cases 2b) and 2c), as it can be see the the Table 4.13. As it can be noticed, the magnitude of $f_{min,MeOH}$ does not change in any way the results. The real effective constraint is the sum of the unit use, as it was explained previously.

The summary of the features of Test 6 is presented in Table 4.14. As it can be seen, the constraint that really helps in speeding up the number of runs is the sum of the integer.

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	Cost1	ε cstr	$\sum y_s$ cstr
6a	23	7	0	30%	10^{-5}	10^{-5}	10^{-5}	none	5
6b	23	7	0	30%	10^{-4}	10^{-4}	10^{-4}	none	5

Table 4.14: Summary of Test 6

Test 7

Another combination of constraints tested is the epsilon constraint combined with $f_{min,s} > 0$. In such case, the features of the test are the following:

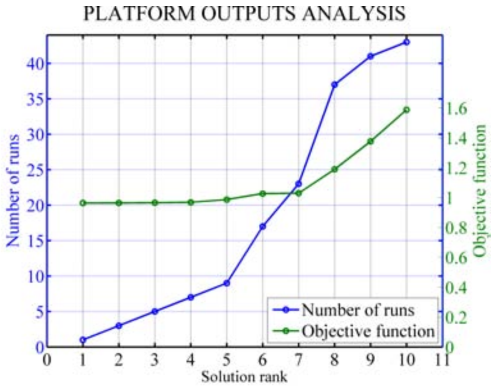
- **Test 7a)** $f_{min,s} = Cost_{1,s} = 1{\cdot}10^{-4}$ and $f_{min,MeOH} = 1$ and $\varepsilon = 0.01\%$;
- **Test 7b)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-4}$ and $f_{min,MeOH} = 1$ and $\varepsilon = 0.1\%$;

The expected result is an increasing number of solutions found because of the use of epsilon constraint. Stating $f_{min,MeOH} = 1$ is equal to impose that the lowest allowed size of the unit is 20 MW, as all the unit are scaled according to a reference size of 20 MW. The graphical results of this test are shown in Figure 4.12.

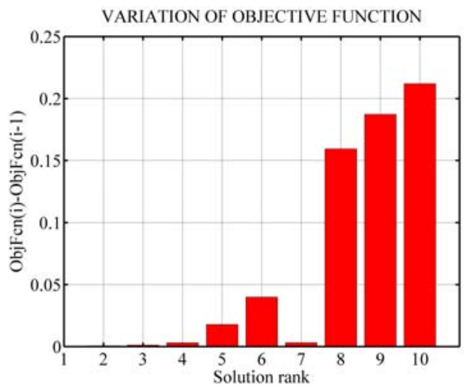
It is clear that the combination of $f_{min,s} > 0$ and epsilon constraint is not really efficient: in case 7a) (the case with the smallest epsilon) the solutions are found in 44 runs with a total amount of iterations equal to the base case. Moreover, even if there are no solutions missing, there is still some meaningless solutions that could not be detected by the cleaning, thus they must be discarded manually. Increasing the epsilon the overall number of iteration decreases but, as in test 4, some solutions are lost as it can be seen in Table 4.15 and in Table 4.16, the summary of the current test.

Rank	**Test**	
	7a	**7b**
1	d+E_{out}	d+E_{out}
2	b+d+E_{out}	b+d+E_{out}
3	b+d	b+d+E_{in}
4	b+E_{in}	b+E_{in}
5	a+d+E_{out}	a+d+E_{out}
6	c+d+E_{out}	c+d+E_{out}
7	a+d	a+d+E_{in}
8	a+E_{in}	a+E_{in}
9	c+d	c+d
10	c+E_{in}	c+d+E_{in}
11		c+E_{in}

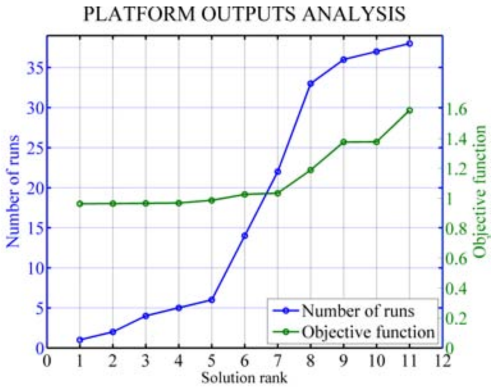
Table 4.15: Results after the cleaning in Test 7



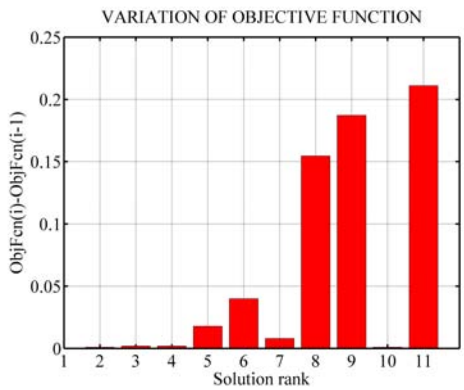
(a) Runs and objective function - Test 7a



(b) Variation of objective function - Test 7a



(c) Runs and objective function - Test 7b



(d) Variation of objective function - Test 7b

Figure 4.12: Results from Test 7.

In case 7b) the solver missed two solutions coming from the base case. There are also in this case a certain number of solutions that does not make sense from an engineering point of view, as a consequence of the use of the epsilon constraint. This proved once again that epsilon constraint is not reliable, neither combined with other kind of constraints.

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	**Cost1**	ε **cstr**	$\sum y_s$ **cstr**
7a	44	7	0	16%	1	10^{-4}	10^{-4}	0.01%	none
7b	38	5	2	13%	1	10^{-4}	10^{-4}	0.10%	none

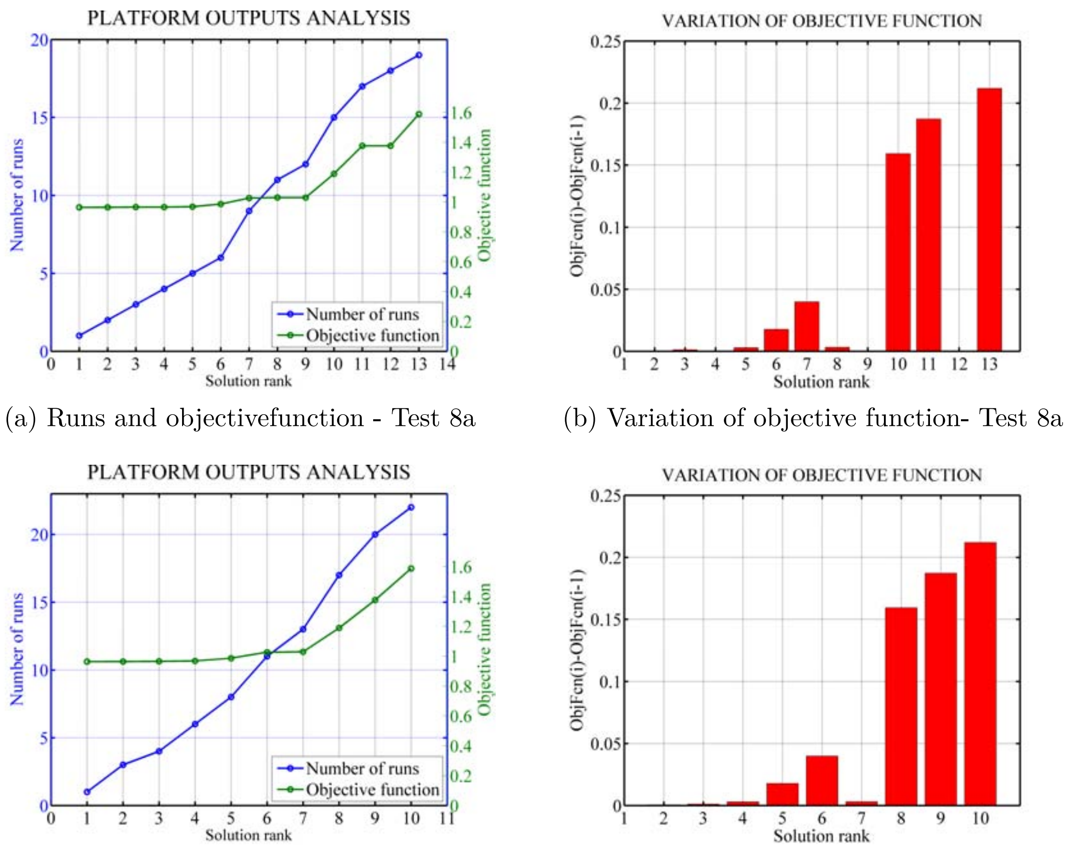
Table 4.16: Summary of Test 7

Test 8

The final test is made combining all the constraints seen in this chapter, according to the behaviour of each one. So for what concerns the epsilon constraint, a small value must be chosen if the aim is to obtain all the results. The sum of unit use is stated to be less equal to 5, because, as it was proved in the test made, it is the best constraint both in term of effectiveness in obtaining all the result and reducing the computational time. Finally, a value of $f_{min,s}$ greater than zero turned out to be useful to improve the stability of the Platform. According to those considerations, a last test is performed:

- **Test 8a)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-5}$ and $f_{min,MeOH} = 1$ and $\sum y_s \leq 5$ and $\varepsilon = 0.01\%$;
- **Test 8b)** $f_{min,s} = Cost_{1,s} = 1 \cdot 10^{-4}$ and $f_{min,MeOH} = 1$ and $\sum y_s \leq 5$ and $\varepsilon = 0.01\%$;

The solution outputs are shown in the graphs below:



(a) Runs and objectivefunction - Test 8a

(b) Variation of objective function- Test 8a

(c) Runs and objective function- Test 8b

(d) Variation of objective function- Test b8

Figure 4.13: Results from Test 8.

The combinations after the result filtering and cleaning are in Table 4.17.

The combination of epsilon constraint, limit in the sum of unit use and $f_{min,s} > 0$ turned out to be a quite good set of constraints because it increases the speed in obtaining the solutions without losing solutions. Increasing the $f_{min,s}$, the number of solutions decreases while the number of runs taken to get the results increases, as it can be seen in Table 4.18.

In this test, even the number of meaningless solution is really small but not zero. Again, the use of epsilon constraint is tricky because it creates

Rank	**Test**	
	8a	**8b**
1	d+E_{out}	d+E_{out}
2	b+d+E_{out}	b+d+E_{out}
3	b+d	b+d
4	b+d+E_{in}	b+E_{in}
5	b+E_{in}	a+d+E_{out}
6	a+d+E_{out}	c+d+E_{out}
7	c+d+E_{out}	a+d
8	a+d	a+E_{in}
9	a+d+E_{in}	c+d
10	a+E_{in}	c+E_{in}
11	c+d	
12	c+d+E_{in}	
13	c+E_{in}	

Table 4.17: Results after the cleaning in Test 8.

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	**Cost1**	ε **cstr**	$\sum y_s$ **cstr**
8a	19	7	0	37%	1	10^{-5}	10^{-5}	0.01%	5
8b	23	7	0	30%	1	10^{-4}	10^{-4}	0.01%	5

Table 4.18: Summary of Test 8.

many meaningless solutions, and some of them could not be detected and discarded automatically by the cleaning and therefore is needed a further post-analysis of the results after the cleaning.

4.6 Conclusions

Gathering the results from all the tests, a global table of the features of the tests can be built up.

Test	$\mathbf{n_{run}}$	$\mathbf{n_{sol}}$	$\mathbf{n_{missed}}$	η_{sol}	$\mathbf{f_{min,MeOH}}$	$\mathbf{f_{min,s}}$	Cost1	ε cstr	$\sum y_s$ cstr
1	44	7	0	16%	0	0	0	none	none
2a	44	7	0	16%	10^{-6}	10^{-6}	10^{-6}	none	none
2b	44	7	0	16%	10^{-5}	10^{-5}	10^{-5}	none	none
2c	44	7	0	16%	10^{-4}	10^{-4}	10^{-4}	none	none
3a	37	7	0	19%	0	0	0	none	6
3b	23	7	0	30%	0	0	0	none	5
3c	5	5	2	100%	0	0	0	none	4
4	37	6	1	16%	0	0	0	0.001%	none
4a	38	6	1	16%	1	0	0	0.001%	none
4b	36	6	1	17%	1	0	0	0.01%	none
4c	35	6	1	17%	1	0	0	0.10%	none
4d	33	5	2	15%	1	0	0	0.50%	none
4e	13	5	2	38%	1	0	0	1.00%	none
5a	15	6	1	40%	1	0	0	0.01%	5
5b	15	6	1	40%	1	0	0	0.05%	5
5c	15	6	1	40%	1	0	0	0.10%	5
5d	13	4	3	31%	1	0	0	0.50%	5
5e	13	4	3	31%	1	0	0	1%	5
6a	23	7	0	30%	10^{-5}	10^{-5}	10^{-5}	none	5
6b	23	7	0	30%	10^{-4}	10^{-4}	10^{-4}	none	5
7a	44	7	0	16%	1	10^{-4}	10^{-4}	0.01%	none
7b	38	5	2	13%	1	10^{-4}	10^{-4}	0.10%	none
8a	19	7	0	37%	1	10^{-5}	10^{-5}	0.01%	5
8b	23	7	0	30%	1	10^{-4}	10^{-4}	0.01%	5

Table 4.19: Comparison of the feature of all the tests.

A more effective comparison can be made by plotting in the same graph the most interesting data about each test: number of runs, number of solutions (meaning the sum of simple and complex solutions) and solutions missed, as it can be seen in Figure 4.14.

A good set of constraints should be able to retrieve all the solutions in the smallest number of iteration possible and avoid creating many meaningless solutions. The tests in which all the solutions were found are:

- 2a) 2b) and 2c) : 7 solutions in 44 runs;
- 3a) and 3b) : 7 solutions found respectively in 37 and 23 runs;
- 6a) and 6b) : 7 solutions found in 23 runs;
- 7a) : 7 solutions found in 44 runs;
- 8a) and 8b) : 7 solutions found respectively in 19 and 23 runs.

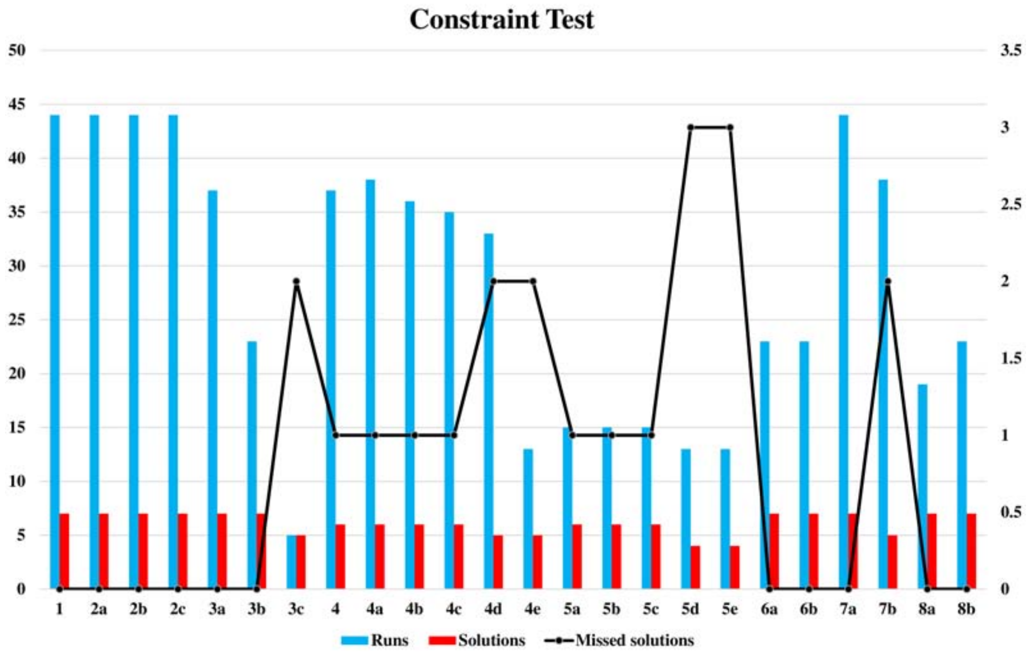


Figure 4.14: Comparison of all the test of the Platform.

All the tests except the base case and 2a,b,c, 3a,b, 6a,b present no meaningless solutions. Finally, the test with the smallest amount of runs (in order):

- 3c) : 5 runs;
- 4e), 5d) and 5e) : 13 runs;
- 5a), 5b) and 5c) : 15 runs;
- 8a) : 19 runs.

The best trade off between number of solutions and number of iterations is obtained in test 8a), in which the overall number of runs needed drops from 44 to 19, with a reduction of the computational time of the 43.6%. The downside of the set of constraints used in test 8a) is the generation of some meaningless solutions that are not cleaned during the filtering of the results. Consequently, it is compulsory a check of the solutions after the running of the platform.

A good set of constraints could be either the one used in test 8b) or the one used in test 6a). In both cases the platform took 23 runs to get the results (-56.8% of runs) but while in test 8b) there are some meaningless solutions, in test 6 this problem is avoided. The difference of the overall amount of runs is small because the platform deals with a limited number of units. The non-heuristic nature of the problem does not allow to make accurate prediction of the behaviour of the platform in different conditions, however this set of tests showed a general trend. The tests done so far are just the first step in the understanding of the behaviour of the platform and give a global idea of the most effective constraint that can be successfully applied. The results of the test are that the sum of the integer is a very effective constraint with no collateral effect. The epsilon constraint is less efficient in speeding the results retrieving, and its efficiency is deeply affected by the value of the epsilon. Moreover, the epsilon constraint has a crucial downside: it increases the number of solutions found by generating some combinations that make no sense from an engineering point of view (meaningless solutions).

In conclusion, the objective of speeding up the platform was achieved using a good set of constraints which can efficiently reduce the number of iterations. Since the nature of the problem is strongly non-heuristic, it is impossible to draw a general law that explains the behaviour of the platform subject to different set of constraints. In the end, the need of retrieving all the solutions without loosing precision is a stronger issue than reducing the number of runs. Consequently, the object of finding the best constraints trade off that speed up the platform is achieved and the most suitable combination of constraints is:

- $\sum y_s \leq N$
- $f_{min,s} = 1 \cdot 10^{-4}$
- $Cost_{1,s} = 1 \cdot 10^{-4}$

In the case study these will be the constraint added to the problem statement in order to sort and rank pathways.

Chapter 5

Application of Wood2CHem Platform to a case study

Abstract

Can wood be a reliable renewable resource for Switzerland? And what are the best processes that can be used to convert biomass into valuable products? These are the questions this case study tries to answer. In order to do so, firstly the Swiss wood potential is analysed, secondly the models and the techno-economic boundary conditions of the Platform are set and explained. The models of conversion processes included in the case study were developed and optimized separately, so the Platform deals with already optimized models. Finally, the Platform is run in two specific conditions, fixing the total input biomass and the results discussed and analysed.

5.1 Introduction

Presently, the share of wooden biomass in Switzerland's total energy consumption is around 4.2% [63], mostly used fore heating purpose. The Swiss National Research Programme "Resource Wood" (NRP 66) [17] aims to increase this share of renewable energy acting both on the side of increasing the conversion efficiency and promoting the use of wooden biomass as a reliable source of energy, pursuing the long term goal of 2000 W Society Challenge [64]. According to [14], the current wood potential in Switzerland is around 717 MW (see Table 5.1) against a current consumption of 430 MW. This means that presently the global amount of wood not yet exploited is from 287 MW (current situation) to 812 (maximum availability in the so called "green scenario" [14]).

The aim of this case study is to evaluate, analyse and rank different biomass-to-fuels technologies, according to the current economic conditions in Switzerland. Some preliminary considerations and assessments on the best technologies can be done, but in order to obtain a complete rank of the top technologies and the preferable combinations of processes it is necessary a systematic approach. For what concerns a preliminary assessment, it is

Wood	m^3/year	MW
Potential (base)	2′904′430	717
Potential (maximum)	5′032′154	1242
Demand (current)	1′742′684	430
Availability (base)	1′161′746	287
Availability (maximum)	3′289′469	812

Table 5.1: Wood availability in Switzerland [14].

clear that the technologies which have the lowest investment and the highest output will lead the chart, but beside that it is hard to evaluate the order for all the processes, because investment and efficiency are not the only indexes that can facilitate one technology if compared to another.

For instance, looking at Table 5.4, a good conversion pathway can be FT-a because, as most of the FT processes included in the case study, it has multiple products (fuel and electricity, which is the most valuable product) and low investment. Consequently, FT-a processes are expected to be in the top-ten. Other preliminary assessments can be done about SNG processes, which have really high efficiency (up to 75% according to [12]) and therefore are expected to be in the top level of the rank.

Starting from this consideration, an analysis of the optimal use of wooden biomass could be done using the Platform developed so far. A similar analysis was done by [65] focusing on the best process from an environmental point of view while in this work the attention is mostly focused on economic and energy issues.

5.2 Definition of the case study

In this Section the boundary conditions and assumptions in the case study are presented. Since a biorefinery is a multi-product facility, evaluating the production cost of the single output is a hard task because there are many ways to allocate costs in a multi-product plant. Consequently, in this case study all the prices of resources and products are assumed from the market statistics in order to compare the renewable output with the fossil counterparts through the break even price. The model of the case study is composed of three sub-models:

1. the **wood model**, in which it is assessed the cost of buying and transport the needed amount of wood from the harvesting site to the plant, according to [40] and [14];

2. the **techno-economic models** of the conversion processes included in this case study, taken from the work of [15] and [12];

3. the **economic boundary condition**, as the prices of resources and products were taken to be equal to the fossil counterparts. Setting

the fossil fuels as a benchmark allows to deduce conclusions on the gap between the renewable production of fuels compared to the oil industry.

5.2.1 Wood model

The first parameters to be assumed are the features of the wooden biomass, as all the calculations are referred to the input energy of the biorefinery. According to [14], the properties of the wood are summarized in Table 5.2.

Property	**Quantity/conversion factor**	**Unit**
Volume solid wood (reference)	1	m^3
Weight	0.96	ton
Energy content (per m^3)	7596	MJ
Average moisture content (w)	50	%
Hardwood fraction	57	%
Softwood fraction	43	%

Table 5.2: Wood property [14].

In the economic assessment of the cost of input wood, two aspects must be taken into account :

1. wood has a harvesting and transportation cost;
2. wood is not free, as the owner of the wood has the choice to sell the biomass on the market.

Consequently, the input wood bears both the cost of harvesting, transporting and the market price.

For what concerns the transport model, data were taken from the excellent work done by [14]. He created a spatial model to analysed different biomass plant locations according to the size and calculated the transport function for each plant location, as it can be seen in Figure 5.1.

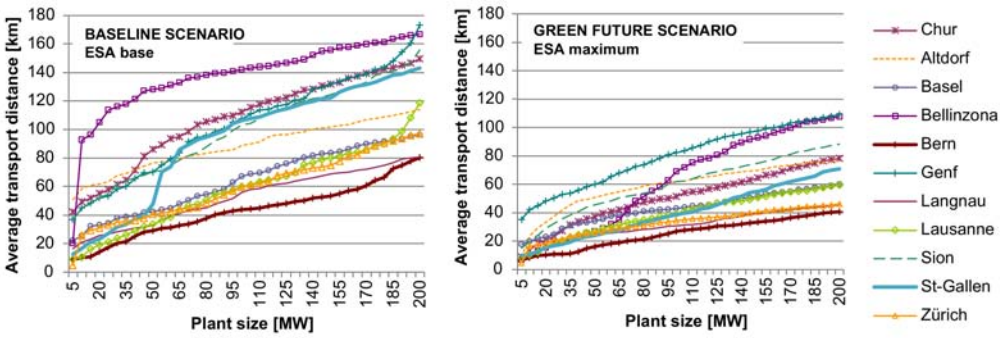


Figure 5.1: Transport distance according to plant size, location and wood availability [14].

In the current work, the reference transport model taken in consideration is Bellinzona. This is a conservative assumption as Bellinzona turned out to be the worst location for a biomass plant. This assumption allows to use the function proposed by [40] for evaluating the average biomass supply distance, coming from the interpolation of the graph in Figure 5.1:

$$d_{average} = t_1 P_{th}^{t_2} \qquad [km] \tag{5.1}$$

Where $d_{average}$ is the average distance between the harvesting site and the plant and t_1, t_2 are the parameters used to calibrate the function to the power of the plant P_{th}, calculated on dry wood input (see Table 5.3).

The specific energy consumption for lorry is assumed to be 10.67 MJ/km for a full-loaded 10 ton lorry and 8.37 MJ/km for and empty one [40], thus giving the average transport fuel consumption:

$$e_{lorry} = e_{full} + e_{empty} \qquad [MJ/km] \tag{5.2}$$

Consequently, the cost of a lorry is calculate as:

$$c_{lorry} = \frac{d_{average} e_{lorry} c_{diesel}}{LHV_{diesel} \rho_{diesel}} \qquad [CHF/lorry] \tag{5.3}$$

Evaluating the number of lorries needed to transport the biomass:

$$N_{lorry} = \frac{m_{wood}}{m_{lorry}} \tag{5.4}$$

Where $m_{wood} = \frac{P_{th} h}{LHV_{wood}}$ is the total amount of wood needed to run the plant and h the amount of working hours of the plant (assuming a capacity factor of 90%, as it is reported in Table 5.5).

Finally, the cost of transportation of biomass is calculated:

$$c_{trasp} = \frac{N_{lorry} c_{lorry}}{P_{th} h} \qquad [CHF/kWh] \tag{5.5}$$

All the parameters used in these calculations are presented in Table 5.3.

Parameter	**Symbol**	**Value**	**Unit**	**Reference**
t_1		18.455	km/kWth	[14, 40]
t_2		0.1776	-	[14, 40]
Fuel consumption (full load)[a]	e_{full}	10.67	MJ/km	[40, 66]
Fuel consumption (empty)[b]	e_{empty}	8.37	MJ/km	[40, 66]
Mean fuel consumption	e_{lorry}	18.99	MJ/km	a+b
LHV diesel	LHV_{diesel}	42.791	MJ/kg	
Diesel density	ρ_{diesel}	0.832	kg/l	
Diesel price	c_{diesel}	1.795	CHF/l	
Capacity lorry	m_{lorry}	10	ton	[40]

Table 5.3: Parameters used in the transport model.

The cost of transporting the biomass turned out to be 0,0052 USD/kWh for a 20 MW plant and 0.0078 USD/kWh for a 200 MW plant. Then it must be added the market price of biomass, which is 8 €/GJ (0.039 USD/kWh). Finally, the total cost of the input biomass can be evaluated: for a 20 MW biomass plant (a typical size for a pilot plant) the global cost of the biomass is 0.045 USD/kWh and the transportation cost constitutes 12% of the total cost. For a 200 MW plant the biomass cost is 0.047 USD/kWh of which 17% is due to the transportation.

5.2.2 Techno-economic process models

As explained in Section 4.3, the models used in the Platform are simple black boxes with fixed efficiency. Each unit (black box) is scaled linearly by the solver multiplying both costs and streams for the multiplication factor of the unit.

For what concerns the investment cost, the cost functions used are obtained linearising the cost function in neighbourhood of the size of the maximum wood available.

Since the data available to deduce the real cost function are limited, the real cost function was assumed to be the exponential regression $y = ax^b$ of the two sets of data available (and collected in Table 5.4). Subsequently, once calculated the interpolated cost function, it is linearised according to the range in analysis. The procedure is the following: first the minimum and the maximum size allowed for each plant must be stated, then the investment versus size is linearised doing a linear regression in that range. The same procedure is applied to the operating cost. According to these hypothesis, the cost function can be linearised in a narrow range, with a good approximation. The approximation is necessary because the main concern is in keeping the problem MILP. In Table 5.4 the reference investment costs are presented together with the reference value of the input/output stream for each technology. The ratio between input energy (wood) and output energy gives the efficiency of the black box. The methanol, the F-T and the DME process models are taken from the work of [15] while the SNG models are taken from [12].

Anyway, there is a lot of uncertainty in stating the investment costs for these kind of plant and for the scaling factor. Instead of taking a fixed scaling factor for all the technologies, as [67] and [68] or by applying the six-tenth rule, each technology has its own exponential function coming from the interpolation of the few data available (investment versus size of the plant given in Table 5.4).

The models presented are therefore integrated in the Platform superstructure, as it can be seen in Figure 5.2, where all units and layers taken into account are highlighted.

5.2.3 Economic boundary conditions

Finally, the boundary conditions of the Platform are assessed. As pointed out in the introduction, the choice is to assign market prices to the output in order to compare the bio-based products with the fossil counterparts.

Parameter	**MeOH-a**	**MeOH-b**	**MeOH-c**	**MeOH-d**	**FT-EF_ind**	**FT-EF_dir**	**FT-a**	**FT-b**	**FT-c**	**DME**	**SNG-a**	**SNG-b**
Gasification Technology	FICFB	FICFB	CFB	CFB	EF	EF	CFB	CFB	FICFB	FICFB	FICFB	CFB
Fuel Output [kW/MW]	570	570	318	318	637	458	303	352	601	561	693	750
Net electricity [kW/MW]	-85	-59	-18	35	-14	55	155	126	-4	-48	37	26
Reference year	2007	2007	2007	2007	2007	2007	2007	2007	2007	2007	2006	2006
20 MW biomass plant												
Investment [M€]	27	28	15	15	7	10	11	12	19	23	24	17
400 MW biomass plant (MeOH-a – DME); *100 MW biomass plant* (SNG-a, SNG-b)												
Investment [M€]	365	363	156	136	88	101	115	133	295	311	103	51

Table 5.4: Techno-economic parameters of the models used in the case study [15, 12].

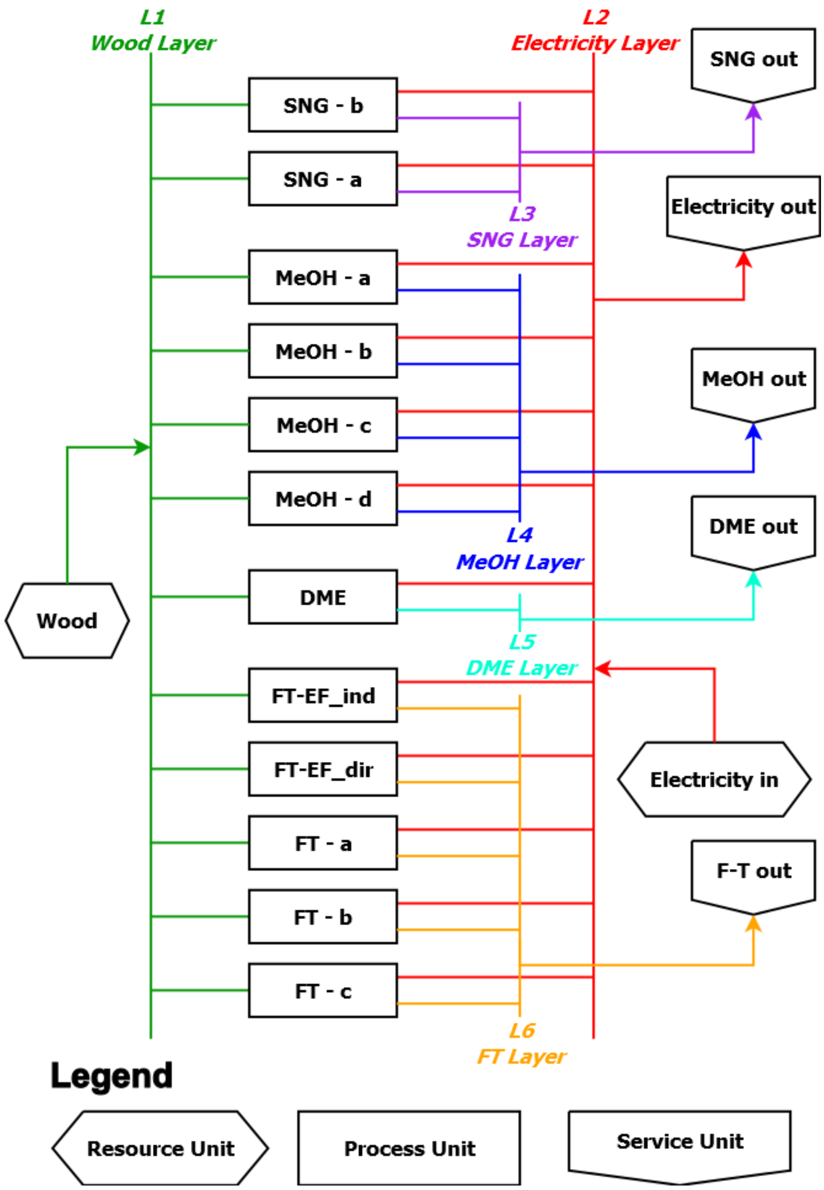


Figure 5.2: Scheme of the case study.

A summary of the economic conditions taken into account could be found in Table 5.5.

The number of operators per shift needed by a plant of 20 MW biomass is 4, according to [12]. Full time operation require 3 shifts of 8 hours per day. If there are 5 working days a week and 48 working weeks per year, each operator per shift corresponds to 4.5 operators. Moreover, in order to consider the scaling of the operators, an exponent 0.7 respect to the reference size of 20 MW was used [70]. Also this non-linear function was linearised with the same method explained in Section 5.2.2.

Parameters	**Value**	**Unit**	**Reference**
CEPCI index (2013)	567.3	-	[16]
Currency exchange rate	1.12	USD/CHF	[69]
Currency exchange rate	1.37	USD/EUR	[69]
Interest rate	6	%	
Plant lifetime	20	years	
Plant availability	90	%	
Operators	4	per shift	[12]
Operators salary	60000	USD/year	[70]
Maintenance cost	5	% of Cgr	
Wood market price	8	EUR/GJ	[71]
	0.039	USD/kWh	
Wood transportation cost (20 MW)	0.0052	USD/kWh	
Wood transportation cost (200 MW)	0.0078	USD/kWh	
Electricity price	0.19	CHF/kWh	[60]
	0.212	USD/kWh	
Methanol price	450	EUR/Mton	[61]
	0.111	USD/kWh	
Crude oil price	107.73	USD/bbl	[72]
	0.063	USD/kWh	
Natural gas price	0.041	€/kWh	[73]
	0.056	USD/kWh	
DME price	450	EUR/Mton	[74]
	0.070	USD/kWh	

Table 5.5: Economic parameters used in the case study.

The scaling of the investment cost C is done according to (5.6) and the CEPCI index is reported in Table 5.6:

$$C_{atA} = C_{atB}\frac{CEPCI_{atA}}{CEPCI_{atB}} \tag{5.6}$$

Year	**Index**
2005	468.2
2006	499.6
2007	525.4
2008	575.4
2009	521.9
2010	550.8
2011	585.7
2012	584.6
2013	567.3

Table 5.6: CEPCI index [16].

For what concerns the assessment of the prices, not all the products are global commodities and thus have a global price. For instance, methanol is a global commodity for chemical industry and it is traded in international market while the dimethyl ether market is not well defined, as the demand is low and localized. Concerning the F-T fuel, its price was assumed to be equal to the crude oil price, as F-T fuel produced by the plant considered, needs a further refinement to be used as an automotive fuel. The SNG produced by the models taken from [12] is methane quality so it can be sent to the grid, thus the European average methane price was assumed. Finally, dimethyl ether is a fuel that can be used in diesel engines, which are the potential major use of DME, owing to its high cetane number (55, compared to diesel's, which is around 40–53). DME could also be used as substitute for propane in LPG or aerosol propellant.

For what concerns the efficiency parameters, two different indexes are evaluated:

1. *Chemical efficiency*, calculated with (5.7), assuming $\eta_{ref} = 55\%$ according to [15]:

$$\eta_{chem} = \frac{E^-_{fuel} + \frac{E^-_{el}}{\eta_{ref}}}{E^+_{wood} + \frac{E^+_{el}}{\eta_{ref}}} \tag{5.7}$$

2. *Total efficiency*, or first-principle efficiency, calculated according to [15] with (5.8):

$$\eta_{tot} = \frac{E^-_{fuel} + E^-_{el}}{E^+_{wood} + E^+_{el}} \tag{5.8}$$

5.3 Rank of conversion pathways with 20 MW biomass input

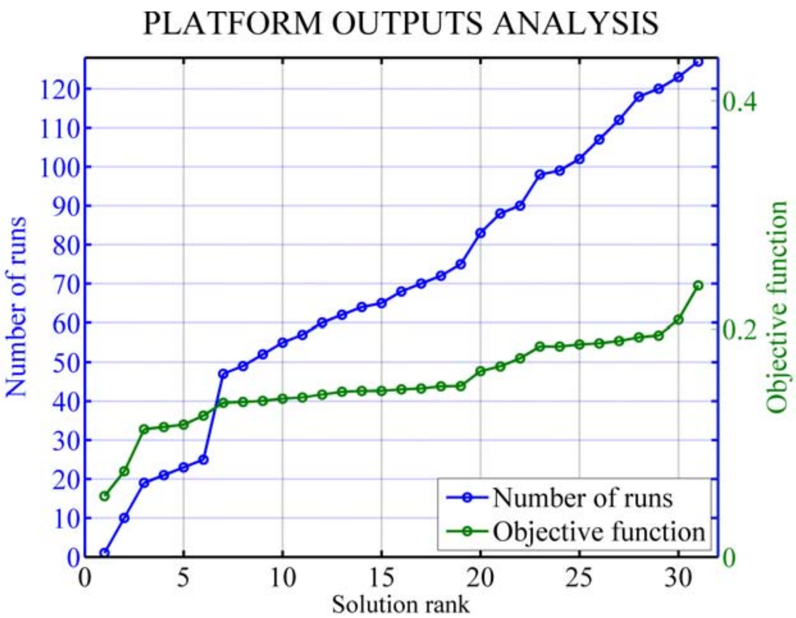
In the first case study, the Platform is run stating a fixed amount of input wood of 20 MW. The object is to see which is the rank of conversion process for a small size pilot plant. The minimum allowed size for the equipment was set to be 5 MW, thus all the cost function are linearised in the range 5 - 20 MW.

The evolution of the objective function versus the rank of the solution and the relative gap between solutions in the rank can be seen in Figure 5.3.

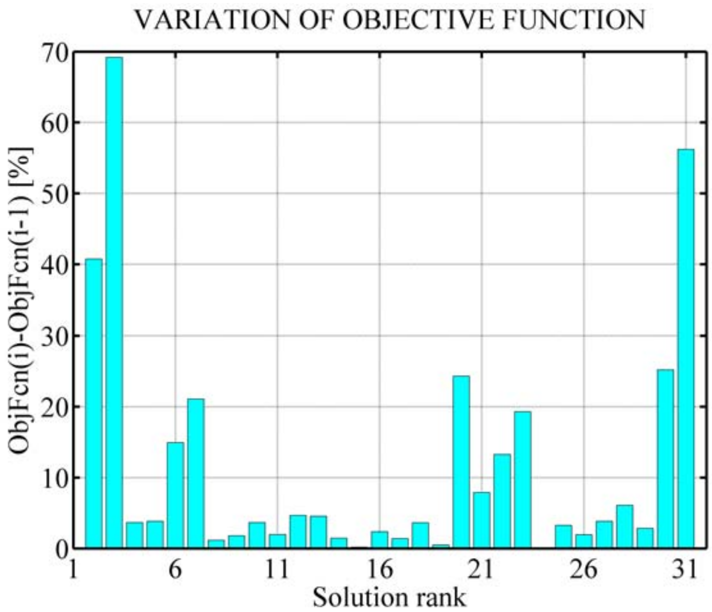
Table 5.7 collects the output of the Platform, i.e. all the possible combination available under the specified set of constraint.

Plotting the data from the table it is possible to have a clear view how the Platform ranks the technologies according to the objective function total cost minus revenues, thus the solutions are also ordered by the break even price of the biomass.

The best technology for a 20 MW biomass plant is FT-a. As it was predicted in the introduction, the first four plants in the rank are processes that have a positive energy production. Electricity is the most valuable product so it is obvious that the best technologies are the one with the possibility of power generation. Beside that, in the central part of the rank



(a) Runs and objective function - 20 MW input biomass



(b) Variation of objective function - 20 MW input biomass

Figure 5.3: Result for the case study (20 MW input biomass).

there are a number of combination of different technologies, most of them are just coupled to mutual fulfill the energy consumption. The processes in the rank from the fifth to the nineteenth position are close to each other both in term of objective function and wood break even, consequently they can be seen as "equivalent solution". All of them are obtained by combining F-T, methanol and SNG such as the external electricity input is zero. Also this results is quite obvious, as it more convenient to have two plant that are perfectly integrated. Surely it will be a great achievement also to assess

Rank	Units activated	η_{chem} %	η_{tot} %	Wood Break Even USD/kWh	OC MUSD	IC MUSD	TC MUSD	Revenue MUSD
1	FT-a + E_{out}	58.5	45.8	0.0354	8.26	16.45	9.70	8.19
2	FT-b + E_{out}	58.1	47.8	0.0315	8.27	17.93	9.83	7.71
3	FT-EFdir + E_{out}	55.8	51.3	0.0249	8.26	14.96	9.56	6.39
4	SNG-a + E_{out}	76.0	73.0	0.0245	8.31	26.14	10.59	7.36
5	E_{in} + FT-EFind	62.1	62.8	0.0241	8.71	10.43	9.62	6.33
6	MeOH-d + E_{out}	38.2	35.3	0.0227	8.29	22.48	10.25	6.74
7	FT-EFind + MeOH-d	54.6	54.6	0.0207	8.48	16.82	9.94	6.11
8	FT-EFind + SNG-a	65.2	65.2	0.0206	8.49	18.77	10.12	6.27
9	FT-a + MeOH-b	49.0	49.0	0.0204	8.57	37.32	11.82	7.94
10	FT-EFind + SNG-b	67.7	67.7	0.0200	8.50	21.43	10.37	6.43
11	FT-b + MeOH-b	49.4	49.4	0.0199	8.56	36.74	11.77	7.80
12	FT-a + MeOH-a	47.5	47.5	0.0194	8.55	34.30	11.55	7.51
13	SNG-b + E_{out}	79.7	77.6	0.0190	8.36	37.18	11.60	7.49
14	FT-EFdir + MeOH-b	50.8	50.8	0.0188	8.54	30.74	11.22	7.09
15	FT-b + MeOH-a	48.2	48.2	0.0188	8.55	33.77	11.50	7.37
16	E_{in} + MeOH-b	50.7	53.0	0.0186	10.35	41.72	13.98	9.82
17	MeOH-b + SNG-a	64.2	64.2	0.0185	8.56	36.34	11.73	7.55
18	MeOH-a + SNG-a	65.6	65.6	0.0181	8.55	34.15	11.53	7.29
19	FT-EFdir + MeOH-a	50.2	50.2	0.0181	8.53	27.60	10.93	6.68
20	MeOH-b + SNG-b	69.2	69.2	0.0157	8.59	41.66	12.22	7.60
21	E_{in} + MeOH-a	49.4	52.5	0.0150	11.21	40.20	14.71	9.98
22	E_{in} + FT-c	59.7	59.9	0.0137	8.45	28.21	10.91	5.97
23	MeOH-c + SNG-a	44.1	44.1	0.0118	8.53	28.12	10.98	5.75
24	MeOH-c + SNG-b	49.5	49.5	0.0118	8.54	30.87	11.23	6.00
25	E_{in} + MeOH-c	30.8	31.2	0.0115	8.89	22.43	10.85	5.57
26	DME + SNG-a	63.6	63.6	0.0113	8.55	33.41	11.46	6.15
27	DME + MeOH-d	42.0	42.0	0.0109	8.54	30.54	11.20	5.83
28	DME + SNG-b	68.4	68.4	0.0104	8.57	38.55	11.93	6.47
29	DME + FT-EFdir	51.3	51.3	0.0101	8.53	27.61	10.93	5.43
30	DME + FT-b	50.3	50.3	0.0077	8.54	32.02	11.34	5.45
31	E_{in} + DME	51.6	53.5	0.0023	9.95	34.24	12.93	6.19

Table 5.7: Global results of the Platform (20 MW input biomass).

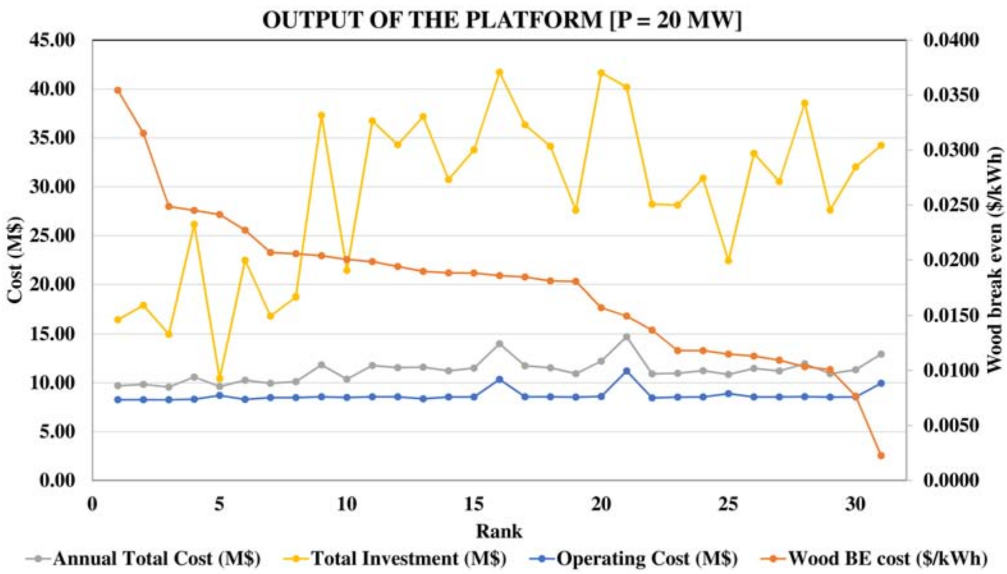


Figure 5.4: Cost and break even price against rank (20 MW input biomass).

and study the energy integration in each complex solution, but this will be left for future studies. Moving toward the end of the set, there is the worst technologies, which is DME.

Giving a closer look to the simple solutions, there are some interesting results about the evaluation of the single technologies. For the case of Switzerland, the leading technology for converting wood into fuels is Fisher Tropsch. The first three position are held by F-T, then comes SNG-a, FT-EFind and MeOH-d. The worst conversion pathways is dimethyl ether.

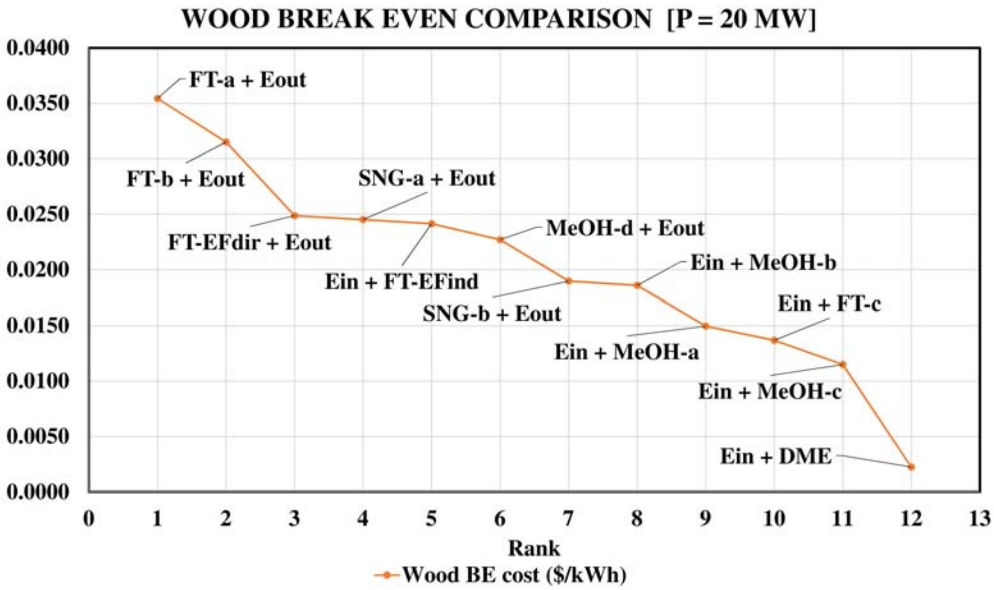


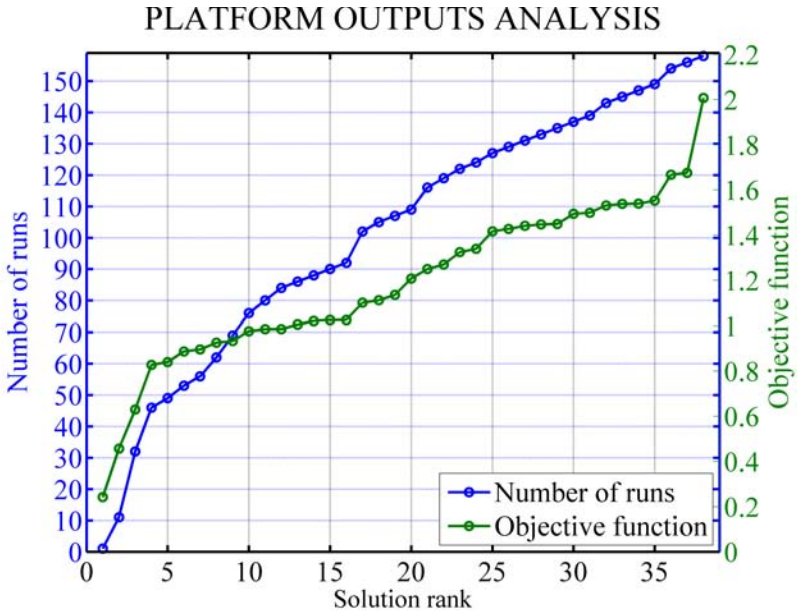
Figure 5.5: Focus on the rank of single technologies (simple solutions) for 20 MW input biomass.

For what concern the economics, the break even cost of wood is always lover than the biomass cost. For the best process (FT-a) the price of biomass should be 21% less. Small biomass plant has the advantage to spend less in harvesting and transporting but they cannot exploited the economy of scale, this explain why the break even is so low. The objective function increased by 94% between the first and the last solution in the rank and simultaneously the wood break even price drops to 6% of the first value found.

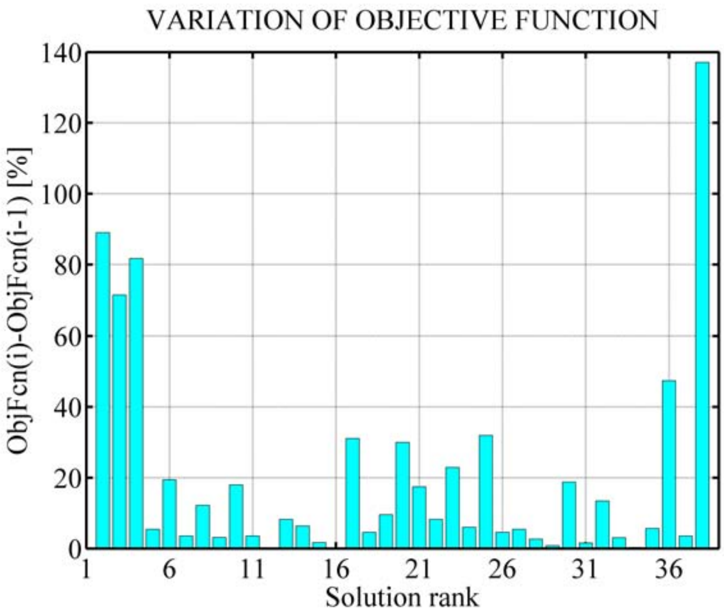
Definitively, the small size bio fuel plant cannot in any way compete with their fossil counterpart without any kind of subsidies. In this perspective, the Platform can be used as a tool to evaluate which are the technologies that worth being supported.

5.4 Rank of conversion pathways with 200 MW biomass input

According to [14], the current wood available and not yet exploited in Switzerland could run a 200 MW plant (see Table 5.1). Consequently, the second size of plant analysed is 200 MW because this is the maximum size currently achievable. A bigger plant can benefit of the economy of scale but, in the other hand, the harvesting area grows and the transport cost increases. The trade off between plant scale and biomass supply should be done according not only to the economics but also to the energy balance, evaluating the overall efficiency of the supply and processing chain. The evolution of the objective function versus the rank of the solution can be seen in Figure 5.3.



(a) Runs and objective function - 200 MW input biomass



(b) Variation of objective function - 200 MW input biomass

Figure 5.6: Result for the case study (200 MW input biomass).

The number of solution found, as it can be seen in Table 5.8, is higher than the previously evaluated case study (38 versus 31). This is due to the fact that the limiting size is 50 MW, consequently the cost function in this case are linearised in the range 50 - 200 MW. The approximation is good because in that range the real cost function is almost linear, the exponent of the real cost functions is around 0.7 - 0.9.

Rank	**Units activated**	η_{chem} %	η_{tot} %	**Wood Break Even USD/kWh**	**OC MUSD**	**IC MUSD**	**TC MUSD**	**Revenue MUSD**
1	FT-a + E_{out}	58.5	45.8	0.0427	80.0	100.0	88.8	81.9
2	FT-b + E_{out}	58.1	47.8	0.0388	80.1	113.9	90.0	77.1
3	SNG-a + E_{out}	76.0	73.0	0.0357	80.2	128.9	91.4	73.6
4	MeOH-d + E_{out}	38.2	35.3	0.0321	80.1	122.4	90.8	67.4
5	FT-EFdir + E_{out}	55.8	51.3	0.0319	80.0	88.5	87.7	63.9
6	FT-a + MeOH-b	49.0	49.0	0.0310	81.8	261.1	104.6	79.4
7	MeOH-b + SNG-a	64.2	64.2	0.0309	81.6	220.4	100.9	75.5
8	FT-b + MeOH-b	49.4	49.4	0.0304	81.8	257.7	104.3	78.0
9	MeOH-a + SNG-a	65.6	65.6	0.0302	81.6	204.0	99.4	72.9
10	E_{in} + FT-EFind	62.1	62.8	0.0294	84.6	73.1	91.0	63.3
11	FT-a + MeOH-a	47.5	47.5	0.0293	81.8	244.1	103.0	75.1
12	FT-EFind + SNG-a	65.2	65.2	0.0293	81.2	109.0	90.7	62.7
13	E_{in} + MeOH-b	50.7	53.0	0.0289	100.6	299.1	126.7	98.2
14	FT-EFdir + MeOH-b	50.8	50.8	0.0286	81.6	209.7	99.9	70.9
15	FT-b + MeOH-a	48.2	48.2	0.0286	81.7	240.9	102.7	73.7
16	FT-EFind + MeOH-d	54.6	54.6	0.0286	81.1	103.8	90.2	61.1
17	FT-EFdir + MeOH-a	50.2	50.2	0.0272	81.5	189.5	98.0	66.8
18	FT-EFind + SNG-b	67.7	67.7	0.0270	81.4	165.6	95.8	64.3
19	SNG-b + E_{out}	79.7	77.6	0.0266	80.9	300.4	107.1	74.9
20	MeOH-b + SNG-b	69.2	69.2	0.0253	82.1	323.0	110.3	76.0
21	E_{in} + MeOH-a	49.4	52.5	0.0245	109.3	296.9	135.2	99.8
22	MeOH-a + SNG-b	70.8	70.8	0.0242	82.1	321.3	110.1	74.1
23	MeOH-c + SNG-a	44.1	44.1	0.0232	81.4	157.0	95.1	57.5
24	DME + SNG-a	63.6	63.6	0.0229	81.6	205.6	99.5	61.5
25	FT-EFdir + MeOH-c	35.3	35.3	0.0215	81.3	138.2	93.3	53.2
26	DME + MeOH-d	42.0	42.0	0.0213	81.5	197.8	98.8	58.3
27	MeOH-c + SNG-b	49.5	49.5	0.0211	81.6	220.3	100.9	60.0
28	FT-a + MeOH-c	31.6	31.6	0.0210	81.3	146.0	94.1	53.0
29	FT-b + MeOH-c	32.2	32.2	0.0209	81.3	147.5	94.2	53.1
30	E_{in} + MeOH-c	30.8	31.2	0.0201	86.2	135.8	98.1	55.7
31	E_{in} + FT-c	59.7	59.9	0.0200	82.0	232.3	102.2	59.7
32	FT-c + MeOH-d	57.2	57.2	0.0195	81.7	240.7	102.7	59.3
33	FT-c + SNG-b	62.1	62.1	0.0193	81.8	257.0	104.2	60.6
34	DME + SNG-b	68.4	68.4	0.0193	82.0	302.5	108.4	64.7
35	DME + FT-EFdir	51.3	51.3	0.0191	81.5	192.6	98.3	54.3
36	DME + FT-b	50.3	50.3	0.0170	81.7	230.5	101.8	54.5
37	DME + FT-a	50.0	50.0	0.0168	81.7	232.2	101.9	54.4
38	E_{in} + DME	51.6	53.5	0.0109	96.8	253.5	118.9	61.9

Table 5.8: Global results of the Platform (200 MW input biomass).

Even for a bigger size, the best conversion pathways are F-T processes. The first two position are held by FT-a and FT.b, then comes SNG-b and MeOH-d, which turned out to be more effective for bigger size. As it can be seen in Figure 5.6, the objective function increases swiftly at the very beginning of the rank, consequently the wood break even price drops rapidly from 0.043 USD/kWh to 0.032 USD/kWh (-25%). After the fourth position, the objective function grows with a lower rate, and most solutions are made by coupling two processes. Consequently, there is a great difference between simple solution (top of the rank) and complex solutions. which are grouped in the central part of the rank. Moreover, complex solution turned out to be really close one to the other, so the difference is not so relevant. The range of variation of the objective function is reduced: in 38 combinations the objective function increases by 74% resulting the last wood break even price is 75% lower than the first one calculated.

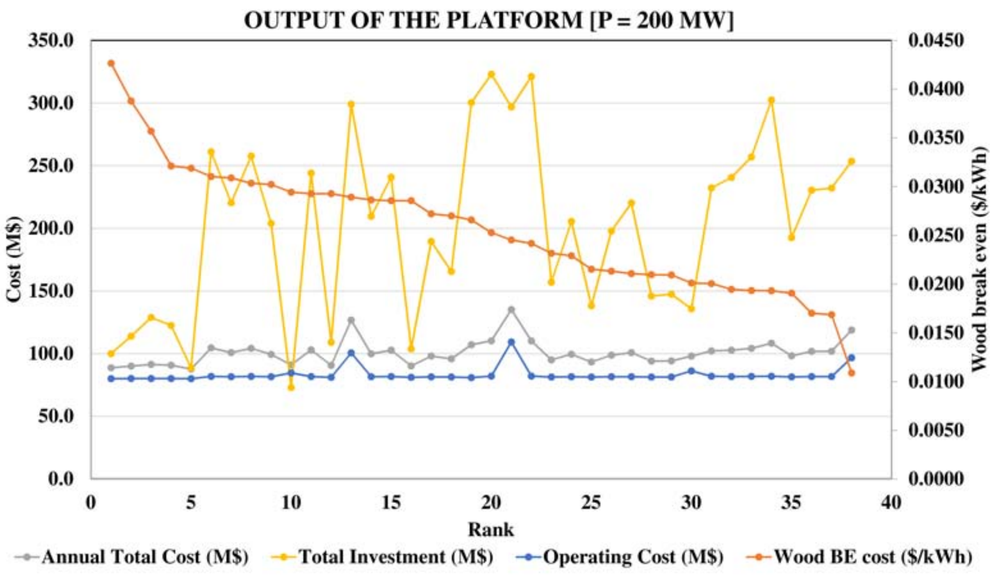


Figure 5.7: Cost and break even price against rank (200 MW input biomass).

For what concern the economics, the 200 MW plant can achieve better performance due to the economy of scale. The best process (FT-a) has a break even price of biomass which is only 9% lower than the cost of biomass.

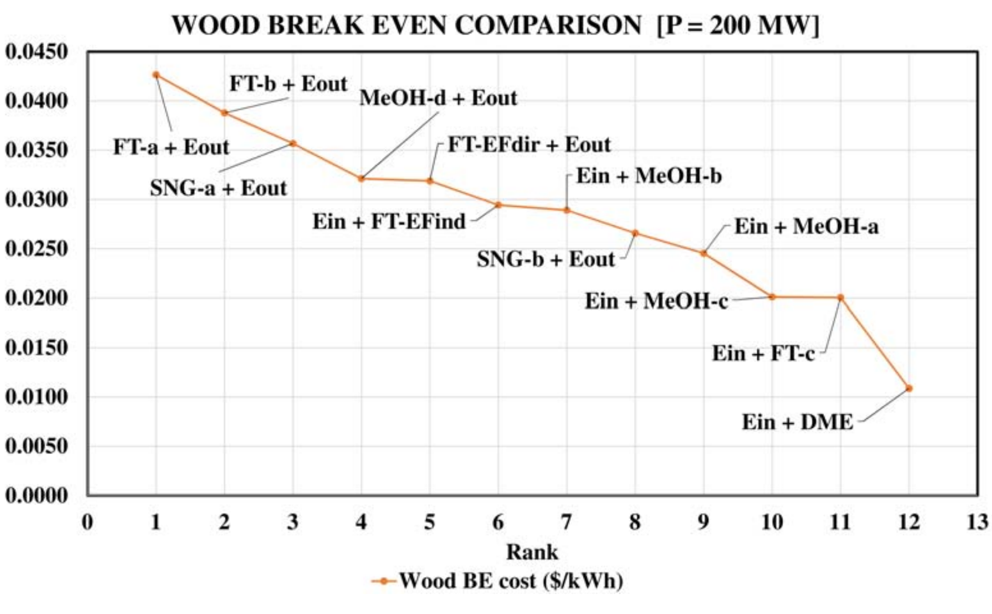


Figure 5.8: Focus on the rank of single technologies (simple solutions) for 200 MW input biomass.

Having a look to the single technologies, we can see which are the solution that can be considered equal. For example MeOH-d and FT-EF with direct heating are really close, as MeOH-c and FT-c. In these cases, the sorting can be done according to other criteria, which is exactly the goal of this work.

5.5 Conclusions

In conclusion, the application of the method developed allows to evaluate and rank different technologies. The set of constraints developed in Section 4.6 permits to accelerate the computational time and the application of Integer-Cuts leads to generate a full rank of pathways.

From the economic point of view, some conclusions can be drawn on the economical feasibility of wooden biomass-to-fuel plants. For what concerns the profitability, the model analysed shows that there is no way for the biomass to compete with the fossil fuels. Anyway the economy of scale pushes towards large scale size while the wood availability represents the stronger limit to the development of a bio-based plant.

In order to make biorefinery economically sustainable, incentives are needed. Or, on the other hand, the biomass should be recovered for free (thus exploiting only waste wooden biomass). The current possible market for bio-based products is a limited market niche of industries that give particular care on the carbon footprint of their products and therefore are ready to pay more to use a renewable raw material. Beside that, the market perspectives for bio-based fuels and materials are narrow in the short term.

The general trend in technologies is clearly kept in both cases: the best group of technologies are the F-T synthesis, which keep the first places for any size. This comparison helps to evaluate how size affects the rank of technologies. Focusing on simple solutions (see Table 5.9), is clear how increasing the size, some technologies are promoted.

Rank	**Technology**	
	20 MW	**200 MW**
1	FT-a	FT-a
2	FT-b	FT-b
3	FT-EFdir	SNG-a
4	SNG-a	MeOH-d
5	FT-EFind	FT-EFdir
6	MeOH-d	FT-EFind
7	SNG-b	MeOH-b
8	MeOH-b	SNG-b
9	MeOH-a	MeOH-a
10	FT-c	MeOH-c
11	MeOH-c	FT-c
12	DME	DME

Table 5.9: Comparison of rank of single technology according to the scale.

The best process, according to the condition stated in this case, is FT-a followed by FT-b, independently from the size of the input biomass. SNG and Methanol are more competitive for big scale (SNG-a and MeOH-d).

The common feature that links these technologies is the positive electricity output, which improves the economic performance of the process.

Another outstanding result coming from the case study is that the top-rank solutions consist in simple solutions, which means that the simplicity of the plant prevails on the integration with other facilities. Moreover, even relaxing the constraints, all the solutions do not consist in more than two plants in parallel because the only integration allowed in this level is through the electricity. In order to keep the cost low, simple plants are preferred and therefore maximum two processes are permitted to work in parallel.

Chapter 6

Conclusions

Throughout the thesis, a systematic methodology to generate a rank of bioefinery pathways for converting biomass into fuels and power is developed and tested. The method is therefore applied to the Wood2CHem Optimization Platform, in order to set up an automated tool able to detect and rank all the technologies according to the economic condition at the boundary. The method itself is simple thus presents many hidden aspects that this work tried to expand and analyse.

The greatest challenge consisted in dealing with the mathematical issue coming from the structure of the problem. The main concern of the work was to keep the problem simple and easy to be handled by a personal computer, without resorting to parallel computing in cluster or to more advanced optimization techniques. Another goal was to keep the structure of the Platform flexible enough to be further expanded without boosting the computational time. Such issue comes together with the need of having a powerful but light tool that can be used instead of multi objective optimization, which needs numerous hours to be run on a commercial personal computer.

These goals were tackled through the application of Constraint Programming set up in order to limit the size of the problem and therefore accelerate the results. The development of the best set of constraint passed through a systematic test because of the non heuristic nature of the problem. Indeed, at the beginning, it was not clear enough the effect that each constraint could have on the achievement of the result and the consequence of different set of constraint on the problem statement. Furthermore, even if the application of Integer-Cut constraint is not new in dealing with generate multiple solutions, the literature about computational issue coming from the application of Integer-Cuts is very scarce. The secondary objective of the test about the methodology is to point out the limits and the advantages of this method, in order to set up scientific bases to further development.

However, the commitment for keeping the MILP imposed to approach carefully to the linearisation of function. The issue was resolved by linearising the function automatically in the range of the allowed size for each technology. This turned out to be a good approach if the range is not so wide and if the cost function can be linearised without loosing accuracy.

Another approach that can increases the accuracy of the cost functions is using linear piecewise cost function or MINLP. This approach boosts the dimension of the problem, thus making it more difficult to be solved. The second approach imposes to change completely the methodology but, potentially, IT could be the most faithful to reality. MINLP could lead to more accurate results, but, as it was pointed out over and over, MINLP robust solving techniques are still yet to come. For instance, the current non-linear solvers still have some lack of accuracy in case of narrow valley. This clarifies why the MILP approach was followed, as it is considered the best problem statement in terms of robustness. MILP are proved to be more effective and robust among all the optimization problem.

In the end the essential trade off is between the coherence of the model with the reality and the robustness of the optimization, because it is as useless to have a perfect model, impossible to be solved as having a too simple model with no relation with the actual situation.

For what concerns the results coming from the application of the methodology to a real case, the most outstanding output is the rank of different technologies. For Switzerland, F-T fuels are the best choice in exploiting wooden biomass. However, even if crude oil price is high, a biomass-to-fuel plant is not yet economically sustainable. Anyway, in case of 200 MW plant, the break even price of wood is not far from the market price (the gap is less than 10%), so there is a real possibility of improving the economics of this kind of processes in order to make them profitable by increasing the efficiency and the integration.

Currently the only way to foster the development to bio-based economy is by subsidies (i.e. feed-in-tariff) or other kind of incentives (such as carbon tax). Anyway, the real issue that delays the bio-based economy is that fossil sources (are), although getting more and more expensive, are still cheaper than bio-based products.

Perspective & Future research

The future development of the Platform involves multiple aspects.

In the next future, the Platform could be enlarged including other technology, connecting also chemical processes to produce bio material. In this way, the Platform could help in comparing processes with output of different nature (energy, chemicals, fuels). The recirculation of mass stream is an issue that must be taken into account to increase the flexibility of the tool. Recirculating flows can create some new computational issue not yet faced.

In the long term period, there is the possibility to switch from black box model for each process to a more sophisticated one, for instance including also heat and power streams, in order to set up not only mass balance but also the heat cascade using pinch analysis and energy integration. The final goal is to achieve an increasingly level of complexity and detail in the structure of the Platform. However, this will cause the complexity of the problem to grow, an issue that must be faced and solved. Currently the Platform could be used to perform energy integration, but the computational time needed to handle such a problem (mass balance and heat cascade) is way too high.

Another interesting field of development of the Platform could deal with the uncertainty of the input. As it was pointed out throughout this work, the cost of the investments for biorefinery processes are still affected by a great uncertainty. Consequently, interesting studies can be addressed on evaluating the effect of cost uncertainty on the rank of technologies. The Platform could be therefore connected to a statistic simulator to create a complete analysis of the most promising pathways, studying the effect of technology learning curve on biorefinery.

Furthermore, the effect of evolution of market prices can be included, thus allowing to draw many scenarios. This last topic could be interesting and help government and public decision makers to address subsidies to the most promising technologies. In this perspective, a tool capable to rank the possible technologies will surely be helpful not only to address environment policy but also for industry to steer their production towards new promising products and developing market.

In the end, there are many possible future developments of the systematic methodology developed in this work. This method applied to such a powerful tool as the Wood2CHem Platform and combined with other models and methods (statistic, forecast, energy integration) can pave the way to a more complex and complete analysis of biomass conversion pathways, being a great add up in helping the development of biorefineries.

Appendices

Apendix A - AMPL code

In this Appendix the AMPL code implemented in the platform is presented. The code was included in the .mod file called by OSMOSE when launching the platform.

```
# $Id: eiampl.mod 2693 2013-11-15 16:08:15 FRIDAY  $
# Authors:  albertomian/ adrianoensinas / stefanomaronese
# This mod file consists in the Integer Cut constraint when
# dealing with Energy Integration mod file. (NO MULTIPERIOD for the moment)



set SolutionRank  ;
param Unit_Use_Old{u in Units, iter in SolutionRank};

subject to IntegerCutConstraint{iter in SolutionRank}:
sum{u in Units}(2*Unit_Use_Old[u,iter]-1)*Units_Use[u]<=(sum{u in Units}(Unit_Use_Old[u,iter]))-1;
```

Figure 1: AMPL syntax for the Integer Cut Constraint

```
subject to EpsCstr:
Costs_Cost['osmose_default_model_DefaultOpCost']+Costs_Cost['osmose_default_model_DefaultInvCost'] >= 0.01
```

Figure 2: AMPL syntax for the Epsilon Constraint

```
subject to MaxNunits:
sum {u in Units} Units_Use[u] <= 6 ;
```

Figure 3: AMPL syntax for the global sum of the unit use constraint

```
subject to sng_sng_units :
        1 * Units_Use['sng_sng_sng_a']  +  1 * Units_Use['sng_sng_sng_b']  <=  1;


subject to ft_ft_units :
        1 * Units_Use['ft_ft_a']  +  1 * Units_Use['ft_ft_b']  +
        1 * Units_Use['ft_ft_c']  +  1 * Units_Use['ft_ft_EFind']  +  1 * Units_Use['ft_ft_EFdir']  <=  1;


subject to meoh_meoh_units :
        1 * Units_Use['meoh_meoh_meoh_a']  +  1 * Units_Use['meoh_meoh_meoh_b']  +
        1 * Units_Use['meoh_meoh_meoh_c']  +  1 * Units_Use['meoh_meoh_meoh_d']  <=  1;
```

Figure 4: AMPL syntax for the limit in the sum of the unit use constraint for each technology

References

[1] Birgit Kamm, Patrick R. Gruber, and Michael Kamm. Biorefineries – industrial processes and products. In *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, 2012.

[2] Ed de Jong, Hans Langeveld, and René Van Ree. IEA Bioenergy Task 42 biorefinery. Technical report, IEA International Energy Agency, 2009.

[3] Francesco Cherubini, Gerfried Jungmeier, Maria Wellisch, Thomas Willke, Ioannis Skiadas, René Van Ree, and Ed de Jong. Toward a common classification approach for biorefinery systems. *Biofuels, Bioproducts and Biorefining*, 3(5):534–546, 2009.

[4] B. Kamm and M. Kamm. Principles of biorefineries. *Applied Microbiology and Biotechnology*, 64(2):137–145, April 2004.

[5] T. Werpy and G. Petersen. Top value added chemicals from biomass: Volume i - results of screening for potential candidates from sugars and synthesis gas. Technical Report DOE/GO-102004-1992, National Renewable Energy Lab., Golden, CO (US), August 2004.

[6] Vishnu Menon and Mala Rao. Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science*, 38(4):522–550, 2012.

[7] P. L. Spath and D. C. Dayton. Preliminary screening - technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas. Technical report, National Renewable Energy Laboratory, December 2003.

[8] John E. Holladay, James F. White, Joseph J. Bozell, and David Johnson. Top value added chemicals from biomass: Volume II - results of screening for potential candidates from biorefinery lignin. Technical Report PNNL-16983, Pacific Northwest National Laboratory (PNNL), Richland, WA (US), October 2007.

[9] Ed de Jong. Bio-based chemicals value added products from biorefineries. Technical report, IEA International Energy Agency, 2011.

[10] Pravat K. Swain, L.M. Das, and S.N. Naik. Biomass to liquid: A prospective challenge to research and development in 21st century. *Renewable and Sustainable Energy Reviews*, 15(9):4917–4933, 2011.

[11] Ronald Backers, Nicole van Klaveren, and Frans Jan Hellenthal. Port of Rotterdam Authority - Rotterdam Bio Port Homepage, 2013.

[12] Martin Gassner. *Process design methodology for thermochemical production of fuels from biomass. Application to the production of Synthetic Natural Gas from lignocellulosic resources.* Tesi di dottorato, Ecole Polytehnique Federale de Lausanne. Laboratoire d'Energetique Industrielle (LENI), 2010.

[13] François M.A. Maréchal. *Méthode d'analyse et de synthèse énergétiques des procédés industriels.* PhD thesis, Université de Liege, Faculté des Sciences Appliquées, 1997.

[14] 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, August 2012.

[15] 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.

[16] Chemical Engineering Magazine January 2014. *Chemical Engineering Magazine*, 1, January 2014.

[17] Thomas Bernhard, Krisztina Beer-Tòth, and Regine Duda. Portrait of the national research programme (NRP 66) resource wood, July 2012.

[18] Wood2CHem: a computer-aided platform for developing bio-refinery concepts - NRP 66 "Resource wood", 2013.

[19] Don J. Stevens. Biomass conversion: An overview of the IEA bioenergy agreement task VII. *Biomass and Bioenergy*, 2(1–6):213–227, 1992.

[20] Biomass production for energy from sustainable forestry | IEA Bioenergy Task 31, 2007.

[21] Biomass combustion and co-firing | IEA Bioenergy Task 32, 2013.

[22] Climate change effects of biomass and bioenergy systems | IEA Bioenergy Task 38, 2013.

[23] Commercialising conventional and advanced liquid biofuels from biomass | IEA Bioenergy Task 39, 2013.

[24] Energy from biogas | IEA Bioenergy Task 37, 2013.

[25] Joint project with the advanced motor fuels implementing agreement | IEA Bioenergy Task 41, 2010.

[26] Pyrolysis of biomass | IEA Bioenergy Task 34, 2013.

[27] Short rotation crops for bioenergy systems | IEA Bioenergy Task 30, 2007.

[28] Socio-economic drivers in implementing bioenergy projects | IEA Bioenergy Task 29, 2010.

[29] Sustainable international bioenergy trade: Securing supply and demand | IEA Bioenergy Task 40, 2013.

[30] Thermal gasification of biomass | IEA Bioenergy Task 33, 2013.

[31] Kamm, Birgit and Kamm, Michael. Biorefinery - system. *Chemical & Biochemical Engineering Quarterly*, 18(1):1–6, 2004.

[32] Sandun Fernando, Sushil Adhikari, Chauda Chandrapal, and Naveen Murali. Biorefineries: current status, challenges, and future direction. *Energy & Fuels*, 20(4):1727–1737, 2006.

[33] Michael FitzPatrick, Pascale Champagne, Michael F. Cunningham, and Ralph A. Whitney. A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. *Bioresource Technology*, 101(23):8915–8922, 2010.

[34] Mehboob Nawaz, Edwin Zondervan, John Woodley, and Rafiqul Gani. Design of an optimal biorefinery. In M. C. Georgiadis E.N. Pistikopoulos and A. C. Kokossis, editors, *Computer Aided Chemical Engineering*, volume Volume 29 of *21st European Symposium on Computer Aided Process Engineering*, pages 371–376. Elsevier, 2011.

[35] Zellstoff Stendal GmbH Homepage. `http://www.zellstoff-stendal.de`, 2013.

[36] Swiss Federal Institute of Technology Lausanne (EPFL) Lausanne: Industrial Energy Systems Laboratory (LENI). OSMOSE Documentation - Introduction. `http://leniwiki.epfl.ch/index.php/OSMOSE`. Last Access: 11/03/2014.

[37] Matthias Dubuis, Laurence Tock, and Leda Gerber. Introduction to LENI software. *Lausanne: Industrial Energy Systems Laboratory (LENI), Swiss Federal Institute of Technology Lausanne (EPFL)*, 2009.

[38] Francesca Palazzi, Z Périn-Levasseur, R Bolliger, and M Gassner. OSMOSE User Manual. *Lausanne: Industrial Energy Systems Laboratory (LENI), Swiss Federal Institute of Technology Lausanne (EPFL)*, 2010.

[39] Atish Jaientilal. Wood2CHem Optimization Platform - User Manual. *Lausanne: Industrial Energy Systems Laboratory (LENI), Swiss Federal Institute of Technology Lausanne (EPFL)*, 2013.

[40] Emanuela Peduzzi, Guillaume Boissonnet, Geert Haarlemmer, and Fran\ccois Maréchalb. Process integration of lignocellulosic biomass pre-treatment in the thermo-chemical production of FT fuels. centralised versus decentralised scenarios. *CHEMICAL ENGINEERING*, 35, 2013.

[41] 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, February 2011.

[42] Raymond R. Tan, Jo-Anne B. Ballacillo, Kathleen B. Aviso, and Alvin B. Culaba. A fuzzy multiple-objective approach to the optimization of bioenergy system footprints. *Chemical Engineering Research and Design*, 87(9):1162–1170, 2009.

[43] Denny Kok Sum Ng. Automated targeting for the synthesis of an integrated biorefinery. *Chemical Engineering Journal*, 162(1):67–74, 2010.

[44] Josef Kallrath. Mixed integer optimization in the chemical process industry: Experience, potential and future perspectives. *Chemical Engineering Research and Design*, 78(6):809–822, 2000.

[45] Singiresu S. Rao. *Engineering optimization: theory and practice*. John Wiley & Sons, Hoboken, N.J, 4th ed edition, 2009.

[46] J. N. Hooker, H. Yan, I. E. Grossmann, and R. Raman. Logic cuts for processing networks with fixed charges. *Computers & Operations Research*, 21(3):265–279, March 1994.

[47] José María Ponce-Ortega, Viet Pham, Mahmoud M. El-Halwagi, and Amro A. El-Baz. A disjunctive programming formulation for the optimal design of biorefinery configurations. *Industrial & Engineering Chemistry Research*, 51(8):3381–3400, February 2012.

[48] Mariano Martín and Ignacio E. Grossmann. On the systematic synthesis of sustainable biorefineries. *Industrial & Engineering Chemistry Research*, 52(9):3044–3064, August 2012.

[49] Antonis C. Kokossis and Aidong Yang. On the use of systems technologies and a systematic approach for the synthesis and the design of future biorefineries. *Computers & Chemical Engineering*, 34(9):1397–1405, 2010.

[50] Alexandre C. Dimian. Renewable raw materials: chance and challenge for computer-aided process engineering. *Computer Aided Chemical Engineering*, 24:309–318, 2007.

[51] 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.

[52] Emilie Danna, Mary Fenelon, Zonghao Gu, and Roland Wunderling. Generating multiple solutions for mixed integer programming problems. In Matteo Fischetti and David P. Williamson, editors, *Integer Programming and Combinatorial Optimization*, volume 4513, pages 280–294. Springer Berlin Heidelberg, Berlin, Heidelberg, 2007.

[53] Belinda Wang, Berhane H. Gebreslassie, and Fengqi You. Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: Integrated life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. *Computers & Chemical Engineering*, 52:55–76, 2013.

[54] Jonathan Moncada, Luis G. Matallana, and Carlos A. Cardona. Selection of process pathways for biorefinery design using optimization tools: A colombian case for conversion of sugarcane bagasse to ethanol, poly-3-hydroxybutyrate (PHB), and energy. *Industrial & Engineering Chemistry Research*, 52(11):4132–4145, March 2013.

[55] Sergio Rech. *Analisi e ottimizzazione della configurazione di un macro-sistema di conversione di energia.* Tesi di dottorato, Università degli Studi di Padova, January 2013.

[56] 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 & Environmental Science*, 5(2):5768–5789, October 2011.

[57] 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, January 2008.

[58] Soterios A. Papoulias and Ignacio E. Grossmann. A structural optimization approach in process synthesis—II: heat recovery networks. *Computers & Chemical Engineering*, 7(6):707–721, 1983.

[59] Samira Fazlollahi, Pierre Mandel, Gwenaelle Becker, and Francois Maréchal. Methods for multi-objective investment and operating optimization of complex energy systems. *Energy*, 45(1):12–22, 2012.

[60] Swissgrid - Tariffs. http://swissgrid.ch/swissgrid/it/home/experts/topics/grid_usage/tariffs.html. Last Access: 11/02/2014.

[61] Methanex Regional Posted Contract Prices. http://www.methanex.com/products/methanolprice.html. Last Access: 11/02/2014.

[62] BIOMASS Energy Centre. http://www.biomassenergycentre.org.uk/portal/page?_pageid=75,59188&_dad=portal. Last Access: 11/02/2014.

[63] Swiss Federal Office of Energy SFOE - Energy Consumption in Switzerland 2012. www.bfe.admin.ch/statistics. Last Access: 11/03/2014.

[64] François Marechal, Daniel Favrat, and Eberhard Jochem. Energy in the perspective of the sustainable development: The 2000 w society challenge. *Resources, Conservation and Recycling*, 44(3):245–262, 2005.

[65] Bernhard Steubing, Rainer Zah, and Christian Ludwig. Heat, electricity, or transportation? the optimal use of residual and waste biomass in europe from an environmental perspective. *Environmental science & technology*, 46(1):164–171, January 2012. PMID: 22091634.

[66] Swiss Centre for Life Cycle Invetories, Ecoinvent. http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/Electricity_and_natural_gas_price_statistics#Natural_gas_prices_for_industrial_consumers. Last Access: 11/02/2014.

[67] Michael W. Jack. Scaling laws and technology development strategies for biorefineries and bioenergy plants. *Bioresource Technology*, 100(24):6324–6330, December 2009.

[68] Mark Wright and Robert C. Brown. Establishing the optimal sizes of different kinds of biorefineries. *Biofuels, Bioproducts and Biorefining*, 1(3):191–200, 2007.

[69] Swiss National Nank SNB. http://www.snb.ch/en/. Last Access: 11/02/2014.

[70] Gael D. Ulrich. *Chemical engineering process design and economics: a practical guide*. Process Pub, Durham, N.H, 2nd ed edition, 2004.

[71] Gustav Resch, Mario Ragwitz, Simone Steinhilber, Barbara Breitschopf, Christian Panzer, Andre Ortner, and Sebastian Busch. RE-Shaping: shaping an effective and efficient european renewable energy market. *A comparative assessment of two recent studies on the future development of renewable electricity support in Europe, a report compiled within the European research project RE-Shaping (work package 4) Intelligent Energy-Europe, ALTENER http://www. reshaping-res-policy. eu/downloads/Quo% 28ta*, 2010.

[72] U.S. Energy Information Administration EIA - Europe Brent Spot Price. http://www.ecoinvent.ch. Last Access: 11/02/2014.

[73] Eurostat - Electricity and natural gas price statistics. http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/Electricity_and_natural_gas_price_statistics#Natural_gas_prices_for_industrial_consumers. Last Access: 11/02/2014.

[74] A. V. Bridgwater, R. Chinthapalli, and P. W. Smith. Identification and market analysis of most promising added-value products to be co-produced with the fuels. Technical report, European Union - Seventh Framework Programme for Research and Technological Development, May 2009.