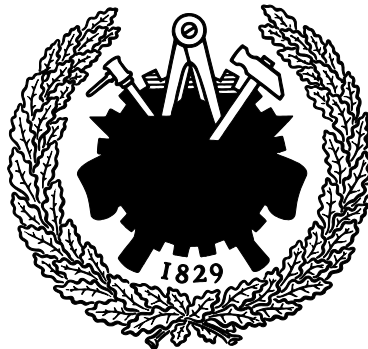


THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

**Production of Hydrogen for Oil Refining by Thermal
Gasification of Biomass:
Process Design, Integration and Evaluation**

JEAN-FLORIAN BRAU



Heat and Power Technology
Department of Energy and Environment
Chalmers University of Technology
Göteborg, Sweden 2013

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Integration and Evaluation

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ABSTRACT

Hydrogen is an important part of crude oil refining operations since it is required in several units for the desulphurization and upgrading of various oil fractions. At present, most of the refineries meet their hydrogen demand through methane steam reforming, a refinery unit that can represent up to 25% of the plant's fossil CO₂ emissions. Processes based on thermochemical gasification of biomass are promising alternatives for hydrogen production. This thesis presents a process integration study of two distinct biomass-to-hydrogen concepts. The focus is put on the integration of these processes with an existing refinery used as a case study for the identification of promising configurations.

The first biomass-to-hydrogen concept is based on indirect, atmospheric steam gasification and proven technologies for gas cleaning and upgrade (IG concept) while the second concept relies on direct, pressurized oxygen-steam blown gasification and more advanced cleaning and upgrading technologies (DG concept). Mass and energy balances for the biorefinery concepts are obtained by process simulation while actual refinery data is used. Simulation results show that based on Higher Heating Values (HHV), the conversion efficiency from biomass to hydrogen is 67% for the IG concept and 65% for the DG concept.

Process integration tools are then used to identify promising integration and heat recovery opportunities. The identified process configurations differ in terms of coproducts: in addition to hydrogen, the production of HP steam and/or electricity is investigated. All configurations are compared in terms of energy and exergy efficiency and their environmental impact is assessed by means of a fossil CO₂ balance.

Results highlight the potential for improvement of process performances by performing biomass drying with low quality refinery excess heat instead of high temperature biorefinery excess heat. This integration allows the export of additional HP steam to the refinery or electricity generation through an integrated steam cycle, which increase the efficiency of the biorefinery. The IG concept is found to consistently outperform the DG concept according to both thermodynamic efficiencies. For both concepts, the configuration where HP steam is exported to the refinery appears most promising in a context of decreasing emissions from the European power sector.

Keywords: Process Integration, Hydrogen, Refining, Energy Systems, Modeling, Biomass Gasification

List of Publications

This thesis is based on the following papers.

- I. Brau J-F, Morandin M, Berntsson T. Hydrogen for oil refining via biomass indirect steam gasification: energy and environmental targets. *Clean Technologies and Environmental Policy*. 2013;15(3):501-12.
- II. Brau J-F, Morandin M. Biomass-based hydrogen for oil refining: integration and performances of two gasification concepts. 2013. *Submitted for publication in International Journal of Hydrogen Energy*.

Jean-Florian Brau is the main author of these papers. Thore Berntsson was the main supervisor of and Matteo Morandin co-supervised the work.

Related work not included in this thesis

- Brau J-F, Morandin M, Berntsson T. Integration of a biomass-to-hydrogen process in an oil refinery. *Chemical Engineering Transactions*. 2012;29:1087-92.

This article is a conference paper that presents results included in Paper I, which is an extended version including also additional work. Including this conference article was not considered instrumental to improving the quality of this thesis and it was thus discarded.

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1. Introduction

As a response to the challenges of global warming and climate change, the European Union (EU) has issued various policy instruments such as the Emissions Trading System (ETS), which objective is to reduce industrial greenhouse gas emissions cost-effectively [1]. A quantitative target for global emission reduction was also set by the EU at a level 20% lower than 1990 as an additional incentive to translate policy into an effective transition (part of the EU 20-20-20 targets [2]). Cuts in emissions from the industrial sector are expected to play a significant role in meeting the target since this sector represented 58% of the total carbon dioxide (CO₂) emissions in the EU-27 in 2007 [3]. As an energy intensive activity, the refining industry holds a significant share of these emissions.

Options for the reduction of fossil CO₂ emissions in the industrial sector include energy efficiency measures and replacement of fossil-based energy with renewable energy. Solar power, wind power and hydropower are alternative technologies to produce renewable electricity but when it comes to the production of chemicals and transportation fuels, biomass appears as a promising renewable substitute for fossil fuels [4].

The use of biomass, when it replaces fossil fuel supply in a given conversion process, leads to a reduction in fossil CO₂ emissions. Additionally, systems making use of biomass are inherently more sustainable than their fossil fuel-based counterparts since biomass is a renewable resource, as opposed to fossil fuel supply which is bound to exhaustion. Biofuel production through biomass conversion processes could thus contribute in meeting two of the EU 20-20-20 targets: global emission reduction and share of energy produced from renewables.

However, renewable does not mean unlimited: the worldwide potential for biomass energy supply is estimated at around 20 to 30% of the current energy demand [5, 6]. Identifying the most efficient biomass conversion pathways is therefore crucial to achieve the transition to a consistent and more sustainable energy system.

The focus of this study is put on the utilization of biomass for hydrogen supply in a complex European oil refinery. The work presented in this thesis is based on the case study of an existing

oil refinery, where the substitution of the existing fossil-based hydrogen production unit by a biomass-based process is investigated. Since a number of different technologies can be used in a biomass-to-hydrogen process, the aim is to determine the most promising concept among some design alternatives.

1.1 Background

Oil refining designates the process of transforming crude oil into a variety of marketable products such as gasoline or diesel. The overall aims of the refining chain are as follow:

- Remove contaminants (essentially sulfur compounds) from crude oil;
- Separate the oil into so-called “fractions”, according to the molecular weight of the hydrocarbon chains. A fraction is composed of hydrocarbons within a certain range of molecular weight;
- Break down long hydrocarbon chains (heavy fractions) into more value-added short chains (light fractions): this is known as cracking;
- Improve quality of the obtained fractions regarding e.g. environmental regulations and combustion behavior.

Several techniques are operated to reach each of these objectives. The refining process therefore consists in a number of operations ranging from simple distillation to heterogeneous, catalytic chemical reactions. Depending on the range of products delivered by a refinery, its organization can take various levels of complexity, from a simple refinery equipped only with atmospheric distillation and a few upgrading operations to a complex refinery operating several distillation trains and extensive upgrading units.

1.1.1 Case study

The case study refinery is located on the Swedish West Coast. The plant is one of the most modern in Europe and has a capacity of 11.4 Mt crude oil/y. Figure 1 shows a flowsheet of the refinery.

The total hot utility demand in the refinery amounts to 408 MW. The plant has an electricity demand of 45 MW, which is entirely satisfied through power import from the grid. A large amount of excess heat is also available from the refinery, mostly in process streams currently cooled by air fans. Fuel gas-fired boilers in the refinery produce 49.4 MW of High Pressure steam (HP steam at 390°C and 39 bars) with an efficiency of 80%.

The total hydrogen requirements in the refinery are 12.5 t/h. Of these, only 5.1 t/h originate from catalytic reforming operations where hydrogen is a byproduct. Therefore, the additional 7.4 t/h (291.5 MW, HHV basis) need to be produced in a dedicated refinery unit.

Ethanethiol + Hydrogen \rightarrow Ethane + Hydrogen sulfide



The toughening of regulations imposes deeper desulphurization and therefore leads to an increase in hydrogen demand in the refinery. As a consequence, most complex refineries are structurally in deficit of hydrogen and therefore operate dedicated Hydrogen Production Units (HPU). As opposed to catalytic reforming units where hydrogen is a byproduct of the upgrading of oil fractions, the sole purpose of these HPUs is to produce hydrogen to meet the refinery's demand.

An overwhelming majority of HPUs consists in steam reforming of light hydrocarbons (e.g. methane) followed by single or dual shift of carbon monoxide (CO) into hydrogen [8]. Figure 2 presents the flowsheet of a typical industrial HPU with indicative temperature levels.

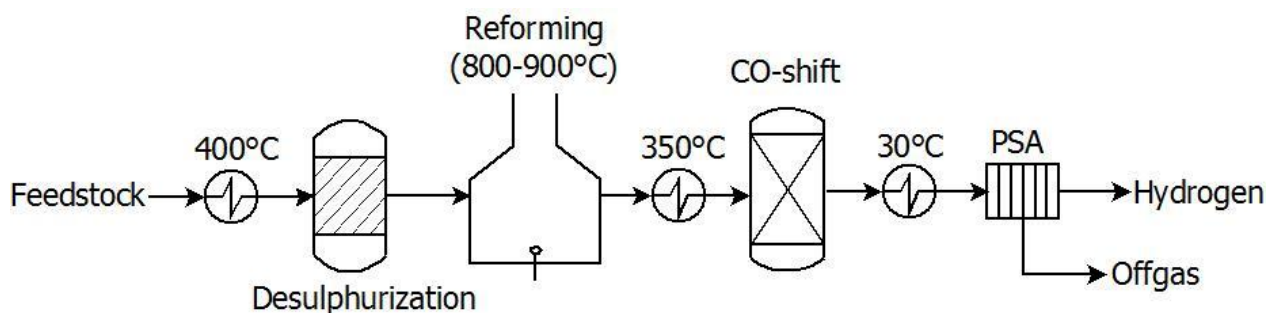


Figure 2: flowsheet of a typical refinery HPU

Steam reforming can represent up to 25% of the total CO₂ emissions in a refinery [9]. It is therefore crucial for the refinery sector to find efficient, environmental-friendly pathways to meet an increasing hydrogen demand without hindering their emission reduction plans. While improving hydrogen recovery within the refining processes and the refinery hydrogen network is a solution that cannot be overlooked [10], the refining industry has the opportunity to take a leading role in the implementation of new, carbon lean technologies for hydrogen production.

Indeed, a range of pathways based on very different approaches is currently under research: electrolysis and thermal dissociation use water as feedstock while several processes rely on biomass. From a sustainability point of view, water electrolysis may prove an interesting pathway if renewable-based electricity is used. Unless combined with large scale electricity storage however, availability issues arise. Thermal dissociation by means of nuclear energy is a source of environmental and social concerns. Biomass fermentation does not seem promising because of low yields and long reaction times [11].

Among biomass-to-hydrogen processes, production through biomass gasification is highly efficient and could reduce dependence on fossil feedstock and, as a consequence, emissions of fossil CO₂ [12]. Compared to the processes discussed previously, biomass gasification is also the

route that is the most likely to comply with the availability and productivity requirements of a refinery.

1.2 Objectives

The overall objective of this thesis is to study hydrogen production through thermal gasification of biomass as a substitution to a fossil fuel-based HPU in a complex European oil refinery. Since a number of different technologies can be combined to form a complete biomass-to-hydrogen process, the aim is to determine the most promising concept among some design alternatives.

To this end, performance indicators are defined. These are general enough to allow comparing these concepts to other biomass conversion pathways but also well adapted to the nature of the processes, material and energy flows involved in this study. The environmental performance of these biomass-based concepts is also determined. This is done by evaluating the change in fossil CO₂ emissions at the refinery after the implementation of each concept.

The necessity of making use of the high temperature excess heat potentially available in biomass gasification processes was highlighted in several previous studies [13]. Additionally, although modern refineries are rather well energy-integrated, a structural excess of heat remains in these plants [14, 15]. However, the temperature levels of this waste heat are usually much lower than those expected in biomass gasification concepts. In this thesis, particular attention is thus paid to opportunities for heat integration, both within the biorefinery and with the oil refinery. The identified opportunities are included in different configurations of the biorefinery that are then compared using the selected performance indicators.

1.3 Related work

Although no industrial plants have been built yet, a large body of literature has been produced on stand-alone hydrogen production through biomass gasification. Detailed design parameters and economic results for a process based on the Battelle Columbus Laboratory gasifier were published by Spath et al. [16]. Williams et al. [17] provided a literature review on existing gasifier concepts with focus on technological challenges associated with hydrogen production. Hamelinck and Faaij studied several stand-alone biomass-to-hydrogen concepts considering two types of gasifiers [18]. They published detailed simulation data and economic evaluations which showed comparable outcomes for the various systems. The concepts using membrane separation appeared to perform well on an economic point of view due to high efficiencies and modest investments.

More recently, Cohce et al. studied one concept of a hydrogen production process based on biomass gasification by applying energy and exergy analysis [19]. With help of a multi-objective optimization framework, Tock and Maréchal designed and optimized the thermo-economic performance of stand-alone biomass-to-hydrogen concepts based on the FICFB gasifier [20].

Some concepts included a gas turbine and/or carbon capture; efficiencies of 60% were reached in some cases. The integration of hydrogen production processes with other industrial plants was also investigated in a number of publications. As an example, Andersson and Harvey compared hydrogen production via black liquor gasification and stand-alone biomass gasification [21].

Among the studies dealing with hydrogen production for refinery applications, Sarkar and Kumar [22] investigated the production of hydrogen via biomass gasification for the upgrading of bitumen from oil sands. However, they considered only stand-alone processes producing hydrogen sent via pipeline to the refining site, which was very specific to the Canadian oil sands industry. Heat integration with the refining plant was not part of their work.

In [23], Johansson et al. investigated CO₂ emission consequences of hydrogen production through biomass gasification compared to standard methane reforming in a simple oil refinery equipped only with atmospheric distillation, naphtha reformer and necessary treatment. Several process designs were included but all had dual shift and pressure swing adsorption in common. Opportunities for the use of refinery excess heat were studied as well. In this latter study, the biomass gasification process was considered as a supplementary capacity installed to satisfy an increase in hydrogen demand and excess heat from the biorefinery was used for steam export only. Results were found to heavily depend on assumptions on the surrounding energy system and biomass availability.

The present work is based on the case study of a much larger and more complex refinery, which is likely to be more representative of the future European refining plants. Besides steam export, electricity generation is also considered for biorefinery excess heat recovery and several technologies are included in process concepts.

1.4 Outline

Chapter 2 is a presentation of the biomass-to-hydrogen gasification pathway and the different steps it consists of. In Chapter 3, the methodology used and the way the work was structured are detailed. Results are then presented in Chapter 4 and discussed in Chapter 5, followed by conclusions in Chapter 6. In Chapter 7, ideas for future work on the project are highlighted.

2. Thermochemical biomass-to-hydrogen conversion

A thermochemical biomass-to-hydrogen process is organized in roughly three sections: biomass drying and gasification, syngas cleaning and upgrading and hydrogen separation. However, several technologies can be applied in each of these sections and the resulting biomass-to-hydrogen concept is a combination of chosen building blocks, see Figure 3.

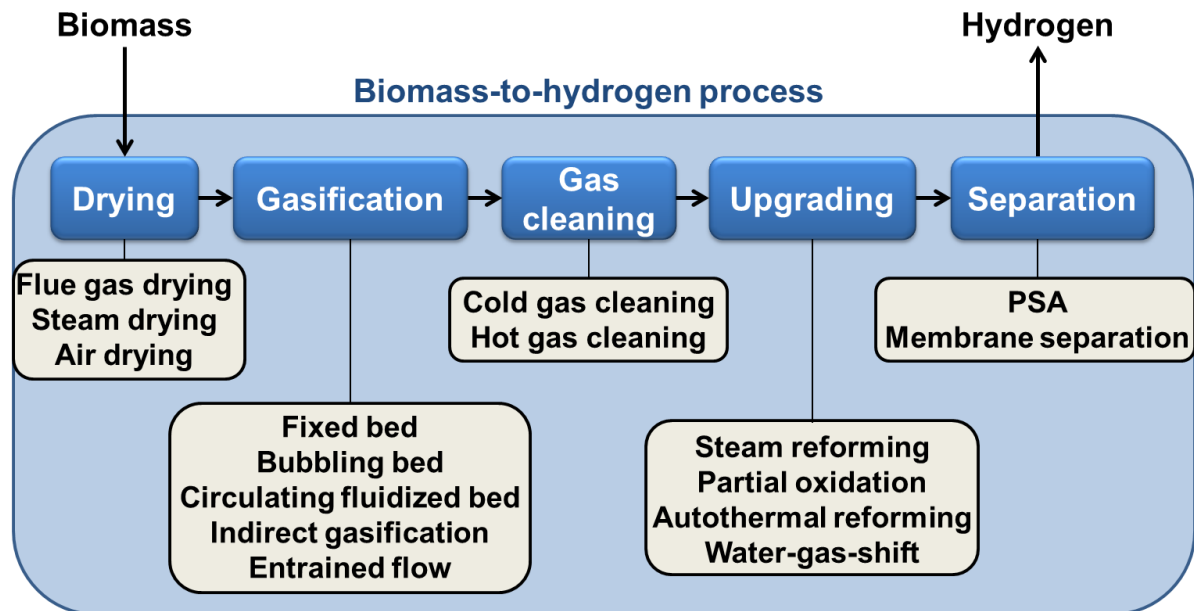


Figure 3: principle diagram of a biomass-to-hydrogen process with alternative technologies

Two process concepts, following two different design approaches, are investigated in this work. The principles of the subsequent steps included in the biomass-to-hydrogen concepts are described in this section, together with the main technologies that can be applied. The design of the two processes, built by assembling these technologies to form a whole biomass-to-hydrogen conversion chain, is explicated in the results section (section 4.1).

2.1 Biomass drying

The usual moisture content of woody biomass is around 50wt%. Gasifying wet biomass implies evaporating this water content with high temperature heat in the gasifier, which leads to additional energy requirements. The first step of a biomass conversion system therefore consists in drying the incoming feed.

Drying is performed prior to gasification to ensure reliable operation of the gasifier and to maximize efficiency [24]. Higher moisture content in the biomass also hinders char combustion which leads to lower gasification temperature and, therefore, to increased methane and lower hydrogen contents in the produced syngas [25]. The optimal moisture content for gasification is a function of the gasifier type and the final desired product but is in a range of 10 to 20wt% [17].

Several drying technologies exist but three are mainly considered in biomass conversion systems:

- Flue gas drying
- Steam drying
- Low temperature air drying

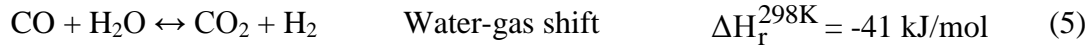
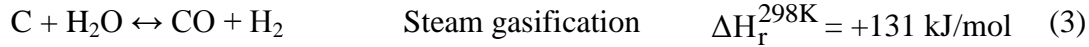
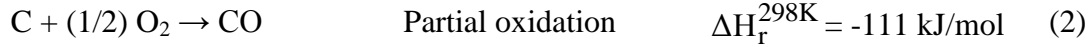
Each technology has a different net specific energy demand for drying [26]. Although steam drying offers the lowest demand, low temperature air drying is of particular interest in case of a biorefinery since it allows recovering low temperature excess heat for biomass drying. This low quality energy can originate either from the biorefinery itself or from a nearby industrial plant with an excess of heat, i.e. the oil refinery in this work. For these reasons, low temperature air drying is the only biomass drying technology included in this thesis.

2.2 Gasification

2.2.1 Principles

Gasification is the conversion of solid biomass into a gas with usable heating value and solid mass residues (ash and unconverted material, i.e. char) [27]. The gaseous phase mainly consists in CO, CO₂, H₂, CH₄ and steam originating from vaporization of the remaining biomass moisture content and potentially from unreacted steam injection. This gas will in the following be referred to as *syngas*.

Thermal gasification of biomass essentially takes place in three subsequent stages. In the first stage, remaining biomass moisture is evaporated. Biomass is then pyrolyzed to char and, simultaneously, condensable and permanent gases are produced. Condensable gases consist in water and TAR, i.e. heavy hydrocarbons. Above 800-850°C, the main chemical reactions occurring in gasification are as follow (adapted from [27]).



Additionally, pyrolysis reactions take place, essentially producing char and TAR.

2.2.2 Technical solutions

Several alternative technologies exist to perform biomass gasification. They have different feed quality requirements, operating and capacity ranges and, most importantly, produce syngas with different compositions. All of them are not adequate for continuous hydrogen supply in a refinery. The different gasifier types are depicted in Figure 4.

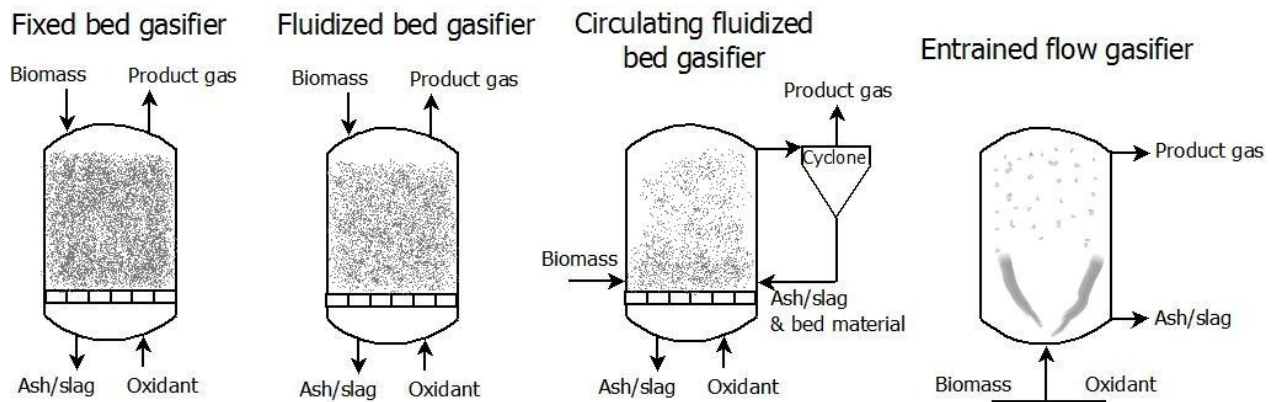


Figure 4: types of gasifier technologies

In a fixed bed gasifier, the oxidant is injected through a fixed bed of biomass where the gasifying reactions take place. In a fluidized bed gasifier, the velocity of the oxidant is increased until bubbles appear in the bed of biomass. Bubbles allow for a more uniform temperature in the bed. If the velocity of the oxidant is further increased, biomass particles are entrained with it. To stabilize temperature and carry heat in the process, bed material (e.g. sand) is added to the bed and a circulating fluidized bed gasifier is obtained. Bed material, ash and slag are separated from the product gas in a cyclone and returned to the gasifying section. Finally, increasing the velocity of the oxidant and the gasification temperature until over 1250°C allows operation in entrained flow mode, i.e. without bed material thanks to quick reaction times and easy fluidization. This is possible only with small size biomass particles.

Fixed bed gasifiers have a tendency to produce large amounts of TAR and/or char (unconverted biomass), have small capacities and are usually operated in batch modes. For these reasons they seem to be rather inadequate for H₂ supply in a refinery. Their main advantage is their ability to handle extremely inhomogeneous feedstock such as municipal solid waste, which makes them good candidates for small-scale waste-to-fuels or chemicals applications [25].

Bubbling fluidized beds are by far the technology the most widely demonstrated for biomass gasification, however not at high enough temperatures (1200-1300°C) to eliminate the need for downstream syngas upgrading. They are possibly the cheapest option among biomass gasification technologies thanks to their simple design, but have lower capacity and potentially less uniform temperature distribution than circulating fluidized beds.

Circulating fluidized beds (CFBs) use higher gas velocities and offer higher conversion rates, efficiencies and throughput. This technology involves direct heating, i.e. in situ combustion of part of the biomass feed to provide energy to the endothermic gasification reactions. If air is used as an oxidant, the syngas is diluted with inert nitrogen and a separation step must be added to the process. Alternatively, combustion can be carried out with pure O₂. Oxygen-fired CFBs are candidates for H₂ and/or liquid fuels production [17].

Indirectly heated gasifiers are inherently more complicated than directly-heated systems, but can produce syngas with a high heating value [25]. Combustion and gasification take place in two different vessels; heat is provided to the gasification reactions by bed material that circulates in loop between the two sections. Compared to directly heated gasifiers, their advantage is that pure O₂ is not required to produce nitrogen-free syngas. This reduces both investment and running costs since air separation units are no longer needed and the avoided dilution of the syngas allows smaller downstream equipment. TAR production remains an issue in indirectly heated gasifiers, although TAR content can be reduced by adding steam to the gasification section [28] [29].

Finally, *entrained-flow gasifiers* have even higher material throughput, thanks to high gas velocities which enable operation without bed material. This type of system is usually oxygen-blown and operates at high temperature (>1250°C). Consequently, little to no TAR or methane is formed. High gas velocities however mean short residence time for biomass particles, which therefore need to be very small. Pretreating and feeding biomass to entrained-flow gasifiers, especially for pressurized systems, remain thus an important issue to overcome for industrial-scale application. Entrained-flow gasifiers are used extensively in oil refining but only pilot plants are currently in operation with biomass feedstock (e.g. bioliq in Karlsruhe or the DBI pilot plant in the Netherlands). An industrial plant, using the Choren technology involving entrained-flow gasification, is currently in the engineering phase for construction in Finland (Ajos BtL project) [30].

2.3 Gas cleaning

2.3.1 Principles

In refineries, feedstock is treated upstream and syngas produced in the HPU is clean from particles or TAR. In the case of biomass gasification though, syngas is contaminated with:

- particles (char, dust, bed material entrained with the gas flow) ;
- heavy, condensable compounds (TAR);
- alkali, sulfur and halogen compounds [31].

All of these can block or deactivate catalysts via e.g. adsorption or chemical reactions and foul downstream equipment through e.g. condensing. Cleaning is thus required before further syngas processing in a biomass conversion system. Indicative maximum allowable impurities concentrations in syngas are given in Table 1.

Table 1: Maximum allowable concentration of impurities in syngas (adapted from [32])

Impurity	Specification
Sulfur compounds (H ₂ S, COS)	< 1 ppmv
Nitrogen compounds (NH ₃ , HCN)	< 1 ppmv
Halogens (HCl)	< 1 ppbv
Alkali metals (Na, K)	< 1 ppbv
Particles	“Almost completely removed”
TAR	Not condensing
Hetero-organic species (incl. S, N, O)	< 1 ppmv

The term “TAR” designates a number of heavy hydrocarbons produced during gasification of biomass. Although the accurate definition varies among scientific publications, TAR can be summarized as heavier hydrocarbons that can potentially condense in colder parts of the process, downstream the gasifier [24]. TAR yield decreases with increasing gasification temperatures, as heavier species are cracked into lighter products. A classification of TAR species according to the order of production through gas-phase thermal cracking is suggested by Milne et al. [33]:

- Primary products: cellulose-derived products such as hydroxyl-acetaldehyde and furfurals, hemicellulose-derived products, lignin-derived methoxyphenols;
- Secondary products: phenolics, olefins;
- Alkyl tertiary products: methyl derivatives of aromatics such as toluene, methyl acenaphthylene, methylnaphthalene, indene;
- Condensed tertiary products: naphthalene, acenaphthylene, anthracene/phenanthrene, pyrene.

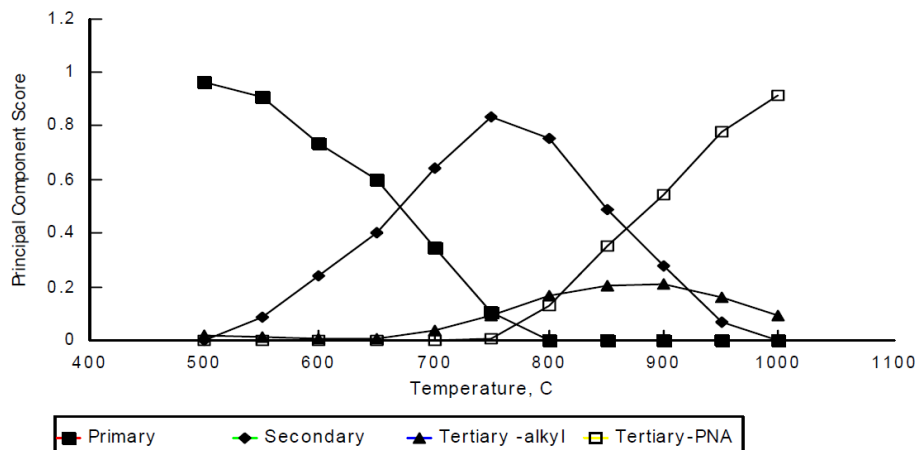


Figure 5: Distribution of the four TAR component classes vs. temperature (adapted from [33])

Figure 5 shows the distribution of these four “classes” vs. gasification temperature. Primary and tertiary products are essentially mutually exclusive, i.e. primary products are destroyed before tertiary products appear in significant amounts.

2.3.2 Technical solutions

Biomass syngas can be cleaned using available, conventional technologies: gas cooling, low temperature filtration (dust and particles removal) and water scrubbing at 150-200°C (TAR condensation and removal, removal of other contaminants) [18]. A cyclone for first solid separation and a ZnO guard bed to remove traces of sulfur contaminants before catalytic treatment might be added [32]. These technologies have been demonstrated and are used in coal gasification combined cycle and Fischer-Tropsch synthesis. This low temperature cleaning strategy will be further referred to as *wet gas cleaning*.

Wet gas cleaning is not always a penalty in terms of feedstock conversion, but in processes involving high temperature operations such as steam reforming, wet gas cleaning reduces the maximum energy efficiency that can be reached by the system. Hot gas cleaning strategies can therefore improve energy efficiency (i.e. the fraction of energy entering the system recovered in useful forms) and reduce equipment costs since cooling and reheating are avoided [34] [18]. This does not apply to atmospheric gasification, where syngas needs compressing, thus cooling, before upgrading. Hot gas cleaning is at research stage and further developments are needed for industrial application. Cleaning takes place between 500 and 1000°C, with 800°C being listed as preferred temperature for heat recovery. Several options are investigated for particles removal, see Table 2.

Table 2: options for particle removal at high temperature (adapted from [34])

Technology	Operating conditions	Advantages	Drawbacks
Cyclone	T up to 925°C P up to 1-2 MPa	Low investment and operating costs Continuous operation without particle accumulation	Inefficient for particles smaller than 5 µm
Candle filter	Up to 1000°C for metal filters, 400 to 700°C reported	Near 100% efficiency	Residual particle deposit, inconvenient cleaning methods Low reliability for ceramic filters
Granular bed filter	High T and P	99% for d>4 µm, 93% for smaller	Few data available
Electrostatic precipitator	Up to 1000°C P from 0,1 to 3,5 MPa	No pressure drop Observed efficiency between 95 and 100% for particle size between 0,01 – 100 µm	Few data in extreme T and P conditions

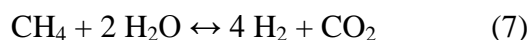
TAR cracking is preferred to scrubbing in hot gas cleaning configurations. In addition to high temperature operation, TAR cracking increases the H₂ and CO content of the syngas. NH₃ can be removed by base absorption or decomposition over Ni catalyst after H₂S removal, which can be performed through chemisorption or absorption [18]. Other contaminants (SO_x, NO_x, HCl, HCN, alkali) are removed by adsorption or absorption [35] [36].

2.4 Gas upgrading

In a biomass-to-hydrogen process, upgrading of the syngas is carried out in two steps: reforming and water-gas-shift.

2.4.1 Reforming

In the reforming step, light hydrocarbons in the syngas react with steam to produce hydrogen and carbon monoxide. With methane (CH₄) as an example, the global balance can be written as follows:



Natural gas is the main feedstock used for hydrogen production through steam reforming – this process is therefore commonly known as Steam-Methane Reforming (SMR). The reformer operates at elevated temperatures, usually around 850-900°C, and moderate pressure (15 to 30 bars). The steam to carbon ratio is typically between 2.5 and 5. Nickel catalysts are used. The syngas obtained has a higher H₂ and CO content than the incoming feed; CH₄ conversion is

around 90%. Reaction (7) is highly endothermic: the reforming reactor is a large high temperature heat sink and the reaction is usually carried out in a furnace where a tubular reactor is disposed.

Two concepts derive from SMR: partial oxidation and autothermal reforming (ATR). They are not as widespread as reforming for hydrogen production, but industrial application was demonstrated or industrial units exist.

Partial oxidation

Partial oxidation can be described as combustion of the feedstock below stoichiometric conditions (i.e. in lack of oxidizing agent). It takes place at high temperature and pressure: 1200 to 1500°C and 20 to 90 bars. The reaction is exothermic, conducted in presence of pure O₂ and a temperature moderator, i.e. steam. Catalysts can be used to lower the required reaction temperature to around 1000°C. The feedstock is first preheated to around 300°C and Reaction (8) (global reaction resulting from numerous chemical equilibria) brings the gaseous mixture to above 1000°C.



Partial oxidation is in fact a partial combustion of the feedstock, carried out in a deficit of O₂ compared to stoichiometric combustion proportions. It can be applied to heavier hydrocarbons compared to reforming (asphalts, petcoke) but also directly to coal and biomass.

Autothermal reforming

Autothermal reforming (ATR) is based on the combination, in a single vessel, of partial oxidation and steam reforming. The energy needed by endothermic reforming reactions is provided by the exothermic partial oxidation section. Heat flows are thus optimally integrated.

Partial oxidation takes place in a combustion zone at the beginning of the reactor. Hot gases are then led to a catalytic section for reforming. Ni-based catalyst is usually used and operating conditions are from 900 to 1100°C and between 20 and 60 bars [8].

ATR allows higher H₂ yields than partial oxidation for any type of feedstock. It is also less sensitive to coking than SMR. According to some sources, ATR could be the only technology able to handle the high CO and C+ content of biomass syngas without excessive coking [18]. Finally, ATR allows recovering the energy content of TAR through either partial oxidation for heat supply or cracking to increase H₂ yield, which eliminates the need for a separate TAR cleaning step.

2.4.2 Water-gas-shift

Following reforming, water-gas-shift (WGS) is applied (Reaction (4)). This enables a first purification of the syngas and an increase in H₂ yield through the conversion of carbon monoxide. This step generates around 15% of the total H₂ produced in a traditional SMR plant. The shift reaction is favored at low temperatures, in excess of steam and is usually operated in two steps. The first step, at high temperature (HTS), favors kinetics and the second, low temperature step (LTS) favors higher CO conversion. Usual characteristics of the two WGS steps are given in Table 3.

Table 3: characteristics of WGS steps [8]

	HTS	LTS
Catalyst type	Iron oxide	Copper oxide, zinc oxide, aluminum oxide
Inlet temperature (°C)	350	200-220
Temperature elevation (°C)	30 to 60	10 to 30

2.5 Hydrogen separation

2.5.1 Pressure-Swing Adsorption (PSA)

The PSA process is the most widespread H₂ purification process. Highly pure H₂ can be produced, at the same pressure level as the syngas feed but at near- or ambient temperature. H₂ recovery rates range from 75 to 95%, depending on purity specifications [37].

This process relies on the adsorption of gas phase molecules on a solid adsorbent. In the case of H₂ production, impurities are selectively retained by the adsorbent because of their greater affinities. A pure H₂ stream is produced at constant pressure level. After a while, the adsorbent bed is saturated with impurities and needs regeneration. This is usually done by lowering the pressure. A single PSA adsorber is thus operated in a cycle and several adsorbers are needed in parallel to obtain a continuous purification unit (typically 5 to 12). Several adsorbents are usually used as subsequent layers in an adsorber: silica gels, activated char and zeolites, with the latter two being the most widely employed.

2.5.2 Membrane separation

Another option for H₂ purification exists, namely inorganic membrane separation. A membrane is a physical barrier allowing selective transport of mass species. The driving force of the membrane separation process is often a pressure or concentration gradient across the membrane, see *Figure 6*. Selectivity and permeation rate (or permeance, i.e. the mass flux through the membrane) are the most basic properties of a membrane. The higher the selectivity, the more efficient the process and the lower the driving force required to achieve a given separation. The higher the permeation rate, the smaller the required membrane area.

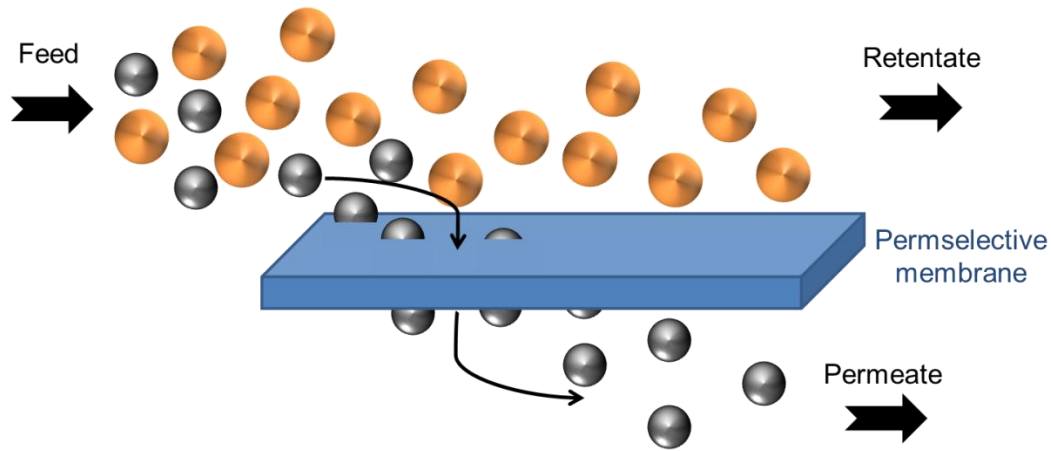


Figure 6: Simplified principle of membrane separation

In hydrogen production, dense phase metal and microporous ceramic membranes have the potential to replace not only PSA systems but also WGS reactors if installed in catalytic membrane reactors. These even have the potential to improve the equilibrium-limited WGS reaction by continually removing the product (H_2) while reactants are retained on the retentate side [38]. Among these types, Pd-based metal membranes and ceramic microporous membranes are showing great potential for the intended applications.

Additionally, these membranes are expected to perform better at high temperature, which would eliminate the need of gas cooling before purification. Costs for heat exchangers and drop in energy efficiency would thus be avoided [18]. Main advantages and current limitations of both Pd-based and microporous membranes are summarized in *Table 4*.

Table 4: advantages and limitations of Pd-based and microporous membranes [38]

Pd-based membranes	Microporous membranes
Advantages	
<ul style="list-style-type: none"> - Commercially available - Generally good mechanical stability - Very high selectivity for H_2 (practically in the order of 10^3) 	<ul style="list-style-type: none"> - Chemically and thermally stable - Higher flux than Pd-base membranes - Better performance than Pd-based membranes for WGS reaction
Current limitations	
<ul style="list-style-type: none"> - Limited life span (months) for best membranes because of cracking or pinhole formation - Pd alloys can undergo surface enrichment from minor metal atoms - Ultrathin, continuous Pd layers needed to maximize H_2 flux - Complex reactor design needed to maximize specific area - High and unpredictable Pd prices 	<ul style="list-style-type: none"> - Hydrothermal stability when applied in vapor-containing gas streams (exposure to humidity at $T > 400^\circ C$ causes rapid densification) - Selectivity generally lower than Pd-based membranes

These membranes offer advantages such as high flux and high operating temperatures and, in reactor applications, could lead to catalyst reductions, reduced equipment size, improved temperature and pressure conditions and ultimately lower costs. Both membrane types have thus great potential for H₂ production and purification but ceramic membranes, especially silica or silica functionalized, seem to take a lead on dense phase metal membranes thanks to their greater ability to improve WGS equilibrium. Developments in ceramic membranes are however more recent in comparison to dense phase metal.

When compared to PSA, ceramic membranes appear promising because cooling is not necessary (especially interesting in hot gas applications, e.g. H₂ production for refining purposes) and the technology is potentially simpler [17]. Both types have already been applied in membrane reactors showing promising results, but it must be stressed that despite the interesting results at laboratory scale-, no industrial application for large scale project was reported to date. Further work is necessary to improve the technology, especially concerning scale up (i.e. efficient, reliable manufacturing process) and stability of membranes.

3. Methodology

The first step of this work is to design and simulate the processes in order to obtain the necessary input to the second step, which consists in the application of process integration tools to identify integration opportunities and select relevant process configurations. Finally, evaluating and comparing these configurations requires choosing adequate indicators; these are presented in the final paragraph of this section.

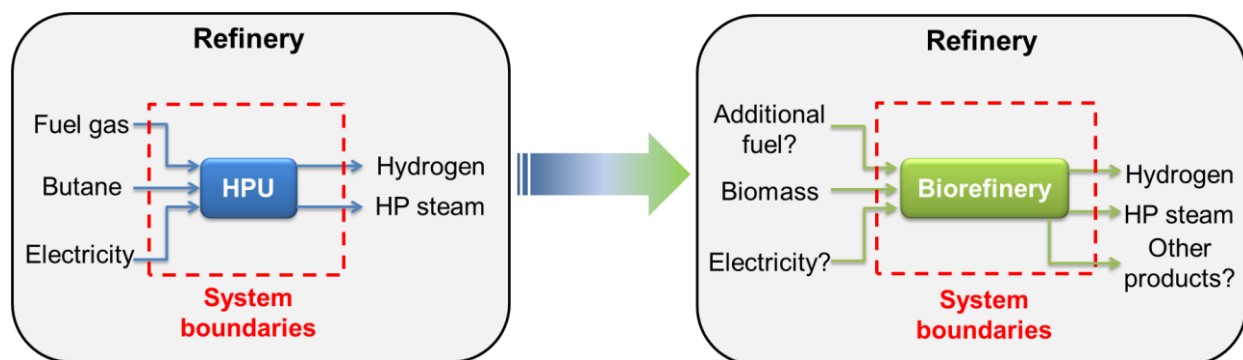


Figure 7: system boundaries for performance evaluation. Left: refinery with current HPU; Right: refinery with biomass-to-hydrogen concept

To match the production of the current HPU, two mandatory outputs are allocated to the biorefinery concepts: 291.5 MW of hydrogen and at least 15.9 MW of HP steam, see Figure 7. As explained in section 1.2, the focus is put on integration opportunities and options for electricity generation, which excludes modifications in the refinery hydrogen and steam networks. System boundaries for the evaluation of process performances are thus put around the hydrogen production process.

3.1 Process simulation

In order to obtain the necessary input to process integration tools, i.e. mass and energy balances, the investigated processes were simulated using ASPEN+. ASPEN+ is a comprehensive chemical process modeling system that provides extensive databases of physical properties to be used in

various equations of states, as well as a number of built-in models of unit operations (e.g. pump, distillation column, reactor) [39].

For gas-phase operations, the Peng-Robinson cubic equation of state with the Boston-Mathias alpha function extension was used. To obtain more accurate results in operations involving only water, steam data tables were used instead. When possible, models were validated against relevant, available literature data. While the model of the indirect gasifier was the result of internal work ([40], updated subsequently by S. Heyne and J.-F. Brau), the model of the direct gasifier was largely built according to Hannula and Kurkela [41]. Some particular species representing TAR in the simulation differ slightly between the two models. The impact on overall mass and energy balances is negligible and results from both models form a consistent basis for process comparison. The chemical species and their relative fractions chosen to represent TAR content in syngas produced through indirect gasification were chosen according to Figure 5.

The following chemical species were accounted for in the simulations:

- Main species: H_2 , CO , CO_2 , H_2O , CH_4
- TAR:
 - Indirect gasifier: toluene (C_7H_8), naphthalene ($C_{10}H_8$), phenol (C_6H_6O);
 - Direct gasifier: acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propane (C_3H_8), benzene (C_6H_6)
- Sulfur, nitrogen and chlorine compounds: H_2S , NH_3 and HCl

Char was modeled as pure solid carbon.

All main modeling assumptions and parameters, together with relevant references, can be found in Articles I and II. Pressure drops in all equipment were included in the simulations in order to determine electricity demands for compression. Apart from hot gas cleaning and the membrane reactor, for which no industrial scale numbers were found, unit operations were modeled based on literature data and experimental or industrial values. When oxygen is needed in the biomass-to-hydrogen concept, production in a cryogenic Air Separation Unit (ASU) is assumed. The ASU was not modeled but an overall power demand for oxygen production was used to determine consistent energy balances. It is assumed that 200 kWh of electricity are required for each ton of pure oxygen produced at 25°C and atmospheric pressure [42]. Oxygen compression up to operating pressures was then included in the model.

Hot gas cleaning essentially consists in chemical and physical adsorption of pollutants present in the raw gas and was simulated as a black box since no heat demand or excess is expected to occur in this section of the process. The adsorbent beds need regeneration and thus, the installation of 2-3 adsorption trains might be necessary to ensure continuous availability. This is important when it comes to cost evaluation but is beyond the scope of the present study. More details on hot gas cleaning strategies can be found in [36]. The membrane reactor was simulated by means of two separate unit models available in ASPEN+. The WGS reaction was simulated via a stoichiometric reactor and hydrogen separation was modelled as a separator block.

3.2 Process integration

Process integration was defined at an IEA expert meeting in 1993 as *systematic and general methods for designing integrated production systems, ranging from individual processes to total sites, with special emphasis on the efficient use of energy and reducing environmental effects* [43]. In its broader sense, process integration covers material as well as thermal integration. Material integration can be performed to e.g. minimize raw material consumption while thermal integration focuses on energy usage and the minimization of external energy or fuel supply to the process. The focus of this study is on thermal integration between hot and cold streams within the biorefinery and between the biorefinery and the existing oil refinery.

Thermal integration is performed in this study by means of Pinch Analysis. This method was first developed by Linnhoff et al. [44] and Umeda et al. [45]; several updated versions of the Linnhoff's user guide on process integration are available, the latest being Ref. [46]. Pinch Analysis was first developed in order to design new, or improve existing heat exchanger networks but was subsequently applied to a number of other problems such as the integration of new process units in existing plants or optimization studies [47]. Other examples where Pinch Analysis has been used include the analyses of hydrogen and freshwater networks [48, 49].

According to Pinch Analysis, the minimum heating and cooling demands of a process can be found by analyzing thermal streams in the process, i.e. streams that require heating (cold streams) or cooling (hot streams). Pinch Analysis is therefore widely applied on industrial processes as a targeting methodology. A common graphical representation of the thermal profile of a process is the Grand Composite Curve (GCC) [50], see Figure 8.

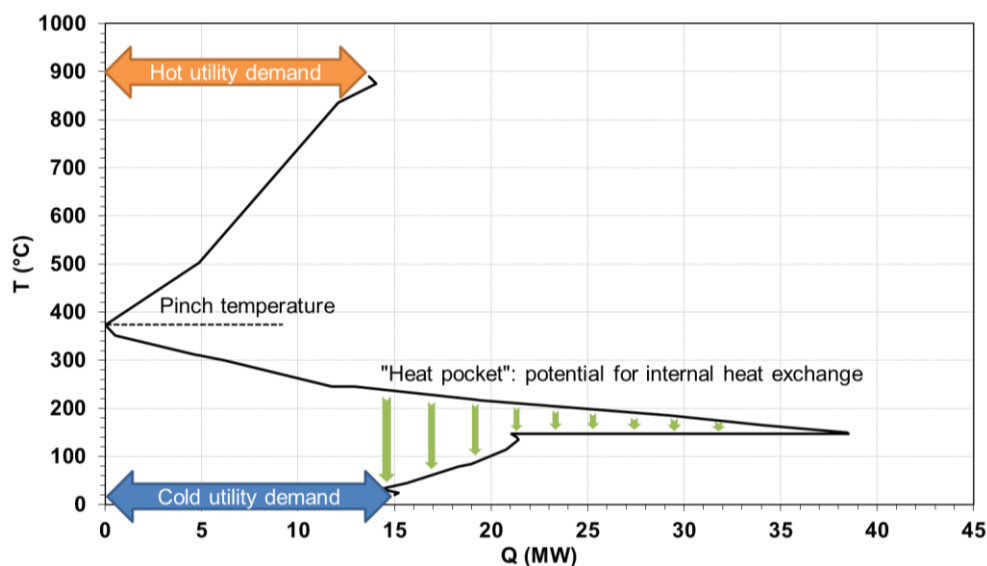


Figure 8: Grand Composite Curve (GCC)

On a GCC, the process heat demand and availability versus the temperature level in the process is represented. The minimum heating and cooling demands of the process can be read on the GCC, as well as the potential for internal heat exchange in so-called “heat pockets”, i.e. parts of the curve where a heat excess is located above a heat deficit. This means that heat available at a given temperature level can be transferred to a lower temperature level, where a net deficit of heat is located. To account for thermodynamic limitations in heat exchange (a temperature difference is needed for heat to flow from a source to a sink) and different stream characteristics (e.g. phase, phase change, composition), individual stream contributions to minimal temperature differences are implemented in this work. The values used in this work are given in Table 5.

Table 5: individual contributions to minimal temperature differences used for Pinch Analysis in this work

Type of stream	$\Delta T_{\min}/2$ (°C)
Gaseous process stream	15
Air	10
Water	5
Steam	2.5

More advanced integration opportunities can also be deduced from the GCC, such as the integration of another process with the plant represented in the GCC. Such opportunities can be quantified by means of a graphical approach, using the so-called *split GCC*.

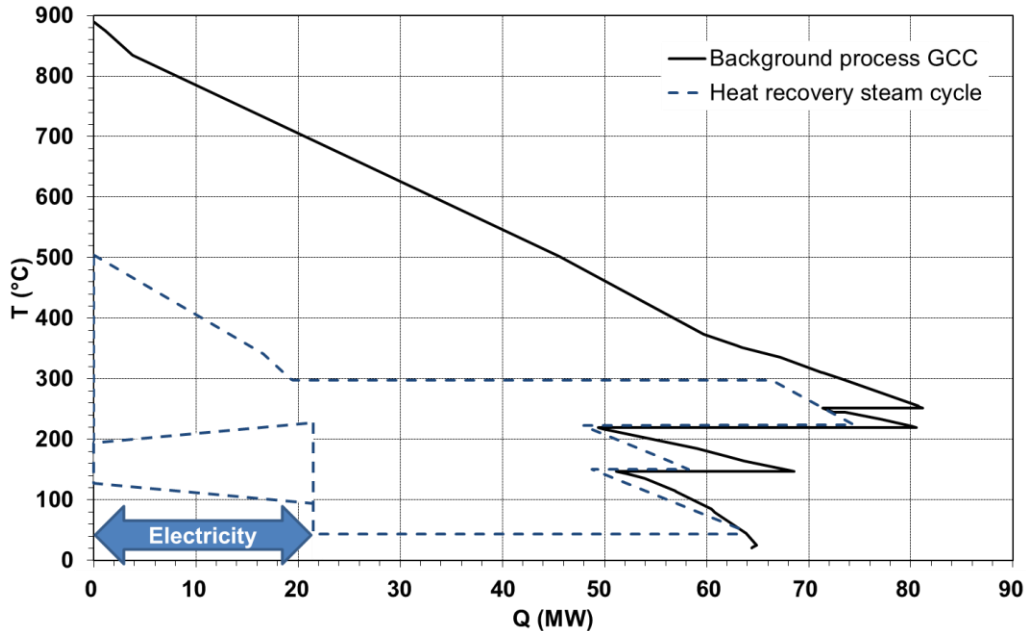


Figure 9: split GCC representation. Black line: GCC of the background process; Blue dotted line: heat recovery steam cycle

Figure 9 represents the split GCC of a fictitious process with an integrated heat recovery steam cycle: the GCC of the heat recovery steam cycle is plotted against that of the process streams.

Accordingly, the maximum steam cycle net power generation is found when at least one pinch point is activated between the steam cycle and the process. Similarly with any new system to be integrated with the background process, the activation of these *utility pinch point(s)* allows exploiting the maximum heat integration potential [51].

3.3 Process evaluation

In order to compare several processes, adequate criteria have to be chosen and clearly defined. The most promising configurations are identified in this study by means of thermodynamic criteria (energy and exergy efficiencies) as well as with an environmental criterion (fossil CO₂ balance).

3.3.1 Performance indicators

The performances of the processes investigated in this study are quantified by means of two thermodynamic performance indicators. The first indicator, energy efficiency η_{tot} , is a measure of the overall performance of the process according to the first law of thermodynamics. Energy efficiency is the ratio between the energy contained in all useful outputs and the energy content of all inputs. Energy efficiency is calculated according to Equation 9:

$$\eta_{tot} = \frac{\sum_o (\dot{m}_o \cdot HHV_o + \dot{Q}_o + P_o)}{\sum_i (\dot{m}_i \cdot HHV_i + \dot{Q}_i + P_i)} \quad (9)$$

where process outputs and inputs are denoted by the subscripts o and i , respectively, \dot{m} represent mass flows, HHV higher heating values¹, \dot{Q} thermal energy flows and P electrical power.

Energy efficiency can be misleading for systems involving inputs and/or outputs of different nature, such as steam, fuels and electricity. According to the second law of thermodynamics, these indeed differ in energy quality, a feature that is not taken into account in energy efficiency calculations where energy contained in steam is equivalent to energy contained in electricity. To include differences in energy quality in efficiency calculations, exergy must be used instead of energy. Exergy is defined as the potential for work generation of an energy commodity, i.e. steam has much lower exergy content than electricity [52]. The exergy content of a stream is always related to a reference state (also called dead state), that is the ambient conditions. The second performance indicator used in this study is the exergy efficiency η_{ex} :

$$\eta_{ex} = \frac{\sum_o \dot{m}_o \cdot (e_o^{PH} + e_o^{CH}) + P_{net}}{\sum_i \dot{m}_i \cdot (e_i^{PH} + e_i^{CH})} \quad (10)$$

¹ To facilitate comparison with other studies, energy efficiency is also calculated on a LHV basis; HHV values for biomass and hydrogen are then replaced by LHV values in Equation 9.

where e^{PH} and e^{CH} represent the physical and chemical exergy. P_{net} represents the exergy content in the net electrical power balance of the process, which has the same value as its energy content.

Although energy efficiency gives an easily understandable picture of a process, exergy efficiency seems more relevant when dealing with multiple energy commodities of various energy quality, as is the case in this study. Furthermore, exergy efficiency might also give a better idea of the economic performance of the process than energy efficiency since energy commodities of high exergy content often are more valuable than those with lower exergy content (e.g. electricity).

3.3.2 Fossil CO₂ balance

In relation to the challenge of GHG emission mitigation, an environmental indicator is also included in this study: the fossil CO₂ balance ΔCO_2 . With this indicator, the difference in fossil CO₂ emissions from the refinery following the implementation of the biomass-based process is evaluated. Biomass is considered to be 100% CO₂-neutral and the current refinery operating the fossil-based HPU is chosen to set the reference for CO₂ emissions. Therefore, any negative value for ΔCO_2 means that the studied configuration has the potential to reduce fossil CO₂ emissions. ΔCO_2 is calculated according to Equation 11.

$$\Delta\text{CO}_2 = e_{el} \cdot \frac{P_{net}}{\eta_{el}} - e_{C4} \cdot \dot{m}_{C4} - e_{fg} \cdot \dot{m}_{fg} \quad (11)$$

where e represents specific CO₂ emissions associated with natural gas consumption for electricity production (subscript el), butane and fuel gas consumption (subscripts $C4$ and fg , respectively); P_{net} is the net electricity balance of the biomass-to-hydrogen process; η_{el} is the efficiency of the marginal electricity producer; \dot{m} represents the avoided mass flows of butane and fuel gas.

When calculating the fossil CO₂ balance, systems where inputs and/or outputs are impacted by the implementation of the biorefinery are taken into account. More specifically, it is assumed that if HP steam is exported from the biomass-to-hydrogen process, the use of refinery fuel gas-fired boilers is decreased by the corresponding load. Also, the impact of the electricity balance of the biomass-to-hydrogen process is included by calculating a change in CO₂ emissions at the marginal electricity producer. In such calculations, the choice of marginal electricity producer is therefore of great importance since different electricity production technologies have different specific CO₂ emissions associated with power production. In this study, two marginal electricity producers are considered: natural gas combined cycle (NGCC) and coal power plant. These were chosen to represent two widespread electricity generation alternatives in Europe [53]. Consequences of future technology changes in marginal power production, e.g. deployment of Carbon Capture and Storage (CCS), are discussed further in this thesis. The parameters used to calculate ΔCO_2 are listed in Table 6 [54].

Table 6: parameters used in calculations of fossil CO₂ balances [54]

Marginal electricity producer		
	Efficiency η_{el}	Specific emissions e_{el} (kg CO ₂ /GJ _{fuel})
NGCC	0.6	57
Coal power plant	0.45	92
Fuel specific CO₂ emissions e (kg CO₂/ kg_{fuel})		
Fuel gas e_{fg}	1.99	
Butane e_{C4}	3.03	

In the configuration where excess fuel gas from the refinery is used for power generation in a gas turbine, the efficiency of the combined cycle is set to 55%. In that case the system boundaries are extended to include this gas turbine, with fuel gas as an input and electricity as an output.

It should be noted that, as opposed to cases where all or part of the automotive fuels produced in the refinery are replaced by biofuels (e.g. Fischer-Tropsch diesel or DME), only hydrogen atoms are ultimately replaced in this work. Combustion emissions of fossil CO₂ from these fuels thus remain unchanged and are not included in the calculation of ΔCO_2 . This is further discussed in section 4.5.

4. Results

Results obtained in the project are summarized in this section. The designs of two biomass-to-hydrogen process concepts are presented first. These serve as a base for the whole study. The configurations selected for detailed investigation and the way these were designed, especially using process integration approaches, are presented afterwards. Values of the performance indicators introduced in Section 3.3 are finally discussed and solutions compared.

4.1 Process design

To achieve the conversion of biomass into hydrogen, building blocks presented in Section 2 were combined according to two different design approaches: one based on indirect heat transfer between a combustion zone and a gasifier zone and well-known technologies, the second involving direct heating via combustion in oxygen and emerging technologies. Both designs are scaled to replace the current refinery HPU, i.e. for a hydrogen production of 7.4 t/h. As mentioned in section 2.1, air drying is used in both concepts. Final hydrogen compression to 27 bars is also common to both concepts for injection in the refinery hydrogen distribution network.

4.1.1 Indirect Gasification concept

The first process concept, based on atmospheric, indirect steam-blown gasification and here referred to as the *IG concept*, is presented in Figure 10. For the upgrading and separation sections, this process relies on technologies that are proven industrially with syngas produced from fossil fuels.

The dried biomass is gasified in an atmospheric, indirect steam-blown gasifier at 850°C. Since compression is needed prior to downstream syngas upgrading, wet gas cleaning is chosen in this concept. The syngas leaving the gasifier is cooled, passed through a filter for particle removal and scrubbed with water to remove TAR and sulfur compounds. The cleaned syngas is then compressed to 15 bars prior to the SMR reactor which is followed by dual CO-shift at 22 bars. Hydrogen is finally separated from the remaining gases via PSA, where it is produced at a pressure of 21 bars.

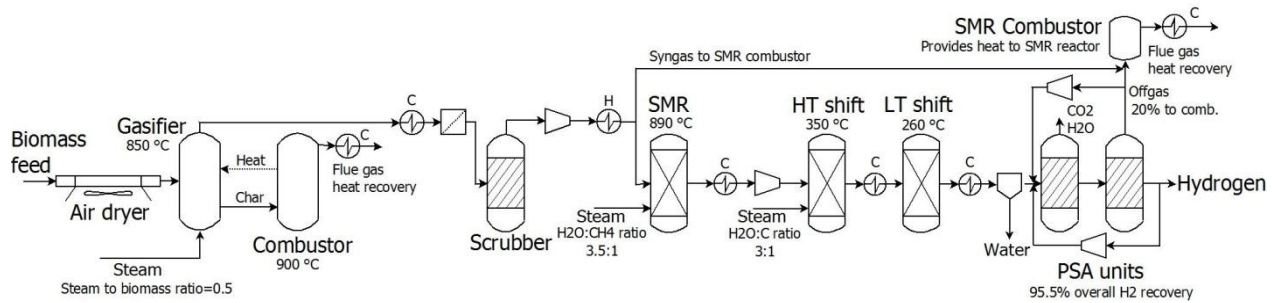


Figure 10: flowsheet of the IG concept

As a result of process simulation, a hydrogen yield of 0.1 ton of H_2 per ton of dry biomass was obtained for the IG concept. This corresponds to a conversion efficiency of biomass to hydrogen of 67% on HHV basis (64% on LHV basis)². The total process steam demand amounts to 11.6 ton of steam per ton of H_2 and the power requirement is 22 MW_{el} .

4.1.2 Direct Gasification concept

As shown in Figure 10, the IG concept consists of several conversion steps which not only implies a rather large number of units, but also that a large amount of heat shall be transferred between thermal streams. Indirect gasification and SMR also imply indirect heat transfer and therefore, technical complexity and possible thermal losses. Finally, wet gas cooling means that if heat is not recovered in appropriate ways, all sensible high temperature heat in the syngas is lost.

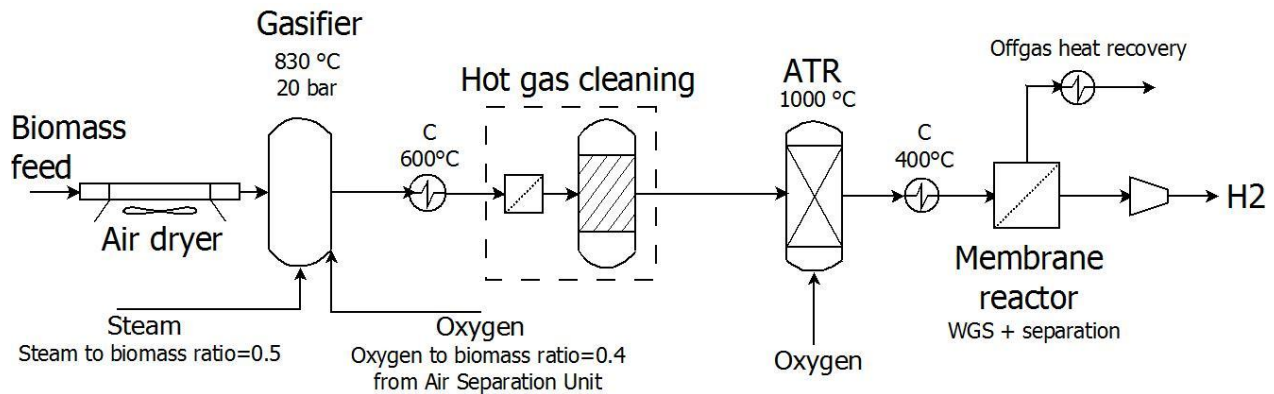


Figure 11: flowsheet of the DG concept

Following a different approach, a second biomass-to-hydrogen concept was designed as shown in Figure 11. This process - further on referred to as the *DG concept* - is based on direct, pressurized oxygen/steam-blown biomass gasification. Pressurized gasification eliminates the need of downstream syngas compression and therefore cooling can be avoided. To avoid loss of high temperature sensible heat, hot gas cleaning is implemented in this concept. SMR is replaced by

² $HHV_{H_2} = 141.8 \text{ MJ/kg}$; $LHV_{H_2} = 120 \text{ MJ/kg}$.

$HHV_{\text{biomass}} = 20.96 \text{ MJ/kg}$ (dry basis); $LHV_{\text{biomass},50\% \text{ moisture}} = 9.26 \text{ MJ/kg}$; $LHV_{\text{biomass},10\% \text{ moisture}} = 18.6 \text{ MJ/kg}$.

ATR, operated at 1000°C with pure oxygen injection. The final step of the DG concept is a membrane reactor where the remaining WGS reaction takes place on the catalyst surface and hydrogen is separated from the offgas. The DG and IG concepts are thus based on very different technologies.

As a result of process simulation, a hydrogen yield of 0.087 ton of H₂ per ton of dry biomass was obtained for the DG concept. This is lower than the yield in the IG concept and corresponds to a biomass to hydrogen conversion efficiency of 65% on HHV basis (63% on LHV basis). The total process steam demand amounts to 5.4 ton of steam per ton of H₂, which is less than half the demand in the IG concept. The total oxygen demand (to gasification and ATR) is 6.7 ton per ton of H₂ while the electricity consumption for the entire concept is 35.1 MW_{el}, including power demand for the ASU.

Compared to the IG concept, the DG concept eliminates the need for indirect heat transfer in the gasifier and the reforming step thanks to in-situ combustion of part of the biomass and the syngas, respectively. This represents potential efficiency increases from reduced heat losses. Furthermore, the implementation of the membrane reactor is a step forward in terms of process intensification since two unit operations are performed in a single vessel. The drawback of these apparent advances is the need for pure oxygen injection into the gasifier and the ATR. This means that an oxygen production plant is required in the concept, which leads to an increase in electricity demand.

4.2 Process integration

As mentioned earlier in this thesis, the focus of this study is put on opportunities for energy integration. Material integration aspects are here essentially limited to the substitution of hydrogen supply, from a fossil fuel-based route to a biomass-based process. Heat integration opportunities, both within the biorefinery concepts and with the oil refinery, were studied by means of pinch analysis graphical tools such as GCCs and Split GCCs.

Integration opportunities are presented in the following section. Once options for heat integration are identified, several relevant system configurations can be determined which are discussed in more detail in section 4.2.2. The main differences between these configurations are the nature and potential amount of additional products such as electricity and steam.

4.2.1 Integration opportunities

As a result of the simulations, data on temperatures and heat loads of the various heating and cooling processes of the biomass conversion plants were obtained and were used to study theoretical heat recovery opportunities with the help of Pinch Analysis. To match the current production in the refinery HPU and to meet steam requirements in the refinery, additional thermal streams representing the production of 15.9 MW of HP steam were added to those of the bioH₂

plant. The details about all thermal streams are summarized in Article II along with the composition of key process streams.

The GCCs obtained for the two biorefinery concepts are represented in the same diagram in Figure 12. It can be seen that both concepts are unpinched and do not present any hot utility demand. The biorefinery concepts are thermally self-sufficient: the biomass feed is used both as feedstock for hydrogen production and as fuel for supply of heat and steam.

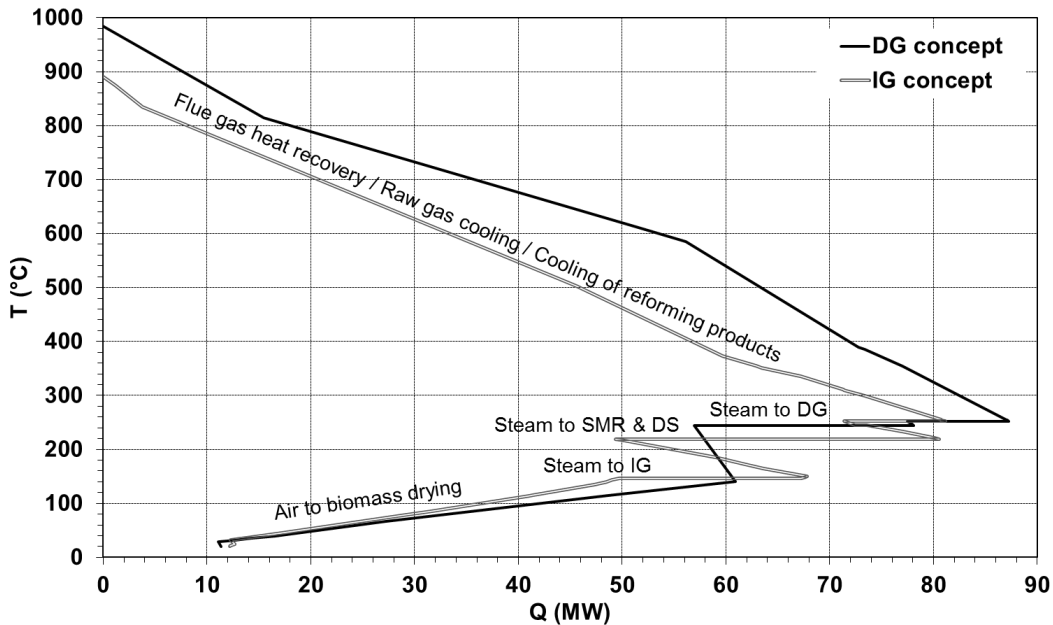


Figure 12: GCCs of both biorefinery concepts. Single black line: DG concept; Double grey line: IG concept

The GCCs of both concepts are rather similar. Heat is available at high temperature levels from syngas cooling while heat demand takes place around 250°C (steam production) and below (air heating for biomass drying). As represented, i.e. including energy demand for biomass drying, there is a net excess of heat in both concepts: 12.2 MW in the IG concept and 11.4 in the DG. This energy is potentially available at high temperature levels if maximum heat recovery is achieved.

It is worth noting that while the IG concept requires steam injection at several pressure levels (injection into gasifier, SMR and dual shift), there is only one steam injection point in the DG concept. Although steam can be throttled to lower pressure levels if needed, having a single-level steam network in the biorefinery lowers the complexity of the plant.

The GCCs also allows pointing out that large temperature differences appear between the heat sources and sinks. This leads to large exergy losses in both biorefinery concepts. In addition to these losses, the GCCs show that heat recovery within the biorefinery concepts would not be constrained by the activation of pinch point(s) with high temperature syngas but strongly limited

by the low temperature energy demand for biomass drying. It would therefore be greatly beneficial to eliminate this energy demand in order to release more high temperature heat from the biorefinery concepts, which could be used for steam export or electricity production. The resulting GCCs of both concepts are shown in Figure 13.

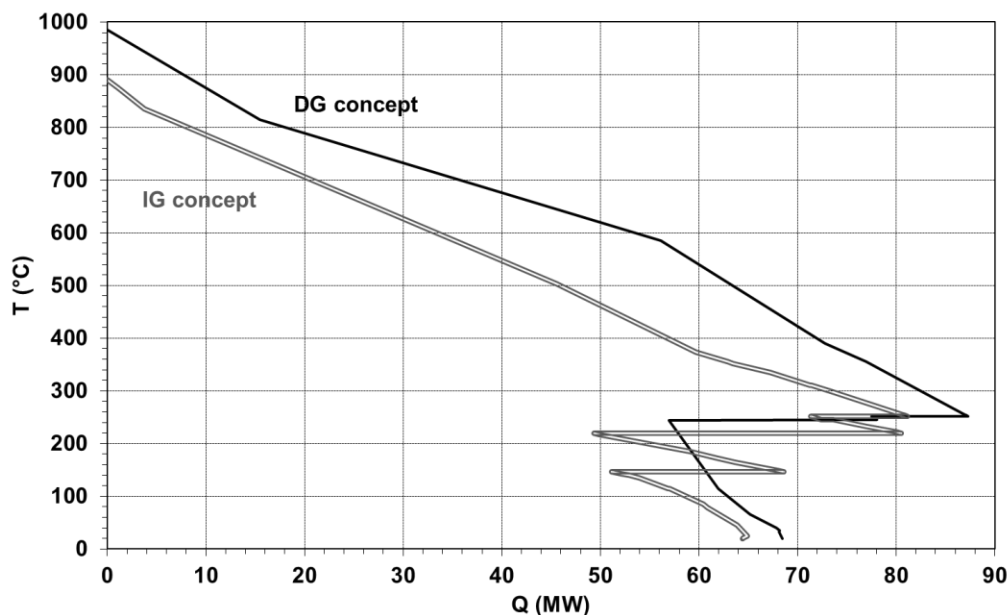


Figure 13: GCCs of the biorefinery concepts without biomass drying; Single black line: DG concept; Double grey line: IG concept

Figure 13 was obtained by removing the stream corresponding to the energy demand for biomass drying from the data set used to build the GCCs. More high temperature heat is now available from the biorefinery concepts since the constraint of low temperature energy demand was removed. The DG concept appears to have an advantage compared to the IG concept in terms of potential for heat recovery since the absence of energy demand for steam production at 150°C and 210°C seems to allow recovering more heat from the biorefinery process for useful applications.

Two alternative ways of taking advantage of the high temperature heat available in the biorefinery process are considered in this work: export of HP steam to the refinery and electricity generation by means of a heat recovery steam cycle. Steam demand in the refinery is partly satisfied through heat recovery steam generation in various units, but the operation of fuel gas-fired boilers is required to satisfy the HP steam demand. Producing HP steam in the biomass-to-hydrogen concepts would allow a net export to the refinery and thus, offloading these furnaces. Ultimately, this would result in fuel gas savings and a reduction of fossil CO₂ emissions.

On the other hand, the implementation of a heat recovery steam cycle allows generating electricity, which has a higher energy quality than HP steam. This electricity can be consumed on-site in the biomass-to-hydrogen process or in the refinery, or can be sent to the grid if a net

excess is created. Thanks to the release of high temperature heat, the export of HP steam and/or electricity is enabled in the biomass-to-hydrogen concepts. This in turn translates into increased overall efficiencies as a greater part of the energy fed to the system is converted in useful products.

Although eliminating the energy demand for biomass drying from the biorefinery concepts is appealing, the need for drying remains. This energy demand is thus shifted from within the biorefinery process to outside the system. Beyond the creation of a more sustainable hydrogen supply, the major advantages of heat integrating the biorefinery concepts with the refinery appear in this context, as shown below.

Results of a complete pinch analysis of the refinery [55] allowed plotting a temperature profile of excess heat available at the refinery, see Figure 14. This excess heat originates from refinery hot streams that are currently not recovered but cooled by means of water or air. It is thus, literally, waste heat. Excess heat is available at temperatures up to 475°C, but as much as 91% of the total amount is available below 150°C.

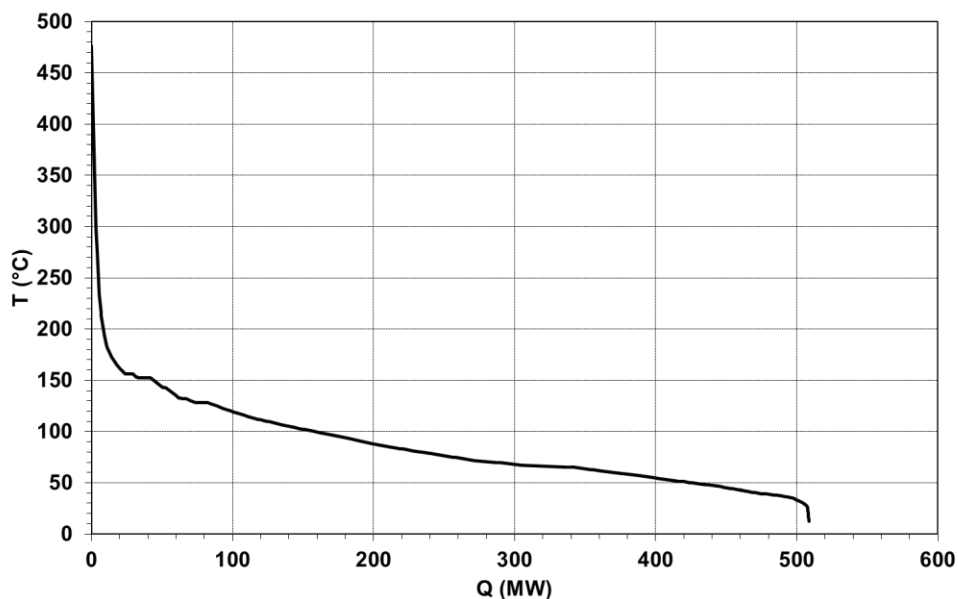


Figure 14: available refinery excess heat

Although emerging applications such as low temperature electricity generation through Organic Rankine Cycles (ORC) can be envisioned below 150°C [56], this low temperature level limits the options for relevant utilization of this excess heat in relation to the biorefinery concepts. Low-temperature air drying of biomass was already identified as a promising option for the use of low temperature industrial waste heat [26].

This latter alternative was confirmed as an option of high interest in this project since it allows releasing high temperature energy within the biomass-to-hydrogen process. Regarding the

specific biorefinery concepts and refinery included in this study, the temperature level and the amount of available refinery excess heat make it possible to cover the entire energy demand for drying in both biomass-to-hydrogen concepts.

4.2.2 Selected configurations

For each concept four system configurations were investigated in this work, corresponding to a frozen setup of the biomass to hydrogen concepts but different integration options with the refinery, as shown in Table 7.

Table 7: description of selected configurations: W – wet biomass input, D – dry input, HP - HP steam production, E - electricity production, FG - use of refinery fuel gas excess.

Configuration	Biomass feed	Products	Use of fuel gas excess
W	Wet (50% moisture)	H ₂ , HP steam	No
DHP	Dry (10% moisture)	H ₂ , HP steam	
DE		H ₂ , electricity	
DFG		H ₂ , HP steam	Yes

In Configuration W, wet biomass is fed to the process; therefore air drying is included and performed with excess heat from the biomass-to-hydrogen concept. In all other configurations, dry biomass is fed to the process. This allows investigating the impact of moisture content in the feed on system performances and, since biomass drying can be performed with refinery excess heat, highlighting the potential interest of locating the biomass-to-hydrogen concept within the oil refinery. Excess heat from the biomass-to-hydrogen concepts is recovered to produce either HP steam in configurations W, DHP and DFG or electricity through a steam cycle in configuration DE.

When HP steam is exported from the biorefinery to the refinery, the boilers are offloaded and thus, an excess of refinery fuel gas is created [57]. However, this fuel gas supply originates from crude oil refining operations and cannot be discontinued. A fourth configuration was therefore included in this work, where the excess of refinery fuel gas is used in a combined cycle to generate electricity (configuration DFG).

4.3 Process performances

Energy balances were determined for each configuration and are presented in Table 8. In all configurations, the hydrogen production amounts to 291.5 MW (HHV basis). The biomass input to the IG concept is 433 MW (HHV basis). Due to the lower hydrogen yield, the biomass feed to the DG concept is 442 MW (HHV basis). In all configurations, 15.9 MW of HP steam are also produced to match the production of the current HPU. The HP steam production listed in Table 8 corresponds to additional steam export from heat recovery.

Table 8: energy balances for the selected configurations

Configuration	HP steam (MW) (+ 15.9 MW in all cases)		Electricity balance (MW) (production – demand = net)	
	IG concept	DG concept	IG concept	DG concept
W	12.2	11.3	0-22 = -22	0-35.1 = -35.1
DHP	49.4	62.5	0-22 = -22	0-35.1 = -35.1
DE	0	0	21.8-22 = -0.2	24.8-35.1 = -10.4
DFG	49.4	62.5	51.1-22 = 29.1	51.1-35.1 = 16

If wet biomass is fed to the systems (Configuration W), a small amount of excess heat is available from the biorefinery; 12.2 and 11.3 MW of HP steam can be exported to the refinery from the IG and the DG concept, respectively. Both concepts are in deficit of electricity but oxygen production in the cryogenic ASU leads to a high power demand in the DG concept: 35.1 MW against 22 MW for the IG concept, i.e. 60 % higher consumption.

The interest of allowing heat integration between the biorefinery and the refinery is visible when comparing Configuration W to all other configurations, where biomass is dried with refinery excess heat. The released high temperature excess heat from the biorefinery allows exporting 49.4 MW and 62.5 MW of HP steam in the IG and DG concept, respectively (config. DHP).

Alternatively, this excess heat can be recovered through an integrated steam cycle (config. DE). This allows generating 21.8 MW and 24.8 MW of electricity in the IG and DG concept, respectively. The IG concept is then energy self-sufficient without supplementary fuel requirement. A power deficit of 10.4 MW remains in the DG concept.

In Configuration DFG, the excess of refinery fuel gas created by the export of HP steam from the biorefinery is used to generate electricity in a gas turbine combined cycle. Other potential utilizations of the fuel gas are discussed in section 7.2. The amount of excess fuel gas being the same regardless of which concept is implemented, 51.1 MW of electricity can be produced in the two cases. This allows both concepts to become net electricity producers, with a net electricity surplus of 29.1 MW in the IG concept and 16 MW in the DG concept. These numbers amount to 65% and 36% of the refinery's total electricity import, respectively. This configuration thus appears very interesting since it would allow an important reduction of power purchase from the grid.

Table 8 shows that heat integration between the biorefinery and the refinery enables the production of HP steam and/or electricity in addition to hydrogen from the same amount of biomass. It also shows that for the same hydrogen output, the DG concept can produce more HP steam or electricity than the IG concept. These results are however not sufficient to evaluate the processes since the DG concept has both higher biomass and electricity demands. Here,

performance indicators such as energy and exergy efficiencies can be advantageously used in order to compare the configurations on a consistent basis.

Energy and exergy efficiencies were calculated for each configuration and are presented in Table 9. Energy efficiency is presented and discussed on HHV basis; results on LHV basis are shown in Table 11 in the Appendix. In the following, results from the two indicators are first commented separately. A discussion and comparison including both indicators is presented.

Table 9: performance indicators results

Configuration	Energy efficiency (%)		Exergy efficiency (%)	
	IG concept	DG concept	IG concept	DG concept
W	70	67	57	51
DHP	78	78	61	57
DE	72	70	66	56
DFG	75	74	53	51

Looking at the configurations from W to DFG, energy efficiency results follow the same trend for both concepts, see Figure 15. Grey bars represent results for the IG concept while black bars those for the DG concept. Feeding wet biomass to the process and using biorefinery excess heat for drying (config. W) yields the lowest efficiencies in both concepts.

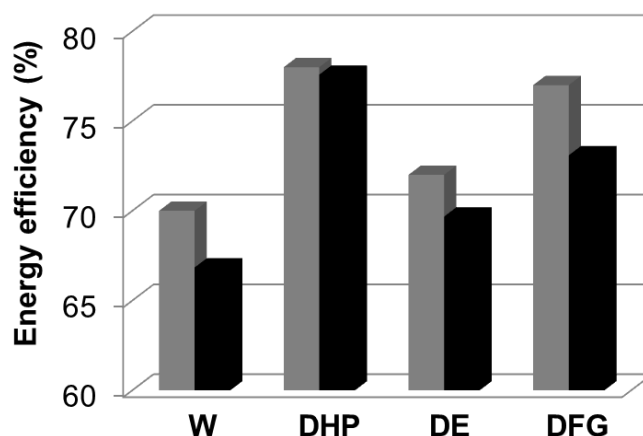


Figure 15: energy efficiency plot for both concepts. Grey bars: IG concept; Black bars: DG concept

Drying biomass with refinery excess heat and exporting HP steam with high temperature biorefinery excess heat yields an increase of 8 and 11 percentage points in energy efficiency for the IG and DG concept, respectively. The higher potential for HP steam export observed in Table 8 for the DG concept allows this greater efficiency improvement; the amount of exported HP steam is sufficient to offset the higher electricity deficit and the same efficiency as the IG concept

is obtained. HP steam export (config. DHP) appears as the most efficient configuration, with an energy efficiency of 78% for the two concepts.

Alternatively, recovering this excess heat by means of a steam cycle for electricity production (config. DE) yields energy efficiencies of 72% and 70% for the IG and DG concept respectively. Since energy efficiency puts the same value on 1 MW of HP steam and 1 MW of electricity, HP steam export appears more efficient than electricity generation because of the higher amount of energy that can be recovered. Therefore, although the IG concept becomes energy self-sufficient with the integration of a heat recovery steam cycle, the energy efficiency remains lower than the value obtained in Configuration DHP.

Finally, the use of excess refinery fuel gas for electricity production (config. DFG) yields energy efficiencies of 75% and 74% for the IG and DG concept, respectively. This configuration appears thus interesting since it makes efficient use of all available resources: the energy efficiencies obtained are the second best of all configurations.

According to exergy efficiency, the selected configurations are ranked differently, see Figure 16. The performances of Configuration W appear rather low, with 57% exergy efficiency for the IG concept and 51% for the DG concept. The higher electricity deficit of the DG concept puts a greater penalty on its performances with exergy efficiency as an indicator because of the high exergy content of electricity.

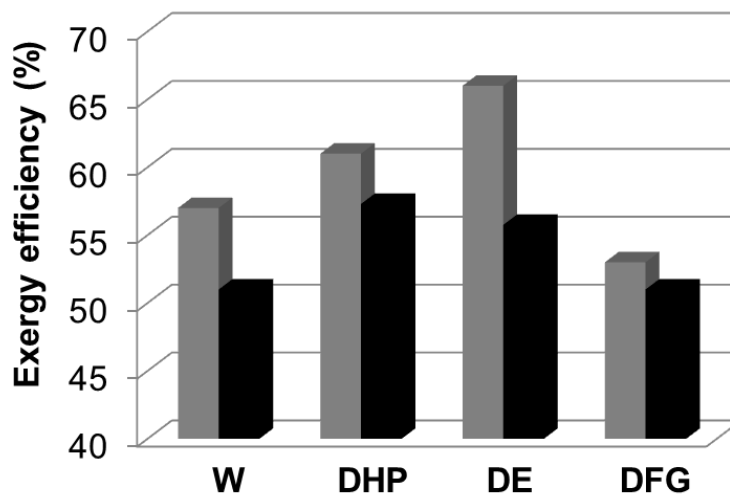


Figure 16: exergy efficiency plot for both concepts. Grey bars: IG concept; Black bars: DG concept

The heat integration opportunities identified in section 4.2.1 also yield efficiency improvements from Configuration W to DHP and DE. The methodology used thus seems relevant to identify and reduce exergy losses in the biorefinery concepts. The highest efficiencies now appear when electricity is produced through the heat recovery steam cycle (config. DE). This is clear with the IG concept, which has an exergy efficiency of 61% with HP steam export (config. DHP) and

66% with electricity production (config. DE). In the case of the DG concept, the higher potential for HP steam export is sufficient to offset the lower exergy content of steam and both configurations yield close exergy efficiencies: 57% with HP steam export and 56% with power generation.

The two performance indicators used in this work give different pictures of the system configurations. According to energy efficiency, export of HP steam to the refinery is the most efficient way to recover high temperature excess heat from the biorefinery concept (config. DHP). On the other hand, since electricity has much higher exergy content than steam, exergy efficiency favors the configuration where electricity is produced by means of a heat recovery steam cycle (config. DE).

Beyond this different result with the two performance indicators, a stronger conclusion can be made regarding the two biomass-to-hydrogen concepts. Indeed, it appears that the IG concept consistently outperforms the DG concept, in every configuration and according to both indicators. The main factors that explain the poorer performance of the DG concept are the higher electricity consumption of the ASU and oxygen compression as well as the lower biomass-to-hydrogen yield. Thermal integration of the ASU with the biorefinery represents an important area for process improvement since increased integration leads to a reduced power demand.

4.4 Fossil CO₂ balance

The environmental performance of the biorefinery concepts was evaluated by means of the fossil CO₂ balance. Results are shown in Figure 17 and Figure 18 with Coal and NGCC as marginal electricity producer, respectively³. Grey bars represent results for the IG concept while black bars those for the DG concept.

Figure 17 shows that, with coal power plants as marginal electricity producer, the IG concept appears to have higher emission reduction potentials than the DG concept in all configurations. This can be explained by the higher electricity deficit found in the DG concept, which has a negative impact on the fossil CO₂ balance since it implies increased power generation from the marginal producer.

³ To facilitate comparison with other biomass conversion pathways, the specific CO₂ balance (t CO₂/t dry biomass) is given in Table 12 in the Appendix.

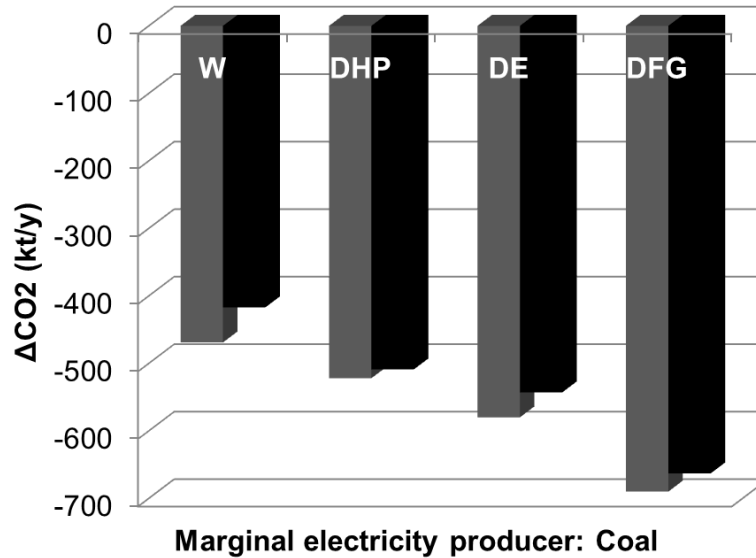


Figure 17: fossil CO₂ balance with coal as marginal electricity producer. Grey bars: IG concept; Black bars: DG concept

The selected configurations are ranked in the same way for both concepts. The integration options chosen to design these configurations seem therefore robust since they lead to comparable benefits for both biomass-to-hydrogen concepts. According to ΔCO_2 , the configuration where biomass is dried with excess heat from the biorefinery performs worst (config. W). This result is not surprising since in the other configurations, heat recovery allows producing HP steam and/or electricity and thus avoiding fossil fuel utilization. Without considering refinery fuel gas utilization, the best configuration appears to be the drying of biomass with refinery excess heat and the implementation of a heat recovery steam cycle for electricity production in the biorefinery (config. DE).

With coal as marginal electricity producer, the use of refinery fuel gas for electricity generation clearly appears of high interest (config. DFG) in terms of emission abatement. Given the much lower CO₂ emissions of refinery fuel gas compared to coal and the net electricity export created, this configuration yields the highest potentials for reduction of CO₂ emissions.

Observations from Figure 18 are slightly different from those drawn from the previous graph. With NGCC as marginal electricity producer, results for the selected configurations are within a narrower range: ΔCO_2 is found between -522 kt/y and -630 kt/y while extreme values were -469 kt/y and -690 kt/y with coal as marginal producer. Larger CO₂ emissions of the marginal power production technology lead to a greater impact on the CO₂ balance when the net electricity balance of the studied system is changed.

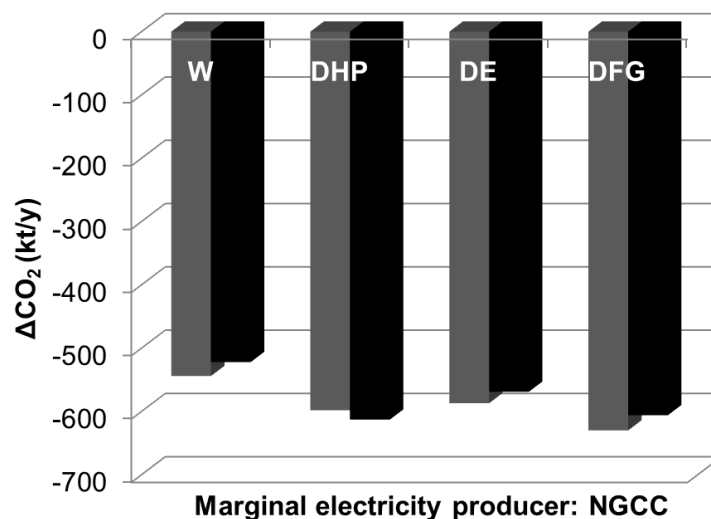


Figure 18: fossil CO₂ balance with NGCC as marginal electricity producer. Grey bars: IG concept; Black bars: DG concept

Since fossil CO₂ emissions from refinery fuel gas are close to those of natural gas, the difference between using either of these to produce electricity is small, as can be seen in Figure 18 (configurations DHP and DFG). Although excess heat from the biomass-to-hydrogen concept is used to produce HP steam in these two configurations, the best concept is not the same in both cases:

- in the configuration where electricity is imported from the grid (config. DHP), the DG concept has an advantage over the IG concept since more steam can be produced. With NGCC as marginal electricity producer, this is enough to offset the negative impact of the higher electricity deficit;
- in the configuration where refinery fuel gas is used to produce electricity (config. DFG), the IG concept performs best. Because of the lower electricity deficit, the net electrical power that can be exported to the grid is higher than in the DG concept, which leads to a higher potential for emission reduction.

While the configuration with the lowest potential for emission reduction remains the same as in Figure 17, i.e. biomass drying carried out with excess heat from the biorefinery; the best configuration does not appear as clearly. Indeed, both configurations discussed previously (DHP and DFG) yield very close ΔCO₂ values.

Results from Figure 17 and Figure 18 show that marginal electricity production technologies have an impact on the calculated environmental performance of biorefineries that should not be neglected. With both marginal electricity producers included in this work, configuration DFG appears the most promising. However, if for any reason such as technical constraints, backup considerations or economic issues, refinery fuel gas cannot be diverted from boilers, this

conclusion does not apply. The most promising configuration becomes then a function of the marginal electricity producer.

In a context where more carbon lean power generation technologies (such as NGCC in this work) are envisioned in the European energy system, it appears from the results above that a polygeneration concept producing hydrogen and HP steam in order to offload refinery boilers is the most promising configuration. This is true even though all electricity demand in the biomass-to-hydrogen concepts must be imported from the grid.

4.5 Relevance and final choice of indicators

Three indicators are used in this study, two of them to evaluate the thermodynamic performance of the biorefinery configurations and the third to assess the environmental impact of the proposed solutions. Using several indicators gives more information on the studied systems and allows identifying influent factors. However, there is a drawback to having several indicators: it can decrease the intelligibility of results, i.e. make them harder to comprehend for the reader. This multiplication also raises a question: what is the most relevant indicator? This is even more important when the selected indicators give different results, as is the case in this work with energy and exergy efficiency. Which one to select to draw the final conclusions?

On a general level, it is my opinion that a researcher should eventually state a clear conclusion that goes beyond writing “the results depend on a number of factors”. In a work of research, very few – if any – conclusions are definitive: they all depend on the achieved work and its scope. However, whatever their limitations and shortcomings, there should be clear conclusions at the end of a study. This is all the more important if a research project is meant to help the general public to gain a better understanding of the subject, let alone if the target audience is decision makers.

Energy and exergy efficiency are both used to evaluate thermodynamic performances. A choice should thus be made between these two indicators, especially since another biorefinery configuration appears best according to each of them. Energy efficiency gives equal value to all material and energy flows, regardless of their nature. Exergy efficiency intrinsically takes into account differences in nature by introducing the concept of “energy quality”. This indicator thus seems much more relevant in cases where energy commodities of different energy quality coexist. With biomass, hydrogen, steam and electricity flows involved in the processes studied in this thesis, exergy efficiency appears to be the indicator of choice. Favoring the best configuration in terms of exergy efficiency makes sure that the energy input is converted with minimal loss of energy quality. However, exergy efficiency does not give information on the environmental impact of a process. It must therefore be used together with another indicator for this purpose, such as the fossil CO₂ balance in this work. Similarly, an indicator of the economy of the process should be added for final decision.

Accordingly, the best configuration among those considered in this work can be selected by plotting the potential for reduction of fossil CO₂ emissions versus the exergy efficiency, see Figure 19 (coal as marginal electricity producer) and Figure 20 (natural gas combined cycle as marginal electricity producer). On these figures, grey markers represent configurations of the IG concept while black markers represent those of the DG concept.

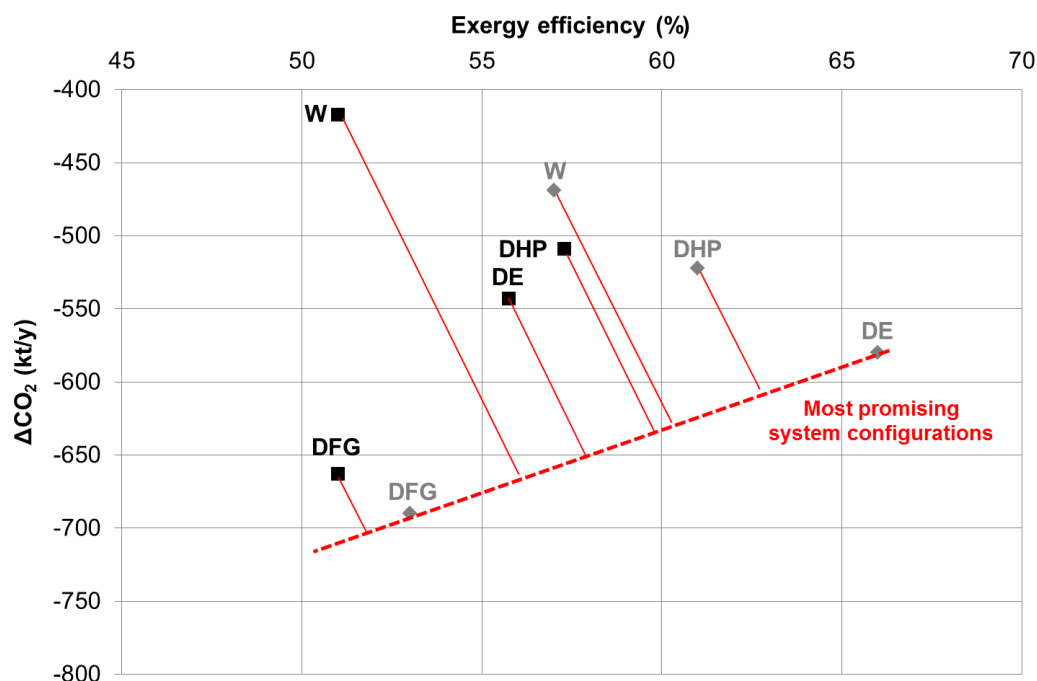


Figure 19: potential for emission reduction versus exergy efficiency, Coal as marginal electricity producer. Grey markers: IG concept; Black markers: DG concept

On Figure 19 and Figure 20, the most promising system configurations are linked by a red dotted line. These are configurations with either the highest exergy efficiency or the highest potential for emission reduction. Accordingly, the further from this line the other points are, the worse are the performances of the associated configurations.

As highlighted earlier, configuration W is the worst performing of all for both concepts. The better performance of the IG concept appears again on Figure 19 since configurations DE and DFG of this concept are located directly on the red dotted line. Configuration DFG of the DG concept is the closest point not located on this line, i.e. the performances of this configuration are the closest to that of configurations DE and DFG of the IG concept.

If the marginal electricity producer is changed from coal to natural gas combined cycle, Figure 20 is obtained. Three of four configurations of the IG concept are especially well performing while configuration DHP is the only one of the DG concept located on the red dotted line. The distance between other configurations and this line is shorter than with coal as marginal electricity

producer, which shows again the impact of the marginal electricity producer on the relative performances of the different system configurations.

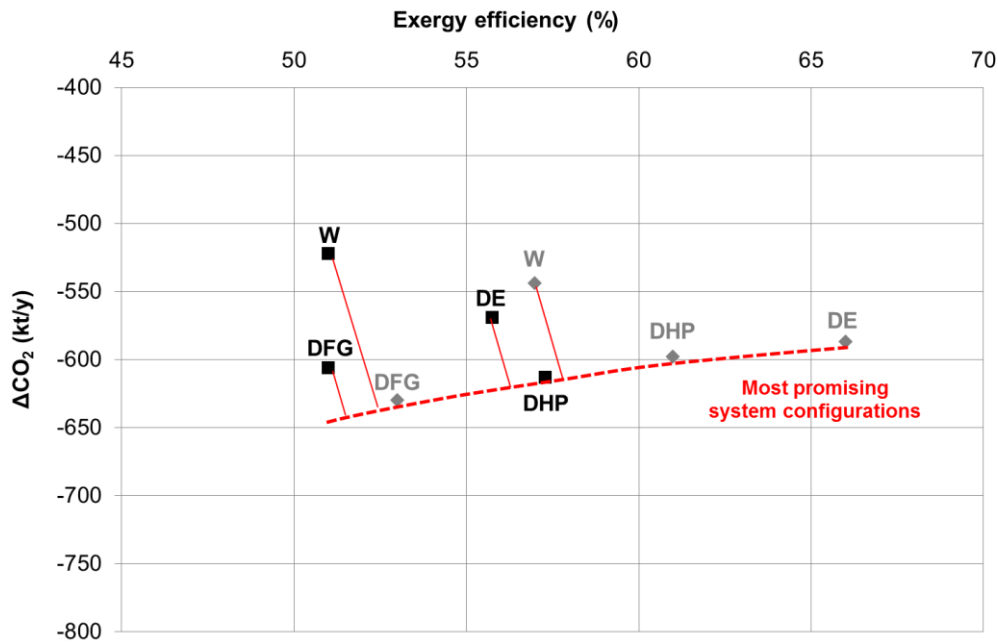


Figure 20: potential for emission reduction versus exergy efficiency, Natural gas combined cycle as marginal electricity producer. Grey markers: IG concept; Black markers: DG concept

These figures confirm that the IG concept outperforms the DG concept. Additionally, comparing the two figures leads to interesting conclusions. From Figure 19 to Figure 20, fossil CO_2 emissions from the marginal electricity producer are decreased. In the range of marginal electricity producers included here, configurations DE and DFG of the IG concept appear as the most robust since they are twice located on the red dotted line. For both concepts, the location of configuration DHP is shifted and is on the line on Figure 20. It is likely that this trend can be extrapolated to less emitting marginal electricity producers, where configuration DHP would shift further down on the graphs and define the red dotted line. Drying biomass with refinery excess heat and exporting HP steam from the biorefinery therefore appears as a promising configuration in the context of a future, more emission-lean European energy system.

5. Discussion

5.1 Future use of biomass

In this study, biomass is used to produce hydrogen for refining purposes. In a longer term perspective, some general questions concerning biomass as a feedstock can arise. Biomass has the advantage of being a very versatile resource since it allows the production of many chemicals, materials and energy commodities. As its use becomes more widespread, users will compete for this resource and it is essential that the most sustainable conversion pathway(s) are promoted. The number of products and processes involved is another argument in favor of the use of exergy efficiency in order to keep track of the most resource efficient routes.

The case study refinery is located in Europe, where sales of hybrid vehicles (vehicles combining an internal combustion engine with one or several electrical motors) are steadily increasing since 2004 [58]. If this trend confirms or if a massive switch to 100%-electrical cars takes place, the market for automotive fuels will shrink dramatically (although not disappear). In such a situation, the production of refining hydrogen or of any automotive fuel does not seem an interesting pathway for biomass conversion while combustion (or co-combustion with coal) for electricity production appears as a more suitable use.

In the near future however, it is likely that the demand for fossil automotive fuels (i.e. gasoline, diesel) will continue to rise and, as a consequence, so will hydrogen requirements in refineries. In developing countries such as China or India, car sales are growing at a fast rate and, in developed countries, traditional combustion engine cars still represent the large majority of new license numbers. Despite the clear upward trend, hybrid vehicles represented an average of less than 1% of the sales in the EU-27 in 2010 although their fraction peaked to 3-4% in the Netherlands.

Several renewable-based automotive fuels, e.g. those produced through upgrading of bio-oils, also require more hydrogen than their crude oil-based counterparts [59]. If the market for these fuels increases, hydrogen will remain an essential part of the production chain.

5.2 Keeping track of the “green”

As mentioned in Section 3.3.2, CO₂ emitted during combustion of the fuels (occurring in car engines) produced at the refinery are not included in the calculation of ΔCO_2 . Indeed, only hydrogen atoms are replaced in these fuels: the fossil CO₂ emissions occurring during combustion in car engines remain unchanged. Only on-site fossil CO₂ emissions are impacted by the implementation of the biorefinery. This is very different from cases where renewable automotive fuels are produced, e.g. Fischer-Tropsch fuels, ethanol or tall oil diesel. In these cases, fossil fuels are replaced by “green” fuels in engines and combustion emissions of fossil CO₂ are avoided.

The location where fossil CO₂ emissions are avoided constitutes a major difference between the production of hydrogen and automotive fuels from biomass. Considering only this parameter, these products are thus likely to be eligible for different kinds of subsidies.

On the other hand, it can be argued that automotive fuels produced in a refinery using biogenic hydrogen also are “green” since, even if the carbon dioxide released during their combustion is 100% fossil, they contain hydrogen atoms originating from renewable feedstock. Similarly, if life cycle fossil CO₂ emissions is the parameter taken into account, should there be a difference between fuels (or blends) containing biogenic carbon and those containing biogenic hydrogen? One can imagine that, if its life cycle specific fossil CO₂ emissions are lower than those of a traditional fossil fuel, a fuel could be marketed as “green” and therefore be eligible for the same type of subsidies as other bio-fuels.

This however requires more advanced accountings of the renewable share of automotive fuels produced with biomass-based H₂ than in the case the whole fuel is based on renewable feedstock, which represents a barrier for both policy makers and the final customer market. Similar issues appear however in the petrochemical sector where large scale productions of chemical intermediates cannot entirely rely on renewable feedstock. There are therefore evidences that a transition towards more sustainable production of conventional fuels and chemicals relies upon more advanced policy instruments and renewable certifications than those currently available.

5.3 Relevance of the case study

This project is based on a case study and the quantitative results presented in this thesis are therefore very specific to the plant considered for the calculations.

However, the studied refinery ranks among Europe’s largest and most complex plants. The structure of these refineries is very similar; especially, most of them operate dedicated HPUs and use byproduct fuel gas in boilers to produce HP steam. This means that the trends identified from the results and the conclusions of this project can most likely be generalized to other refineries of the same type.

The implementation of large-scale gasification-based biorefineries of the type discussed in this thesis is likely to take place in the medium-term future. The economies of scale and the versatility of the large, complex refineries have allowed them to adapt to feedstock and market changes for a long time. These characteristics will most likely allow these plants to remain in operation for several more decades, which makes this case study relevant in terms of time perspective. Additionally, this type of refineries appears as a relevant candidate for the implementation of large scale gasification-based biorefineries.

6. Conclusions

The results presented in this work highlighted the importance of including integration aspects in the design phase to build efficient biomass-to-hydrogen concepts and select sound heat recovery options. Two process concepts were designed, following two approaches. The IG concept, based on indirect, atmospheric steam gasification, relies on well-proven unit operations for gas cleaning and upgrading. On the other hand, the DG concept is based on pressurized, direct gasification and involves emerging technologies such as a membrane reactor. This technology puts together chemical reactions and hydrogen separation and represents a step forward in terms of process intensification.

Both biomass-to-hydrogen concepts were found to be self-sufficient in terms of heat and steam but in deficit of electricity; this deficit being highest in the DG concept. A higher biomass-to-hydrogen yield was found in the IG concept, but this process also requires twice as much steam as the DG concept. In both concepts, large exergy losses were identified between high temperature heat sources and low temperature heat sinks.

Heat integration opportunities were identified and proved to increase both energy and exergy efficiencies of the selected configurations. Especially, the integration of low-temperature biomass drying with refinery excess heat appears to be of high interest since it allows releasing high temperature excess heat in the biorefinery. Taking advantage of this opportunity, several configurations could then be designed, where this high quality energy is recovered in the form of either HP steam or electricity. Although the DG concept allows for larger HP steam and electricity production, it was found to be consistently outperformed by the IG concept according to energy and exergy efficiency.

The environmental impact of biomass-based hydrogen production through the designed concepts was evaluated by calculating a fossil CO₂ balance after their implementation. It was found that all selected configurations led to potential reductions of fossil CO₂ emissions. Because of the electricity deficit of both concepts, the reduction potential was found higher with natural gas combined cycle as marginal electricity producer.

Combining exergy efficiency and potential for reduction of fossil CO₂ emissions allowed identifying the most promising configurations. In a context of decreasing emissions from the marginal electricity producer, two configurations of the IG concept were found to be well performing and the most robust in the considered range:

- Configuration DE, where biomass is dried with refinery excess heat and electricity is produced with biorefinery excess heat.
- Configuration DFG, where biomass is dried with refinery excess heat, HP steam is produced with biorefinery excess heat and electricity is generated through a fuel gas combined cycle. This configuration is also the one yielding the highest potential for emission reduction.

If the trends identified in the results of this work are extrapolated to less emitting marginal electricity producers, which is likely to represent a future European energy system [60], the configuration of both concepts where HP steam is exported to the refinery appears promising.

Much like oil refining in the fossil industry, biomass gasification is a key technology that enables the production of various chemicals and energy commodities from renewable feedstock. Among these, hydrogen appears as a product of interest since it can be produced through high efficiency routes and can contribute to on-site emission reduction at the refinery. Its use in the production of automotive fuels is not likely to decrease in the near to medium-term, whether for fossil or renewable fuels. Other, emerging and much researched applications can also be envisioned for hydrogen, such as its use in fuel cells [61]. Hydrogen production thus appears as a relevant pathway for biomass conversion.

7. Future work

The type of work described in this thesis often involves the same options for further work, i.e. improvements of the models used for process simulation and economic calculations. Although the performance indicators used in this project give a clear picture of the biorefinery concepts, their actual implementation indeed strongly depends on the process economy. Together with its environmental impact, the economy of a process is likely to be the governing indicator on which decision makers will base their choices. In the case of this project, the economic study should also include an evaluation of the possibility to use existing HPU equipment for the upgrading of biomass syngas.

It was also shown that a promising way of recovering low temperature refinery excess heat was biomass drying. Biomass is used on-site for hydrogen production in this work but it could be interesting to evaluate the potential for drying and export to other locations where biomass would be used. As mentioned in the introduction of this thesis, hydrogen production is one of many pathways for biomass conversion. Other potential products include e.g. pellets, methanol, synthetic natural gas and FT-crude. These different biorefinery routes should ultimately be compared in order to determine the most promising pathway to achieve the transition to a consistent, more sustainable energy system.

The main opportunities for further studies directly related to the work described in this thesis are presented in the following sections. These can be divided into two parts according to their focus: the first part consists in more detailed work on parts of or the whole biomass-to-hydrogen concepts investigated in the project. The main objective would be to investigate the options for changing either the type or the operating parameters of single equipment units and how these changes could impact the performance of the biorefinery process and the energy integration options between the biorefinery and the refinery. The second part involves working at a higher scale and expanding the system to match resources (biomass and refinery fuel gas) with products and energy commodities (hydrogen, steam and, optionally, electricity).

7.1 Design optimization

Based on sound simulations and performances indicators, the results presented in this thesis are rather close for each concept. It was shown that the IG concept consistently outperforms the DG concept and some main reasons can be pointed out such as a lower hydrogen yield and a greater electricity demand. Although the first parameter is largely fixed by known chemical equilibriums, these can be influenced by the operating conditions (T, P) applied in the various reacting steps of the process. The electricity consumption essentially consists in the electricity demand for oxygen production in the Air Separation Unit and its subsequent compression and for hydrogen compression at the process output.

Thus, it might be interesting to optimize process operating conditions such as temperature and pressure and to increase the overall performance of the biorefinery processes. Temperature can have an impact on heat integration opportunities described in this thesis while pressure levels will change compression requirements and therefore, electricity demands.

Perhaps the most interesting trail for performance improvement involves the Air Separation Unit (ASU) in the DG concept. This unit has a large electricity demand and its integration with the rest of the process was not included in the work accomplished so far. Opportunities for such integration have however been identified in other publications [42] and investigating in this direction could lead to substantial performance improvements for the DG concept.

7.2 Process synthesis

When excess heat from the biorefinery is used to export HP steam to the refinery, an excess of fuel gas is created since boilers are offloaded. This fuel gas supply cannot, however, be discontinued since it is a byproduct of crude oil refining. In this work, the use of this fuel gas in a gas turbine combined cycle to generate electricity was considered. However, this is not the only potential application of this resource.

Refinery fuel gas contains around 20% of hydrogen. Combustion of this fuel gas therefore allows producing electricity with low CO₂ emissions, but in a context of hydrogen deficit in the refinery the recovery of the hydrogen content is also of interest. Similarly, the light hydrocarbon fraction of fuel gas could be sent to a reforming unit to produce hydrogen.

The general aim of the work accomplished so far was to study the substitution of a traditional refinery HPU with a biomass-based process. Nevertheless, biomass can be used for other purposes in a refinery, especially for steam production in boilers. It thus appears that the formulation of a problem of resource management or of resource allocation can be of interest. Indeed, it would be very interesting to consider biomass and refinery fuel gas as available resources that could be used in various processes in order to satisfy the refinery demands in hydrogen and steam. Electricity can be added as an optional product.

Figure 21 presents an example of a system that can be considered for resource allocation. The system consists in a variety of technologies and equipment that can be used for the production of steam, electricity and hydrogen from fuel gas and biomass. The solutions to the problem will thus consist in sets of sizes of these different technologies and the respective input flow of fuel gas or biomass.

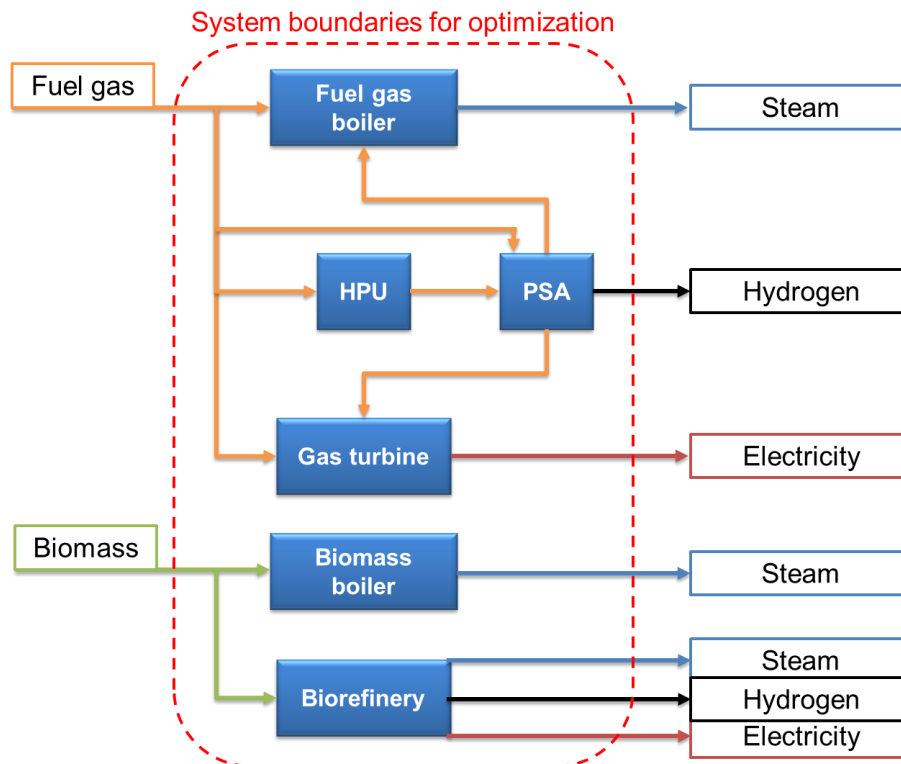


Figure 21: example of system for an optimization problem

This type of problem can be solved by means of linear programming in order to determine optimal ways of allocating the resources to the different users. The optimization can be performed for several targets: lowest fossil CO₂ emissions, highest overall efficiency, best economic performance or lowest overall net electricity import.

Nomenclature

Symbols

\dot{m}	mass flow
\dot{Q}	thermal power
ΔH_r^{298K}	enthalpy of reaction at 298K
e	specific fossil CO ₂ emissions
e^{CH}	chemical exergy
e^{PH}	physical exergy
HHV	Higher Heating Value
η_{el}	efficiency of marginal electricity producer
η_{ex}	exergy efficiency
η_{tot}	total energy efficiency
P	electrical power
wt%	weight percent (mass-based composition)
ΔCO_2	fossil CO ₂ balance
ΔT_{min}	individual contribution to minimum temperature difference for heat exchange

Subscripts

$C4$	butane
fg	fuel gas
i	input
net	net output
o	output

Abbreviations

ASU	Air Separation Unit
ATR	AutoThermal Reforming
CCS	Carbon Capture and Storage
CFB	Circulating Fluidized Bed
DE	biorefinery configuration with dry biomass input and electricity production
DFG	biorefinery configuration with dry biomass input, HP steam export and utilization of refinery excess fuel gas
DG concept	biorefinery concept based on Direct Gasification
DHP	biorefinery configuration with dry biomass input and HP steam export
DME	DiMethylEther
ETS	Emission Trading System
EU	European Union
EU-27	European Union with 27 member countries (from 2007-01-01 to 2013-06-30)
GCC	Grand Composite Curve
HP	High Pressure
HPU	Hydrogen Production Unit
HTS	High-Temperature Shift
IG concept	biorefinery concept based on Indirect Gasification
LTS	Low-Temperature Shift
NGCC	Natural Gas Combined Cycle
P	Pressure
ppbv	part per billion, volume based
ppmv	part per million, volume based
PSA	Pressure-Swing Adsorption
SMR	Steam Methane Reforming
T	Temperature
W	biorefinery configuration with wet biomass input
WGS	Water-Gas Shift

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Vill du plocka svamp?

Appendix

Table 10: Composition of forest residues used in simulations

Proximate analysis (wt% dry basis)	
Fixed carbon	20.6
Volatile matter	76.8
Ash	2.6
Ultimate analysis (wt% dry basis)	
C	51.3
H	6.1
N	0.5
Cl	0
S	0.05
O	39.5
Ash	2.6
Moisture content, wet biomass (wt%)	50
Moisture content, after drying (wt%)	10

Table 11: Energy efficiencies on HHV and LHV basis

Configuration	Energy efficiency (%) HHV basis		Energy efficiency (%) LHV basis	
	IG concept	DG concept	IG concept	DG concept
W	70	67	62	58
DHP	78	78	70	69
DE	72	70	64	61
DFG	75	74	68	66

Table 12: specific potential for emission reduction

Configuration	δCO_2 IG concept (t CO₂/t dry biomass)		δCO_2 DG concept (t CO₂/t dry biomass)	
	<i>NGCC</i>	<i>CPP</i>	<i>NGCC</i>	<i>CPP</i>
W	-0.92	-0.79	-0.77	-0.61
DHP	-1.01	-0.88	-0.90	-0.75
DE	-0.99	-0.98	-0.84	-0.80
DFG	-1.06	-1.17	-0.89	-0.97