THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Assessing Integrated Gasification-Based Biorefinery Concepts for Decarbonisation of the Basic Chemicals Industry

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ABSTRACT

Direct substitution of chemicals with drop-in biomass-based equivalents is a promising approach to achieving the transition to a fossil-free chemical industry. This work contributes to the development of a screening methodology for identifying and assessing energy-efficient decarbonisation options, based on the integration of gasification-based biorefinery concepts into existing chemical processes. The work was conducted as a case study that focused on the largest chemical complex site in Sweden. Two key plants were considered, an oxo synthesis plant (processing natural gas-derived syngas and light olefins into specialty chemicals) and a steam cracker plant (processing a fossil-derived mix into light olefins). The methodology builds upon systematic comparisons of different drop-in approaches and different platform chemicals that target the same drop-in chemical (syngas or light olefins). The impacts of substitution on the host site material and energy balances and process integration opportunities are investigated. Performance indicators considered include thermodynamic performance, GHG emissions balances, and process economics.

The results indicate that both the drop-in point and the composition of the feed to the host process value chain affect significantly the host site material, steam, and fuel gas balances. This is particularly the case for a drop-in point located downstream of the main fossil feedstock conversion unit. Direct conversion to the target chemical, while avoiding "chemical detours", yields favourable thermodynamic and economic performances. The choice of intermediate platform chemical is not so critical; using methanol or dimethyl ether for the production of light olefins gives similar thermodynamic and carbon conversion profiles. The investigated gasification-based biorefinery concepts release high-temperature excess heat which can be recovered for the (co-)generation of steam and/or electricity. By co-locating such processes with other industrial processes, thereby enabling the export of steam, it is possible to completely eliminate or significantly reduce natural gas firing in the existing site utility boilers. The introduction of drop-in bio-chemicals can significantly reduce GHG emissions, mainly through the "storage" of biogenic carbon in the targeted products. The heat recovery option (and location) and the assumed reference grid electricity generation technology affect the ranking of the options. Under specific energy market conditions, switching to syngas-based production of biomass-based chemicals can be economically competitive with current fossil-based operations.

Keywords: Biorefinery, Gasification, Syngas, Platform chemical, Process integration, Chemical industry

Appended papers

This thesis is based on the studies described in the following papers:

I.   Biomass Gasification-Based Syngas Production for a Conventional Oxo Synthesis Plant — Process Modeling, Integration Opportunities, and Thermodynamic Performance
Arvidsson M, Morandin M, Harvey S (2014)
Energy & Fuels **28** (6), 4075-4087. DOI: 10.1021/ef500366p.

II.   Biomass Gasification-Based Syngas Production for a Conventional Oxo Synthesis Plant - Greenhouse Gas Emission Balances and Economic Evaluation
Arvidsson M, Morandin M, Harvey S (2015)
Journal of Cleaner Production **99**, 192-208.
DOI: 10.1016/j.jclepro.2015.03.005.

III.   Integration of Biomass Gasification-Based Olefins Production in a Steam Cracker Plant - Consequences for Steam Balances
Arvidsson M, Johansson E, Pettersson L, Morandin M, Harvey S (2015)
Proceedings of the 23rd European Biomass Conference and Exhibition, EUBCE 2015, Vienna, Austria, pp 1774-1777.

IV.   Integration of Biomass Gasification-Based Olefins Production in a Steam Cracker Plant - Global GHG Emission Balances
Arvidsson M, Johansson E, Morandin M, Harvey S (2015)
Chemical Engineering Transactions **45**, 787-792. DOI: 10.3303/CET1545132.

Also presented at the 18th International Conference on *Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction*, PRES 2015, Kuching, Malaysia, 23-27 August, 2015.

V.   Comparative Thermodynamic Analysis of Biomass Gasification-Based Olefins Production Using Methanol or DME as Platform Chemical
Arvidsson M, Haro P, Morandin M, Harvey S
Submitted to *Chemical Engineering Research & Design*

Co-authorship statement

Maria Arvidsson is the main author of all appended papers. Professor Simon Harvey was the main supervisor and Dr Matteo Morandin co-supervised the work. Erika Johansson and Lars Pettersson conducted the modelling and the energy balance calculations of the steam cracker plant investigated in **Paper III** and **Paper IV**. Dr Pedro Haro co-supervised the study in **Paper V**.

Parts of the earlier work presented in this thesis are based on the author's Licentiate thesis:

Assessing the Integration of Biomass Gasification-Based Production of Chemicals – Case Study of an Oxo Synthesis Plant
Arvidsson M (2014)
Licentiate thesis, Chalmers University of Technology, Göteborg, Sweden.
Available through Chalmers Publication Library (CPL)
publications.lib.chalmers.se/records/fulltext/205836/205836.pdf

Related papers that are not included in this thesis:

- Process Integration Study of a Biorefinery Producing Ethylene from Lignocellulosic Feedstock for a Chemical Cluster
  Hackl R, Arvidsson M, Lundin B, Harvey S (2011)
  Proceedings of the *6th Dubrovnik Conference on Sustainable Development of Energy, Water and Environment Systems*, SDEWES 2011, Dubrovnik, Croatia, 25-29 September 2011, pp 21 (Paper 928).

- Integration Opportunities for Substitute Natural Gas (SNG) Production in an Industrial Process Plant
  Arvidsson M, Heyne S, Morandin M, Harvey S (2012)
  Chemical Engineering Transactions **29**, 331-336. DOI: 10.3303/CET1229056.

  Also presented at the *15th International Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction*, PRES 2012, Prague, Czech Republic, 25-29 August, 2012.

The first paper is based on the fermentation of biomass. The second paper includes a definition of the problem and initial results, which were subsequently developed and investigated in **Paper I** and **Paper II**.

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Regarding the alarming threat of climate change that we are facing and the lack of necessary actions taken to curb current trends.

> *"The revolution is not an apple that falls when it is ripe.*
> *You have to make it fall."*
> Ernesto Guevara, 1965

1 Introduction

To motivate this work, this chapter provides an overview of the future challenges and opportunities for the chemical industry. Thereafter, the objectives and scope of this thesis are stated, and this is followed by a general overview of the appended papers and a presentation of the thesis outline.

Finding sustainable pathways for the transition to a competitive low-carbon economy, so as to mitigate the build-up of greenhouse gases (GHG) in the atmosphere, is one of the greatest challenges of our times. The current annual global primary energy demand is estimated at approximately 150 PWh. Approximately 13% of the energy that meets this demand originates from biomass, waste, and other renewables such as hydro, solar, and wind (IEA, 2015). The main sectors for the end-use of energy are industry, transport, and buildings. No single solution that satisfies all the criteria for a transition to a sustainable society has been identified. Instead, it seems likely that a variety of energy resources and conversion pathways, in addition to some behavioural changes, will be required. In a roadmap (EC, 2011) that was formulated by the European Commission (EC) to cut European Union (EU) GHG emissions to 80% lower than the 1990 levels by Year 2050, it was emphasised that "*all sectors need to contribute*" (Figure 1). For the energy-intensive industry sector, it is projected that emissions could be cut by more than 80%.
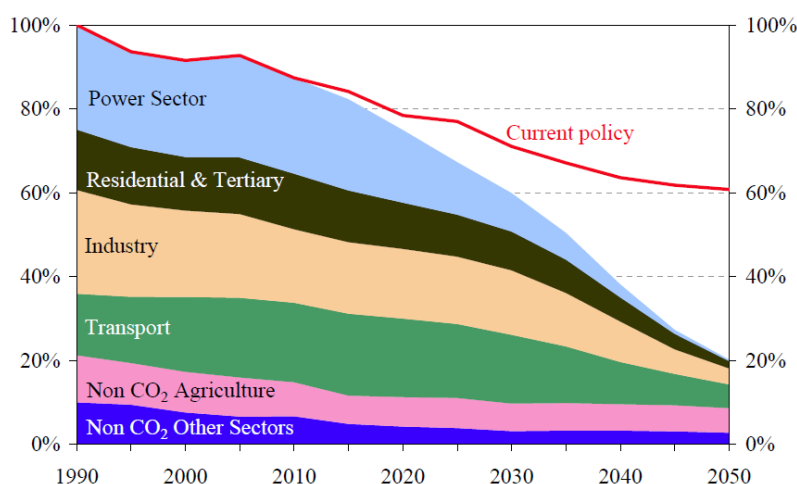

Figure 1. Projections of the decreases in GHG emissions by sector in the EU required to achieve an 80% decrease in the 1990 emissions levels by Year 2050 (EC, 2011).

Ongoing research projects related to the transition to using renewables focus mainly on the energy supply and transportation fuels. These sectors have also received substantial attention from the political sphere in terms of visionary goals and policy instruments. For the supply of heat and power and to a certain extent transportation energy demand, several promising alternative technologies for harnessing non-carbon-based renewable energy sources have been developed. However, for the production of chemicals and materials a source of carbon is generally required. The long-term option for reducing the use of fossil-based carbon in these commodities is to switch to renewable sources of carbon, with biomass as the prime alternative. As the number of viable decarbonisation options for the chemical industry is limited compared to other sectors, this could be considered a key motivation for biomass conversion-related research to focus more attention on this sector.

1.1 Challenges and Opportunities for the Chemical Industry

The chemical industry is energy-intensive and highly fossil-feedstock-dependent. In Year 2012, the use of energy and feedstock in this sector accounted for approximately 30% of industrial energy use (equivalent to approximately 11 PWh) (IEA, 2015). More than half of this demand is attributable to feedstocks. Biomass, waste, and other renewables currently account for only 0.3% of the total energy use of the chemical industry (equivalent to approximately 0.03 PWh). The manufacturing of chemicals is responsible for approximately 20% of industrial GHG emissions (IEA *et al.*, 2013), which in 2005 corresponded to approximately 2.1 Gt CO_2 equivalents ($CO_{2,eq}$) (ICCA, 2009). It should be noted that there are also significant emissions related to the extraction phase of feedstock and fuels (0.3 Gt $CO_{2,eq}$) and the disposal phase of produced chemicals (0.9 Gt $CO_{2,eq}$).

The global annual production of chemicals and polymers is approximately 330 Mt (IEA, 2012a). Three principal intermediate chemical bases, or platform chemicals, can be identified in the chemical industry (IEA, 2007): light olefins (C_2 to C_4); aromatics (C_6 to C_8); and others, including syngas. Ethylene and propylene (i.e., C_2 and C_3 olefins) are the two largest by volume hydrocarbon intermediates with global demands of approximately 145 and 90 Mt, respectively, in Year 2014 (Oil & Gas Journal, 2014; IHS, 2014), and they are expected to grow (ICIS, 2015). In Year 2014, the global chemical sector's turnover was valued at €3,232 billion, of which the EU market accounted for 17% (€549 billion) (Cefic, 2016). The sales of chemicals within the EU (excluding pharmaceuticals) can be broken down as follows: 60% base chemicals; 26% specialty chemicals; 12% consumer chemicals, refer to Section 2.1 for sub-sectors within the chemical industry.

In the chemical industry, fossil hydrocarbons, such as crude oil and natural gas, comprise the dominant feedstock. There is a distinct trend to shift from a liquid or solid feedstock to a gaseous feedstock (IEA, 2012b). The transition to natural gas only offers a short- to medium-term solution, as its combustion contributes directly to increasing atmospheric levels of GHGs [approximately 40% and 15% less per unit of energy content compared with coal or oil, respectively (Gode *et al.*, 2011)]. There are environmental concerns

associated with some of the methods used for natural gas extraction (e.g., hydraulic fracturing, or fracking, of shale rock formations). Furthermore, the current shift in feedstock from naphtha towards inexpensive shale gas-based ethane for the production of light olefins [which generally result in ethylene/propylene ratios of 2.2 and 45 to 50 (mass basis), respectively (Zimmermann and Walzl, 2012)], is expected to result in a so-called "propylene gap" calling for "on-purpose" propylene production (Plotkin, 2014). The production of butylenes (i.e., C_4 olefins) is also expected to be affected, since butylene is a product of naphtha steam cracking (Geilen *et al.*, 2014).

The global annual usage of fossil-derived syngas (i.e., from natural gas, coal or refinery by-products) is approximately 2 PWh (Boerrigter and Rauch, 2006). Fossil-derived syngas is used for a number of different products: 50% ammonia, 25% hydrogen, 10% methanol, 15% other types of syngas, such as Fischer Tropsch (FT) synthesis, oxo synthesis, iron ore reduction gas, and electricity. According to a market tracker report that identifies global trends and forecasts to 2018, the market for syngas and derivatives is expected to grow (Markets and Markets, 2013). The syngas derivatives discussed in that report include methanol, ammonia, hydrogen, oxo chemicals, n-butanol, and dimethyl ether (DME). For the future production of chemicals and fuels, biomass and waste utilisation (as well as underground coal gasification) offer major opportunities.

As fossil resources start to deplete and only available in limited geographical areas, consumer demand for more sustainable products, as well as political concerns about the security of supply become important drivers for increasing the motivation for the chemical industry to engage actively in the transition to a bio-based economy (IEA, 2012a).

1.1.1 Efficient Decarbonisation – Biorefinery Concepts

The primary option for the conventional chemical industry to reduce their long-term fossil feedstock dependence and GHG emissions is to switch to renewable feedstock. The International Energy Agency (IEA) has identified biomass-based technologies as important "game changers" for the chemical industry in its efforts to reduce dependence on fossil feedstock and future GHG emissions (IEA *et al.*, 2013). The IEA's definition of a biorefinery is "*the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)*" (IEA, 2012a).

Lignocellulosic materials, such as forest residues, represent one of the most relevant renewable resources from the medium-term perspective for the production of chemical and energy commodities. The potential harvest for forest residues[1] in Swedish forests under current conditions is estimated at 31–68 TWh per year [higher heating value (HHV) basis], which combined with the harvest of stubs can be increased to 66–172 TWh per year, which further increases expected (Börjesson *et al.*, 2013; Skogsstyrelsen, 2008). From the long-

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[1] Forest residues such as tops and branches not fulfilling quality requirements for producing pulp or sawn goods.

term perspective, aquatic biomass (algae) is also of interest. Although potentially renewable, biomass is likely to become a scarce and limited resource in the future as demand grows, due to the limited availability of land, underlining the importance of optimising the efficiency of utilisation of biogenic feedstock.

Biomass can be converted *via* thermochemical, chemical, biochemical, and mechanical routes. For the conversion of lignocellulosic biomass, thermochemical gasification is considered to be a particularly promising technology. During gasification, biomass is thermally decomposed into syngas (which is rich in CO and hydrogen), and this can be processed into virtually any hydrocarbon. Biomass-derived syngas exhibits physical and chemical characteristics that are similar to conventional fossil-derived syngas, thereby facilitating integration of gasification-based biorefinery concepts with existing fossil syngas-based facilities. Furthermore, biomass gasification-based routes are generally associated with the production of high-temperature excess heat, which makes these processes particularly attractive from an energy integration point of view.

1.1.2   Efficient Decarbonisation – Approaches

In principle, all chemicals and materials that have been traditionally produced from fossil resources can be exchanged for the corresponding bio-equivalent. As discussed by Vennestrøm *et al.* (2011), two general approaches can be adopted to introduce biomass-based production of chemicals (i.e., bio-chemicals): emerging bio-chemicals; drop-in bio-chemicals (Figure 2).
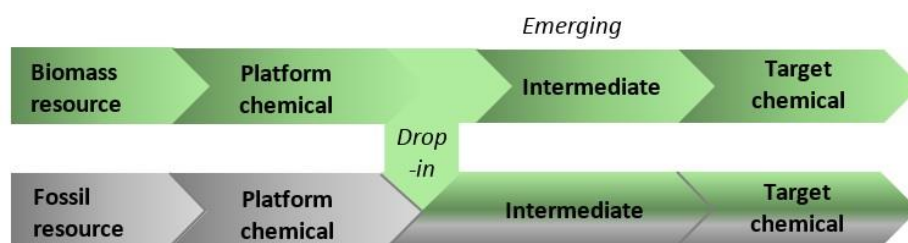
Figure 2. General overview of the two different approaches to introducing production of bio-chemicals in the process value chains.

Note that Figure 2 illustrates a general process value chain for the production of chemicals. For instance, for a given process value chain, the definition of what is a platform chemical and what is an intermediate may differ. For further discussion refer to Section 2.1. The point in the value chain that indicates the drop-in (arrow in Figure 2) distinguishes the two approaches.

Emerging Bio-Chemicals

The production of emerging bio-chemicals involves target chemicals that have novel structures and properties. As no equivalent fossil value chain or product exists, this strategy entails the development and deployment of new value chains, infrastructure, and markets.

This is also the case for the substitution of a fossil-based product that has similar functionality (but is not the identical chemical equivalent). An advantage of this approach is that direct competition with fossil products is avoided. The intrinsic functionality in the biomass feedstock can be retained to a greater extent. One example of the emerging bio-chemicals approach is in the production of the bio-degradable plastic polylactic acid (PLA), which can replace the traditional fossil-derived plastic polyethylene terephthalate (PET) in some applications.

Drop-in Bio-Chemicals

The drop-in approach involves the production of bio-chemicals that can directly substitute for the fossil-based hydrocarbon equivalent. Thus, the bio-chemical can be introduced directly into existing and established value chains, infrastructure and markets. An example of the drop-in strategy is the production *via* fermentation to ethanol (the 'platform chemical' depicted in Figure 2), which can be processed *via* dehydration to ethylene (the 'intermediate' in Figure 2), and thereafter converted to a number of products through a series of processes, such as polymerisation to polyethylene (the 'target chemical' in Figure 2) (Vennestrøm *et al.*, 2011).

Different versions of the drop-in approach, with different drop-in points in the existing fossil-based value chain, could be applied. For example, switching from the current feedstock or a conventional platform chemical to a biomass-derived equivalent could be considered. The different switching approaches have advantages and drawbacks related to issues such as changes to existing core process, infrastructure, back-up systems, (co-)location and integration opportunities, and intrinsic conversion losses related to total route-to-target chemical.

The advantages of producing chemicals that are identical to the platform and bulk chemicals in the current fossil-based petrochemical industry have been highlighted by van Haveren *et al.* (2008). In their study, the feasibility of substitution in the production routes of different biomass-based bulk chemicals were reviewed using the port of Rotterdam in the Netherlands as a case study. Routes based on syngas or pyrolysis oil were not included. Six important platform chemicals were identified: ethylene; propylene; C_4-olefins; benzene; toluene; and xylene. Cherubini and Strømman (2011) discussed the opportunities, perspectives, and potential options for the production of platform chemicals from lignocellulosic biomass, which primarily involve bio-chemical processes, using the existing infrastructure of the petrochemical industry. For the synthesis of short-carbon-chain chemicals, such as ethylene and propylene, thermochemical conversion was highlighted as a particularly promising technology.

Chemical plants are complex systems, making it challenging to identify and evaluate appropriately all the important effects of introducing drop-in bio-chemicals at various drop-in points. Thus, systematic comparisons that apply holistic perspectives are crucial to identifying sustainable opportunities for decarbonising the chemical industry.

1.2 Objectives and Scope

The aim of this study is to identify and assess different energy efficient decarbonisation options, based on the integration of gasification-based biorefinery concepts, to support the chemical industry in the transition to a bio-based economy and towards reducing global GHG emissions. Different drop-in approaches, associated with different points in conventional process value chains to integrate biorefinery concepts, as well as different platform chemicals, for the same target drop-in chemical are considered. The consequences of substitution for site materials and energy balances and process integration opportunities across the biorefinery concepts and host plants are investigated. A methodology to handle systematically the relevant changes to a surrounding system, related to the decarbonisation concepts, is developed. The process performances of the different biorefinery concepts are compared for thermodynamic performance, global GHG emission balances, and process economics. In general, this thesis aims to increase the body of knowledge regarding those parameters that have significant impacts on the above-mentioned process performance measures, and which are therefore important factors in decision-making by chemical companies, third-party companies, and policy makers.

This thesis adopts a case study-based approach. The scope of this thesis is limited in terms of selection of host plants for the integration of biorefinery concepts, i.e., a conventional oxo synthesis plant and a conventional stream cracker plant. While the quantifications are case-specific, the conclusions can be considered as generally applicable, since both plants are representative for the plants of this type, which can be found in many places around the world. All the biorefinery concepts considered are based on future expected commercial-scale thermochemical gasification systems. The feedstock considered for the gasifier is forest residues, which are assumed to be harvested from sustainably managed forests. Two target drop-in bio-chemicals in the host plants are selected: syngas and light olefins. The approach is to compare different routes to the same final product *via* different drop-in points in the existing fossil process value chain or *via* different platform chemicals. In total, five different biorefinery concepts are assessed that involve the production of: synthetic natural gas (SNG); syngas; crude light olefins (*via* methanol); light olefins *via* methanol; and light olefins *via* DME. The process performance evaluation is based on theoretical targeting. A European energy market is assumed. The main differences between the work conducted for this thesis and other studies that have addressed integration of biomass gasification concepts with existing industrial sites are the:

- Selection of the host plants, i.e., conventional chemical process plants;
- Decarbonisation approach, i.e., replacing current fossil-based platform chemicals with drop-in bio-chemicals;
- Focus on the consequences of substitution, i.e., detailed investigation of changes made to on-site materials and energy balances;
- Comparison approach, i.e., comparing different approaches that replace the same final target chemical.

1.3 Overview of the Appended Papers

The work presented in this thesis is based on the five appended papers (hereinafter referred to as **Papers I** to **V**). A general overview of the papers is illustrated in Figure 3, which shows that the papers investigate different targeted drop-in, or platform, bio-chemicals associated with different case study plants. All the biorefinery concepts considered are based on thermochemical gasification of lignocellulosic biomass.

In **Paper I** and **Paper II**, full substitution of the natural gas feed to the syngas generator in the oxo synthesis plant is investigated by comparing two different integration points for the biorefinery concepts in the process value chain. The options considered are: (*i*) replacing the feedstock with biomass-derived SNG (bio-SNG) (BioSNG2Syngas); and (*ii*) replacing syngas with biomass-derived syngas (Bio2Syngas). Both co-location and stand-alone operation of the biorefinery concepts are considered, and associated integration consequences and opportunities are investigated. The various biorefinery process concepts are compared in relation to thermodynamic performance (in **Paper I**), global GHG emission balances, and process economics (in **Paper II**).

In **Paper III** and **Paper IV**, partial substitution of several cracker units in the steam cracker plant with crude biomass-based light olefins production *via* methanol-to-olefins (MTO) units fed with biomass-based methanol (Bio2CrudeOlefins), is investigated. The existing olefin separation equipment is retained for upgrading of the crude MTO stream. Both co-location and stand-alone operation of the methanol production process are considered and associated integration consequences and opportunities are investigated. In **Paper III**, a detailed analysis of the cracker site steam balance consequences resulting from the partial feedstock switch is conducted. In **Paper IV**, the partial feedstock switch options are compared with respect to global GHG emission balances.

The production of biomass-based light olefins *via* alternative platform chemicals (Bio2Olefins) is investigated in **Paper V**. The options considered are: (*i*) methanol synthesis and MTO synthesis; and (*ii*) DME synthesis and DME-to-olefins (DTO) synthesis. Only stand-alone operation is considered. The two investigated biorefinery processes are compared in relation to thermodynamic performance.
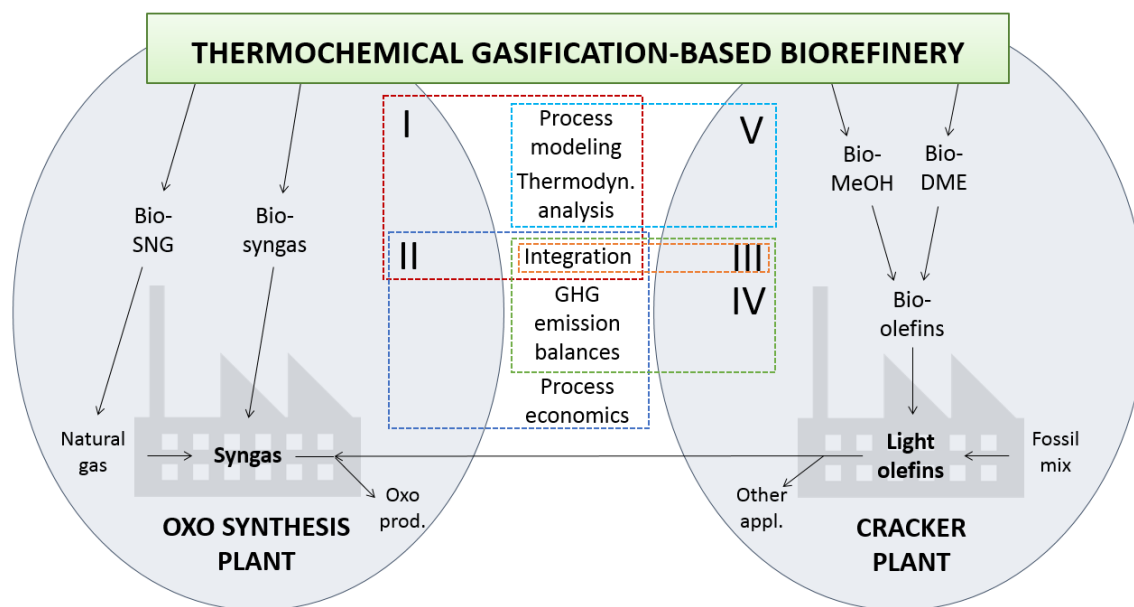
Figure 3. Overview of the appended papers, their inter-relationships and main applied focus.

1.4 Thesis Outline

This thesis starts by motivating the present work through a description of the challenges and opportunities that the chemical industry is currently facing, followed by the objectives and scope of this work, as well as an overview of the appended papers.

An overview of the studies and activities related to biomass-based production of chemicals in general, and *via* biomass gasification in particular, is provided in Chapter 2. Special attention is focused on previous studies concerned with the integration of gasification-based biorefinery processes with existing industrial plants, and gaps in current knowledge are identified.

The methodology employed in this study is described in Chapter 3. The case study involving the chemical complex site and the investigated biorefinery concepts are described in Chapter 4. In Chapter 5, an overview of the main findings taken from the appended papers are presented and discussed, followed by a more general discussion in Chapter 6. The conclusion drawn from this work are summarised in Chapter 7, and some suggestions for additional research are presented in Chapter 8.

2 Literature Review and Research Needs

This chapter presents an overview of the studies and activities that have been conducted in relation to the production of bio-chemicals in general, and production via gasification in particular. Studies of the integration of gasification-based biorefinery processes into existing industrial plants are highlighted, and various research needs are identified.

2.1 Biorefinery Concepts for the Production of Chemicals

To aid the reader of this thesis, this chapter starts by defining the terminology related to the production of chemicals that is used in this thesis.

The chemical industry can generally be divided into sub-sectors, such as the production of bulk chemicals, fine chemicals, and specialty chemicals (Pollak, 2007). Bulk chemicals, which are also referred to as basic chemicals or commodity chemicals, are high-volume, low-value, homogeneous, standardised chemicals that are used in a wide range of applications. Bulk chemicals cover, for example, traditional petrochemicals, polymer derivatives thereof, and basic inorganics (Cefic, 2016; Pollak, 2007). Fine chemicals are low-volume, high-value, complex, single, pure chemicals that are used in a wide range of applications (Pollak, 2007). Fine chemicals can be further sub-categorised on the basis of added value (building blocks, advanced intermediates, and active ingredients) or the type of business (standard or exclusive products). Specialty chemicals are relatively small-volume and high-value chemicals that are produced on the basis of their performance or function with one or more fine chemicals as the active ingredient (SOCMA, 2016; Pollak, 2007). Sub-categories of specialty chemicals include adhesives, agrochemicals, biocides, pigments, flavours and fragrances, food and feed additives, and pharmaceuticals. In practice, it is difficult to distinguish between fine and specialty chemicals. In general, fine chemicals can be said to be sold on the basis of *"what they are"* and specialty chemicals on the basis of *"what they can do"* (Pollak, 2007).

As noted in Section 1.1.2, what is considered to be a platform chemical or an intermediate chemical in a specific process value chain can vary. Following the general value chain

described in Vennestrøm *et al.* (2011), platform chemicals are the building-block chemicals derived from the raw materials, whereas intermediate chemicals are the derivatives of platform chemicals that act as an 'intermediate' step in the process to the final target chemical. A prerequisite of this general process value chain is that only two steps are needed to reach the target chemical. Furthermore, that which is considered to be the final target chemical may also differ depending on the perspective taken, such that the target chemical in one system may very be a platform chemical or an intermediate chemical (or feedstock) in another system. In this thesis, the term 'platform chemical' refers to a key intermediate chemical of strategic importance for the studied route to a specific target chemical, while the term 'intermediate chemical' refers to a general "intermediate" along the studied route.

In this thesis, the term 'drop-in chemical' refers to a chemical that can be introduced into existing process value chains.

2.1.1 Commercial Implementation of the Production of Bio-Chemicals

Biorefinery concepts for the production of chemicals is not novel. Most of the investigations conducted to date on the development of new processes for the production of biomass-based chemicals have focused on the production of low-volume, high-value fine or specialty chemicals, for which functionality is often significant, *via* bio-chemical and chemical conversions of easily accessible carbohydrates, such as sugar- and starch-based feedstocks. However, the use of agricultural feedstocks for the production of value-added products (chemicals, materials, fuels, *etc.*) raises major concerns, as it is inevitably comes into direct competition with food production.

The global annual production of bio-based chemicals and polymers is approximately 50 Mt (IEA, 2012a). The main products are non-food starch, cellulose fibres and derivatives, tall oils, fatty acids, and fermentation products (e.g., ethanol and citric acid). Several biomass-based chemical and material production plants, which are primarily based on agricultural feedstock resources, such as plant oils, sugars, and starch, exist at the commercial scale. For example, NatureWorks LLC began producing bio-degradable PLA plastic, primarily from corn, in the USA in 2002 with an annual production capacity of 140 kt (NatureWorks LLC, 2014).

Traditional platform and speciality chemicals that are conventionally produced from fossil-based feedstocks can also be produced from biomass feedstocks. In Year 2010, Braskem commercialised the production of ethylene (production capacity of 200 kt per year) *via* the dehydration of sugar-cane ethanol in Brazil (Braskem, 2013). In the same year, BioAmber in France began producing biomass-based succinic acid through the fermentation of wheat-derived glucose (BioAmber, 2014).

Several of the companies involved in the production of bio-chemicals would prefer that their future products be produced from cellulosic materials, biomass wastes or non-food plants, once the associated challenges have been overcome.

Biogenic methane (often referred to as biogas) can be produced by anaerobic digestion of organic waste, manure, and sewage sludge. Biogas, which is currently produced in a multitude of small-scale plants, is mainly used as a fuel for transportation and energy applications rather than as a feedstock for the production of chemicals. The usage of upgraded biogas in the Swedish transportation sector was 0.6 TWh in Year 2010, and the potential exists to increase production to approximately 11 TWh per year (Energimyndigheten, 2012; Linné *et al.*, 2008).

2.1.2 Systems Evaluation of the Production of Bio-Chemicals

The U.S. Department of Energy has identified 12 platform chemicals (including succinic acid, levulinic acid, glycerol, sorbitol, and xylitol) that could be derived from sugars *via* biological or chemical conversion and would be suitable for further conversion into a range of high-value chemicals and materials (Werpy *et al.*, 2004).

In a comprehensive review of life cycle assessment (LCA) studies on the production of chemicals, it was noted that there is a lack of studies into the value chains for the production of biomass-based chemicals other than biofuels (Tufvesson *et al.,* 2013). This trend was also identified in a review of GHG emissions from biorefinery chains for the production of chemicals (Kajaste, 2014).

Clancy *et al.* (2013) highlighted the importance of assessing the shift from petroleum-based materials to biomass-based materials by comparing the sustainability characteristics of the products associated with the different routes. By reviewing the available assessment approaches, the study found that while several methods exist, there are no guidelines for case-specific interpretations and there is a general lack of adequate assessment parameters for comparing the use of wood or petroleum as a feedstock. This lack is mainly attributed to difficulties associated with assessing the impacts of land and water use, resource depletion, and social impacts.

Some comparative assessments of the environmental impacts of biomass-based and petroleum-based products have been conducted. For example, in a case study conducted by Ekman and Börjesson (2011), the environmental impact of producing propionic acid by the biological conversion of agricultural by-products was compared with conventional methods using a fossil-derived feedstock. Zhao *et al.* (2014) compared the environmental impacts of producing polyols from corn and petroleum feedstocks. Both studies showed that the biomass-based routes reduced the GHG emissions over the entire life cycle. In the latter study, corn was treated as a carbon sink, i.e., CO_2 absorption during growth was included. In fact, one review concluded that most comparative LCAs of bio-chemicals have shown favourable environmental performances for the biomass-based option, particularly with respect to the global warming potential (GWP) impact and energy use (Tufvesson *et*

al., 2013). However, the review also noted significant variability among the reported environmental performances as a result of uncertainties connected with raw material production. Some environmental concerns were also identified in the review, such as eutrophication and land use. These concerns are of particular importance in the case of agricultural feedstocks.

2.2 Gasification-Based Biorefinery Concepts for the Production of Chemicals

The use of sustainable lignocellulosic feedstock, such as agricultural residues and forest residues, is one opportunity to overcome some of the concerns related to agricultural feedstock. However, the required feedstock processing is more complex. As mentioned in Section 1.1.1, thermochemical gasification is considered to be a particularly promising technology for the conversion of lignocellulosic biomass. In this thesis, the feedstock considered is forest residues, which are assumed to be harvested from sustainably managed forests.

During gasification, a carbonaceous feedstock is converted into a raw syngas, which consists primarily of hydrogen, CO, CO_2, and methane, in an oxygen-deficient environment at high temperature (in the range of 500°–1300°C). The feedstock can be: solid, such as forest residues (or coal); liquid, such as black liquor (or residual liquids); or gaseous, such as biogas (or natural gas). There are a number of different reactor types for conducting gasification (listed here in order of increasing up-scalability): fixed bed; fluidised bed [bubbling (BFB) or circulating (CFB)]; and entrained flow. Heat for the endothermic gasification reactions can be supplied directly (by *in situ* combustion of part of the feedstock) or indirectly (e.g., by heat transfer with an inert bed material). Depending on the gasifier type and the eventual application, the gasification agent can be oxygen, air, and/or steam. The gasification reactions can be conducted under atmospheric or pressurised conditions. Different gasification technologies and conditions yield different qualities of raw syngas in terms of gas composition, gas purity, and heating value. The obtained syngas can be processed into a spectrum of products, as shown in Figure 4.

Thermochemical gasification of fossil-based material is commercially available, whereas the utilisation of biomass feedstock for advanced applications needs to be proven on a large scale, as discussed below. The diversity of application areas is an attractive feature of gasification-based biorefinery concepts. A key aspect for realisation of these concepts is efficient biomass utilisation to achieve favourable environmental and economic performances. Therefore, systematic comparisons of different process pathways are necessary to facilitate the search for robust solutions.
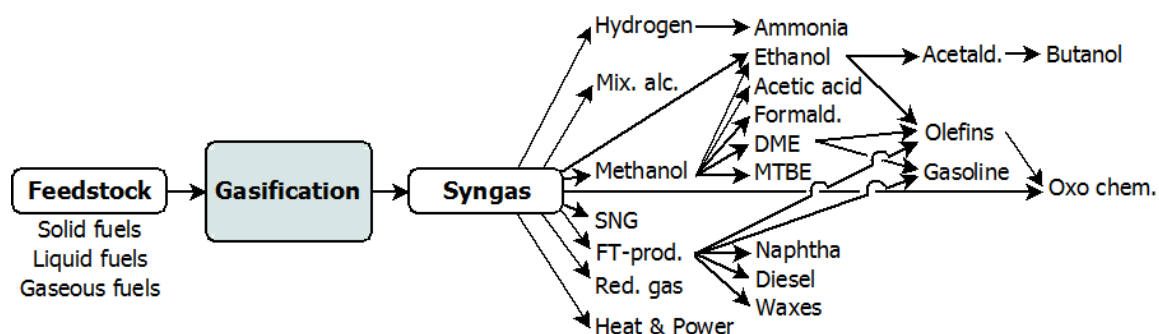
Figure 4. Overview of possible production routes for bulk chemicals based on thermochemical gasification. Abbreviations: Acetald., acetaldehyde; Formald., formaldehyde; FT-prod., FT products; Mix. alc., mixed alcohols; Oxo prod., oxo products; Red. gas, reduction gas.

2.2.1 Commercial Implementation of Gasification-Based Biorefinery Concepts

The only commercial-scale biomass gasification concepts currently in existence are direct combustion applications connected to a boiler for heating or combined heat and power (CHP) operation. The world's (currently) largest biomass (primarily forest residues) gasifier, which has a capacity of 140 MW (thermal), has been in operation since early 2013 at the Vaskiluodon CHP plant in Vaasa, Finland (Isaksson and Tiilikka, 2014). The plant consists of an atmospheric air-blown CFB gasifier and a modified steam boiler, in which the generated syngas is combusted together with pulverised coal.

Gasification concepts for solid biomass in more advanced applications, i.e., where the syngas requires extensive cleaning for further upgrading, are currently being used in pilot- or demonstration-scale plants. A brief overview of some of the ongoing biomass gasification projects is presented below. For a relatively recent review of syngas utilisation projects, see Rauch et al (2014).

In Güssing, Austria, an 8 MW (thermal) biomass CHP plant, which is based on fast internally circulating fluidised bed (FICFB) steam gasification technology and tar scrubbing with bio-oil, has been in operation since 2002 (Hofbauer *et al.*, 2003; Rauch *et al.*, 2014). Using the syngas slip-streams, research and development is performed with respect to downstream conversion for the production of SNG, FT, mixed alcohols, and hydrogen.

In the Netherlands, the Energy Research Centre of The Netherlands (ECN) has demonstrated the production of SNG based on an indirect gasification technology (MILENA gasifier technology) at the laboratory scale (30 kW; thermal) and the pilot scale (800 kW; thermal) (van der Meijden *et al.*, 2009). Based on the same technology, several demonstration plants are being planned: 1 MW of power to be generated from agricultural waste in India; 4 MW of SNG production from waste wood in the Netherlands; and a 7-MW (power) waste-to-energy plant in the UK (van der Meijden, 2014).

The Gothenburg Biomass Gasification (GoBiGas) project developed by Göteborg Energi, which is an energy company in south-western Sweden, includes a proof-of-concept bio-SNG plant developed in two stages (Gunnarsson, 2011; Göteborg Energi, 2014). The construction of the initial phase (phase 1) began in Year 2012 and the technology has been proven feasible, producing 20 MW (lower heating value (LHV) basis) of SNG since late-2014. The design of the first phase is based on the Güssing FICFB gasification technology, and the gas upgrading and methanation units are based on the Haldor Topsøe technology. After evaluation of the demonstration plant, a second phase (phase 2) aimed at the production of 80 MW (LHV basis) of SNG was planned. However, following a recent political decision, the project has been put on hold. In Year 2014, E.ON was awarded EU funding *via* the NER300[2] program for the Bio2G project, which encompassed a 200-MW SNG plant in southern Sweden. The gasification and tar-reforming process is similar to that of the Gas Technology Institute (GTI) concept (see below).

At the GTI, which is located in Des Plaines, Illinois, USA, successful test campaigns of a biomass gasification pilot plant that produces gasoline have been conducted (GTI, 2014). The system is based on the oxygen-blown, pressurised, CFB gasification system developed by Andritz-Carbona, followed by a catalytic tar-reforming process that was jointly developed by Andritz-Carbona and Haldor Topsøe. The gasoline synthesis process is based on Haldor Topsøe's TIGAS system using methanol/DME.

The results obtained from the pilot and demonstration projects indicate that gasification-based biorefinery concepts are, technology-wise, mature enough to be scaled up to commercial size. Some issues remain to be resolved, such as syngas cleaning and compression, and feedstock feeding, as well as high investments costs. However, the main obstacle facing up-scaling is the lack of stable policy frameworks, resulting in investor hesitation.

2.2.2 Systems Evaluation of Gasification-Based Biorefinery Concepts for the Production of Chemicals

Numerous studies have investigated different gasification-based biorefinery concepts, most of which have evaluated stand-alone operation with a techno-economic focus. As this thesis is focused on integration with existing industrial process plants (which is covered in a separate section in this literature review; see Section 2.3), these studies are mentioned only briefly here. Furthermore, as in the case of biorefinery concepts in general, current research on gasification-based biorefinery concepts focus mainly on the production of transportation fuels. Although, some biofuels (e.g., methanol, ethanol, DME, and hydrogen) could have also chemical applications, these studies are not specifically commented on in this section.

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[2] NER300 is an EU funding program for demonstration of innovative low-carbon energy projects, such as carbon capture and storage (CCS) and renewable energy (RES) technologies, on commercial scale.

There are a few studies investigating gasification-based biorefinery concepts for the production of chemicals and fuels. Ciferno and Marano (2002) reviewed comprehensively and benchmarked existing (at that time) near-commercial biomass gasification technologies for the production of fuels and chemicals (FT fuels, methanol, hydrogen, and fuel gas). The study identified directly heated BFB biomass gasification as a particularly promising technology for the investigated syngas applications and that further research to establish operating limits in general was needed. Haro *et al.* (2013a) reviewed potential thermochemical biorefineries routes for the multi-production of chemicals and fuels. Products investigated were e.g., alcohols, light olefins, and fuels (gasoline, diesel, and jet fuel). The use of applying a platform chemical was highlighted. The platform chemicals considered were: methanol; DME; and ethanol. The study emphasised the importance of the selection of mix of co-products and commented on the need for a general sustainability criteria. In a related study (Haro *et al.*, 2013b), a techno-economic assessment of producing chemicals and fuels via DME as platform chemical was conducted. The feedstock considered was low-grade lignocellulosic biomass. Three products were considered (in different combinations): synthetic gasoline; ethylene; and propylene. Similar total energy efficiencies were achieved for the investigated concepts (ranging from 38-41%). All concepts resulted in a higher specific production cost compared with the current market price. The implementation of CO_2 sequestration certificates and tax reductions was investigated. The results indicated that the light olefins concept required the lowest CO_2 sequestration certificates price to achieve profitability.

Ren and Patel (2009) conducted a comprehensive comparison of energy use and CO_2 emissions associated with the production of high-value basic petrochemicals (HVCs), such as light olefins from crude oil, natural gas, coal, and biomass (including lignocellulosic biomass, maize starch, and sugar cane). Biomass conversion routes included in the investigation were gasification and fermentation, and the syngas-based routes considered were: FT synthesis to FT-naphtha followed by steam cracking; and methanol synthesis followed by MTO and methanol-to-propylene (MTP). The energy demand levels of the biomass gasification-based routes were found to be significantly higher than those of the conventional steam cracking routes. However, biomass-based routes also showed the potential to reduce global fossil-derived CO_2 emissions. In Ren *et al.* (2009), the future production costs for the different configurations for a wide range of projected energy prices were estimated. The gasification-based biorefinery routes showed promising results, particularly if CO_2 emissions are associated with high charges.

Liptow *et al.* (2015) conducted a comparative LCA of the production of ethylene from lignocellulosic biomass *via* a fermentation-based route (ethanol dehydration) and *via* a gasification-based route (MTO synthesis). The results were compared with commercial ethylene production from sugarcane and fossil oil. A cradle-to-gate perspective was considered. The investigated impact categories included GWP, acidification, photochemical ozone creation, and eutrophication. The gasification-based route showed lower environmental impacts compared with the fermentation routes.

2.3 Systems Evaluation of Integrated Gasification-Based Biorefinery Concepts at Industrial Sites

Co-location of biorefinery concepts at existing industrial process sites offers interesting integration opportunities for heat and material flows, as well as the possibility to make use of the existing infrastructure.

2.3.1 Integration with Pulp and Paper Industry

Several process integration studies of different thermochemical biorefinery concepts at industrial sites have been reported. A sector that stands out in the literature is the pulp and paper industry, which with its long experience of forestry management and wood feedstock handling, is currently seeking opportunities to widen its product portfolio, so as to improve profitability. A pulp and paper mill that is co-located with a sawmill has also been investigated (Isaksson *et al.*, 2012). The targeted end-products have typically been motor fuels (e.g., DME, FT liquids, ethanol-rich alcohols, and SNG) or electric power, as well as ammonia production (Andersson and Lundgren, 2014). A common assumption made in most of these studies is to size the biorefinery concept under investigation to specific mill conditions, for example, replacing the recovery boiler with a black liquor gasifier that is sized to process the same volume of black liquor, or replacing the bark boiler with solid biomass gasification (including both forest residues and bark). For studies focusing on black liquor gasification, see e.g., Larson *et al.* (2006), Pettersson and Harvey (2012), and Joelsson and Gustavsson (2012). An overview of studies analysing the integration of solid biomass gasification concept with pulp and paper industry is provided in Isaksson (2015).

Consonni *et al.* (2009) investigated the integration of several biofuel production configurations with a large hypothetical pulp and paper mill. The results showed that the integrated cases achieved higher biofuel yields, reduced capital investments, and favourable process economics under several investigated scenarios, as compared with the stand-alone cases.

Wetterlund *et al.* (2011) investigated the integration of two biomass gasification concepts with pulp and paper production. The studied biorefinery concepts showed potentials to become profitable, however, a high dependence on assumed energy market parameters, particularly policy support, was identified. The integrated cases showed considerably better economic performance. The potentials to reduce CO_2 emissions and energy use were shown to be very dependent on assumptions about the surrounding system, particularly alternative biomass use and electricity production.

Isaksson *et al.* (2012) investigated the integration of several biomass gasification concepts, with a pulp and paper mill co-located with a saw mill. The results showed that that the integrated cases achieved larger CO_2 emissions reductions than stand-alone operation. However, the CO_2 emissions reductions levels achievable by co-firing biomass in coal in a coal power plant could not be reached unless storage of separated CO_2 was assumed. The

assumed reference electricity production technology affected the ranking of the investigated cases.

Tunå et al. (2012) investigated the integration of several biofuel production set-ups with an efficient pulp and paper mill. The results showed that the integration was not advantageous (in terms of electrical equivalence efficiency) in all cases. All investigated cases showed potentials to reduce CO_2 emissions. A correlation between the electrical equivalence efficiency and the CO_2 emissions reduction compared with the stand-alone operation was identified.

Ljungstedt et al. (2013) investigated the integration of FT crude production with a typical Scandinavian pulp and paper mill, considering a number of development pathways at the mill. It was shown that the integrated co-located cases achieved higher wood-to-fuel efficiencies and generally lower production costs than stand-alone operation. The integrated cases showed comparatively larger potentials to reduce GHG emissions, for reference electricity production technologies emitting equal or less than a natural gas combined cycle (NGCC) power plant. Andersson and Lundgren (2014) also found favourable process economics and energy performances for integrated cases, as compared with stand-alone operation. They studied the integration of ammonia production with a pulp and paper mill.

Andersson et al. (2014) conducted a techno-economic analysis of the integration of methanol production, considering different set-ups, with a pulp and paper mill. An improved overall plant efficiency (based on electricity-equivalents) was identified for the integrated cases. In the economic analysis, it was found that an economic policy support was necessary for the investigated concepts to be competitive under all studied market scenarios.

2.3.2 Integration with Industries Other than Pulp and Paper

Process integration studies of different thermochemical biorefinery concepts at industrial sites other than the pulp and paper industry have also been reported.

Heyne et al. (2012) investigated the integration of a bio-SNG process (based on indirect gasification technology) with a biomass-fired CHP plant, whereby the existing steam boiler was modified to serve also as a heat supplier for the gasification reactions. This integration was considered technically feasible and it was concluded that the possibility to use the existing infrastructure represented a valuable opportunity for maximum exploitation of the excess heat from the SNG process.

The option to replace liquefied petroleum gas (LPG) with bio-SNG (based on pressurised, oxygen-blown CFB gasification technology) as the fuel in steel industry reheating furnaces was investigated by Johansson (2013b). The results showed that profitability could not be achieved (for any of the studied energy market scenarios), and that the global CO_2 emissions reduction potential relied on marginal biomass user assumptions. Lundgren et

al. (2013) investigated the opportunities for methanol production from steel-work off-gases and biomass gasification in a steel plant. The key critical integration factors related to balancing the biorefinery steam system and satisfying the local district heat demand. The results showed that integration of methanol production in steel plants could be economically feasible and could result in CO_2 emissions reductions and higher overall plant energy efficiency.

There are several studies that looked at the integration of gasification-based biorefinery concepts in oil refineries. Some of these studies have focused on biomass-based hydrogen (bio-hydrogen) production, while others are concerned with the production of biomass-based Fischer-Tropsch (bio-FT) fuels. In Johansson *et al.* (2012), the integration of bio-hydrogen production (based on different gasification concepts) to meet the future increased demand for hydrogen in a hydro-skimming refinery was investigated. The results show that the global CO_2 emissions balance depends on marginal biomass user assumptions. Brau *et al.* (2013) explored the opportunity to substitute gradually the current fossil-based hydrogen production unit in a large European oil refinery with bio-hydrogen (based on indirect gasification technology). In a related paper, the integration of two bio-hydrogen concepts (based on different gasification technologies, gas cleaning, upgrading, and hydrogen separation) with an oil refinery was investigated (Brau and Morandin, 2014). Heat recovery options that targeted steam export to the refinery showed the highest energy efficiencies, whereas electricity generation generally showed the highest exergy efficiencies. All the investigated cases showed significant CO_2 emissions reduction potentials, although they were dependent upon the assumed reference grid electricity generation technology. Johansson *et al.* (2013; 2014) investigated the integration of bio-FT fuels (based on CFB gasification technology) into a complex oil refinery. The option to upgrade the bio-FT crude into existing refining units was investigated. The capacity of existing units was assumed to be sufficient, i.e., it was deemed that no changes were necessary and that the current crude oil feed could be maintained. Heat integration with an oil refinery yielded greater potentials for GHG emissions reductions than stand-alone operation (Johansson *et al.*, 2014). Co-upgrading of the bio-FT crude in existing units had a marginal effect on the GHG emission balances (compared with upgrading in new units). For the bio-FT fuel production to be profitable, policy support for biofuels was found to be essential (Johansson *et al.*, 2013). The heat-integrated cases showed better economic performance than stand-alone operation (which did not show profitability in any of the studied scenarios).

A techno-economic assessment of integrating the production of methanol or FT fuels into a South African sugar mill was conducted by Petersen *et al.* (2015). Different process concepts were considered (based on indirect or direct CFB gasification technology and conventional or advanced synthesis routes). The feedstock was sugar-cane residues and bagasse. None of the investigated cases were shown to be sufficiently economically viable to attract investment. The advanced bio-FT case could satisfy the overall mill energy demands, whereas the advanced methanol case could not (as it required the import of

electricity). Nevertheless, the advanced methanol case performed better in term of internal rate of return.

Optimal geographical locations for future biofuel production plants in Sweden have been explored by Wetterlund *et al.* (2013). By applying a geographically explicit approach, the minimum cost of the entire studied system (including raw material supply, production, transportation and distribution, sales of co-products, and policy instruments) can be identified. The objective is to identify robust (under various boundary conditions) and cost-effective biofuel plant locations. Seven future biofuel technologies (based on gasification of solid biomass or black liquor) are considered for integration with existing industry. The industrial sites considered include pulp mills, paper mills, saw mills, refineries, and bio-CHP plants. Two future biofuel production targets are investigated: 4 TWh per year; and 9 TWh per year. The results suggest that the biofuel production targets can be met using only domestic resources for all the modelled scenarios. The leading solutions include black liquor gasification with DME production and gasification of solid biomass with SNG production, due to their high biomass-to-biofuel system efficiencies. A weak requirement for biomass transportation was identified as a key factor, for which chemical pulp mills and saw mills appeared to be the most attractive. The solutions encompass the entire range of small to large plants. In general, systems that have a mix of biofuels achieve lower system production costs, as compared with more homogeneous systems, which indicates that future policies should be carefully designed to foster a diversity of technologies and fuels. Further refinement of the model has been reported by Pettersson *et al.* (2015), whereby the focus was on the integration of future biofuel production facilities in the existing forest industry (including pulp mills, pulp and paper mills, and saw mills). The leading solutions included the integration of black liquor gasification with DME with (by default) chemical pulp mill production and solid biomass gasification with SNG production with (mainly) saw mills. In general, low specific investment costs (i.e., large plants) and/or low specific biomass transportation costs were identified as key factors.

2.3.3   Integration of Drop-in Bio-Chemicals into the Chemical Industry

Drop-in bio-chemicals are expected to achieve the easiest market penetration since they are able to benefit from the existing infrastructure (IEA, 2012a). A few process integration studies on this topic are available in the literature. The focus has been on light olefins, which can be produced indirectly from syngas *via* a suitable intermediate, such as methanol or DME, in chemical clusters (or steam cracker plants). The required upgrading of the resulting MTO or DTO crude-olefins mixture is similar to that of the conventional fossil-based olefin production processes, which allows for obvious synergistic effects in the case of feedstock substitution or capacity expansions of existing light olefins processes. Oxo synthesis is an alternative application for drop-in biomass-derived syngas (Boerrigter and Rauch, 2006; Spath and Dayton, 2003), for which no detailed integration study has been performed to date.

Holmgren *et al.* (2014) compared in a chemical cluster (the case study chemical complex) the GHG emissions balances of two alternative applications for biomass gasification-based methanol production: 1) use as a vehicle fuel; and 2) further conversion to light olefins *via* MTO. Stand-alone operation was used for comparison and involved the delivery of heat to a district heating network. Heat integration opportunities considered in the study included the use of low-temperature heat from the cluster for drying the biomass feedstock, as well as steam and heat delivery to the cluster utility system [as identified by Andersson *et al.* (2011)] and the local district heating system, respectively. In addition, the opportunity to boost methanol production by adding hydrogen (which at that time was available within the cluster) to the syngas was investigated. Data for the MTO process were based on data from the literature, and the upgrading of the crude bio-olefins was assumed to occur using existing equipment at a cracker plant in the cluster. No systematic analysis of the integration consequences of the drop-in was conducted. The integrated cases showed higher GHG emissions reduction potentials than stand-alone operation. The results showed similar GHG emissions reduction potentials when methanol replaced motor fuels (petrol) and when methanol was used for the production of light olefins to replace conventional olefins (naphtha-based). However, in comparison with using biomass for co-combustion in a coal power plant (i.e., replacing coal), the GHG emissions reduction potentials achieved in the investigated cases were modest.

Hannula and Arpiainen (2015) performed a techno-economic assessment of the production of light olefins and transportation fuels *via* biomass gasification and methanol synthesis, in which the possibilities for material and heat integration into a steam cracker plant were discussed. The economic evaluation showed that the costs associated with olefins production could be reduced by integrating the MTO section with an existing plant, thereby allowing for equipment sharing and avoiding the investment costs linked to the upgrading sequence. However, no systematic analysis of the specific integration consequences was performed, and the environmental performance was not investigated. In a related study, it was found that similar economic performance levels for producing bio-fuels and bio-chemicals (light olefins) could be achieved by applying the same low-carbon policies (Hannula, 2015).

In the Swedish "Forest Chemicals" ("*Skogskemi*") project, options for the production of forest-based bulk chemicals (including butanol, methanol, and light olefins), were investigated (Joelsson *et al.*, 2014). Two routes for converting lignocellulosic feedstock to key platform chemicals were included: fermentation to ethanol (Jönsson, 2014); and gasification with methanol production (Andersson, 2014; Morandin and Harvey, 2015). Several different set-ups (configurations, locations, integrations etc.) were investigated. A chemical cluster (the case study chemical complex) and several pulp mills in Sweden were included among the considered host sites. The conversion of ethanol and methanol to light olefins was investigated by Johansson and Pettersson (2014).[3] For the MTO route,

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[3] From which results, **Paper III** and **Paper IV** are based upon.

upgrading of crude bio-olefins within existing units was considered. Furthermore, an LCA (including several environmental impact categories) of the investigated options was conducted within the project (Joelsson and Mossberg, 2014). For the light olefins value chain, which involved partly switching the current production at a chemical cluster to a biomass-based process (*via* both ethanol and methanol), the results showed that there was potential to reduce the GHG emissions from the cluster. This decrease mainly covered cradle-to-gate and end-of-life (assumed incinerated or decomposed) activities. The number of set-ups included in the project was high and the set-ups were quite specific[4]. For the LCA of the olefins value chain, a cluster perspective was taken (the functional unit being "*the total production of the Stenungsund cluster in 1 year*"). Moreover, the ethanol and methanol routes were considered simultaneously. Additional work will be required to analyse the reported results so as to identify and evaluate the specific integration consequences in more detail. One outcome from the economic assessments was that some of the investigated set-ups were potentially feasible, if sold on the motor fuel market (with current policies), whereas production for the chemical markets appeared to be less promising.

2.4 Research Needs

Based on the background given in Section 1.1 and the above literature review, the rationale of this thesis can be motivated. The main aim is to compare systematically different energy-efficient decarbonisation options, based on gasification-based biorefinery concepts, for the chemical industry. The focus is on investigating different drop-in approaches and platform chemicals, substitution consequences, and process integration opportunities.

Studies that have investigated decarbonisation options for the chemical industry are scarce, with a particular lack of studies on the integration of gasification-based biorefinery concepts. While drop-in bio-chemicals have been identified as particularly promising, no systematic comparison of different drop-in approaches and platform chemicals has been conducted. Studies of drop-in concepts are generally based on the assumption that no significant change to the host plant will ensue as a consequence of the integration. There is therefore a need to analyse systematically the substitution consequences related to different decarbonisation options, as these might have significant influences on overall process performance.

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[4] For example, one of the methanol production options is to produce SNG (*via* gasification) at a pulp mill. This SNG is thereafter injected into the natural gas grid, to be reformed into syngas at the chemical cluster and mixed with syngas produced from another gasification plant at the chemical cluster. Finally, the syngas is fed to a methanol synthesis plant. Excess heat from processing is utilised in different ways depending on the opportunities at the respective locations.

In addition, as no ready-to-use methods exist for comparing different decarbonisation options for complex chemical plants, a methodology that can systematically handle relevant changes to the surrounding system needs to be developed.

3 Methodology

This chapter presents the methodological framework applied in this thesis. Descriptions of the methods and tools used in the appended papers, as well as the key assumptions are provided.

This work aims to identify and assess systematically different opportunities for plants that employ fossil-based production of chemicals to switch to biomass-based routes, based on the integration of gasification-based processes. The long-term goal is to contribute to the development of a screening methodology that rapidly identifies robust decarbonisation options for specific systems. The methodological framework developed and applied in this work has the following elements:

- Selection of case study host plants (see Section 3.1)
- Identification of target drop-in bio-chemicals and drop-in approaches that constitute systematic comparisons (see Section 3.1)
- Selection of performance indicators (see Section 3.4)
- Definition of system boundaries and surrounding reference systems (see Section 3.4)
- Selection of biorefinery layouts and calculation of mass and energy balances (see Section 3.2)
- Identification & quantification of process integration opportunities (see Section 3.1 and 3.3)
    - o Material integration opportunities
    - o Consequences of substitution at host site
    - o Heat integration opportunities
- Quantification and comparison of process performance targets (see Section 3.4)

Note that the above actions are not listed in strict order of implementation or importance, as some of them may occur in parallel and some may affect previous actions in an iterative manner.

3.1 Selection of Case Study Host Plants and Target Drop-in Bio-Chemicals

In this work, different energy-efficient decarbonisation options for the chemical industry are evaluated based on a case study approach. While this approach inevitably involves case-specific quantifications, the selection of plants that are typical for their genre and the fact that similar plants are operating around the world, allows the drawing of general conclusions.

The largest chemical complex site in Sweden was selected for studying decarbonisation of the chemical industry (for details, refer to Section 4.1). Two key plants, together accounting for approximately 85% of the total CO_2 emissions of the cluster, are identified as being particularly promising for targeting the decarbonisation of the complex: (*i*) an oxo synthesis plant; and (*ii*) a steam cracker plant. The former plant produces specialty chemicals (from natural gas-derived syngas and light olefins) and the latter constitutes the core of the complex, producing high-volume intermediates (light olefins from light alkanes and naphtha) for supply to the surrounding plants. In this work, the drop-in decarbonisation approach is considered (see Section 1.1.2). By matching the material flows (feedstocks, platform chemicals, intermediates, and targeted products, according to Figure 2) in the complex (and in particular, the identified host plants) with possible pathways for gasification-based biorefinery concepts (see, for example, Figure 4) two key target drop-in bio-chemicals are identified: (*i*) syngas; and (*ii*) light olefins. Given the expected growth of the syngas market (in addition to the obvious overlap with gasification-based processes) and the fact that light olefins constitute the largest-by-volume hydrocarbon intermediates (see Section 1.1), the selected target drop-in bio-chemicals can be considered as being of general interest.

For decarbonisation of the oxo synthesis plant (studied in **Paper I** and **Paper II**) , the following options to substitute completely the currently used natural gas-derived syngas are considered: (*i*) retaining the existing conventional syngas production and substituting the natural gas feedstock with bio-SNG (BioSNG2Syngas route); and (*ii*) scrapping the existing syngas production unit and directly substituting with biomass-based syngas (bio-syngas) (Bio2Syngas route) (fulfilling the specifications, such as purity and H_2/CO ratio, for downstream oxo synthesis). The comparison approach is, to compare the two different routes having different introduction points in the fossil process value chain to replace the same product (i.e., syngas). Both co-location and stand-alone operations for the biorefinery concepts are considered, and the associated integration consequences and opportunities are investigated. The current fossil-based production of syngas is used as the reference in the comparisons (Base Case).

For decarbonisation of the steam cracker plant (studied in **Paper III** and **Paper IV**) the option to substitute partially (approximately 25% of the total capacity) the current fossil-only production of light olefins (in several cracker units) with crude light olefins produced

via biomass-based methanol (bio-methanol) and MTO (Bio2CrudeOlefins), while making use of existing olefin separation equipment, is considered. The Bio2CrudeOlefins cases are sized to match the Base Case ethylene production. Both co-location and stand-alone operations for the biorefinery concept are considered, and the associated integration consequences and opportunities are investigated. The current fossil-based production of light olefins is used as the reference in the comparisons (Base Case).

For the production of biomass-based light olefins (bio-olefins) (Bio2Olefins route), two alterative platform chemicals (studied in **Paper V**) are considered: (*i*) methanol; and (*ii*) DME. The approach is to compare two different platform chemicals (i.e., methanol and DME) that replace the same product (i.e., light olefins). The production of biomass-based light olefins is adjusted to satisfy the specifications of the cracker light olefins, so as to allow for drop-in to the cluster. Only stand-alone operation is considered. One potential substitution for the biomass-based ethylene-fraction (not further investigated in this thesis) could be to replace the current cluster import of ethylene. Further processing of biomass-based light olefins, either for drop-in as crude or in a form that already fulfils the specifications, could be considered in any relevant cluster plant, for example in the oxo synthesis plant (not investigated further in this thesis).

3.2 Process Layout and Modelling

The purpose of this work is to assess different decarbonisation options and to compare them with current operational practice (Base Case). To establish the data for the investigated (future) biorefinery concepts, process flowsheet layouts are created based on findings from the literature and previously performed work (at the division). The process layouts applied in the systematic comparisons are kept the same/similar as much as possible. For an overview of the process layout for syngas production (gasification) and target drop-in bio-chemical production (downstream upgrading and synthesis), the reader is directed to Section 4.2 and Section 4.3, respectively (and, for more details, to the relevant papers). The mass and energy balances for the selected biorefinery process designs and some fossil-based reference processes (syngas production at an oxo synthesis plant) are obtained from process simulation models established in the commercial flow-sheeting software Aspen Plus (Aspen Tech, 2014). For other fossil-based reference processes and partially switched processes (steam cracker plant), the mass and energy balances are provided by a plant-specific production planning simulation program (Johansson and Pettersson, 2014).

The assumed process flow-sheet layout for the bio-SNG process investigated in **Paper I** and **Paper II** is similar to that for the proof-of-concept demonstration plant known as GoBiGas phase 1 (see Section 2.2.1). The assumed process layout for the direct bio-syngas process is basically a combination of the layouts for the bio-SNG and existing fossil-based syngas processes. Therefore, the comparison is conducted based on the same gasification technology, to allow for generalised conclusions. The process flowsheet layout (and model) for the bio-methanol process (which is fed to an integrated MTO unit) used in **Paper III**

and **Paper IV** is based on previous work (Isaksson *et al.*, 2012; Johansson, 2013a; Morandin and Harvey, 2015). The process flowsheet layouts for the two bio-olefin production concepts (*via* methanol or DME) investigated in **Paper V** are assumed to be the same, to allow for generalised conclusions to be drawn. The process layout is determined based on findings from the literature.

The mass and energy balances for the investigated biorefinery concepts (bio-SNG, bio-syngas, and bio-olefins) studied in **Paper I**, **Paper II**, and **Paper V** and for the fossil-based syngas production at the oxo synthesis plant studied in **Paper I** and **Paper II** are obtained by establishing process simulation models in the Aspen Plus software. For the detailed modelling assumptions, data, and relevant references used, refer to **Paper I** and **Paper V**. The mass and energy balances for the biorefinery concept (bio-methanol) studied in **Paper III** and **Paper IV** are based on previous results (Isaksson *et al.*, 2012), which were recently updated (Johansson, 2013a; Morandin and Harvey, 2015). The mass and energy balances for the steam cracker plant, including the fossil-only Base Case and the feedstock-switch case involving integration of an MTO unit, as studied in **Paper III** and **Paper IV**, are obtained using an in-house production planning simulation program provided by the cracker site, as discussed in the paper of Johansson and Pettersson (2014).

In addition, the required oxygen is assumed to be produced in an air separation unit (ASU), for which the power consumption is accounted for in the calculations.

3.3 Process Integration

The IEA definition of process integration is "*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*" (Gundersen, 2002).

In this study, two process integration aspects are analysed: (*i*) material integration of biorefinery product streams into conventional fossil-based value chains at different entry points, including full and partial substitutions; and (*ii*) energy targeting of the biorefinery concepts to estimate heat recovery targets for co-generation and heat integration with host plants, as well as of the fossil-based syngas production to estimate targets for current steam production. The consequences of substitution for the host site material and energy balances are investigated.

3.3.1 Material Integration and Substitution Consequences

The key material integrations considered in the oxo synthesis plant (**Paper I** and **Paper II**) involve full substitution of the currently natural gas-derived syngas with bio-SNG or bio-syngas. The drop-in of bio-SNG does not (by definition) affect the host plant's material and energy balances. However, for the drop-in of bio-syngas (i.e., further downstream in the value chain), substitution consequences are introduced. The material (and energy) streams

exchanged between the syngas production unit and the other sections of the oxo synthesis plant (e.g., hydrogen and tail gas from the H_2/CO adjustment step and steam produced through heat recovery) are considered fixed in the analysis (determined by the Base Case). In addition, the current net steam demand (i.e., for which extra fuel gas needs to be purchased) is included. Streams that are affected by the feedstock switch (particularly in the direct bio-syngas case) are adjusted for using increased/decreased imports (of for example, hydrogen) from a reference system (see Section 3.4.2). By developing steam and fuel gas balances, heat integration opportunities (by means of steam export from the biorefinery processes) are investigated.

The key integration of material considered in the steam cracker plant (**Paper III** and **Paper IV**) is the partial substitution of current cracker light olefins with crude bio-olefins. The MTO section is assumed to be located at the cracker site, thus allowing for utilisation of the existing olefin separation equipment. The integrated crude MTO-stream has a different composition (and usually higher purity) than the conventional cracker crude (regardless of the fossil-based feedstock used). As a result, other material (and energy) inlet and outlet streams (e.g., ethane, propane, light olefins) are affected by the partial feedstock switch. The analysis considers a fixed amount of products (determined by the Base Case). To achieve this, the partial feedstock cases are sized to match current ethylene production, and the remaining product mix is (if necessary) adjusted with imports/exports from a reference system (refer to Section 3.4.2). By deriving steam and fuel gas balances, heat integration opportunities (through steam export from the biorefinery processes) are investigated.

In **Paper V**, the production of drop-in light olefins is considered. However, no specific substitution is investigated in detail. The conducted analysis considers a fixed input.

3.3.2 Energy Targeting

In this study, heat recovery targets for the different biorefinery concepts are estimated using pinch analysis tools. Pinch analysis is a method for systematically estimating process heat recovery targets. The concept was originally introduced by Linnhoff and Flower (1978), and was later developed into the first pinch analysis user guide (Linnhoff *et al.*, 1982). Updated descriptions, which include new developments, are provided by Smith (2005) and Kemp (2007).

The investigated biorefinery concepts require heating and cooling at different temperature levels. Ideal heat recovery targets can be estimated by analysing the thermal cascades of the process' heating and cooling requirements. This is done without pre-definition of the heat exchanger network (HEN) layout. Instead, a minimum temperature difference (ΔT_{min}) for heat exchange is imposed. The process thermal cascades can be represented in the grand composite curve (GCC). The GCC provides graphical insights into the required and available amounts of heat and the temperature levels for the conditions of ideal heat recovery. To access the potential integration of two process parts (or two different

processes), one GCC can be plotted against another GCC while applying the principles of split-GCC graphical analysis (Kemp, 2007). An alternative approach is to also include all the required utility streams in addition to the biorefinery process streams, and balance the overall thermal cascade.

Biomass gasification-based processes are generally associated with high-temperature excess heat, which can be recovered for the co-generation of electric power and useful thermal heat. The split-GCC analysis is applied for estimating heat recovery targets in **Paper I**, **Paper III**, and **Paper IV**. In these studies[5], steam generation targets are estimated by representing the GCC of the steam production against the GCC of the process under investigation and then iteratively maximising the recovery of process excess heat. Similarly, power generation targets are estimated by including the GCC of a heat recovery steam network, which allows for steam extractions to be iteratively matched with process heat demands. For the assumptions made regarding the steam productions and steam networks, the reader is directed to the relevant papers.

In **Paper V**, heat recovery targets for the co-generation of electric power and refrigeration work requirements are estimated by introducing the thermal cascade contributions of the corresponding steam and refrigeration cycles and other cold utilities (collectively referred to as the "utility system"). The maximum power generation is estimated by balancing the overall thermal cascade through solving a linear programming problem (Morandin *et al.*, 2011). For the assumptions made regarding the utility system, refer to **Paper V**. To highlight the integration of the biorefinery concept and the utility system, the overall thermal cascade is split and graphically represented in a balanced, split GCC.

For the decarbonisation options investigated for the oxo synthesis plant (**Paper I** and **Paper II**) and the steam cracker plant (**Paper III** and **Paper IV**), two biorefinery concept locations associated with different integration opportunities are considered: co-location (i.e., on-site); and stand-alone (i.e., off-site). For the biorefinery concepts compared in **Paper V**, only stand-alone operation is considered. For the co-location cases, heat integration with the host plant (*via* the export of steam) is prioritised, whereas in the stand-alone cases, maximum production of electricity is targeted.

3.4 Performance Indicators

In a screening of the different decarbonisation options, it is useful to select a set of performance indicators to assess quantitatively and compare the different alternatives.

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[5] In addition to the biorefinery concepts investigated in **Paper I**, **Paper III**, and **Paper IV**; this method was applied to estimate the current HP steam production for fossil-based syngas production in **Paper I**.

In general, for systems that are characterised as energy conversion processes, it is of interest to examine how much of the input ends up in useful products. This is of particular importance to consider when investigating different pathways that utilise the same limited resource. For this purpose, the evaluation of the thermodynamic performance of the processes is useful (see Section 3.4.1). Thermodynamic performance indicators can also provide valuable insights for comparing the applications of the various conceptual approaches, such as the comparisons of different drop-in approaches and routes that target the same final chemical and the selection of heat recovery options.

When considering the implementation of new processes and products it is of importance to assess the associated environmental burdens. The preferred methodology for these evaluations is to conduct a full-scale LCA, covering several impact categories over the entire life cycle (i.e., from cradle-to-grave). Although LCA is a standardised methodology (ISO, 2006a; ISO, 2006b), different methods are allowed, and depending on the goal and scope, assumptions, and input data [many of which are associated with uncertainties caused by (future direct and indirect) land-use changes], the results obtained for similar systems may differ significantly. Furthermore, to conduct a full-scale LCA is time-consuming and therefore, it is not ideal for an initial screening. One of the key incentives for making the transition to a low-carbon economy is mitigation of the build-up of GHGs in the atmosphere. Therefore, this work focuses on estimating the GHG emissions savings that can be realised by the different decarbonisation options (see Section 3.4.2).

To enable the realisation of any kind of project, it must be economically attractive to investors. Several methods are available for assessing the profitability or economic performance of an investment, of which the preferred ones are based on cash flow projections over the project life-time (Smith, 2005). The inputs required to calculate the cumulative cash flows for an investment consist of fixed and variable costs and revenues (or avoided costs). In addition, assumptions regarding the project life-time and interest rates are required. Establishing reasonable costs for the feedstock, energy commodities, and sale prices of products are major challenges when conducting an economic assessment. In this thesis, the objective is to conduct a screening and to compare different decarbonisation options with each other and with the current fossil fuel-only operation. For this purpose, the annuity method is assumed to be adequate for evaluating the process economics (see Section 3.4.3). Furthermore, by calculating the change in production cost relative to the fossil fuel route, fixed inputs are eliminated from the calculations and no sales prices for the products are necessary.

3.4.1 Thermodynamic Performance

Depending on the purpose of the analysis, thermodynamic performance can be defined using several approaches. As discussed by Lind *et al.* (2014), defining efficiency is especially difficult for multi-product systems. In this thesis (**Paper I** and **Paper V**), the performance indicators used to compare the thermodynamic conversion efficiencies of the investigated biorefinery concepts are based on energy and exergy efficiencies. In the

definition of the energy performance indicator, all energy flows (chemical energy, thermal heat, and electric power) are treated equally. In the exergy performance indicator, the quality of the energy content of the flows is considered; this is particularly useful when comparing different heat recovery options (i.e., maximising electricity production or prioritising steam export).

Energy efficiency

Energy efficiency can be defined in several ways (Lind *et al.*, 2014; Haro *et al.*, 2014). In this thesis (**Paper I** and **Paper V**), the energy efficiency (η_{en}) is defined as the ratio of the net useful energy products to the net required energy inputs, according to Eq. (1):

$$\eta_{en} = \frac{\sum_p \dot{n}_p \cdot HHV_p + \sum \dot{W}^- + \sum \dot{Q}^-}{\sum_f \dot{n}_f \cdot HHV_f + \sum \dot{W}^+ + \sum \dot{Q}^+} \tag{1}$$

where $\dot{n}_p$ and $\dot{n}_f$ are the molar flows (kmol·s^{-1}), HHV_p and HHV_f are the corresponding HHVs (MJ·kmol^{-1}) of the net products (index p) and net feeds (index f), respectively, $\dot{Q}^-$ and $\dot{Q}^+$ are the net useful thermal heat production and net useful thermal heat demand (MW), respectively, and $\dot{W}^-$ and $\dot{W}^+$ are the net electric power production and net electric power demand (MW), respectively. Note that the energy efficiency is based on net flows, in other words a given energy stream is considered either as a product from or a feed into the system.

To compare the different process steps in more detail (**Paper V**), the cold gas efficiency ($\eta_{cg,i}$) of the various intermediate products along the process value chain is defined according to Eq. (2):

$$\eta_{cg,i} = \frac{\sum_i \dot{n}_i \cdot HHV_i}{\sum_f \dot{n}_f \cdot HHV_f} \tag{2}$$

where $\dot{n}_i$ and $\dot{n}_f$ are the molar flows (kmol·s^{-1}), and HHV_i and HHV_f are the corresponding HHVs (MJ·kmol^{-1}) of the net intermediate products (index i) and net feeds (index f), respectively.

In addition, to track the carbon flows in the process chain, the carbon conversion ($C_{conv,i}$) was defined according to Eq. (3):

$$C_{conv,i} = \frac{\sum_i \dot{n}_{C,i}}{\sum_f \dot{n}_{C,f}} \tag{3}$$

where $\dot{n}_{C,i}$ and $\dot{n}_{C,f}$ are the carbon molar flows (kmol C·s^{-1}) in the net intermediate products (index i) and net feeds (index f), respectively.

Exergy efficiency

The exergy or energy "quality" of an energy or material flow is quantified as the maximum theoretical amount of mechanical work that can be generated by bringing it to an equilibrium state, usually defined as the environmental reference state, by a reversible process (Szargut *et al.*, 1988). In this study, the environmental reference state (P_0 and T_0) is set at 1.01325 bar and 25°C.

The exergy efficiency (η_{ex}) is defined (**Paper I**) as the ratio of the exergy content of the net useful products to the exergy content of the net required inputs, according to Eq. (4):

$$\eta_{ex} = \frac{\sum_p \dot{n}_p \cdot e_p + \sum \dot{E}_{W-} + \sum \dot{E}_{Q-}}{\sum_f \dot{n}_f \cdot e_f + \sum \dot{E}_{W+} + \sum \dot{E}_{Q+}} \tag{4}$$

where $\dot{n}_p$ and $\dot{n}_f$ are the molar flows (kmol·s⁻¹), e_p and e_f are the corresponding exergy contents (MJ·kmol⁻¹) of the net products (index p) and net feeds (index f), respectively, $\dot{E}_{Q-}$ and $\dot{E}_{Q+}$ are the exergy content of the net useful thermal heat production and net useful thermal heat demand (MW), respectively, and $\dot{E}_{W-}$ and $\dot{E}_{W+}$ are the exergies of the net power production and net power demand (MW), respectively. Similar to the energy efficiency, exergy efficiency is based on net flows (i.e., a given energy stream is considered either as a product from or a feed into the system).

The exergy content of a product or feed stream (e_i) is equal to the sum of its chemical, physical, kinetic, and potential exergies. The kinetic and potential exergies can usually be neglected, as their variability is null or negligible compared to that of the remaining terms. The values and group contributions for the standard chemical exergies of the components in the reference state (MJ·kmol⁻¹) are tabulated in Szargut *et al.* (1988). For biomass, the chemical exergy is estimated from its elemental composition and heating value, as described by Szargut *et al.* (1988).

3.4.2 Global Greenhouse Gas (GHG) Emissions Balances

The environmental performance indicator used in this study (**Paper II** and **Paper IV**) is the GHG emissions reduction potential ($E_{Reduction}$) of switching fossil-based processes to biomass-based processes by introducing drop-in bio-chemicals to existing value chains. The conventional fossil-based processes are used as reference cases.

A life cycle approach is applied. Thus, to account for both on-site and off-site GHG emissions effects that are associated with the processes in the global GHG emission balances, the considered system boundary is expanded. The considered GHG emissions sources are those that cross the system boundary of the "expanded system", as shown in

Figure 5. All included emissions are considered to be $CO_{2,eq}$, i.e., considering CO_2, methane, and N_2O in accordance with their respective GWP over a 100-year period[6].

This approach implies that cradle-to-gate emissions (i.e., those associated with extraction and transportation to the plant battery limit) are considered. In this work, indirect impacts, such as changes caused to the carbon stock by utilising forest residues, are not taken into account. To account for the introduction of biogenic carbon to the system, CO_2 uptake associated with photosynthesis during biomass growth is included. Consequently, all process-related and combustion-related emissions (of both fossil and biomass origin) are included. The final use of the fossil- and biomass-based products (which in the case of chemicals is particularly difficult to define due to the infinite number of applications) is assumed to be identical. In this way, emissions associated with the end-use do not affect the results when comparing the changes in GHG emissions between the biomass-based concepts and the fossil reference case. The final use for the considered products is not considered and is beyond the expanded system boundary.
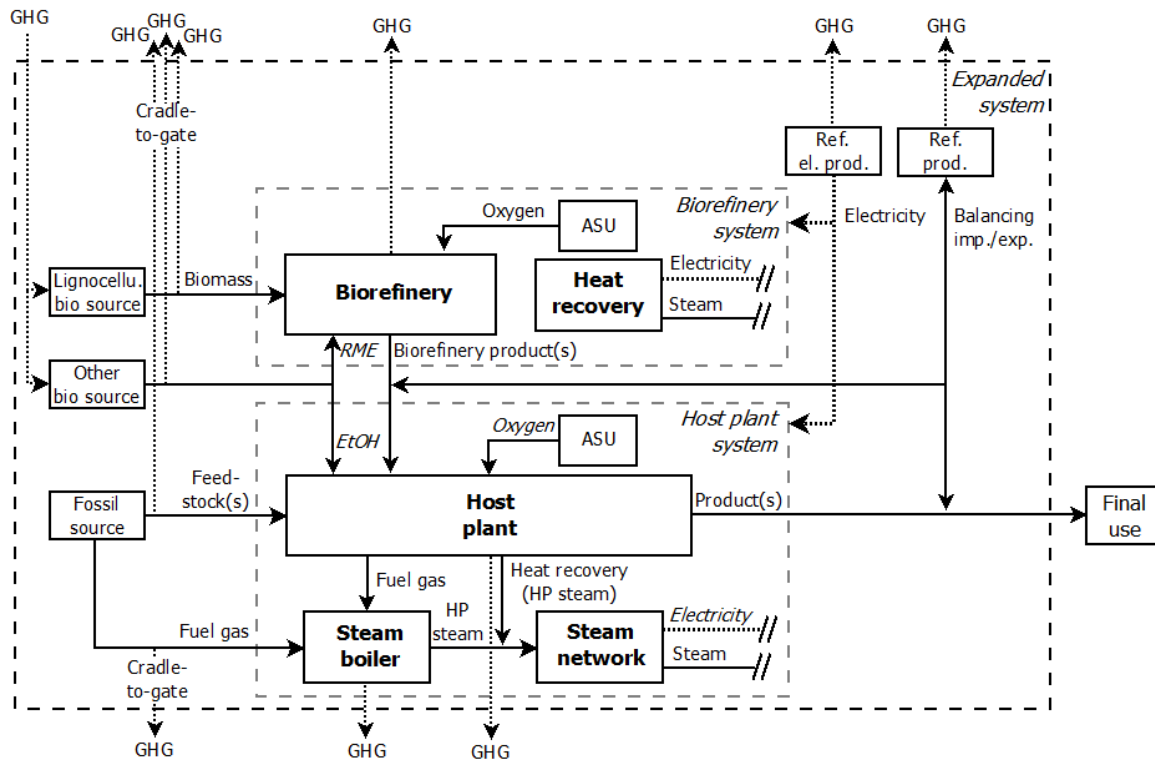
Figure 5. General overview of the system expansion approach applied in the GHG emissions balance evaluation. The materials and energy streams indicated in italics are only relevant for one of the case study plants.

Regarding the changes in the net import of electricity at the site, the electricity generation in a reference base-load grid power plant is assumed to be affected. In this study, the

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[6] GWP conversion factors: CO_2 = 1 CH_4 = 25, and N_2O = 298 (Forster *et al.*, 2007).

reference grid power plant from a European perspective is assumed to be a fossil fuel-fired condensing power plant (Sköldberg *et al.*, 2006), which is represented by modern, highly efficient coal power plants (coal PP) with (low-emitting) and without (high-emitting) carbon capture and storage (CCS); for information on specific GHG emissions refer to Table 1. Using this approach, a wide range of electricity mixes can be assumed to be covered.

Table 1. Specific GHG emissions (electricity basis) with coal-fired grid power generation technologies (in Year 2030).

Reference grid technology	coal PP	coal PP with CCS
GHG emissions (kg $CO_{2eq} \cdot MWh^{-1}$)[a]	816	273

[a] Based on GHG emissions associated with coal utilisation (Gode *et al.*, 2011; Uppenberg *et al.*, 2001). Assumed electric efficiencies (for Year 2030) are based on Odenberger et al. (2008). A CO_2 capture efficiency of 88% is assumed for the CCS technology (Axelsson and Pettersson, 2014).

The comparison is conducted by considering a fixed level of products, i.e., both from the syngas production unit to the downstream oxo synthesis plant (**Paper I** and **Paper II**) and for the crude light olefin production cases (**Paper III** and **Paper IV**). To account for variations in production, a fossil-based reference production site is assumed to be affected.

The GHG emission reduction potential ($E_{Reduction}$) is estimated according to Eq. (5):

$$E_{Reduction} = e_{Fossils} + e_{FuelGas} + e_{Process} + e_{Biomass} + e_{NetEl} \qquad (5)$$

where,

$E_{Reduction}$ is the potential reduction of GHG emissions released to the atmosphere; where a positive value corresponds to reduced emissions compared with the fossil reference case.

$e_{Fossils}$ is the avoided (positive value) cradle-to-gate emissions due to reduced use of fossil feedstock(s)[7].

$e_{FuelGas}$ is the change [i.e., avoided (positive value) or increased (negative value)] in cradle-to-gate and combustion emissions due to reduced or increased fuel gas import to the host plant steam boiler.

$e_{Process}$ is the change [i.e., avoided (positive value), increased (negative value), or unchanged (zero)] in host plant process-related emissions; this

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[7] Note that in this factor, the change (i.e., increased import (negative value) or avoided import/increased export (positive value)) of emissions related to balancing the product mix affecting a fossil-based reference production site (**Paper II** and **Paper IV**) are included.

includes all on-site emission changes not accounted for by the change in fuel gas import.

$e_{Biomass}$ is the net GHG emissions reduction potential contribution (positive value) from the introduced biomass feedstock[8]; it includes CO_2 uptake, cradle-to-gate emissions, and biorefinery process-related emissions.

e_{NetEl} is the change [i.e., increased import (negative value) or avoided import (positive value)] in emissions related to changes in the site's net electricity import produced in a fossil-based reference grid power plant.

Note that Eq. (5) is in a general form, i.e., without a pre-defined functional unit. Note also that the reported GHG emissions reduction potentials can be illustrated using a break-down categorisation to highlight interesting case-specific features, i.e., not strictly following the categorisation applied in Eq. (5).

The resulting GHG emissions reduction potential can be expressed using a number of different functional units, depending on the goal and scope. The objective in **Paper II** is to compare two different drop-in approaches to replacing the same final product (i.e., syngas) in the production of oxo products (assumed to be primary aldehydes). By applying the expanded system boundary, one product (oxo product) could be isolated, and the functional unit for the comparison could be defined on a per-mass (t) output basis. The objective in **Paper IV** is to evaluate partial feedstock-switching options for the production of light olefins. In this case, however, a single product could not be isolated by applying the expanded system boundary due to the diverse set of products obtained from the cracking process. Therefore, in this case, the functional unit for the comparison is defined on a per-year (y) basis. An alternative approach could be to allocate the GHG emissions reduction potentials to the different products, e.g., based on energy content.

3.4.3 Economic Evaluation

The economic performance indicator used in this work (**Paper II**) is the change in specific production cost (ΔSPC) of switching to biomass-based production relative to that of the fossil route (Base Case). The ΔSPC, on per-mass (t) basis, for producing oxo products from biomass-derived syngas compared with fossil-derived syngas is based on the annual incremental capital investment and changes in the fixed and variable operating costs, and it is estimated according to Eq. (6):

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[8] Note that in this factor, the net GHG emissions reduction potential impacts (negative values) related to the introduced RME import (which is eventually combusted) (**Paper II**) and the reduced import of ethanol (which is further processed to ETBE) (**Paper IV**) are included.

$$\Delta SPC = \big[a \cdot C_F + C_{O\&M} + C_{lb}$$
$$+ \big(\dot{E}_{BIO} \cdot p_{BIO} + \dot{E}_{EL} \cdot p_{EL} - \dot{E}_{NG} \cdot p_{NG} - \dot{E}_{FG} \cdot p_{FG} - \dot{E}_{H2}$$
$$\cdot p_{H2} \big) \cdot t - \dot{m}_{CO_2} \cdot p_{CO_2} \big] / \dot{m}_{oxo\ product} \qquad (6)$$

where a is the annuity factor (y^{-1}), C_F is the incremental capital investment (€), $C_{O\&M}$ is the change in operation and maintenance (O&M) costs (€), C_{lb} is the change in labour cost (€), $\dot{E}_i$ is the change in the energy/material flow i (MW), which includes biomass import (BIO), change in net electricity import (EL), avoided NG import (NG), avoided fuel gas import (FG), and avoided hydrogen import (H_2), $\dot{m}_{CO_2}$ is the avoided annual on-site fossil CO_2 emissions (t $CO_2 \cdot$y^{-1}), p_i is the price of the energy/material flow i (€$\cdot$MWh^{-1}), which includes biomass (BIO), electricity (EL), NG (NG), fuel gas (FG), hydrogen (H_2), and on-site fossil CO_2 emissions (CO_2), t is the operating time (h y^{-1}), and $\dot{m}_{oxo\ product}$ is the annual production level of oxo products (t$\cdot$y^{-1}).

The incremental capital investments (C_F) are estimated using the factorial approach described by Smith (2005), which is based on the delivered equipment cost at a base rate for the different process units. The accuracy range for estimating the capital investment using the factorial approach is ±30% (Smith, 2005). The changes in fixed operating costs are estimated from the changes in O&M costs ($C_{O\&M}$) and changes in labour costs (C_{lb}), which are estimated based on the total capital investment and the required number of man-hours, respectively. The general economic assumptions applied in the annual capital investment and fixed operating cost estimations are listed in Table 2. The changes in variable operating costs are estimated from the changes in material and energy flows and on-site fossil-derived CO_2 emissions. Note that the import of light olefins required for the production of oxo products (refer to Figure 7) is fixed in the analysis (regardless of syngas origin) and consequently, the relative change from the Base Case is zero.

Table 2. General economic assumptions.

Parameter	Value
Annuity factor (a)	0.1 y^{-1}
Operating hours (t)	8000 h$\cdot$y^{-1}
O&M costs	5% of the tot. cap. inv.

It is crucial to base the economic evaluation on realistic costs for the feedstock and energy commodities. The prediction of future energy market conditions (i.e., future prices for chemical feedstock, energy commodities, and policy instruments) is a complex task. In this analysis, the economic assessment is conducted for possible energy market scenarios for Year 2030 (which is assumed to be a representative operating year for the considered investments). Prices for fossil fuels (i.e., natural gas and coal) and CO_2 emission charges are obtained from two of the scenarios reported in the IEA's 2013 World Energy Outlook

(WEO): the current policies scenario[9] (denoted as WEO current policies); and the 450 ppm scenario[10] (denoted as WEO 450 ppm) (IEA, 2013).

Based on fossil fuel prices and assumed policy instruments, the prices of biomass and electricity are projected using the Energy Price and Carbon Balance (ENPAC) tool (Axelsson and Harvey, 2010; Axelsson and Pettersson, 2014). The biomass price is projected by estimating the willingness to pay for low-grade woody biomass (such as forest residues) assuming co-firing in coal PPs as the marginal price-setting user. The electricity price is projected by estimating the production cost of electricity, assuming coal PP and coal PP with CCS as the base load build margin technology for the WEO current policies and WEO 450 ppm scenarios, respectively.

In this analysis, the only policy instrument that is considered is the CO_2 charge, which is assumed to be harmonised across the different sectors. The CO_2 emissions considered in the economic evaluation comprise the on-site fossil CO_2 emissions (see Table 4). Note that few policy instruments have been developed, e.g., in the form of subsidies, for the chemical sector. The price of hydrogen is estimated based on the hydrogen levelised costs reported by the US Department of Energy (US DOE) (Dillich *et al.*, 2012).

The projected prices for the chemical feedstock, energy commodities, and CO_2 charge for the two WEO scenarios are summarised in Table 3. In the variable operating cost estimation, the cost for oxygen is assumed to be included in the electricity cost and the cost for scrubbing media is assumed to be included in the O&M costs. For the detailed calculation assumptions and relevant references, see **Paper II**.

Table 3. Projected prices for material and energy flows and CO_2 emission charges.

Variable	Unit (basis)	Price	
		WEO current policies	WEO 450 ppm
Biomass price (p_{BIO})	€·MWh^{-1} (HHV)	13	26
Electricity price (p_{EL})	€·MWh^{-1} (el.)	63	78
NG & FG price[a] (p_{NG} & p_{FG})	€·MWh^{-1} (HHV)	41	32
Hydrogen price (p_{H_2})	€·MWh^{-1} (HHV)	145	148
CO_2 charge (p_{CO_2})	€·t^{-1} (CO_2)	19	74

[a] Excluding the CO_2 charge.

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[9] Only policies enacted by mid-2013 are considered.
[10] The implementation of policies required to attain 50% probability to limit the long-term increase in average global temperature to 2°C is assumed.

4
Studied Processes

This chapter presents an overview of the site of the chemical complex in general and the selected case study of host industries in particular. Moreover, a description of the studied concepts regarding the gasification-based biorefinery is provided.

4.1 Case Study – Chemical Complex

A chemical process complex of large size (by Swedish standards) located in Stenungsund on the west coast of Sweden has formulated a joint vision called "Sustainable Chemistry 2030", which aims to switch progressively to renewable feedstocks and to decrease overall GHG emissions. The chemical complex site is the largest agglomeration of its kind in Sweden and consists of six different process sites: an ASU (producing industrial gases); an amines and surfactants plant; a steam cracker plant (producing e.g., light olefins); a polyethylene plant; a polyvinyl chloride (PVC) plant; and an oxo synthesis plant (producing specialty chemicals). Figure 6 shows an overview of the material and energy flows at the chemical complex site. The steam cracker plant is at the core of the complex, supplying feedstocks, such as light olefins and hydrogen, as well as fuel gas to the neighbouring sites. The chemical complex site also imports ethylene and natural gas, whereby the latter is used for both fuel and feedstock purposes.

The annual level of CO_2 emissions from the chemical complex is approximately 900 kt CO_2 (Naturvårdsverket, 2016). The steam cracker plant is the single major emission source, accounting for approximately 70% of the total CO_2 emissions of the complex. The second largest emitter is the oxo synthesis plant, which is responsible for approximately 10%–15% of the total emissions at the complex site. Note that the reported values are limited to CO_2 emissions and moreover, they only describe the on-site emissions.

As shown in Figure 6, several opportunities to substitute flows of fossil origin with drop-in bio-chemicals exist within the chemical complex site. The steam cracker plant and the oxo synthesis plant, which are identified as key plants for the targeting of decarbonisation plans for the chemical complex site (combined, they account for approximately 80%–85% of the total CO_2 emissions from the complex site), were selected as case study sites for the integration of gasification-based biorefinery concepts in this thesis. Another important

detail, not shown in Figure 6, is that syngas production (currently based on partial oxidation of natural gas) is an essential process in the oxo synthesis plant.
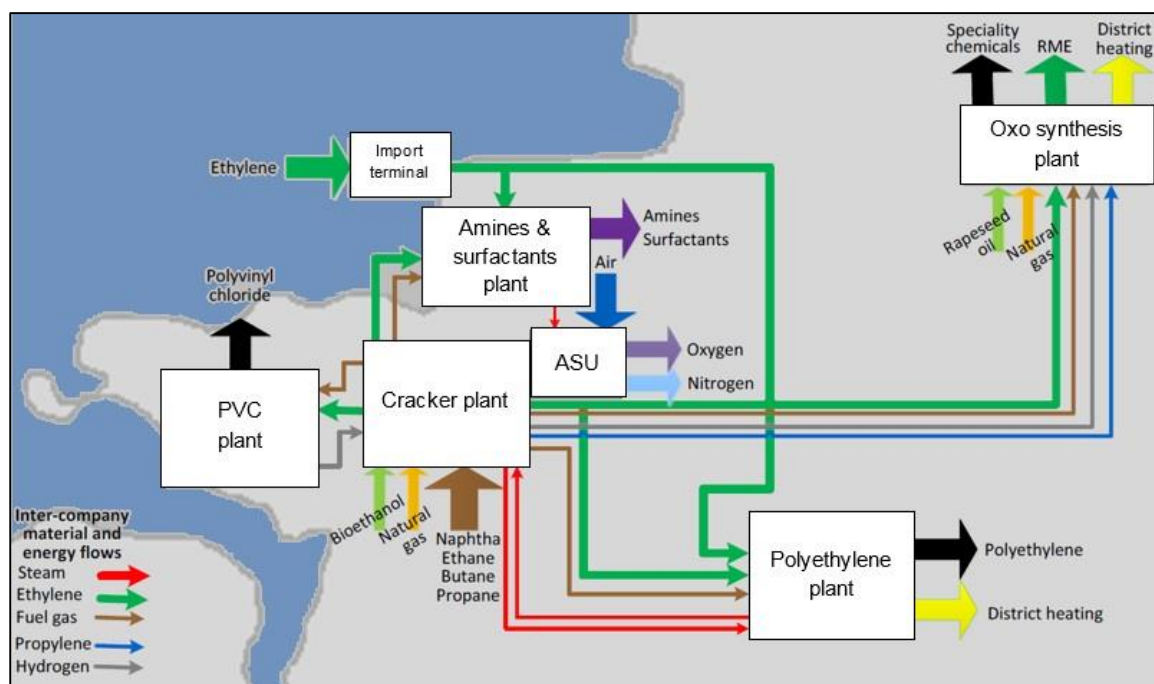

Figure 6. Overview of the chemical complex site in Stenungsund. Adapted from Jönsson *et al.* (2012).

4.1.1 Conventional Oxo Synthesis Plant

A wide spectrum of bulk as well as high-value specialty chemicals can be produced *via* oxo synthesis. There are many applications of established oxo products, such as pharmaceuticals, paints, solvents in coatings, resins and dyes, specialty plasticisers, synthetic lubricants, safety glass, animal feedstuffs, and crop preservatives. In 2009, the total annual worldwide oxo production capacity for aldehydes and alcohols was approximately 12 Mt (Bahrmann *et al.*, 2013).

During oxo synthesis, olefins (i.e., unsaturated hydrocarbons) react with syngas (CO and hydrogen) in the presence of a homogeneous catalyst (e.g., cobalt or rhodium complexes) to form aldehydes. The olefin carbon chain is thereby extended by one carbon atom. Oxo synthesis, or hydroformylation, can be described by the following reaction (Matar and Hatch, 2001):

$$2RCH=CH_2 + 2CO + 2H_2 \rightarrow RCH_2CH_2\overset{\overset{O}{\|}}{C}H + RCH-\overset{\overset{O}{\|}}{C}H \qquad \text{(R1)}$$
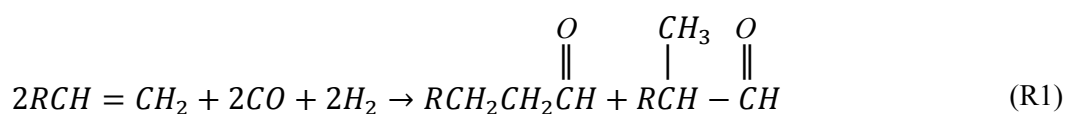
The oxo products usually range from C_3 to C_{19}, of which butyraldehyde is the predominant species, accounting for approximately 75% of the total global production (Bahrmann *et al.*, 2013). Oxo synthesis (R1) is an exothermic reaction and, as R1 implies, the applied H_2/CO

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ratio is usually around 1. Typically, commercial oxo synthesis is conducted in stirred-tank reactors, operating at 60°–130°C and 15–100 bar (rhodium-based catalysts), with high overall aldehyde selectivity, high selectivity for unbranched aldehyde products (or high *normal:iso* ratio), and low-level hydrogenation (Bahrmann *et al.*, 2013).

The primary aldehydes can subsequently be reacted to generate a wide spectrum of different secondary products, such as other aldehydes, alcohols and carboxyl acids. Secondary aldehydes can be created by so-called 'aldol condensation' followed by hydrogenation. Alcohols are formed by catalytic (e.g., with copper or nickel) hydrogenation of the corresponding aldehyde. Carboxylic acids are formed by (catalytic or non-catalytic) oxidation of the corresponding aldehyde.

A general overview of the main material flows in the case study oxo synthesis plant (**Paper I** and **Paper II**) is illustrated in Figure 7. The production of oxo products at the studied site is approximately 360 kt per year[11]. As shown in Figure 7, the first conversion step at the site involves the production of syngas. Originally, the syngas was produced at the site by partial oxidation of oil feedstock. In 2004, the oil was replaced by natural gas when the plant connected to the West Swedish natural gas grid. Oxygen is produced in an ASU located in another cluster plant. Light olefins are imported (ethylene:propylene ratio of around 1:8) from the neighbouring steam cracker plant. At the case study plant, the primary aldehydes can be further processed into other aldehydes, alcohols, and carboxyl acids (see Figure 7). The site's hydrogen demand is covered by hydrogen produced in the syngas production (owing to a higher-than-required fraction of hydrogen in the syngas) and additional hydrogen imports from the stream cracker plant.
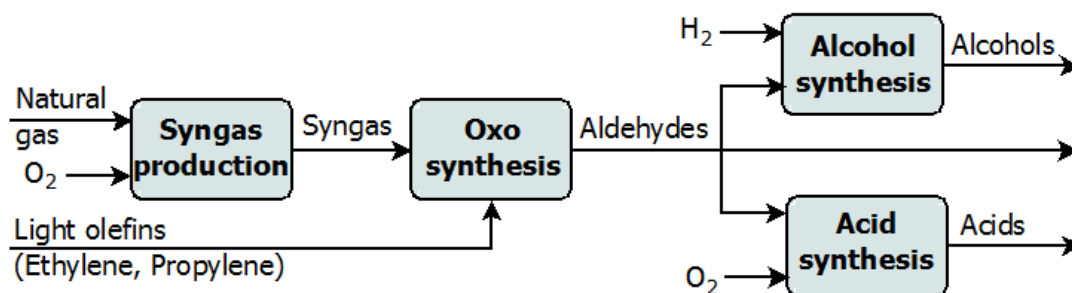

Figure 7. General overview of main material flows in the case study oxo synthesis plant.

As shown in Figure 7, the oxo synthesis plant involves several (exothermic) reaction steps. The oxo synthesis plants also involves several separation operations, e.g., absorption, adsorption, vapour-liquid separation, distillation, decanting, and evaporation. From the separation steps, various energy-containing by-product streams are obtained, which are

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[11] The oxo synthesis plant is product-flexible which implies that the primary aldehydes (from the oxo synthesis step) can be further reacted to several different final products depending on market and demand. In this thesis, the "oxo product" refers to the resulting primary aldehyde production (i.e., propionaldehyde and butyraldehyde).

subsequently fired in the steam boilers available on-site. The oxo synthesis plant steam network consists of several pressure levels connected by let-downs. High-pressure (HP) steam (at 41 bar) is produced by heat recovery during syngas production (through process cooling of the hot raw syngas) and by the firing of by-product fuel gas and (when required) the firing of purchased fuel gas and natural gas fuel in steam boilers. The net steam demand at the oxo synthesis site (i.e., for which extra fuel gas needs to be purchased) is estimated at 20 MW of the low-pressure (LP) steam (at 3 bar). The amount of electricity imported at the oxo synthesis site is approximately 10 MW (Perstorp Holding AB, 2010).

The Base Case for syngas production is determined from the specified flows of natural gas (Table 4). The produced syngas must satisfy the requirements for downstream oxo synthesis (in terms of H_2/CO ratio and molar purity). In addition, the current hydrogen import and net LP steam demand are considered. The material and energy streams exchanged between the syngas production plant and the other oxo synthesis plant units (i.e., syngas, hydrogen, tail gas, LP and HP steam, and off-gases) are specified accordingly. The Base Case results determine the design specifications for the biorefinery cases. For detailed descriptions, refer to **Paper I**.

4.1.2   Conventional Steam Cracker Plant

The bulk production of the two largest (in terms of volume) hydrocarbon intermediates in the chemical industry, ethylene and propylene, is based on thermal steam cracking or pyrolysis (Zimmermann and Walzl, 2012; Eisele and Killpack, 2012). Ethylene and propylene are highly reactive intermediates that can be used for many applications, such as in the production of plastics (where polymerisation accounts for more than half of the usage), textiles, detergents, pharmaceuticals, paints, solvents, cosmetics, speciality plasticisers, synthetic lubricants, foams, rubber, and various specialty oxo products.

During thermal steam cracking, the feed hydrocarbon is degraded to shorter and/or more unsaturated molecules by breaking the carbon-carbon bonds and/or carbon-hydrogen bonds in the absence of a catalyst. The complex cracking reactions can generally be described by three main steps: initiation; propagation; and termination (Zimmermann and Walzl, 2012). During initiation, radicals (where, "•" in R2 to R5 symbolises an electron) are formed according to the following reactions:

$$R_1R_2 \rightarrow R_1 \bullet + R_2 \bullet \tag{R2}$$

$$RH \rightarrow R \bullet + H \bullet \tag{R3}$$

The propagation step comprise reactions that involve radicals. There are many possible propagation reactions, both desirable and undesirable, for example:

$$R_3\text{-}C\text{-}C \bullet \rightarrow R_3 \bullet + C = C \tag{R4}$$

$$R_3\text{-}C\text{-}C \bullet \rightarrow R_3 = C + C \bullet \tag{R5}$$

The termination step involves reactions in which two radicals form stable molecules (e.g., the reverse reactions for R2 and R3)

Typically, commercial steam cracking is carried out in fired tubular reactors, operating at 750°–875°C, with controlled residence time (0.1–0.5 s), temperature profile, and partial pressures, to achieve the desired product mix (Zimmermann and Walzl, 2012).

A general overview of the main material flows in the case study steam cracker plant described in **Paper III** and **Paper IV** is illustrated in Figure 8. The annual production of light olefins at the studied site is approximately 825 kt[12]. As shown in Figure 8, the steam cracker plant basically involves a key conversion step, i.e., the cracking of various fossil hydrocarbons, followed by a very complex and energy-intensive separation and upgrading scheme. At the case study site, cracking is conducted in several parallel cracking furnace units. Some of these units are dedicated to a specific feedstock, such as ethane, propane, butane, and naphtha, while others are feedstock-flexible. The furnace feeds are mixed with diluting medium-pressure (MP) steam (at 10 bar). The heat required for the endothermic cracking reactions is provided by firing a hydrogen- and methane-rich fuel gas, which is a by-product of the cracking itself.
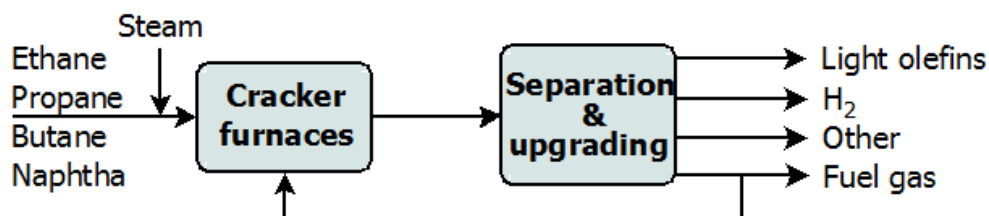

Figure 8. General overview of the main material flows in the case study steam cracker plant.

A wide range of cracking products is retrieved from the subsequent separation and upgrading step, which includes quenching, primary fractionation, compression, a caustic wash, a stripper, dryers, reactors, and several distillation columns. Cracker products "other" than light olefins, hydrogen, and fuel gas (as indicated in Figure 8) include: carbon black feedstock (CBFS); steam cracked naphtha (SCN): and ethylene-tert-butyl-ether (ETBE).

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[12] The steam cracker plant is feedstock-flexible, generating various product mixes, whereby the feedstock (and to some extent, the products) can be altered depending on the market and demand (within the cracker furnace and separation capacity limits). In general, the operating conditions are set so as to maximise ethylene production. In this thesis, the term 'light olefins' refers to the combined production of ethylene, propylene, and butylenes, whereby the latter is a mixture of mainly C_4 olefins and butane (sometimes referred to as 'Raff 2').

As mentioned above, fuel gas is an additional by-product that is primarily used in the cracker furnaces and steam boilers available on-site and exported to neighbouring sites. Unreacted ethane and propane are recycled to the cracker or used as fuel gas (not indicated in Figure 8). The cracker plant steam network consists of several pressure levels, which are connected by various turbines and let-downs (see **Paper III**). HP steam (at 86 bar) is produced through heat recovery in the cracker process (process cooling of the hot cracked gas) and by the firing of fuel gas and purchased natural gas fuel (when required) in the steam boilers. Several of the cracker plant compressors and pumps are steam turbine-driven, requiring HP or MP steam. Other steam requirements include HP steam export to other site users, diluting MP steam, and various process heaters. Steam can also be expanded in a turbo-generator. The net import of electricity for the steam cracker site is approximately 42 MW (Borealis AB, 2011).

4.2 Biorefinery Concepts – Syngas Production

Figure 9 presents a general overview of the different process steps in a gasification-based biorefinery. The choice of technology for each step very much depends on the choice made for each other step. The following sections focus on describing the key conversion steps, i.e., the thermochemical gasification (see Section 4.2) and the synthesis (see Section 4.3), included in this thesis work. For more detailed information, see **Paper I**, **Paper III**, and **Paper V**.
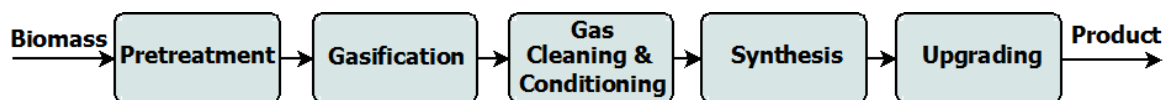

Figure 9. General process scheme for a gasification-based biorefinery.

Several different reactor types are used for biomass gasification (refer to Section 2.2). Different gasification technologies and operating conditions result in raw syngases of different qualities, in terms of gas composition, gas purity, and heating value.

For the studies described in **Paper I** and **Paper II**, syngas production (for both the bio-SNG process and the direct bio-syngas process) is assumed to be similar to the that in the GoBiGas phase 1 layout, i.e., based on atmospheric indirect steam gasification and rapeseed methyl ester (RME)-based tar scrubbing. This set-up can be assumed to generate an essentially nitrogen-free syngas with some initial methane (10 vol-%, dry gas) content (Hofbauer and Rauch, 2001). In the case of direct bio-syngas production, the methane content is reformed in an autothermal reformer (ATR).

In **Paper III** and **Paper IV**, the production of syngas is based on previous work (Isaksson *et al.*, 2012; Morandin and Harvey, 2015) , which involved pressurised oxygen steam-blown direct CFB gasification, similar to the concept proposed by the VTT Technical Research Centre of Finland (Hannula and Kurkela, 2012). The tar and methane contents of

the raw syngas are reformed in an advanced CFB catalytic reformer and an ATR, respectively.

The syngas production described in **Paper V** is based on work conducted within the settings of the Swedish "Forest chemicals" ("*Skogskemi*") project (Morandin and Harvey, 2015). The concept entails torrefaction followed by pressurised entrained flow gasification. Data regarding the torrefaction step were adapted from Nordin *et al.* (2014) and Prins (2005). This set-up can be assumed to result in a pressurised, practically tar-free, low-methane-containing syngas, in addition to a combustible fuel gas. The option of including a decentralised torrefaction arrangement is not included.

Prior to gasification, the incoming biomass is assumed to be dried from its initial moisture content (for which a typical value of 50 wt-% is assumed for forest residues) in a low-temperature air drier (Heyne and Harvey, 2009; Holmberg and Ahtila, 2005). The drying of the purchased forest residues is assumed to be co-located with the biorefinery in all the studied cases.

Depending on gasification technology and downstream applications and synthesis used, adjustments to the H_2/CO ratio may be necessary. If a higher content of hydrogen is required, the gas is shifted in a partial water-gas shift (WGS) reactor (see R6). If a lower content of hydrogen is required, the hydrogen is separated from the syngas and purified by means of an integrated membrane and pressure swing adsorption (PSA) unit (Doshi *et al.*, 1989).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad\qquad (R6)$$

Removal of CO_2 and sulphur is conducted by chemical absorption, using an amine wash (in **Paper I** and **Paper II**), a caustic wash (in **Paper V**), or physical absorption with organic solvents, such as methanol in the Rectisol process (in **Paper III**, **Paper IV**, and **Paper V**). This is also used in combination with chemical adsorption, using ZnO guard beds for trace sulphur removal, or physical adsorption, using activated carbon or zeolites for the removal of non-polar or polar compounds.

4.3 Biorefinery Concepts – Drop-in Bio-Chemical Production

In this thesis, different biorefinery concepts to produce the targeted drop-in bio-chemicals (syngas and light olefins) are considered.

4.3.1 Synthetic Natural Gas (SNG)

In the case of bio-SNG production, syngas is converted to a methane-rich gas. Methanation of syngas is conducted in either conventional adiabatic fixed-bed reactors in series or unconventional single isothermal fluidised bed reactors, according to the following reactions:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{R7}$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{R8}$$

where the methanation of CO_2 (R8) is essentially the linear combination of the methanation of CO (R7) and the WGS reaction (R6). As R7 implies, the applied H_2/CO ratio for the incoming syngas is generally approximately 3.

The SNG synthesis studied in **Paper I** and **Paper II** is achieved using conventional technology similar to that of the GoBiGas phase 1 layout, i.e., based on the Haldor Topsøe technology using three adiabatic fixed-bed reactors in series, operating at approximately 35 bar, with intercooling and a recycle step in the first reactor for temperature control (Harms *et al.*, 1980). To satisfy the specifications for injection to the natural gas grid or downstream synthesis, the gas undergoes a final drying step.

4.3.2 Syngas

The production of direct bio-syngas, studied in **Paper I** and **Paper II**, is set to match the energy content (MW HHV basis), H_2/CO specifications, and state (temperature and pressure) of the current fossil-based syngas produced at the oxo synthesis plant. The final H_2/CO ratio adjustment of the syngas results in a very pure hydrogen stream and tail gas, which are used in the downstream synthesis and steam boiler, respectively.

4.3.3 Light Olefins *via* Methanol

In the case of light olefin production *via* methanol, syngas is first converted to methanol, followed by methanol-to-olefins (MTO) synthesis. Methanol synthesis from syngas is conducted in either conventional adiabatic or quasi-isothermal gas-phase (i.e., fixed bed) or unconventional isothermal liquid-phase (i.e., slurry bed) reactors, according to the following reactions:

$$CO + 2H_2 \rightleftharpoons CH_3OH \tag{R9}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \tag{R10}$$

where the hydrogenation of CO_2 (R10) is essentially the linear combination of the hydrogenation of CO (R9) and the WGS reaction (R6). For optimal methanol synthesis, the molar composition of the incoming syngas can be characterised by the stoichiometric number [SN = (H_2 - CO_2) / (CO + CO_2)], which should range from 2 to 2.05 (Ott *et al.*, 2012).

The MTO process involves a very complex reaction scheme. In brief, the MTO process involves the conversion of methanol into DME and thereafter into mainly light olefins, according to the following simplified reactions (Chang and Silvestri, 1977):

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \tag{R11}$$

$$CH_3OCH_3 \rightarrow Light\ olefins + other \tag{R12}$$

Where the term *other* in R12 includes alkanes, light gases, coke, and water. The overall carbon selectivity for C_2 to C_4 olefins is approximately 90%, and the ethylene/propylene ratio can range from 0.7 to 1.4 depending on the process conditions and catalyst used (Vora *et al.*, 2001).

The methanol synthesis studied in **Paper III** and **Paper IV** (Morandin and Harvey, 2015), is carried out using conventional technology, i.e., in a quasi-isothermal gas-phase reactor operating at 250°C and approximately 85 bar, with a syngas recirculation ratio of 3. Water-free methanol is achieved through distillation. The MTO process studied in **Paper III** and **Paper IV** (Johansson and Pettersson, 2014) involves a CFB reactor with continuous catalyst regeneration in a separate unit, operating in high-propylene mode, in similarity to the UOP/Hydro technology (Vora *et al.* 2001). Upgrading of the crude-MTO stream is conducted in the existing separation equipment at the cracker plant.

The methanol synthesis studied in **Paper V** involves conventional technology, i.e., a quasi-isothermal gas-phase reactor operating at 260°C and 80 bar, with a syngas recirculation ratio set to achieve an overall CO conversion of 95%. The once-through conversion of CO is limited to 25% (Bertau *et al.*, 2014). No side-reactions are accounted for in this process. Separation and purification of the methanol stream is conducted by flashing and distillation. The MTO process studied in **Paper V** utilises a CFB reactor with continuous catalyst regeneration in a separate unit, operating in high-propylene mode at 430°C and 4 bar (Vora *et al.* 2001). The product recovery from the crude-MTO stream is conducted in an extensive separation sequence, very similar to that used in a conventional fossil-based olefin production process, and including a quench, a compressor, a stripper, a caustic wash, dryers, reactors, and several distillation columns. The various by-product streams produced during the light olefin process are assumed to be combusted in the boiler used for heat recovery.

4.3.4 Light Olefins *via* Dimethyl Ether (DME)

In the case of light olefin production *via* DME, syngas is converted to DME, and this is followed by DTO synthesis. Current commercial DME synthesis involves two separate steps: methanol synthesis from syngas, and methanol dehydration. One interesting emerging option is to bypass the methanol synthesis equilibrium limit by allowing for *in situ* dehydration. Thus, DME synthesis is conducted directly from syngas in a single step, in either gas-phase (i.e., fixed bed) or liquid-phase (i.e., slurry bed) reactors, according to the following reaction:

$$3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2 \tag{R13}$$

where direct DME synthesis (R13) is essentially the linear combination of the methanol synthesis (R9), methanol dehydration (R11), and the WGS reaction (R6). As R13 implies, the applied H_2/CO ratio for the incoming syngas in direct DME synthesis is usually approximately 1.

The DTO process is similar to the MTO process. In fact, Chang and Silvestri (1977) found that the only difference between methanol and DME conversion to olefins, to be the methanol dehydration, without effect on the hydrocarbon distribution.

The DME synthesis studied in **Paper V** comprises an isothermal slurry-bed reactor operating at 280°C and 50 bar, with a syngas recirculation ratio set to achieve an overall CO conversion of 95%. The once-through conversion of CO was limited to 53% (Ogawa *et al.*, 2003). In addition to DME, the production of methanol is accounted for in this process. Separation and purification of the DME stream is conducted by flashing and distillation. The DTO process studied in **Paper V** is similar to the MTO process, whereby the hydrocarbon distribution is assumed to be identical (Chang and Silvestri, 1977). Product recovery from the crude-DTO stream is also conducted in a similar fashion to that from the crude-MTO stream, and the various by-product streams are assumed to be combusted in the boiler used for heat recovery.

4.4 Utility System

In the case of integration with a heat recovery steam network as studied in **Paper I**, **Paper IV**, and **Paper V**, the steam turbine inlet data (maximum pressure of 100 bar and maximum temperature of 530°C are assumed) and steam extraction and turbine outlet pressures (minimum pressure of 0.1 bar is assumed) are set to match the corresponding background process steam pressure levels (based on the GCC shape and/or actual levels). The resulting condensate is pumped back to the desired turbine inlet pressure.

In the case of integration with a cascaded compression refrigeration cycle as studied in **Paper V**, the evaporator temperatures are set to match the corresponding background process refrigeration demands (based on GCC shape).

5 Overview of Main Findings

In this chapter, the key results from the appended papers are presented, commented upon, and summarised. The results are divided into two sections. The first section deals with the decarbonisation of an oxo synthesis plant, while the second is concerned with the decarbonisation of a steam cracker plant.

5.1 Decarbonisation of an Oxo Synthesis Plant

For decarbonisation of the oxo synthesis plant (**Paper I** and **Paper II**), two options towards fully substituting the currently natural gas-derived syngas are considered: (*i*) replacing the feedstock with biomass-derived SNG (BioSNG2Syngas); and (*ii*) replacing syngas directly with biomass-derived syngas (Bio2Syngas) (fulfilling the specifications for downstream oxo synthesis). The different biorefinery process concepts are compared for thermodynamic performance (**Paper I**), global GHG emissions balances, and process economics (**Paper II**). The current fossil-based syngas production is used as a reference in the comparisons (Base Case).

5.1.1 Process Models

This section presents the results from the process simulation models. Data for the conventional oxo synthesis plant based on fossil-derived syngas (Base Case) are listed in Table 4. Table 5 presents the calculated mass and energy balances for the investigated syngas production routes. Note that relevant energy flows are reported at HHV basis.

Base Case

In Table 4, data for the total supply to the oxo synthesis plant ("Total") are presented, and breakdown details are presented for the syngas production ("Syngas") and the other units at the oxo synthesis plant ("Oxo"). Oxygen and electricity flows to, and on-site fossil CO_2 emissions from, the syngas production unit, which are presented in Table 4, are estimates based on the mass and energy balance calculations presented in **Paper I**.

Table 4. Data for the conventional oxo synthesis plant based on fossil-derived syngas (Base Case). The values are reported as mass flow rate (energy flow rate) in kt per year (MW).

	Natural gas	Ethylene	Propylene	H$_2$	O$_2$[a]	Power[b]	Oxo product[c]	CO$_2$[d]
Syngas	95	-	-	5.7	124	-	-	54 (-)
	(175)	(-)	(-)	(28)	(6.9)	(3.9)	(-)	
Oxo	-	24	190	-	21	-	364	30 (-)
	(-)	(42)	(322)	(-)	(1.2)	(6.1)	(-)	
Total	95	24	190	5.7	145	-	364	84 (-)
	(175)	(42)	(322)	(28)	(8.1)	(10)	(-)	

[a] The oxygen demand for the syngas production is estimated in **Paper I**. The energy flows (in MW) for the oxygen flows, which correspond to the power consumption to support production in an ASU, are added to the electricity demand reported in the "Power" column.

[b] The total electric power demand is based on the reported average annual values (Perstorp Holding AB, 2010), and the electricity demand of the syngas production unit is estimated in **Paper I**. The electricity demands listed here do not include the power demand for oxygen production, which is listed separately as an energy flow rate in the "O$_2$" column.

[c] The annual production of oxo products (assumed as primary aldehydes) is estimated by closing the carbon balance of the oxo synthesis plant; see **Paper II**.

[d] The total of the on-site CO$_2$ emissions is based on the reported average annual values (Perstorp Holding AB, 2010). The on-site CO$_2$ emissions from syngas production include CO$_2$ that is separated during processing (estimated in **Paper I**) and CO$_2$ emissions from the LP steam boiler [based on usage-related emissions (Gode *et al.*, 2011)]. The on-site CO$_2$ emissions from other units at the oxo synthesis plant are estimated by closing the carbon balance; approximately 45% of the incoming carbon originates from syngas or tail gas and the remaining 55% originates from olefins (**Paper II**).

The results for the conventional syngas process (Base Case) determine the size specifications for the investigated biorefinery concepts. The results show that by processing 175 MW of natural gas (and 2.4 MW of off-gases), the Base Case delivers 115 MW of syngas, 29 MW of hydrogen, and 6.7 MW of tail gas to the downstream oxo synthesis plant (Table 5). The electricity demand, which includes the power required for oxygen production, of the Base Case is estimated at 11 MW. To cover the oxo synthesis plant's net LP steam demand (20 MW), 27 MW of fuel gas must be imported. In addition, 28 MW hydrogen is imported (not indicated in Table 5).

Decarbonisation options

For the route that entails intermediate bio-SNG production (BioSNG2Syngas), the results show that 262 MW of biomass are required to substitute completely the natural gas feed (175 MW). For the direct route to syngas (Bio2Syngas), the results show that 216 MW of biomass (and 2.4 MW of off-gases) are required to satisfy the syngas requirements of the oxo synthesis plant (115 MW). In addition, RME is required for gas cleaning in both cases. The hydrogen and tail gas production levels of the direct bio-syngas process are slightly higher than those for the Base Case (+2.5 MW and +0.5 MW, respectively). Thus, the amount of hydrogen that must be imported can be decreased by the corresponding amount.

The extra tail gas can be utilised for other purposes, e.g., for LP steam production. The amount of oxygen required in the gas conditioning and clean-up section (ATR) corresponds to 40% of the oxygen demand in the Base Case.

Table 5. Summary of the results for the investigated syngas production routes (in MW).[a]

		Base Case	BioSNG2Syngas		Bio2Syngas	
			Case El	Case LP	Case El	Case LP
Input						
Natural gas	(en)	175	0 (-175)	0 (-175)	0 (-175)	0 (-175)
	(ex)	165	0 (-165)	0 (-165)	0 (-165)	0 (-165)
Off-gases	(en)	2.4	2.4 (0)	2.4 (0)	2.4 (0)	2.4 (0)
	(ex)	2.3	2.3 (0)	2.3 (0)	2.3 (0)	2.3 (0)
Biomass	(en)	-	262 (+262)	262 (+262)	216 (+216)	216 (+216)
	(ex)	-	277 (+277)	277 (+277)	228 (+228)	228 (+228)
RME	(en)	-	4.2 (+4.2)	4.2 (+4.2)	3.5 (+3.5)	3.5 (+3.5)
	(ex)	-	4.2 (+4.2)	4.2 (+4.2)	3.5 (+3.5)	3.5 (+3.5)
Fuel gas	(en)	27	27 (0)	0 (-27)	27 (-0.4)	9.4 (-18)
	(ex)	26	26 (0)	0 (-26)	26 (-0.4)	8.9 (-17)
Power (net)		11	11 (+0.2)	14 (+3.1)	10 (-0.8)	21 (+9.7)
Production						
Syngas	(en)	115	115 (0)	115 (0)	115 (0)	115 (0)
	(ex)	105	105 (0)	105 (0)	105 (0)	105 (0)
Hydrogen (net)	(en)	29	29 (0)	29 (0)	31 (+2.5)	31 (+2.5)
	(ex)	24	24 (0)	24 (0)	26 (+2.1)	26 (+2.1)
Tail gas (net)	(en)	6.7	6.7 (0)	6.7 (0)	6.7 (0)	6.7 (0)
	(ex)	5.8	5.8 (0)	5.8 (0)	5.8 (0)	5.8 (0)
HP steam	(en)	16	16 (0)	16 (0)	16 (0)	16(0)
	(ex)	6.8	6.8 (0)	6.8 (0)	6.8 (0)	6.8 (0)
LP steam	(en)	20	20 (0)	20 (0)	20 (0)	20 (0)
	(ex)	5.3	5.3 (0)	5.3 (0)	5.3 (0)	5.3 (0)

[a] The energy (en) and exergy (ex) flows are reported as absolute values. The change in value compared with the Base Case is reported in parenthesis. For the flows that appear as both inputs and outputs, only the net demand or production is reported and denoted as (net).

5.1.2   Energy Targeting

This section presents the results from the energy targeting analysis and the consequences of the eventual use of recovered process heat for the overall energy balances (Table 5).

Base Case

The target for HP steam production in the Base Case is estimated as 16 MW (refer to split-GCC in **Paper I**).

Decarbonisation options

Pinch analysis indicates high levels of high-temperature excess heat and a large heat pocket in the two biomass-based processes (see split-GCC for the bio-SNG process in Figure 10 and the split-GCCs in **Paper I**). By integrating a heat recovery steam cycle, the heat pocket and the high-temperature excess heat can be exploited for the co-generation of heat and power. The high-temperature excess heat can be alternatively recovered for the production of useful thermal heat (LP steam). The eventual usage of the recovered process heat affects the levels of electricity and fuel gas imports to the oxo synthesis plant. Targeting for maximum electricity production (Case El) minimises the level of electricity imported to the overall system, whereas targeting for prioritised export of LP steam (Case LP) decreases the amount of fuel gas that needs to be imported.
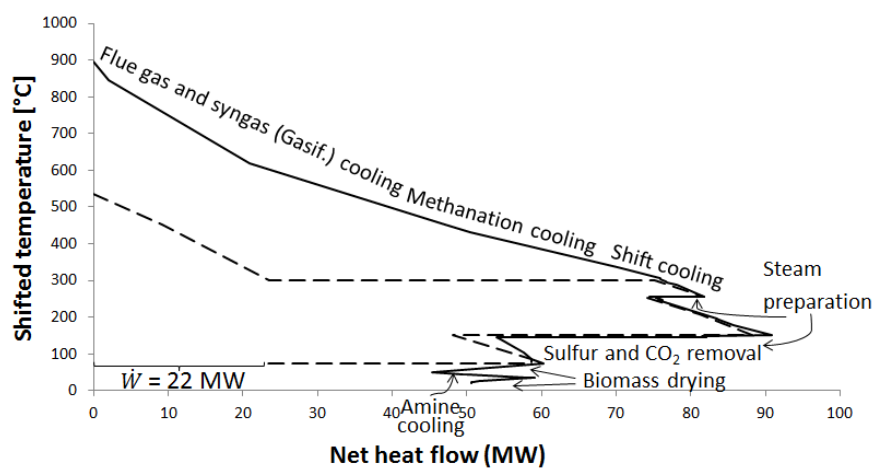
Figure 10. Split-GCC of the bio-SNG process (solid line) and a heat recovery steam cycle (dashed line) (BioSNG2Syngas Case El).

For stand-alone operation of the bio-SNG process, i.e., targeting for maximum electricity production (Case El), the electric power generation potential is 22 MW. Regarding its electricity demand (23 MW), the bio-SNG process can be considered almost self-sufficient, with a small net electricity demand of 0.2 MW. As no extra LP steam generation *via* heat recovery is considered in this case, the level of fuel gas importation at the oxo synthesis plant remains similar to that in the Base Case (27 MW). The co-location case, i.e., targeting the prioritisation of LP steam production (Case LP), could produce enough LP steam to eliminate completely the current need to purchase fuel gas. The electric power co-generation potential is estimated at 19 MW (3.4 MW less than the stand-alone case). This increases the level of electricity imported to the overall system by 3.1 MW, as compared with the Base Case.

For the direct bio-syngas process, the HP steam production is set to match the Base Case. The electric power generation potential for maximum electricity production (Case El) is estimated at 11 MW. The level of electricity imported to the overall system of this set-up is thereby reduced by 0.8 MW, as compared with the Base Case. As no extra LP steam

generation *via* heat recovery is considered in this case, the level of fuel gas import remains similar to that of the Base Case (27 MW). The target for prioritised LP steam production (Case LP) is estimated at 13 MW. The site's current level of purchased fuel gas for LP steam production can be reduced (but not eliminated) by this arrangement; however, an additional 9.4 MW of fuel gas still needs to be purchased. In this set-up, the potential for electricity co-generation is non-existent, and the level of electricity imported to the overall system is increased by 9.7 MW, as compared with the Base Case.

5.1.3 Performance Evaluation

This section presents and discusses the results obtained from the evaluations of process performance, i.e., the thermodynamic performance (energy and exergy efficiency; **Paper I**), global GHG emissions (GHG emissions reduction potential; **Paper II**), and process economics (change in production cost; **Paper II**). The main results are listed in Table 6.

Thermodynamic Performance

The calculated energy (η_{en}) efficiency and exergy (η_{ex}) efficiencies for the investigated biomass-based syngas production concepts are in the range of 60%–75% and 46%–57%, respectively (**Paper I**). For comparison, the conventional fossil route (Base Case) achieves higher energy (86%) and exergy (72%) efficiency values, since the thermochemical conversion of natural gas is significantly less energy-intensive than biomass conversion and entails lower requirements for gas cleaning and conditioning. Table 6 shows a summary of the results.

Table 6. Summary of the process performance targeting results for the investigated decarbonisation options for the oxo synthesis plant.

Performance indicator	Unit	Base Case	BioSNG2Syngas		Bio2Syngas	
			Case El	Case LP	Case El	Case LP
η_{en}	%	86	60	66	73	75
η_{ex}	%	72	46	49	55	57
GHG_{RedPot}[a]	kg $CO_{2,eq}\cdot t^{-1}$		773 / 775	858 / 895	855 / 845	754 / 871
ΔSPC[b]	€·t^{-1}		97 / 200	73 / 176	-14 / 75	-25 / 67

[a] Reference grid electricity generation technologies are coal PP/coal PP with CCS.
[b] Price projections are based on the WEO's current policies scenario/WEO's 450 ppm scenario (IEA, 2013).

The direct route to bio-syngas (Bio2Syngas) is associated with higher energy and exergy efficiencies than the route *via* bio-SNG (BioSNG2Syngas), with a difference of 12/9.1 (Case El/Case LP) energy efficiency points and 9.4/7.2 (Case El/Case LP) exergy efficiency points, respectively. These findings reflect the intrinsic conversion losses that occur during the methanation and subsequent partial oxidation steps, which are avoided in the direct route to bio-syngas. However, the heat recovery targets for CHP production are reduced. The gain in terms of avoided intrinsic conversion losses is more significant than

the decrease in the CHP production potential linked to the direct Bio2Syngas route (as compared with the BioSNG2Syngas route).

For both of the investigated bio-syngas concepts, the option to (co-)generate LP steam to eliminate or reduce the level of fuel gas import (Case LP) gives better performance than the option to maximise the electricity production (Case El). For the BioSNG2Syngas option, the thermodynamic efficiency penalties for a remote location (Case El) compared with an on-site location (Case LP) are estimated at 5.2/3.6 (energy/exergy) efficiency points.

Global GHG Emissions Balances

The calculated specific GHG emissions reduction potentials for the biomass-based syngas production concepts (relative to the Base Case) are in the range of 773–895 kg $CO_{2,eq}$ per t of oxo product, corresponding to a reduction of the Base Case total emissions in the range of approximately 45%–60%. This corresponds to a GHG emissions reduction potential in the range of 281–326 kt $CO_{2,eq}$ per year. The totals and further breakdown details are shown in Figure 11. The results are presented in Table 6.
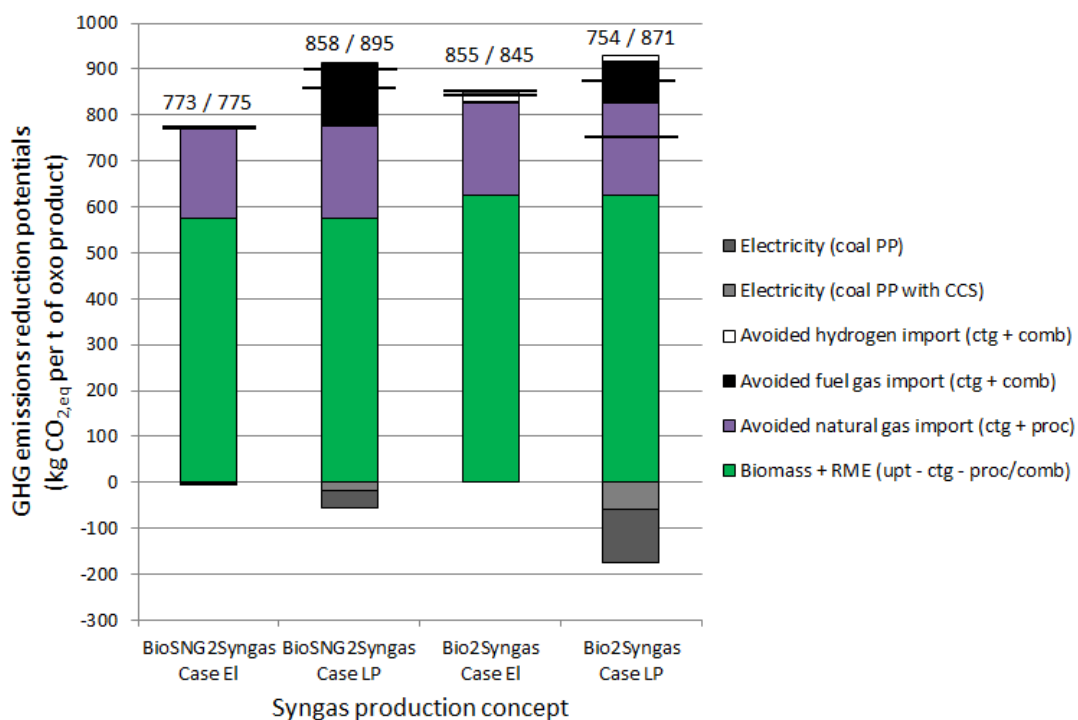
Figure 11. Breakdown of the GHG emissions reduction potentials (kg $CO_{2,eq} \cdot t^{-1}$) for the investigated biomass-based syngas production concepts. The total GHG emissions reduction potentials are indicated with ticks and values (where the reference grid electricity generation technologies are coal PP/coal PP with CCS). Note that only one reference grid electricity generation technology can be considered at a time. In this figure, the emissions contribution of coal PP should be considered as the sum of the coal PP with CCS and the coal PP emissions contributions.

The BioSNG2Syngas Case LP concept achieves the highest GHG emissions reduction potential (858/895 kg $CO_{2,eq}$ per t of oxo product; coal PP/coal PP with CCS). The subsequent ranking of the biorefinery concepts' GHG emissions reduction potentials varies according to the reference grid electricity generation technology. Bio2Syngas Case LP achieves the lowest or the second-highest GHG emissions reduction potential (754/871 kg $CO_{2,eq}$ per t of oxo product) for the high-emitting or low-emitting reference grid electricity generation technologies (coal PP/coal PP with CCS), respectively.

The Case LP heat recovery option achieves higher GHG emissions reduction potentials than Case El, with the exception of Bio2Syngas with coal PP as the reference grid electricity generation technology. The GHG emissions reduction potentials for Case LP show a dependence on the electricity balance (and the reference grid electricity generation technology), particularly for the Bio2Syngas option (in which no electricity generation occurs). The GHG emissions reduction potentials for Case El options show minimal dependence on the electricity balance (and the reference grid electricity generation technology). Note that Bio2Syngas Case El shows a higher GHG emissions reduction potential for the high-emitting reference grid electricity generation technology (coal PP), as compared with the low-emitting reference grid electricity generation technology (coal PP with CCS). This is the case because (in contrast to the remaining investigated concepts) the net electricity import is slightly reduced compared with the Base Case.

The three main emission factors that contribute to the GHG emissions reduction potential are:

- introduced renewable feedstock (accounting for 55%–75%)
- avoided natural gas as feedstock (accounting for 20%–25%)
- avoided fuel gas firing for steam production (accounting for 0%–15%)

Combined, these items account for 83% to almost 100% of the total GHG emissions reduction potential.

The GHG emissions reduction potential that results from introducing renewable feedstock is somewhat higher for the direct Bio2Syngas concept than for the BioSNG2Syngas concept, given that intrinsic conversion losses are minimised and less thermal input is required to replace the same product in the former case. During the production of syngas, approximately 60% and 70% of the CO_2 fixed during biomass growth is released to the atmosphere as part of the Bio2Syngas and BioSNG2Syngas concepts, respectively. The remaining biogenic-carbon is "stored" in the final oxo product.

The GHG emissions reduction potential attributable to avoided natural gas as feedstock is identical for all the investigated biorefinery concepts. The GHG emissions reduction potential due to reduced fuel gas usage is dependent upon whether LP steam is (co-)produced from recovered heat (Case LP) or not (Case El). The fuel gas firing can be

entirely eliminated or reduced in the BioSNG2Syngas and Bio2Syngas Case LP concepts, respectively.

Economic Evaluation

The fixed costs (incremental capital investment plus fixed operating costs) for the investigated biorefinery concepts, as compared with those for the Base Case, are summarised in Table 7. The results show that annual fixed costs of approximately 65 M€ and 30 M€ are required to switch completely to biomass-derived syngas *via* intermediate bio-SNG production (BioSNG2Syngas) and directly (Bio2Syngas), respectively. For the detailed equipment costs, see the Supplementary Material provided with **Paper II**.

Table 7. Annualised incremental capital investment (An. incr. cap. inv.) and fixed operating (op.) costs for the investigated biorefinery concepts (relative to the Base Case). Monetary value in 2012.

		BioSNG2Syngas		Bio2Syngas	
		Case El	Case LP	Case El	Case LP
Incr. cap. inv. (C_F)	M€	403	399	301	281
An. incr. cap. inv. ($a \cdot C_F$)	M€·y^{-1}	40	40	30	28
Change in O&M costs ($C_{O\&M}$)	M€·y^{-1}	20	20	0.9	0
Change in labour costs (C_{lb})	M€·y^{-1}	4.1	4.1	1.6	1.6
An. incr. cap. inv.&fixed op. costs[a]	M€·y^{-1}	65	64	33	30

[a]Sum of $a \cdot C_F + C_{O\&M} + C_{lb}$

The calculated change in the specific production cost of oxo products for the biomass-based syngas production concepts relative to the Base Case range from -14 € to 200 € per t of oxo product. The totals and the breakdowns of the changes in the production costs of oxo products based on two possible future energy market scenarios, WEO current policies and WEO 450 ppm (IEA, 2013), are illustrated in Figure 12. The results are presented in Table 6.

The direct route to syngas (Bio2Syngas) achieves a production cost that is more similar to the production cost of the Base Case compared with the route *via* intermediate bio-SNG production (BioSNG2Syngas), for price projections based on the two scenarios (Figure 12). For prices based on the WEO current policies scenario, the Bio2Syngas routes shows a negative change in production costs (-14 €/-25 € per t of oxo product for Case El/Case LP), i.e., a lower production cost than that for the conventional fossil-based route. Particularly interesting results are obtained with the heat recovery option to (co-)produce LP steam (Case LP).
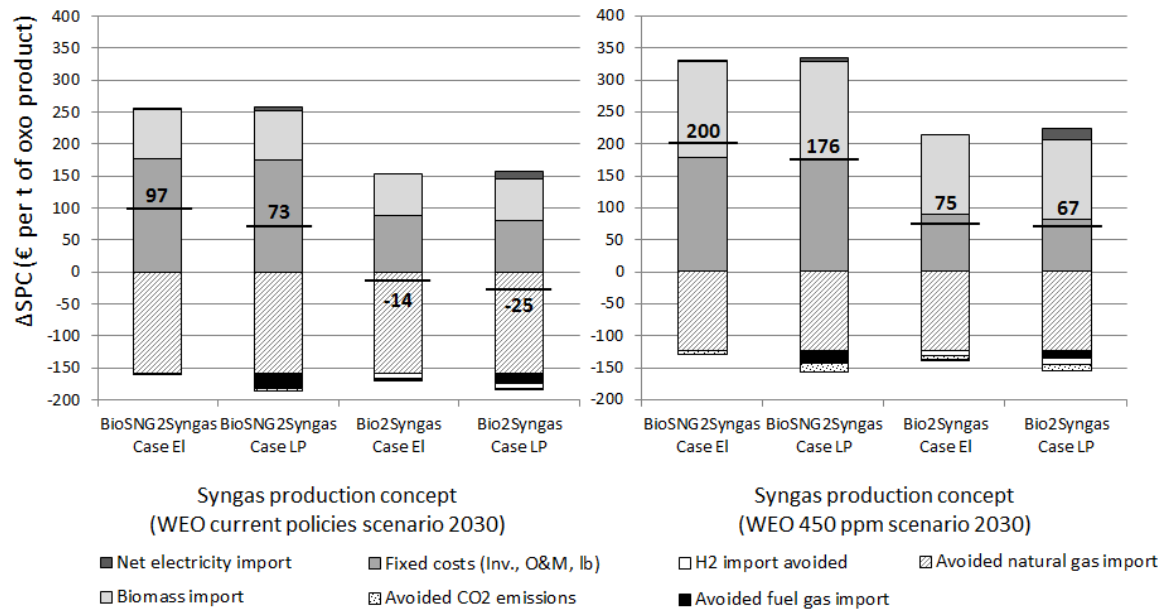
Figure 12. Breakdown of the changes in production cost of oxo products (€·t^{-1}) for the investigated biomass-based concepts based on prices projected from the WEO current policies scenario (left) and the WEO 450 ppm scenario (right). The total changes in production costs are indicated with ticks and absolute values.

Producing oxo products from biomass-based syngas can be cost-competitive with natural gas-derived syngas under the current policies scenario. However, if drastic changes were introduced to current policies (such as the implementation of the WEO 450 ppm scenario), biomass-based syngas would become less competitive for replacing fossil syngas in the production of oxo products. This would be the result of an increase in the charge for CO_2, which is projected to stimulate an increased willingness to pay for biomass and reduce demand (and thereby, the price) for fossil fuels. However, in a carbon-constrained world other policy instruments that are not considered in this study would be expected to influence the costs for materials and energy.

As shown in Figure 12, the factors that have the strongest impacts on the change in production costs are the:

- fixed costs
- avoided natural gas import
- biomass import

Together, these cost items represent ≥90% of the total new expenditures and savings. The results indicate that the incremental capital investment and the changes in feedstock costs have much stronger impacts on the changes in production costs of oxo products than changes in the costs of supporting energy flows (i.e., net electricity import and fuel gas import) and changes in the costs due to energy and climate policies (i.e., here, a CO_2 charge

for on-site fossil CO_2 emissions) (with price projections based on two possible future scenarios).

Although the same amount of natural gas is saved in the investigated biorefinery concepts, the natural gas price has a significant influence on profitability. This affects both the opportunity and driving force to switch to a renewable feedstock for the production of the syngas that will be required for synthesis of oxo products in the future. This finding is interesting considering the rapid changes that have recently occurred in the natural gas market due to the surge in shale gas production. The price of biomass also has a significant impact. The prices of feedstock and the energy commodities in the energy systems market are closely connected.

With ±30% price variation in the prices of natural gas and biomass (compared with price projections based on the WEO current policies scenario), the changes in production costs for the Bio2Syngas Case LP concept are ±54 € and ±19 € per t of oxo product, respectively (**Paper II**). This indicates that the price of natural gas has a stronger impact on the change in production cost. As expected, the fossil route benefits from low natural gas prices, especially when they occur concomitant with high biomass prices, whereas the biorefinery concepts become more competitive when natural gas prices are high, particularly when biomass prices are simultaneously low. In terms of price dependence, similar trends would be observed for the remaining investigated biomass-based concepts, albeit with different absolute values.

Due to uncertainties in the capital investment estimation (±30%), the changes in production costs for BioSNG2Syngas Case El/Case LP and Bio2Syngas Case El/Case LP could be in the ranges of approximately ±50/±49 and ±39/±37 € per t of oxo product, respectively, as compared with the estimates reported here.

5.1.4   Summary of Key Results

In this study, the thermodynamic performances of different integration points and different heat recovery options were estimated. As expected, the results indicate that compared with the direct bio-syngas route, a "chemical detour" through intermediate SNG production carries a penalty with respect to the process economics. For all the investigated options, the thermodynamic performance shows a direct correlation to the change in production cost for the oxo products. For example, the Bio2Syngas Case LP demonstrates the highest thermodynamic (energy and exergy) efficiency and the most competitive economic results. In the following discussion, only these consequences related to process economics and GHG emissions are considered.

Figure 13 maps the changes in the production costs of oxo products (estimated for price projections that are based on the WEO current policies scenario) versus the corresponding GHG emissions reduction potentials for the investigated biorefinery concepts. The most competitive and promising concepts are located in the lower-right corner and the least

beneficial concepts are shown in the upper-left corner of the graph (Figure 13). While the figure is not intended to be a rigorous optimisation tool, it can be used to draw some general conclusions about process performance from economic and environmental perspectives.
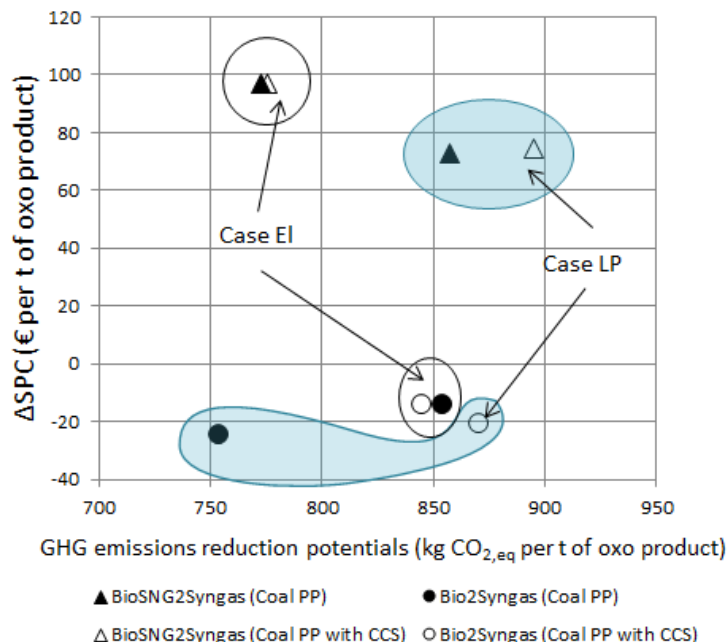

Figure 13. Changes in production costs of oxo products ($€·t^{-1}$) based on prices projected from the WEO current policies scenario versus the corresponding GHG emissions reduction potentials (kg $CO_{2,eq}·t^{-1}$) for the investigated biorefinery concepts.

The Bio2Syngas Case LP concept shows a promising performance profile from the economic and GHG emissions reduction perspectives, assuming coal PP with CCS as the reference grid electricity generation technology, as shown in Figure 13. The Bio2Syngas Case El concept shows a similar performance profile but with minimal dependence on reference grid electricity production. The Case LP option achieves better performance than the Case El options, with the exception of Bio2Syngas's GHG emissions reduction potential, for which high-emitting reference electricity production (coal PP) is assumed.

In this assessment, the CO_2 charge for fossil emissions is the only energy and climate policy instrument that is considered. The results show that there is no economic incentive to switch to biomass-based syngas for the production of oxo products when there is an increase in the CO_2 charge for on-site fossil emissions (i.e., price projections based on the WEO 450 ppm scenario, which increases willingness to pay for biomass and reduces natural gas prices). To create more potent economic incentives and to reduce the risks associated with the transition to biomass-based production of chemicals, alternative policies, such as a reward for the "replaced fossil carbon" or "stored" biogenic carbon, may warrant further investigation.

5.2 Decarbonisation of a Steam Cracker Plant

For decarbonisation of the steam cracker plant (**Paper III** and **Paper IV**), the option to substitute partially (25% of the total capacity) the current fossil-only production of light olefins (in several cracker units) with biomass-based production of crude light olefins production *via* methanol and MTO (Bio2CrudeOlefins), thereby making use of existing olefin separation equipment, is considered. The different biorefinery concepts are compared based on global GHG emissions balances (**Paper IV**). The current fossil-based production of light olefins is used as reference in the comparisons (Base Case).

Also considered is the production of biomass-based light olefins (Bio2Olefins) *via* two alternative platform chemicals (**Paper V**): (*i*) methanol; and (*ii*) DME. The different biorefinery concepts are compared for thermodynamic performance (**Paper V**).

5.2.1 Process Models

This section presents the results obtained from the process models and the established steam, fuel gas, and electricity balances. Table 8 presents the calculated mass and energy balances for the investigated light olefin production routes (Bio2CrudeOlefins) considered in the partial feedstock switch study (**Paper III** and **Paper IV**). Note that relevant energy flows are reported at HHV basis.

Base Case

The results for the conventional fossil-based production of light olefins (Base Case) established the requirements for the investigated partial feedstock concepts. Approximately 825 kt of light olefins [ethylene, propylene, and butylenes (sometimes referred to as Raff 2)] are produced annually in the Base Case (Table 8). The detailed site steam balance characteristics (**Paper III**) for the fossil-only Base Case are reported in Figure 14. In addition, the balances for fuel gas and electric power are investigated (**Paper IV**). To cover the Base Case steam cracker plant's steam demand, the results show that 53 MW of natural gas must be imported. The net electricity import of the Base Case is estimated at 42 MW.

Decarbonisation Options

For the partial feedstock switch option (Bio2CrudeOlefins), the results show that 758 MW of biomass are required to replace approximately 25% of the Base Case light olefin production (corresponding to approximately 220 kt per year). The partial switch of feedstock, achieved by integrating a biomass-based crude light olefin stream (with a different composition and generally higher purity), affects the site material and energy balances. For example, by fixing the ethylene production in the Bio2CrudeOlefins case at 590 kt per year, the production levels of propylene and butylene are increased, even though the level of butane imports is halved.

Table 8. Summary of the results for the light olefin production routes considered in the partial feedstock switching study.[a]

| | | Base Case | Bio2CrudeOlefins | |
			Case El	Case HP
Input				
Ethane	kt·y⁻¹	525	520 (-5.2)	520 (-5.2)
	MW	946	936 (-9.4)	936 (-9.4)
Propane	kt·y⁻¹	0	0 (0)	0 (0)
	MW	0	0 (0)	0 (0)
Butane	kt·y⁻¹	523	275 (-248)	275 (-248)
	MW	899	473 (-426)	473 (-426)
Naphtha	kt·y⁻¹	169	168 (-1.7)	168 (-1.7)
	MW	283	280 (-2.8)	280 (-228)
Ethanol	kt·y⁻¹	13	8.7 (-4.6)	8.7 (-4.6)
	MW	14	9.0 (-4.7)	9.0 (-4.7)
Biomass	kt·y⁻¹	0	2093 (+2093)	2093 (+2093)
	MW	0	758 (+758)	758 (+758)
Natural gas[b]	kt·y⁻¹	32	85 (+54)	16 (-15)
	MW	58	157 (+99)	30 (-28)
Power[c]	kt·y⁻¹	-	-	-
	MW	42	38 (-4.6)	75 (+33)
Production				
Ethylene[d]	kt·y⁻¹	590	590 (0)	590 (0)
	MW	1030	1030 (0)	1030 (0)
Propylene	kt·y⁻¹	149	210 (+61)	210 (+61)
	MW	254	357 (+103)	357 (+103)
Raff 2	kt·y⁻¹	86	96 (+11)	96 (+11)
	MW	144	161 (+18)	161 (+18)
ETBE	kt·y⁻¹	29	19 (-10)	19 (-10)
	MW	40	26 (-14)	26 (-14)
SCN	kt·y⁻¹	115	113 (-2.1)	113 (-2.1)
	MW	167	164 (-3.1)	164 (-3.1)
CBFS	kt·y⁻¹	18	14 (-3.5)	14 (-3.5)
	MW	26	21 (-5.2)	21 (-5.2)

[a] The mass flow rates and energy flow rates are reported as absolute values. The change compared with the Base Case is reported in parenthesis. The mass and energy balances are based on the work of Johansson and Pettersson (2014).

[b] The level of natural gas import is calculated by developing a steam balance (**Paper III**) and fuel gas balances (**Paper IV**) for the Base Case and the Bio2CrudeOlefins cases.

[c] The Base Case electricity import is based on reported average annual values (Borealis miljörapport, 2011). The amount of electricity imported in the Bio2CrudeOlefins case is calculated by developing an electricity balance for the cracker plant with an MTO unit and conducting an energy targeting analysis of the biomass-based methanol process.

[d] The partial feedstock switch options (Bio2CrudeOlefins) are sized to match the Base Case ethylene production.

The resulting detailed site steam balance characteristics for the fossil-only Base Case and the Bio2CrudeOlefins cases are reported in Figure 14. Differing steam mass flow values are indicated for the Base case/Bio2CrudeOlefins cases. The results show that the site's steam balance is substantially affected by partially replacing the production of light olefins in the cracker furnaces. The main consequences for the steam balance associated with the partial feedstock switch are (highlighted in Figure 14):

- Increased (by ca. 70%) requirement for HP steam production in the steam boilers
- Reduced (by ca. 15%) HP steam production from the cracker furnaces
- New heat demand (HP steam) for the MTO process
- Reduced (by ca. 20%) demeand for dilution (MP) steam in the cracking process
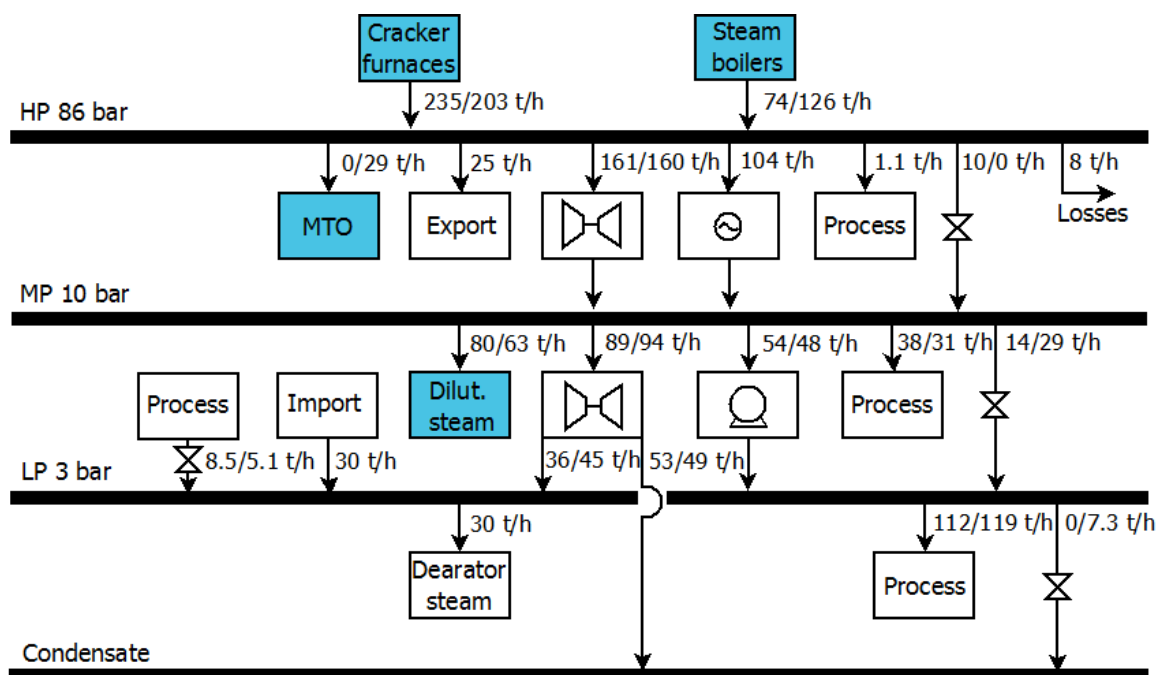
Figure 14. Site steam balance characteristics of the Base Case/Bio2CrudeOlefins cases.

The approximately 70% increase in the requirement for HP steam production in the steam boilers, as compared with the Base Case, corresponds to approximately 50 MW of fuel gas. Other consequences for the main fuel gas balance caused by the feedstock switch include a reduction (of approximately 20%) in fuel gas production and a reduction (of approximately 15%) in fuel gas demand in the cracker furnaces. The overall fuel gas demand decreases by approximately 1%. Nevertheless, the demand for natural gas import is significantly increased (by approximately 170%) compared with the Base Case, corresponding to approximately 100 MW, due to the decreased production of fuel gas.

The net electricity import at the steam cracker plant, accounting for a reduction (of 2.0 MW) in the power demand of the raw cracked gas compressor (Johansson and Pettersson, 2014) and the estimated electricity demand for the MTO process (Joosten,

1998), is estimated at 41 MW. The electricity demand of the bio-methanol process is estimated at 61 MW.

In the platform chemical comparison (Bio2Olefins) (**Paper V**), the results show that approximately half of the energy content of biomass (50 MW) is transferred into light olefins (ethylene, propylene, and butylenes) for the route *via* methanol and the route *via* DME. The production of light olefins is only 0.83 MW higher in the DME case than in the methanol case. Looking more closely at the carbon flows, it becomes clear that regardless of whether one targets methanol or DME as the platform chemical, a certain fraction of the renewable carbon in the feedstock is lost as CO_2. The difference lies in where in the process value chain most of the CO_2 is formed and removed (see below for discussion of carbon conversion).

5.2.2 Energy Targeting

This section presents the results derived from the energy targeting analysis and the consequences for the overall energy balances of the final use of recovered process heat (see Table 8).

Decarbonisation Options

Pinch analysis of the biomass-based methanol production process (Bio2CrudeOlefins) the presence of high levels of high-temperature excess heat and a heat pocket (refer to the split-GCC in **Paper III**). By integrating a heat recovery steam cycle, the heat pocket and the high-temperature excess heat can be exploited for the co-generation of heat and power (investigated in **Paper IV**). The final use of the recovered process heat affects the electricity and fuel gas (i.e., natural gas) imports to the steam cracker plant, where targeting maximum electricity production (Case El) minimises the level of electricity imported to the overall system and targeting prioritised export of HP steam (Case HP) decreases the imports of natural gas.

For stand-alone operation of the biomass-based methanol process, i.e., targeting maximum electricity production (Case El, referred to as MTObioOFF in **Paper IV**), the electric power generation potential is estimated at 65 MW. Regarding its electricity demand (61 MW), the bio-methanol process can be considered self-sufficient, with low-level net electricity export. Compared with the Base Case, the level of electricity imported to the overall system is decreased by approximately 10%. As no extra HP steam generation *via* heat recovery is considered in this case, the amount of fuel gas imported at the cracker plant is increased by approximately 170%, as discussed above.

The co-location configuration of the biomass-based methanol process, i.e., targeting prioritised export of HP steam (Case HP, referred to as MTObioON in **Paper IV**), can potentially produce enough HP steam to offload completely the cracker steam boiler. This corresponds to a reduction in natural gas imports of approximately 50%, as compared with the Base Case. The electric power co-generation potential is estimated at 27 MW.

Compared with the Base Case, the level of electricity import to the overall system of this set-up is increased by approximately 80%.

Pinch analysis of the biomass-based production of light olefins processes (Bio2Olefins) *via* methanol or DME indicates high levels of high-temperature excess heat and a heat pocket refer to the split-GCCs in Figure 15 (and **Paper V**). There are two key differences between the two investigated cases. The DME synthesis releases more heat than the methanol synthesis, represented as horizontal lines at 275°C and 255°C (shifted temperature), and the DME case has a lower demand for steam production (due to a lower requirement for WGS) compared with the methanol case, represented as horizontal lines at ca. 240°C (shifted temperature) (Figure 15).
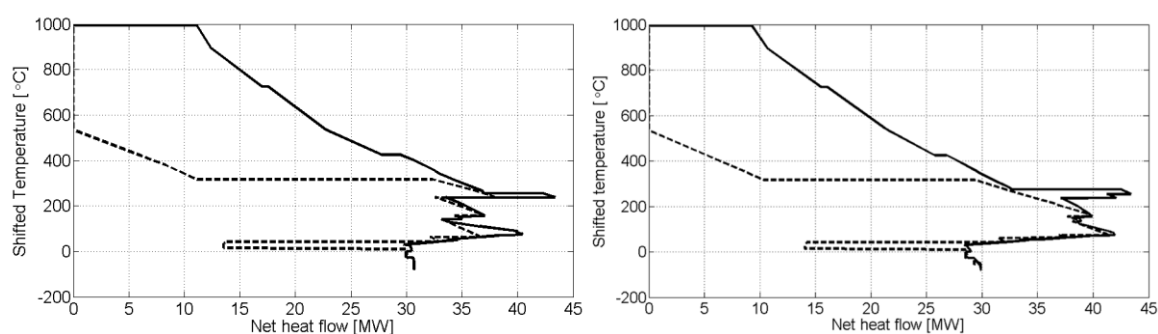
Figure 15. Balanced split-GCCs of the production processes for light olefins (solid lines) *via* methanol (left panel) and *via* DME (right panel) and the utility system (dashed line).

Energy targeting shows that approximately 14 MW of electric power can be co-generated in both cases. The DME case shows a slightly higher (+0.52 MW) co-generation potential. The refrigeration work targets are estimated at 0.29 MW and 0.63 MW, resulting in total process electricity demands of 10 MW and 9.7 MW (including the power required for oxygen production) for the methanol case and DME case, respectively. As a result, the net electricity exports are estimated as 3.3 MW and 4.4 MW for the methanol case and DME case, respectively.

5.2.3 **Performance Evaluation**

This section presents and discusses the results of the process performance evaluations results, including the thermodynamic performance (energy efficiency, cold gas efficiency, and carbon conversion; **Paper V**) and global GHG emissions (GHG emissions reduction potential; **Paper IV**).

Thermodynamic Performance

The calculated energy efficiency (η_{en}) values for the investigated biomass-based light olefin production concepts (Bio2Olefins) are >50% for methanol (52%) and DME (54%) as the platform chemicals. The two routes show similar performance levels, with a

somewhat higher energy efficiency for the case with DME as the platform chemical (+2.0 energy efficiency points). Table 9 shows a summary of the results.

Table 9. Summary of the results for the process performance targeting the production of light olefins using two different platform chemicals.

Performance indicator	Unit	Bio2Olefins	
		Methanol	DME
η_{en}	%	52	54
$\eta_{cg,i}$	%	49	50
$C_{conv,i}$	%	34	35

Figure 16 presents the cold gas efficiency ($\eta_{cg,i}$) and carbon conversion ($C_{conv,i}$) values for key intermediate streams along the light olefin production value chain (for process layout and stream details, refer to **Paper V**). Note that the biomass input and the raw syngas at the gasifier outlet are identical for the two cases. The cold gas efficiency along the process value chain is similar for the two investigated concepts, in that 49% and 50% of the energy content of the biomass input end up as light olefins in the methanol and DME cases (corresponding to a difference of 0.83 cold gas efficiency points), respectively. The most significant drops in cold gas efficiency occur during the torrefaction and gasification steps (between "Biomass" and "Raw syngas" in Figure 16) as well as in the methanol and DME syntheses (between "Syngas" and "Platform chemical" in Figure 16).

Furthermore, the rates of carbon conversion to final product are similar. Thus, 34% and 35% of the carbon content of the biomass input end up in the light olefins for the methanol and DME cases (corresponding to a difference of 0.59 carbon conversion points), respectively. However, as mentioned above, the difference lies in where in the process value chain the carbon losses occur. The most dramatic drop in carbon conversion occurs in the WGS section and subsequent CO_2 removal unit (between "Raw syngas" and "Syngas" in Figure 16) for both cases, although this drop is more significant for the methanol case (from 85% to 41%) than for the DME case (from 85% to 58%). After the platform chemical synthesis step and removal of light gases (between "Syngas" and "Platform chemical" in Figure 16), the carbon conversions rates drop to a similar value.
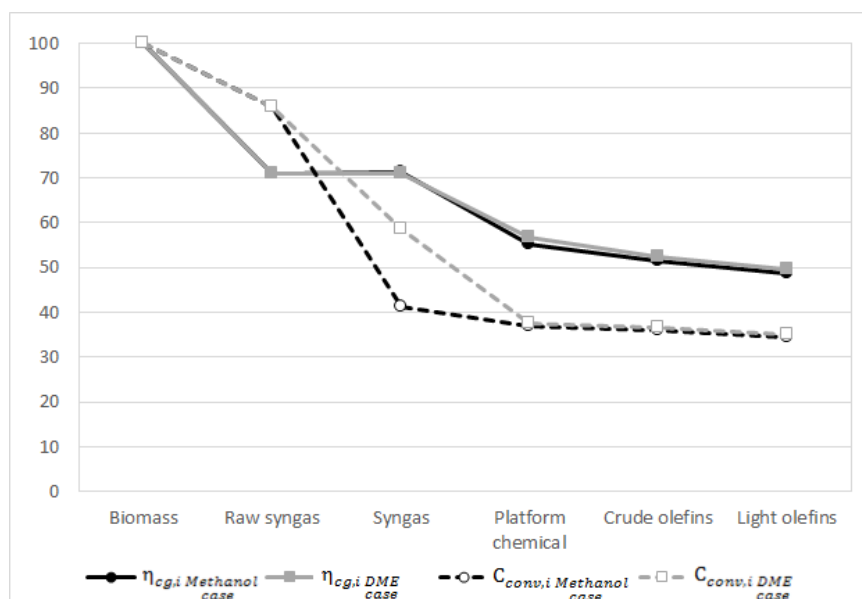
Figure 16. Cold gas efficiency (solid lines) and carbon conversion (dashed lines) for selected intermediate streams along the biorefinery-based light olefin production value chain *via* methanol (circles) and *via* DME (squares). "Platform chemical" refers to methanol/DME at the MTO/DTO synthesis inlet; for other process layout and stream details, refer to **Paper V**.

Global GHG Emissions Balances

The calculated GHG emissions reduction potentials for switching in part the production of light olefins to biomass feedstock (Bio2CrudeOlefins) are in the range of 963–1105 kt CO_{2eq} per year, corresponding to a reduction of approximately 50% to 70% of the Base Case total emissions. This corresponds to a specific GHG emissions reduction potential in the range of 919–1055 kg $CO_{2,eq}$ per t of light olefins (allocated based on energy content). The annual totals and further breakdown details are shown in Figure 17.

The Bio2CrudeOlefins Case El and Case HP have the highest GHG emissions reduction potentials (989 and 1105 kt CO_{2eq} per year) for the high-emitting and low-emitting reference grid electricity generation technologies (coal PP and coal PP with CCS), respectively. The GHG emissions reduction potentials for Case HP show a dependence on the electricity balance (and the reference grid electricity generation technology). The GHG emissions reduction potentials for the Case El options show minimal dependence on the electricity balance (and the reference grid electricity generation technology).
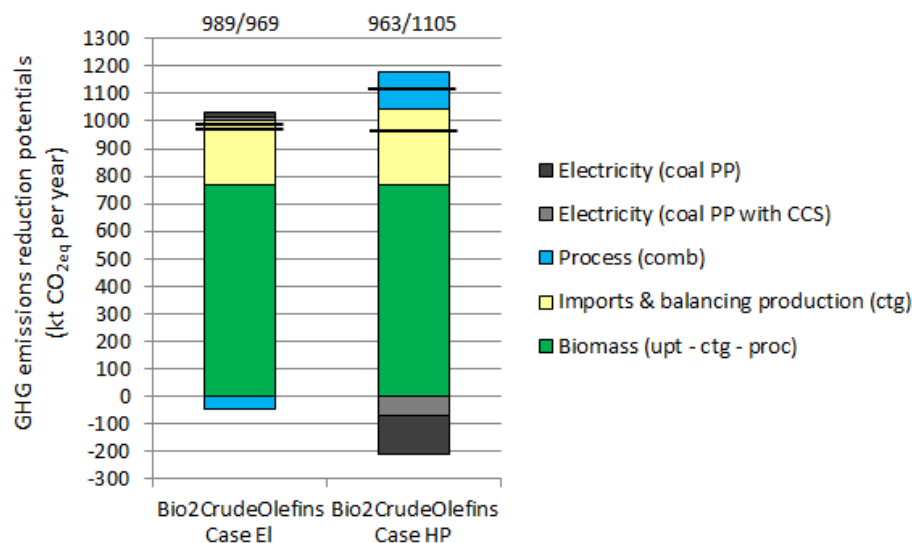
Figure 17. Breakdown of the GHG emissions reduction potentials (kg $CO_{2eq} \cdot y^{-1}$) for the investigated partial feedstock cases. The total GHG emissions reduction potentials are indicated with ticks and values (where the reference grid electricity generation technologies are coal PP/coal PP with CCS). Note that only one reference grid electricity generation technology can be considered at a time. In this illustration, the emission contribution of coal PP should be considered as the sum of the coal PP with CCS and the coal PP emission contributions.

The two main emission factors that contribute to the GHG emissions reduction potential are:

- Introduced renewable feedstock (accounting for 55%–70%)
- Changes in the levels of imports and the balancing product mix (accounting for approximately 20%)

Together, these items account for between 75% and 95% of the total GHG emissions reduction potential.

The GHG emissions reduction potentials that result from introducing a renewable feedstock are identical for the investigated biorefinery concepts. During the production of light olefins, it can be assumed that approximately 65% of the CO_2 that is fixed during biomass growth is released to the atmosphere for the integrated Bio2CrudeOlefins concept (assuming a carbon conversion to light olefins of 35%; **Paper V**).[13] The remaining biogenic-carbon is "stored" in the light olefin product.

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[13] It should be noted that some biogenic carbon ends up as light alkanes (e.g., ethane and propane) in the MTO unit, of which some is recirculated to the cracker furnaces and thus partly turned into light olefins or other products, and some is used as fuel gas in the steam boiler. For a system overview refer to **Paper IV**. However, considering the small drop in the carbon conversion during the MTO synthesis (between "Intermediate" and "Light olefins" in Figure 16), the biogenic fraction taking this detour to light olefins or other products can be assumed to be rather low.

The GHG emissions reduction potentials brought about by the changes in import levels and the balancing product mix is mainly attributable to the avoided butane feed. The difference between Case El and Case HP lies in the levels of natural gas imports (i.e., the cradle to gate-related emissions), as discussed below.

The GHG emissions that relate to the change in natural gas imports (i.e., combustion-related emissions included in the "Process" emissions in Figure 17) reflect whether HP steam is (co-)produced from the recovered heat (Case HP) or not (Case El). The natural gas fuel imports can be entirely eliminated in the on-site case (Case HP), whereas natural gas imports must be significantly increased in the off-site case (Case El), so as to satisfy the overall steam balance. The process-related and electricity-related emissions show opposite trends because of the trade-off that occurs between the co-generated products from the heat recovery opportunities.

6 Discussion

This chapter presents some general reflections on the research results contained in this thesis.

An overall goal of this thesis is to add to current knowledge about how to utilise biomass efficiently in the transition to a bio-based economy. The results from this work alone are not sufficient to determine whether decarbonisation of the chemical industry, based on introducing biorefinery concepts, should be given priority over other sectors. However, as highlighted in the literature overview (Chapter 2), there is a general lack of research into this topic. Furthermore, as stated in Chapter 1, a key argument in favour of introducing biorefinery concepts to achieve decarbonisation of the chemical industry is that a renewable source of carbon is generally required, for which feasible alternatives are currently very limited. Current policy frameworks focus primarily on decarbonising the energy supply and transport sectors. The question is, if the overall goal is to mitigate GHG concentrations in the atmosphere, is it appropriate to introduce sector-specific support instruments? Such policies would confer on selected sectors valuable economic benefits in the competition for the limited resource of biomass.

In this thesis, a case study approach was applied, so although the quantifications are case-specific, general conclusions can be drawn since the considered plants are typical for their category. The primary aim of the comparisons was to quantify the differences between the considered decarbonisation options, rather than focus the absolute values.

The heat integration opportunities considered in this work (in the case of co-location) are limited to the export of steam (produced from heat recovery) from the biorefinery to the host plant (at suitable pressure levels). Heat export from the host plant to the biorefinery [e.g., the recovery of low-temperature excess heat (if available) from the host plant for drying biomass feedstock for the biorefinery plant] has not been considered. For the stand-alone options, no heat integration with external sources or sinks (as in a district heating network) has been considered.

The integration of biorefinery concepts at chemical process plants affects the demand for biomass and purchased electricity, as well as reducing or eliminating certain fossil feedstock and energy carriers. For all the studied cases, the demand for biomass increases,

which leads to competition with other biomass users for a limited resource. To switch fully the syngas production at the oxo synthesis plant (**Paper I** and **Paper II**) and to switch 25% of the current production of light olefins at the steam cracker plant to a biomass-based process (**Paper III** and **Paper IV**), lignocellulosic biomass of approximately 8 TWh per year (ca. 1000 MW if assuming steady-state operation) would be required. This corresponds to approximately 50% of current harvest of forest residues (ca. 17 TWh per year) from Swedish forests used for CHP applications and approximately 5%–12% of the future harvest potential for forest residues and stubs (66–172 TWh per year) (Börjesson *et al.*, 2013; Skogsstyrelsen, 2008). To put this into perspective, a standard large Swedish pulp mill handles approximately 7 TWh per year (ca. 860 MW) of woody biomass (Pettersson and Harvey, 2012). The implementation of biorefinery concepts also affects the electric power sector, either increasing or decreasing the demand for electricity imports. The relative change of the electricity import affects overall process performance. Furthermore, the nature of the purchased electricity mix influences the overall GHG emissions balance. As this factor could have a significant impact on the outcome of the comparisons, one high-emitting and one low-emitting reference grid electricity production technology have been considered, so as to cover a wide range of possible outcomes.

The comparison of different drop-in points in the process value chain (syngas production for downstream oxo synthesis) (**Paper I** and **Paper II**) indicates that the shortest route to the target chemical (direct conversion to syngas), avoiding a "chemical detour" (*via* SNG), appears to be more promising (in terms of the investigated performance indicators). However, it should be noted that this option has the disadvantage that there is no backup for the feedstock supply, in contrast to the feedstock-switch option (for which the natural gas grid provides feedstock back-up). From the perspective of the chemical plant owner, the option to switch to a feedstock of biogenic origin might very well be a viable option, particularly if a third-party company operates the biorefinery process and either delivers the feedstock directly (co-located biorefinery) or delivers *via* the existing infrastructure. An example of this option could be if the GoBiGas plant (see Section 2.2.1) initiates its next phase, injecting bio-SNG into the grid, and with further processing occurring at the case study plant.

In some cases, there is a risk associated with the choice of platform chemical (methanol or DME) used to produce a given target chemical (light olefins) (**Paper V**). For the two investigated routes, similar thermodynamic performances were achieved. Therefore, for a stand-alone plant that covers the entire value chain from biomass to target chemical, there should be no major concerns regarding the market value of the platform chemical (assuming that the processes works as intended and that there are no significant differences in the other process performance indicators). However, in the case of partial switching at an existing plant (steam cracker plant) through the integration of a new platform chemical converter (MTO or DTO reactor) to produce a crude product (crude bio-olefins) (**Paper III** and **Paper IV**), the current market value of the relevant platform chemicals is of

importance. This is particularly true in the case of stand-alone operation of the platform chemical, i.e., where the modified plant imports the platform chemical.

All the biorefinery concepts investigated in this study show potential to reduce (by 45%–70% of current fossil-only operation) the global GHG emissions of the investigated chemical plants (**Paper II** and **Paper IV**). The main contributor to the GHG emissions reduction potential is the introduction of a renewable feedstock (accounting for more than 50% of the total), whereby biogenic carbon is "stored" in the final products. In a related study, it has been shown that similar GHG emissions reduction potentials (from a life-cycle perspective) can be achieved by replacing motor fuels and materials (if currently based on the same fossil resource) (Holmgren *et al.*, 2014). Note that the impact of increased removal of forest residues on the forest carbon stock or biodiversity has not been investigated. The eventual release of CO_2 (and possibly other GHGs) to the atmosphere depends on the product application, which is assumed to be identical for the fossil and biogenic cases. The timing of the CO_2 release could have an overall climate impact, although this issue is outside the scope of the present work.

Another feature of gasification-based biorefinery concepts is that the CO_2 is generally separated during gas processing, resulting in the release of a relatively pure (biogenic) CO_2 stream to the atmosphere. The implementation of (bio-)CCS might further increase the GHG emission reduction potentials of such systems. Note that this process [separation and release of a relatively pure (fossil-derived) CO_2 stream] also applies to conventional gas processing. Although (bio-)CCS is included in several decarbonisation strategies (EC, 2011), the impact of implementation of CCS technology in the chemical industry has not been investigated in the present work.

Industrial-scale implementation of biorefinery concepts requires that investors are willing to invest in profitable value chains. The only climate policy instrument taken into account in this work is a CO_2 charge for fossil-derived emissions, which is assumed to be harmonised across various sectors. The economic evaluation results indicate that gasification-based biorefinery concepts (syngas directly) can be cost-competitive with conventional natural gas-derived syngas-based processes for the production of specialty chemicals (oxo products), as long as current policies are not significantly modified (as in the WEO current policies scenario) (**Paper II**). By increasing the CO_2 charge (as in the WEO 450 ppm scenario, which assumes increased willingness to pay for biomass and reduced fossil fuel prices), no economic incentive for switching to biomass-based production is achieved. However, in a carbon-constrained world, other policy instruments that are not considered in this study can be expected to influence the pricing of material and energy flows. For example, a reward for "replacing fossil carbon" or "carbon storage" in bio-chemicals could act as an incentive. In a related study, it was found that similar economic performance levels for producing bio-fuels and bio-chemicals (light olefins) could be achieved by applying the same low-carbon policies (Hannula, 2015).

7
Conclusions

This chapter draws some general conclusions based on the results described in the appended papers.

A number of different opportunities exists to substitute fossil feedstocks and energy carriers at chemical complex sites by integrating gasification-based biorefinery concepts. In this thesis, different energy-efficient decarbonisation options for the chemical industry were identified and systematically compared using a case study approach. The aims were to contribute to the development of a screening methodology for identifying robust options for specific systems, and to expand the current body of knowledge regarding the efficient utilisation of biomass in the transition to a bio-based economy. Important process integration parameters that should be incorporated into such a screening methodology are described below.

The results of this work highlight the importance of adopting an appropriate systems perspective to capture the relevant consequences of substitution when applying drop-in decarbonisation approaches to complex chemical processing plants. The importance of applying sound material and energy integration to enable this transition is also emphasised.

Two key plants (typical of their genre) within the largest existing chemical complex site in Sweden were identified that would allow substantial decarbonisation of the complex (case study host plants): an oxo synthesis plant; and a steam cracker plant. The former plant produces specialty chemicals (from syngas and light olefins), while the latter plant constitutes the core of the complex, producing high-volume intermediates (light olefins) for the neighbouring plants. Two target drop-in bio-chemicals in the host plants were considered: syngas and light olefins.

The results indicate that the considered drop-in approach, i.e., selected integration points for the biorefinery concepts in the host process value chain (syngas directly or *via* SNG and crude light olefins), as well as the composition of the drop-in stream (crude light olefins), i.e., how similar the substituting stream was to the current stream, can have substantial effects on the host site material, steam, and fuel gas balances. In particular, adopting an integration point downstream from the main fossil feedstock conversion unit (generally energy-intensive, as well as associated with high-temperature excess heat) can have

significant consequences in terms of the substitution. The comparison of integration points in the host process value chain indicates clearly favourable thermodynamic and economic performances for the shortest route to the target chemical (syngas directly), i.e., avoiding the "chemical detour" (*via* SNG) introduced into the feedstock switching option. However, this syngas directly option entails a certain risk as there is no back-up for the feedstock supply. In the comparison of different platform chemicals (methanol and DME) used to target the same drop-in chemical product (light olefins), no difference could be identified for the investigated processes from the thermodynamic and carbon conversion perspectives.

All the investigated gasification-based biorefinery concepts are associated with high-temperature excess heat, which can be recovered *via* a steam network. In the case of co-location, i.e., prioritises steam export, this provides the opportunity to eliminate completely or reduce significantly current natural gas firing in utility boilers. In most cases, the co-generation of electric power can be maintained but at a reduced level. From the thermodynamic (energy and exergy) and economic (change in production cost) points of view, co-location (targeting for steam export) achieves better performance levels than a stand-alone operation (targeting for maximum electricity).

The results of this work indicate that by substituting fossil-derived chemicals with drop-in bio-chemicals, significant GHG emissions reductions can be achieved. The main contributing factor is the introduction of a renewable feedstock, i.e., the "storage" of biogenic carbon in the targeted products. The targeted heat recovery option and reference grid electricity generation technology influence the ranking of the options. In general, co-location and stand-alone operations benefit from a low-emitting and a high-emitting reference technology, respectively. Both the highest and lowest (absolute values) GHG emissions reduction potentials are achieved in the co-location case, with the stand-alone options being less dependent upon the reference power technology.

The results of the economic evaluation indicate that the assumed policy instrument has a significant impact on the projected energy prices and thereby, also impacts upon the profitability. Under certain conditions (current policies scenario), switching to biomass-based production of specialty chemicals (syngas directly) shows good potential to become economically competitive with conventional means of production. However, if there is a change to the policy instrument (for example, an increase in the CO_2 charge), there will be no economic incentive to switch to biomass feedstock.

8 Future Research

A number of different aspects, some of which are presented in this chapter, have been identified as interesting topics for further analysis.

The results obtained from this work indicate that the substitution of fossil-derived intermediate chemicals with drop-in bio-chemicals could yield significant GHG emissions reductions for basic chemical plants. This work only covers a few of all the possible opportunities. It is desirable to keep filling this research gap so as to enable sound decision-making regarding where biomass would be best utilised in the basic chemical sector. In addition, systematic comparisons with uses in other sectors should be carried out in the future.

There is a need to develop an efficient methodology for rapidly screening competitive drop-in decarbonisation options for specific systems. For this to happen, intensified interdisciplinary research is needed. There is also a need for more research that combines the process engineering approach with new developments in LCA, as well as strategies for predicting the evolution of process economics.

For the process engineering approach, some important process integration parameters that warrant further development are highlighted in this thesis (e.g., drop-in approach, platform chemical selection, substitution consequences, biorefinery location, and heat integration opportunities). Other interesting topics to investigate further within this field are the role of flexibility, both in terms of feedstock flexibility, in connection with using other unconventional feedstocks such as waste and unrecyclable plastics, as well as (large) flexible multi-product concepts. In general, research is needed into how best to measure integration benefits versus potential risks.

From the LCA perspective, new insights about the complex consequences of rapid ramp-up of forest biomass usage, as well as timing of CO_2 emissions could be incorporated in the new methodology.

To estimate more accurately the process economics of future biorefinery concepts, there is a need for generic methodology development, so that screening studies can be easily updated as more reliable investment cost data become available. Furthermore, there has to

be improved understanding of the dynamics of future energy market scenarios. In particular, it will be important to investigate the factors (e.g., different policy instruments) that influence price projections for forest residues. In general, work on how to create stronger economic incentives that promote the transition towards a bio-based economy should be prioritised in the future. In this context, business models that are geared towards joint venture investments, rather than having a single large investor assume the entire risk (e.g., for a chemical plant, pulp mill or energy company), are needed.

Acknowledgements

Abbreviations

ASU	air separation unit
ATR	auto-thermal reformer
Base Case	fossil-based reference case
Bio2Syngas	biomass-based syngas production
BioSNG2Syngas	biomass-based syngas production *via* SNG
Bio2CrudeOlefins	biomass-based crude light olefins production
Bio2Olefins	biomass-based light olefins production
BFB	bubbling fluidised bed
CBFS	carbon black feedstock
CCS	carbon (carbon dioxide) capture and storage
CFB	circulating fluidised bed
CHP	combined heat and power
DME	dimethyl ether
DTO	dimethyl ether-to-olefins
EC	European Commission
ETBE	ethylene-tert-butyl-ether
EU	European Union
FICFB	fast internally circulating fluidised bed
FT	Fischer-Tropsch
GCC	grand composite curve
GHG	greenhouse gas
GoBiGas	Gothenburg biomass gasification project
GWP	global warming potential
HHV	higher heating value
HP	high pressure (steam)
IEA	International Energy Agency
LCA	life cycle assessment
LHV	lower heating value
LP	low pressure
MP	medium pressure
MTO	methanol-to-olefins
MTP	methanol-to-propylene
O&M	operation and maintenance
PLA	polylactic acid
PP	power plant

Raff 2	mix of mainly C_4 olefins and butane
RME	rapeseed oil methyl ester
SCN	steam cracked naphtha
SNG	synthetic natural gas
WEO	world energy outlook
WGS	water-gas-shift

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