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Assessing the Integration of Biomass Gasification-Based Production of Chemicals — Case Study of an Oxo Synthesis Plant

MARIA ARVIDSSON

Heat and Power Technology
Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
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CHALMERS UNIVERSITY OF TECHNOLOGY
SE-412 96 Göteborg
Sweden
Phone: +46 (0) 31 772 10 00

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ABSTRACT

The chemical industry sector is energy-intensive and highly dependent on fossil feedstock. The primary long-term option to reduce fossil feedstock dependence and greenhouse gas (GHG) emissions is to switch to renewable feedstock. One promising technology is thermochemical gasification of lignocellulosic biomass feedstock into a raw syngas which can be processed into a spectrum of possible products. This study aims at assessing different opportunities to integrate biomass gasification-based processes in the production of chemicals. The work was conducted in the form of a case study involving a conventional oxo synthesis plant processing syngas derived from partial oxidation of natural gas, and olefins into various specialty chemicals. The following options were investigated: (*i*) retaining the existing syngas production unit and fully substituting the natural gas feedstock by either importing or producing biomass-derived synthetic natural gas (bio-SNG) onsite; (*ii*) scrapping the existing syngas generator and directly producing biomass-derived syngas fulfilling the specifications for downstream oxo synthesis.

The results show that the direct route to bio-syngas requires less lignocellulosic biomass compared with the route via intermediate bio-SNG production. Although the bio-SNG route features a higher heat recovery target for production of heat and power, the direct route achieves the highest thermodynamic performance, particularly if LP steam is exported to the oxo synthesis plant. Furthermore, the direct bio-syngas route shows promising opportunities to perform well from both an economic and GHG emission reduction perspective. For price projections based on current policies, a production cost lower than via the fossil route is indicated. The results also indicate that for future energy market conditions associated with major climate emission constraints, there is no direct economic incentive for switching to biomass-based syngas production, suggesting that other policy measures than a CO_2 emissions charge will be necessary to achieve switching from fossil to biomass feedstock in the chemical process industry.

Keywords: process integration, biorefinery, gasification, syngas, chemicals production, oxo synthesis

List of Publications

This thesis is based on the following papers:

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

II. Arvidsson, M., Morandin, M., Harvey S. (2014) Biomass Gasification-Based Syngas Production for a Conventional Oxo Synthesis Plant — Global GHG Emission Balances and Economic Evaluation. *Submitted to Journal of Cleaner Production*.

Related work not included in this thesis:

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

This paper is a conference paper that presents a problem definition and initial results that are further developed and investigated in Papers I and II.

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1. INTRODUCTION

With global population growth (and increasing energy and material demand), depleting fossil resources, and the threat of climate change due to an increased concentration of atmospheric greenhouse gases (GHGs), a transition to sustainable systems and processes is crucial.

In the 1987 United Nation's *Our Common Future* report (also known as the Brundtland report), sustainable development was defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (United Nations General Assembly, 1987).

The current annual world primary energy demand is estimated at approximately 540 EJ; approximately 13% of this demand originates from biomass, waste, and other renewables such as hydro, solar, and wind (IEA, 2014). The main end-user sectors of energy are industry, transport, and buildings. Although no single solution for achieving a transition to a sustainable society has been attained, a diversity of energy resources and conversion pathways and some behavioural changes will be required.

Ongoing research projects related to the transition to renewables focus on energy supply and transportation fuels. These sectors have also received substantial attention from the political arena in terms of visionary goals and policy instruments. For the supply of heat and power and to a certain extent transportation energy demand, a number of promising alternative technologies for harnessing non-carbon-based renewable energy sources have been developed. For the production of chemicals and materials, however, a source of carbon is required. Biomass is the only renewable option for the sustainable production of these commodities. The International Energy Agency (IEA) has identified biomass-based technologies as important "game changers" for the chemical industry to reduce the 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).

The availability of biomass, which is dependent on a number of different factors, can be divided into theoretical, technical, sustainable, and market potentials (Berndes, 2014). The estimation of the technical potential considers factors such as crop yields, land availability, and biomass competition for food production. The future global biomass potentials reported in the literature vary significantly depending on the applied methodology and assumptions regarding types of biomass, land availability, and yield levels (Berndes et al., 2003; Dornburg et al., 2008). For example, in a review of several biomass potential studies, the reported global biomass potentials for 2050 range between 0 EJ and 1500 EJ per year (Dornburg et al., 2008; Dornburg et al., 2010). When water limitations, biodiversity protection, and food demand are considered, the technical biomass potential in 2050 is reduced to approximately 200 EJ to 500 EJ per year. An overview of the global technical potential for different land-based biomass supply conditions is presented in a report by the Intergovernmental Panel on Climate Change (IPCC) (2011). Lignocellulosic material, such as forest residues, is one of the most relevant renewable resources to be considered from a medium-term perspective for the production of chemical and energy commodities. From a long-term perspective, aquatic biomass (algae) is also of significant interest. Although it is renewable, biomass must be considered as a scarce and limited resource in the future, which emphasises the importance of the utilisation efficiency of biogenic feedstock.

1.1 Challenges for the Chemical Industry

The chemical industry sector is energy-intensive and highly dependent on fossil feedstock. The use of energy and feedstock in this sector accounted for approximately 10% of the total global final energy demand (equivalent to approximately 40 EJ) in 2011 (IEA, 2014). Biomass, waste, and other renewables currently account for only 0.5% of the final energy demand of the chemical industry (equivalent to approximately 0.2 EJ) (IEA, 2014).

The global annual production of chemicals and polymers is approximately 330 million tonnes (IEA, 2012a). In 2012, the global chemical sector's turnover was valued at 3 127 billion €, of which the European Union (EU) market accounted for 18% (558 billion €) (cefic, 2014). The EU sales consisted of: 63% base chemicals (i.e., large volume production of petrochemicals, polymers, and basic organics that are frequently traded within the industry), 25% specialty chemicals (i.e., relatively small volume production of auxiliaries for industry, paints and inks, crop protection, and dyes and pigments), 12% consumer chemicals (i.e., chemicals that are sold to the final costumer, e.g., soaps and detergents, perfumes and cosmetics).

In the chemical industry, fossil hydrocarbons such as crude oil and natural gas (NG) comprise the dominant feedstock. The distinct trend is to shift from liquid or solid feedstock to gaseous feedstock (IEA, 2012b). The transition to NG only offers a short- to medium-term solution as its combustion directly contributes to an increased concentration of atmospheric GHGs (approximately 40% and 15% less per unit of energy content compared with coal or oil, respectively (Gode et al., 2011)). Additional environmental concerns are also associated with some of the methods of NG extraction (e.g., hydraulic fracturing in shale rock formations).

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. As discussed in Vennestrøm et al. (2011), two general approaches are employed to introduce biomass-based production of chemicals, as shown in Figure 1:

- Emerging bio-chemicals
- Drop-in bio-chemicals

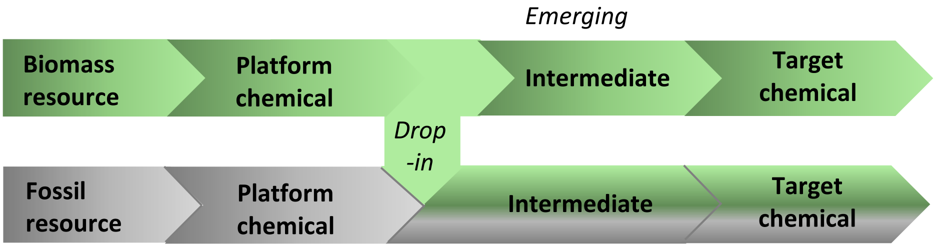

Figure 1. General overview of two different approaches to introduce biomass-based value chains in the production of chemicals.

Note that Figure 1 illustrates a general process value chain for the production of chemicals. For instance, what is considered to be a platform chemical or an intermediate in a specific process value chain can differ. The point that indicates the division of drop-in and emerging bio-chemicals illustrates the difference between the two approaches.

The production of emerging bio-chemicals implies target chemicals with new chemical structures and properties. As no equivalent fossil value chain or product exists, this strategy involves the development of new value chains, infrastructure, and markets. This is also the case for the substitution of a corresponding fossil-based product with similar functionality (but not the identical chemical equivalent). An advantage of this approach is that direct competition with fossil products can be prevented. The intrinsic functionality in the biomass feedstock can be retained to a larger extent. An example of the emerging bio-chemicals approach is the production of the bio-degradable plastic polylactic acid (PLA) that can replace the traditionally fossil-derived plastic polyethylene terephthalate (PET) for some applications.

The drop-in approach involves the production of biochemicals that can directly substitute the fossil-based hydrocarbon equivalent. The biochemical can be directly introduced into existing and established value chains, infrastructure and markets. Note that the entry point of the biomass-based value chain does not have to involve a platform chemical, as illustrated in Figure 1; refer to the discussion in Section 1.2. An example of the drop-in strategy is the production of ethanol (platform chemical) via fermentation, which can be processed to ethylene (intermediate) via dehydration and converted to a number of products via several processes, such as polymerisation to polyethylene (target chemical) (Vennestrøm et al., 2011). Drop-in bio-chemicals are expected to achieve the easiest market penetration (IEA, 2012a).

In principal, almost all chemicals and materials traditionally produced from fossil resources can be switched with their corresponding bio-equivalent (IEA, 2012a). In addition to increasing oil prices and population growth, the consumer demand of environmentally friendlier products and security of supply are important drivers that increase the attractiveness for the chemical industry of transitioning to a bio-based economy (IEA, 2012a).

1.2 Biomass-Based Production of Chemicals

The IEA considers effective integration into existing industrial processes as a key factor for successful transition to a bio-based economy (IEA, 2012a). The advantages of producing chemicals that are identical to the platform and bulk chemicals in the current fossil-based petrochemical industry were 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, C4-olefins, benzene, toluene, and xylene).

Cherubini and Strømman (2011) discussed opportunities, perspectives, and potential options for the production of platform chemicals from lignocellulosic biomass, which primarily involve biochemical processes, using existing infrastructure in 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.

Examples of switching the feedstock in the fossil value chain with a biomass-based equivalent, could involve replacing fossil naphtha with biomass-derived naphtha, such as Fischer Tropsch (FT) naphtha, or NG with biomass-derived methane, such as synthetic NG (bio-SNG) from thermochemical gasification or bio-gas from anaerobic digestion. The advantage of this approach is that existing downstream energy and chemical infrastructure can be retained. Examples of switching conventional platform chemicals or intermediates in the fossil value chain, as shown in Figure 1 could involve replacing fossil-based methanol[1] or syngas with a biomass-derived equivalent.

Various switching approaches have pros and cons. For example, the feedstock switching approach implies only minor changes to the existing core process. This approach also provides some freedom of choice in the location of the biomass conversion process as logistics infrastructure (for the fossil equivalent) already exists (e.g., harbours handling naphtha or NG grid). An additional advantage is that the fossil equivalent can serve as a back-up or buffer. However, this route involves taking a “chemical detour”, which is likely to be associated with intrinsic conversion losses compared with finding a shorter/the shortest biomass-based route to the target chemical.

The platform chemical or intermediate switching approach will most likely utilise less of the existing infrastructure (as it is introduced further downstream in the fossil process value chain). Depending on the transportation possibilities for the switched product, different locations of the biomass conversion process can be considered. In the case of methanol, for example, both stand-alone operation and colocation could be considered. In the case of bio-syngas, however, colocation is the most likely option. Depending on the location of the biomass conversion process, different energy and material integration opportunities exist. In the case of colocation, opportunities for heat and material integration that are not practically possible for the stand-alone option emerge. Compared with switching the corresponding feedstock, switching the platform chemical or

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[1] Having the third largest global production in 2010, methanol is one of the most common bulk chemicals (UNEP, 2013). For each specific chemical site, a bulk chemical such as methanol can serve either as a feedstock, a platform chemical, an intermediate, or a final product.

intermediate may prevent a “chemical detour” (associated with inherent conversion losses) if the total route to the target chemical is short.

1.2.1 Commercial Scale Biomass-Based Production of Chemicals

The global annual production of bio-based chemicals and polymers is approximately 50 million tonnes (IEA, 2012a). The main products include non-food starch, cellulose fibres and derivatives, tall oils, fatty acids, and fermentation products (e.g., ethanol and citric acid).

Biomass can be converted via several optional routes, such as thermochemical, chemical, biochemical, and mechanical routes. The majority of the effort regarding the development of biomass-based chemicals production has focused on the production of high-value fine or specialty chemicals via bio-chemical and chemical conversion (where the functionality has frequently been significant) of easily accessible carbohydrates (such as sugar- or starch-based feedstock).

A number of biomass-based chemical and material production sites, which primarily are employing agricultural resources such as plant oils, sugars, and starch, exist at the commercial scale. For example, NatureWorks LLC began producing the bio-degradable plastic PLA in the USA in 2002 (NatureWorks LLC, 2014). The current production capacity is 140 kt per year and the primary feedstock is corn.

Traditional fossil-derived chemicals and materials are also being produced from renewables. In 2010, Braskem commercialised the production of ethylene (production capacity 200 kt per year) from sugarcane ethanol via dehydration in Brazil (Braskem, 2013). In the same year, BioAmber began producing biomass-based succinic acid via fermentation of wheat-derived glucose in France (BioAmber, 2014).

Several of the companies involved in the production of bio-chemicals indicate that their respective products in the future will preferably be produced from cellulosic materials, biomass wastes or non-food plants (when associated challenges have been overcome).

1.2.2 Biomass Gasification-Based Production of Chemicals

For the conversion of lignocellulosic biomass such as forest residues, thermochemical conversion is considered to be a particularly promising technology. Thermochemical conversion includes the processes of combustion, pyrolysis, liquefaction, and gasification (Basu, 2010).

During gasification, a carbonaceous feedstock is converted into a raw syngas that primarily consists of hydrogen, CO, CO_2, and methane in an oxygen-deficient environment at high temperatures (500 °C to 1300 °C). The gasification reactions are endothermic. The obtained syngas can be processed into a spectrum of possible products, as shown in Figure 2. The feedstock can be either solid, such as forest residues (or coal), liquids, such as black liquor (or residual liquids), or gaseous, such as bio-gas (or NG), which indicates that one product in one gasification-based process can be the feedstock in another gasification-based process. For example, an energy carrier such as FT-naphtha or synthetic NG (SNG) can be produced via gasification-based processes, which subsequently enable further conversion in another gasification-based process. Thermochemical gasification of fossil material is commercially available, whereas the utilisation of biomass feedstock needs to be proven at a large scale, as shown in Section 2.1. Additional information regarding the conceptual design, status, and challenges of biomass gasification-based processes is provided in Section 2.2.

Considering the vast number of possible material flows, as shown in Figure 2, several potential opportunities for integrating a gasification-based biorefinery in the chemical industry can be identified.

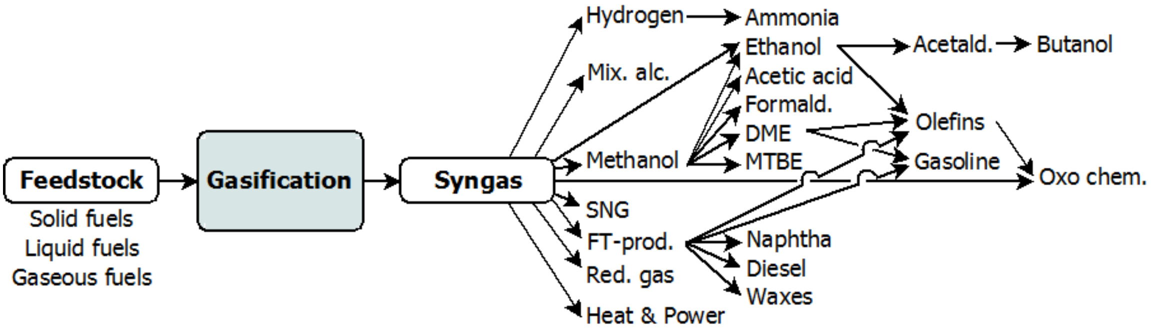


Figure 2. Overview of possible production routes for thermochemical gasification.

The global annual use of fossil-derived syngas (i.e., from NG, coal or refinery by-products) is approximately 6 EJ (Boerrigter and Rauch, 2006). Fossil-derived syngas is used for a number of different applications: 50% ammonia, 25% hydrogen, 10% methanol, 15% other types of syngas, such as FT synthesis, oxo synthesis, iron ore reduction gas, and electricity (Boerrigter and Rauch, 2006).

According to a recent market tracker report that identifies global trends and forecasts to 2018, the market for syngas and derivatives is expected to grow (MarketsandMarkets, 2013). The syngas derivatives discussed in the 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) are noted as major opportunities.

Current studies related to biomass gasification-based chemicals production are focusing on bulk chemical production. An example is the production of methanol as a final product (e.g., transportation purposes) (Bludowsky and Agar, 2009) or as a platform chemical e.g., for the production of olefins (Hannula et al., 2014; Haro et al., 2013). The production of hydrogen has also been substantially investigated as a final product (Ciferno and Marano, 2002; Hamelinck and Faaij, 2002) or specifically for ammonia production (Gilbert et al., 2014).

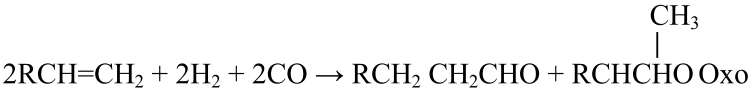
An interesting alternative to conventional removal or conversion has been identified by the Energy Research Centre of The Netherlands (ECN). This option involves direct selective separation of high-value molecules in the syngas (e.g., ethylene, benzene, and methane) (van der Drift, 2013). Experimental tests of this technology are currently planned.

The integration of different thermochemical biorefinery concepts at different existing industrial sites have been reported in the literature, such as the integration of an ammonia production process in a pulp and paper mill (Andersson and Lundgren, 2014); a gas turbine, methanol, or FT synthesis and a mechanical pulp and paper mill colocated with a sawmill plant (Isaksson et al., 2012); methanol production from steel-work off-gases and biomass gasification in a steel plant (Lundgren et al., 2013); methanol production (for use as vehicle fuel or further conversion to olefins) in chemical clusters (Holmgren et al., 2014); and hydrogen production in oil refineries (Brau et al., 2013; Johansson et al., 2012).

Biomass-derived syngas exhibit physical and chemical characteristics that are similar to conventional fossil-derived syngas, which enables relatively easy integration of gasification-based biorefinery concepts with existing fossil syngas-based facilities. Oxo synthesis is an alternative application of biomass-derived syngas (Boerrigter and Rauch, 2006; Spath and Dayton, 2003). No detailed study of the integration of biorefinery concepts in oxo synthesis plants has been performed.

1.3 Case Study — Conventional Oxo Synthesis Plant

During hydroformylation, or oxo synthesis, olefins (i.e., unsaturated hydrocarbons) react with syngas (CO and H_2) in the presence of a catalyst, such as cobalt or rhodium complexes, to form aldehydes, according to reaction R1:



$$2RCH{=}CH_2 + 2H_2 + 2CO \rightarrow RCH_2\,CH_2CHO + RCH\overset{\overset{CH_3}{|}}{C}HO\ \text{Oxo} \qquad \text{(R1)}$$

R1 is an exothermic reaction, in which approximately 118 kJ per mol carbon-carbon double bond converted is released (Kohlpaintner, 2002). The applied H_2/CO ratio is usually approximately 1 mol per mol, as shown in R1.

The carbon chain of the olefin is extended with one carbon atom. In the case of ethylene and propylene, propionaldehyde and butyraldehyde (*normal* and *iso*), respectively, are formed. The oxo products usually range from C_3-C_{19}, in which butyraldehyde (butanal) is dominant, which accounts for 73% (Bahrmann et al., 2013). The aldehydes can subsequently be reacted to an extensive range of different secondary products, such as alcohols and carboxyl acids (Matar and Hatch, 2001). Many applications of established oxo products, such as pharmaceuticals, paints, solvents in coatings, resins and dyes, specialty plasticisers, synthetic lubricants, safety glass, animal feed and crop preservatives, exist. In 2009, the total annual worldwide oxo production capacity for aldehydes and alcohols was approximately 12 million tonnes (Bahrmann et al., 2013).

A large chemical process cluster on the west coast of Sweden has formulated a joint vision, in which the goal is to increasingly switch to renewable feedstock (Kemiföretagen i Stenungsund, 2013). One of the industrial process sites bases its production of specialty chemicals on oxo synthesis. The main material flows in the conventional oxo synthesis plant are illustrated in Figure 3 (IKEM, 2013).

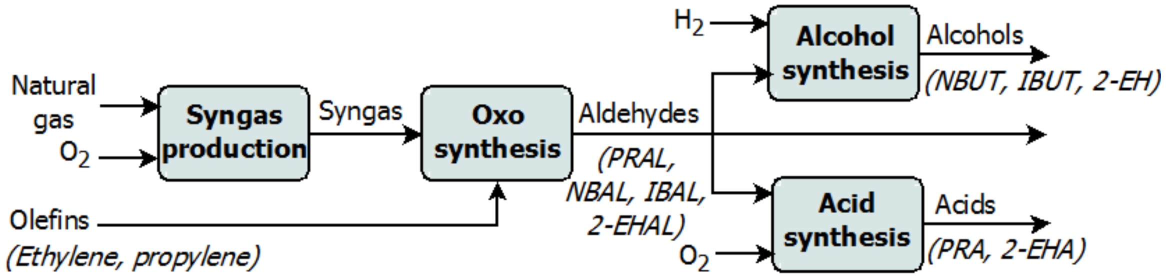


Figure 3. Main material flows in a conventional oxo synthesis plant (IKEM, 2013). Note that 2-EHAL is not a product of the oxo synthesis but was obtained from a subsequent step, in which NBAL is reacted with hydrogen. Adapted from Arvidsson et al. (2014).

Originally, the syngas at the site was produced by partial oxidation of oil feedstock. In 2004, oil was replaced by NG when the plant connected to the West Swedish NG grid. As shown in Figure 3, the oxo synthesis plant is typically fed with fossil feedstock such as NG (for syngas production) and chemical intermediates such as ethylene, propylene, and hydrogen, which in principle can be produced in a biomass gasification-based biorefinery. The conventional oxo synthesis plant is employed as a case study in this work.

1.4 The Objective

The objective of this thesis is to investigate and assess different opportunities for switching fossil-based process routes in the production of chemicals to biorefinery-based routes that are based on thermochemical gasification. Different integration points of the biorefinery concept in the process value chain and the biorefinery location are considered.

Heat recovery targets for the production of useful thermal heat and/or the cogeneration of electric power, as well as material integration opportunities, are investigated and quantified. The different biorefinery process concepts are compared based on thermodynamic performance, global GHG emission balances, and process economics.

1.4.1 The Scope

In this study, the production of syngas in a conventional oxo synthesis plant is considered as a case study. The option of retaining the existing conventional syngas production and either importing or producing bio-SNG onsite, which is denoted as BioSNG2Syngas, is compared with the option of scrapping the existing syngas production unit and investing in a new biomass-based syngas unit, which is denoted as Bio2Syngas. The conventional NG-based syngas production, which is denoted as the Base Case, is used as a reference in the comparison.

The main differences from other studies that address the integration of biomass gasification concepts at existing industrial sites reported in the literature are the selection of the host plant, i.e., an oxo synthesis plant, and the comparison approach, i.e., comparing two different routes with different introduction points in the fossil process value chain by replacing the same product (i.e., syngas fulfils the requirements for downstream oxo synthesis). Both routes are based on the same gasification technology and are associated with different heat recovery targets.

1.5 Thesis Outline

This licentiate thesis presents a summary of the progress accomplished during the first part of a PhD research project. A general overview of ongoing projects, conceptual design issues, and related studies associated with gasification-based biorefineries is provided in Chapter 2. The methodology employed in this study is described in Chapter 3. In Chapter 4, the results of the investigated syngas production routes are presented and discussed. The concluding outcomes of this study are summarised in Chapter 5 and suggestions for additional studies are presented in Chapter 6.

2. ENERGY EFFICIENT BIOMASS GASIFICATION-BASED CONVERSION PLANTS

A number of biomass gasification-based projects are in operation at the pilot and demonstration scale. Some commercial-scale projects are currently planned. The most common end products are heat and/or power and/or transportation fuels. This chapter presents an overview of ongoing biomass gasification-based projects and the status and challenges for different technology options in the conceptual design phase, as well as an overview of related studies on the integration of biomass gasification-based conversion plants in the industry.

2.1 Biomass Gasification-Based Conversion Plants — Ongoing Projects

An overview of some ongoing biomass-gasification projects is presented in Table 1. Some of the projects are briefly described in this section. For a recent review of syngas utilisation projects, refer to Rauch et al (2014).

In Güssing, Austria, an 8 MW_{th} biomass combined heat and power (CHP) plant that is based on fast internally circulating fluidised bed (FICFB) steam gasification technology has been in operation since 2002 (Hofbauer et al., 2003; Rauch et al., 2014). From syngas slip streams, research and development are performed using different applications, such as the production of SNG, FT, mixed alcohols, and hydrogen.

In the Netherlands, the ECN has demonstrated the production of SNG based on indirect gasification technology (MILENA gasifier technology) at the laboratory scale (30 kW_{th}) and the pilot scale (800 kW_{th}) (van der Meijden et al., 2009). Based on the same technology, several demonstration plants are being planned: 1 MW power generation from agricultural waste in India; 4 MW SNG production from waste wood in the Netherlands; and a 7 MW_{el} waste-to-energy plant in the UK (van der Meijden, 2014).

Table 1. Overview of ongoing and planned biomass gasification projects.

Organisation	Location	Gasification technology	Capacity	Products	Startup year
TU Vienna	Güssing, Austria	Indirect (FICFB)	8 MW_{th}	CHP, SNG, FT, etc.	2002
ECN	Petten, the Netherlands	Indirect (MILENA)	30 kW_{th} 0.8 MW_{th}	SNG CHP	2004 2008
ECN collab.	Washim, India	Indirect (MILENA)	1 MW_{el}	Power	2014[a]
ECN collab.	Alkmaar, the Netherlands	Indirect (MILENA)	4 MW_{SNG}	SNG	Planned
ECN collab.	Grimsby, the UK	Indirect (MILENA)	7 MW_{el}	Power	2016
Chalmers	Göteborg, Sweden	Indirect	2-4 MW_{th}	Syngas	2007
I/S Skive Fjernvarme	Skive, Denmark	ANDRITZ Carbona BFB	28 MW_{th}	CHP	2008
Luleå TU (Chemrec)	Piteå, Sweden	Entrained flow	3 MW_{th}	DME	2011
Karlsruhe Institute of Technology	Karlsruhe, Germany	Pyrolysis + Entrained flow (bioliq®)	5 MW_{th}	Gasoline via DME	2013
Göteborg Energi (*GoBiGas*)	Göteborg, Sweden	Indirect (FICFB)	20 MW_{SNG} 80 MW_{SNG}	SNG SNG	2014[b] Planned
Six partners[c] (*BioTfueL*)	Venette and Dunkirk, France	Torrefaction + Entrained flow (PRENFLO®)	15 MW_{th}	FT	2020
Choren Industries GmbH[d]	Freiberg, Germany	Low temp. + Entrained flow (Carbo-V®)	1 MW_{th} 45 MW_{th} 640 MW_{th}	FT FT FT	2002 On hold Planned
E.ON. (*Bio2G*)	Skåne, Sweden	Direct O_2	200 MW_{SNG}	SNG	Decision pending
Vapo Oy (*Forest BtL*)	Kemi, Finland	Carbo-V®	150 kt y^{-1} (products)	FT-diesel FT-naphtha	On hold

[a] Under construction, planned startup.

[b] Startup is ongoing.

[c] Axens, CEA, IFP Energies Nouvelles, Sofiprotéol, ThyssenKrupp Uhde, and Total.

[d] Since 2012, Linde Engineering Dresden GmbH.

The Gothenburg Biomass Gasification (GoBiGas) project developed by Göteborg Energi, which is a local energy company in south-western Sweden, includes a proof-of-concept bio-SNG plant in two stages (Gunnarsson, 2011; Göteborg Energi, 2014). The construction of the initial phase began in 2012 and full-time operation of the production of 20 MW SNG is planned in 2014. The design of the first phase is based on the 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 aimed at the production of 80 MW SNG is planned.

In 2014, E.ON. was awarded 204 million € by the EU via the NER300 program[2] for the Bio2G project, which encompassed a 200 MW SNG plant in southern Sweden (European Commission, 2014).

2.2 Biomass Gasification-Based Conversion Plants — Process Design

Figure 4 presents a general overview of the different process steps in a biomass gasification-based conversion plant and highlights some process alternatives for each step. The different process design options for each step are briefly detailed in the following sections. For the technology choices in this study, refer to Section 4.1.2 and **Paper I**.

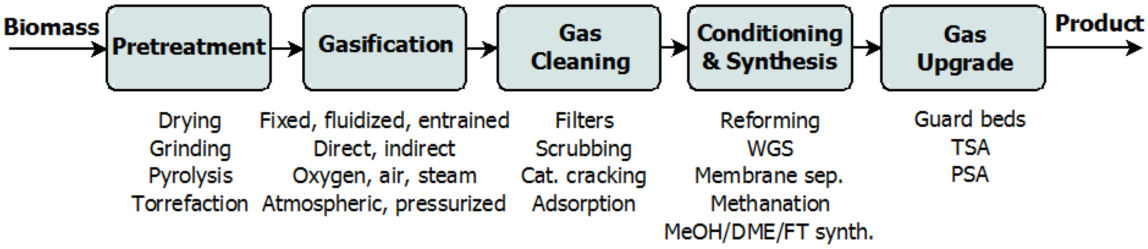


Figure 4. General process scheme of a biomass gasification-based conversion plant. Some examples in each step are highlighted.

2.2.1 Pretreatment and Gasification

Thermochemical gasification of lignocellulosic biomass involves numerous complex chemical reactions. Gasification generally involves three subsequent steps: evaporation of moisture, pyrolysis or devolatilisation of the feedstock (formation of char and volatiles such as hydrogen, water, CO, CO_2, methane, and condensable compounds (tars)), and

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[2] NER 300 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.

char combustion and gasification. In addition to the pyrolysis reactions, the main chemical reactions that occur during the gasification process are as follows:

$$C + \tfrac{1}{2}O_2 \rightarrow CO \qquad \Delta H_r^{298\,K} = -111\ \text{kJ mol}^{-1} \qquad \text{Partial oxidation} \qquad (R2)$$

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H_r^{298\,K} = +172\ \text{kJ mol}^{-1} \qquad \text{Reverse Boudouard} \qquad (R3)$$

$$C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H_r^{298\,K} = +131\ \text{kJ mol}^{-1} \qquad \text{Steam gasification} \qquad (R4)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_r^{298\,K} = -41\ \text{kJ mol}^{-1} \qquad \text{Water-gas-shift (WGS)} \qquad (R5)$$

$$CH_4 + H_2O \leftrightarrow CO + 3\ H_2 \qquad \Delta H_r^{298\,K} = +206\ \text{kJ mol}^{-1} \qquad \text{Steam reforming} \qquad (R6)$$

There are a number of different reactor types for conducting biomass gasification. They are typically grouped in three categories based on the fluid dynamic conditions inside the gasifier:

- fixed bed (updraft, downdraft, or cross-draft)
- fluidised bed (bubbling (BFB) or circulating (CFB))
- entrained flow

Another developing gasification technology, which is not discussed in this thesis, is plasma gasification.

Heat for the endothermic gasification reactions can be directly supplied (by simultaneous oxidation of part of the substrate) or indirectly supplied (e.g., by heat transfer with an inert bed material). Depending on the gasifier type and the final application, the gasification agent can be oxygen, air, and/or steam. The production of pure oxygen is expensive, whereas air is inexpensive but it dilutes the resulting syngas with nitrogen. Steam also shifts the composition of the resulting syngas according to reaction R5. The gasification reactions can be conducted at atmospheric or pressurised conditions. Different gasification technologies feature different raw syngas qualities in terms of gas composition, gas purity, and heating value. The capacity range is a very important characteristic for the commercialisation of biomass gasifiers. The different gasification technologies are suited for upscaling (listed here in increasing upscaling ability): fixed bed, fluidised bed, and entrained flow.

Prior to gasification, the incoming biomass (which usually has approximately 50 wt% moisture content) is dried to minimise the in-bed heat requirements for evaporating the moisture. Consequently, the energy efficiency of the gasification process and the gas quality are increased. Several biomass drying technologies are available, such as: steam drying, flue gas drying, and low-temperature air drying. Additional pretreatment such as pyrolysis or torrefaction, are particularly interesting in the case of entrained flow gasification, in which a very small feedstock size is required due to short residence times for the biomass in the gasification reactor.

The reactor design and conditions (pressure and temperature) and the gasification agent affect the resulting syngas quality in terms of the gas composition, purity, and heating value. The reactor design (e.g., feeding point of the feedstock and the gasification agent and the outlet point of the syngas) will determine the location and temperature in the reactor for the different chemical reactions. For example, arranging a fixed bed in downdraft or updraft mode will result in tar concentrations of less than 1 g/Nm^3 and concentrations higher than 100 g/Nm^3, respectively (Basu, 2010; Milne et al., 1998). Entrained flow gasifiers, which operate at high temperatures, contain a low concentration of tar or methane in the resulting syngas. A fluidised bed gasification operation results in a syngas that contains tar and methane. If the desired product is SNG, the methane concentration in the syngas can be advantageous. However, the methane concentration must be reformed for most alternative applications. Tar is considered to be one of the main challenges for biomass gasification and extensive cleaning is required for tar removal (Basu, 2010; Milne et al., 1998).

For directly heated gasifiers, heat for the endothermic gasification reactions is supplied by in-situ combustion of part of the biomass feedstock. To prevent dilution of the syngas with nitrogen, oxygen (not air) is required. In the case of fluidised bed gasification, the gasification and combustion reactions can occur in two separate chambers and the heat can be indirectly transferred by circulation of the bed material (frequently referred to as a dual bed). No pure oxygen is required to produce a nitrogen-free syngas, and steam can be used as a gasification agent (and air for combustion).

A pressurised operation of the gasification unit is desirable to reduce the equipment size and the downstream gas compression demands. Pressurising the solid material is complex and requires an advanced feeding system. Note that the gasification reactions and the syngas composition are affected by the operating pressure. The atmospheric operation is less complex but requires a larger gasification unit and a downstream syngas compression step.

2.2.2 Gas Cleaning

As discussed in the previous section, the syngas quality (gas composition, purity, and heating value) significantly varies depending on the gasification technology, the operating setup and the process conditions. The impurities in the syngas are highly dependent on the feedstock composition (Dayton et al., 2011). Impurities associated with biomass-derived syngas include particles (e.g., char, dust, and bed material), tars (e.g., phenol, toluene, and naphthalene), sulphur compounds (e.g., H_2S and COS), nitrogen compounds (e.g., ammonia and HCN), halogens (e.g., HCl), and alkali metals.

Woody biomass generally contains relatively low amounts of sulphur, chlorine, and ash. To prevent the fouling of downstream equipment and deactivation of a catalyst in downstream gas upgrading and synthesis, the removal of these impurities is usually necessary. However, the level of required syngas cleaning varies for different applications.

The removal of particulates can be conducted by fabric or barrier filters, electrostatic precipitators, or scrubbing.

If tar condensation is to be prevented, the operating temperature should be maintained above the tar dew point. Tar removal is particularly necessary to prevent extensive fouling in downstream equipment, such as pipes, particulate filters, compressors, and heat exchangers. The formation of tar can be reduced using catalytic bed material in the gasifier. Post-gasification tar removal can be conducted using thermal and catalytic cracking or technologies such as filters and advanced scrubbing. A combination of technologies can also be applied, e.g., filter and subsequent scrubbing or catalytic reforming. Tar scrubbing has been demonstrated as feasible using water (Teislev, 2002) or organic liquids (e.g., rapeseed methyl ester (RME) scrubbing) (Rauch and Hofbauer, 2003; Zwart et al., 2009). Scrubbing has been demonstrated as feasible both below and above the water dew point in the syngas. Operation below the water dew point requires a phase separator unit and causes wastewater treatment issues thus, operation above the water dew point is preferred.

Thermal losses are generally inevitable in gas scrubbing. Catalytic tar cracking is an interesting option for reducing these losses, whereas the syngas is retained at a high temperature and the undesired tar compounds are converted to desired compounds (CO and H_2), i.e., the chemical energy is be retained in the syngas. However, catalytic tar cracking continues to occur at the research stage.

Sulphur is extremely poisonous to catalysts thus, almost complete removal is necessary for applications involving catalytic processes. The removal can be conducted by chemical (using amine wash) or physical (using organic solvents) absorption in combination with either chemical (using ZnO beds for sulphur trace removal) or physical (using activated carbon or zeolites for removal of non-polar or polar compounds) adsorption. Physical adsorbents can be thermally regenerated or regenerated with pressure. Sulphur recovery, such as by the Claus process, may not be economically viable for low sulphur-containing feedstock, such as woody biomass (Zwart, 2009). Most of the previously mentioned technologies also simultaneously remove CO_2 however, the selectivity differs.

For other impurities, such as nitrogen compounds, halogens, and alkali metals, purification technologies similar to the previously mentioned technologies can be employed. For example: ammonia is soluble in water and can be removed by water scrubbing; HCl can be removed using adsorbents or scrubbing with water or caustic water solution; alkali vapours can be condensed onto solid particulates by syngas cooling and can be removed with the particles (Zwart, 2009).

2.2.3 Conditioning and Synthesis

For syngas containing methane and for applications in which it is not desired, the methane can be reformed into CO and H_2 by steam reforming (refer to R6) or autothermal reforming (ATR). Reforming reactions are endothermic. Using Ni-based catalysts, the kinetics can be improved and the required reaction temperature can be reduced. Steam reforming is a conventional technology that is generally performed in tubular reactor furnaces. In an ATR, oxygen and steam are added to enable exothermic partial oxidation reactions that supply heat to the endothermic steam reforming reactions in the same reactor. The ATR technology has been proven at an industrial scale.

Depending on downstream applications and synthesis, adjustments to the H_2/CO ratio may be necessary. If a higher H_2 content is required, the gas can be shifted in a water-gas-shift (WGS) reactor (refer to R5). The WGS reactions can be conducted using sulphur tolerant (sour) or nontolerant (sweet) catalysts. The reactions can also be set up as a partial WGS reactor or operate in one or two steps. If a lower H_2 content is required, H_2 can be separated from the syngas to be used elsewhere. The separation process can be conducted using membrane technology. To achieve a pure H_2 byproduct stream, the membrane can be integrated with a pressure swing adsorption (PSA) unit.

After syngas purification and conditioning, the desired product (e.g., methanol, SNG, DME, or FT-products) is synthesised. In the case of SNG production, the syngas needs to be converted to a methane-rich gas. Methanation of CO is conducted by the following reaction:

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ $\Delta H_r^{298\ K} = -206\ kJ\ mol^{-1}$ Methanation of CO (R7)

As seen in R7, the optimal H_2/CO ratio for the incoming syngas is three. By combining the CO methanation reaction (R7) with the WGS reaction (R5), methanation of CO_2 can occur as follows:

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_r^{298\,K} = -164\ kJ\ mol^{-1}$ Methanation of CO_2 (R8)

Note that the CO methanation reaction (R7) is highly exothermic, which provides interesting integration opportunities. Methanation of syngas can be catalytically conducted using two different reactor concepts: adiabatic fixed-bed reactors in series with intercooling and an optional recycle or single isothermal fluidised bed reactor (Kopyscinski et al., 2010). The syngas conversion processes for methanol, DME, and FT are also exothermic, which can provide interesting integration opportunities.

2.2.4 Gas Upgrade

To fulfil the product specifications, some final upgrading steps are necessary, such as final drying or the removal of trace impurities. The requirements for injecting SNG to the NG grid or for synthesis in downstream chemical reactions need to be satisfied. A harmonisation of recommended gas quality for possible injection to the NG grid within the EU is underway, including Wobbe index, sulphur, and CO_2 content (EASEE-gas, 2005).

3. METHODOLOGY

The objective of this study is to investigate and assess different opportunities for switching traditionally fossil-based production of chemicals to biomass-based routes, particularly via thermochemical gasification. Different drop-in approaches at different integration points in the conventional process value chain are considered. A conventional oxo synthesis plant, which currently converts NG to syngas to be reacted with olefins into various oxo products, is used as a case study. In this study, the option to fully switch the NG feedstock to bio-SNG (BioSNG2Syngas) is compared with the option to fully switch to an intermediate, i.e., replacing syngas with bio-syngas (Bio2Syngas). The conventional NG-based syngas production is used as a reference in the comparison (Base Case).

The investigated biorefinery options are compared based on their thermodynamic performance, global GHG emission balances, and process economics. First, appropriate system boundaries for the investigated systems are set up. Process simulation of the different routes is conducted to obtain mass and energy balance. Heat and material integration opportunities for the investigated biomass-based options are investigated and quantified. To enable a comparison on an equal basis, heat recovery targets for the production of useful thermal heat and/or the cogeneration of electric power are systematically estimated using pinch analysis targeting tools.

3.1 Selection of System Boundary

Three system boundary levels are applied in the assessment. The first level (the Syngas system) is applied in **Paper I**. The second level (the Oxo system) and third level (the Expanded system) are applied in **Paper II**. A general overview of the investigated systems with the main input and output streams is presented in Figure 5.

As explained in the following sections, not all boxes or streams indicated in Figure 5 apply to each of the investigated cases.

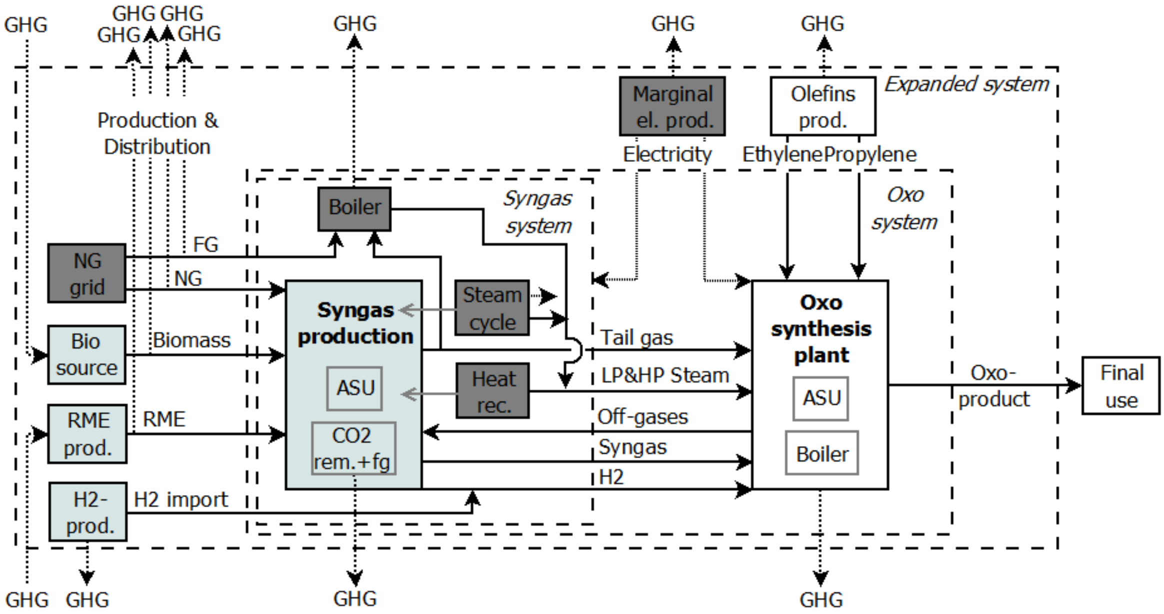

Figure 5. General overview of the investigated systems. The black dashed boxes indicate the system boundary levels applied in this study: the Syngas system (**Paper I**), the Oxo system (**Paper II**), and the Expanded system (**Paper II**). The light gray- shaded boxes highlight the differences between the BioSNG2Syngas and Bio2Syngas concepts. The dark gray-shaded boxes highlight the differences among all investigated systems.

3.1.1 The Syngas System

In the thermodynamic performance analysis (**Paper I**), the considered system boundary includes the syngas production, where syngas (refer to Section 4.1.1) is produced via three different routes to fulfil the required specifications for downstream oxo synthesis: conventional fossil-based (Base Case), biomass gasification-based via SNG (BioSNG2Syngas), and direct biomass gasification-based (Bio2Syngas). In the case of BioSNG2Syngas, this approach implies that conventional syngas production (i.e., converting bio-SNG to syngas) is included within the system boundary.

The material and energy streams exchanged between the Syngas system (fossil- or biomass-based) and the oxo synthesis plant (i.e., syngas, H_2, tail gas, steam, and off-gases) are considered to be fixed in the analysis. The design specifications for the biorefinery cases are determined by the material and energy streams that are currently delivered from the fossil-based syngas production unit to the oxo synthesis plant, i.e., the flows of syngas, H_2, tail gas, and high-pressure (HP) steam at a bar level of 41 in the Base

Case process. In addition, the oxo synthesis site's net low pressure (LP) steam demand that is currently produced by the firing of purchased fuel gas is included in the investigated systems.

High-temperature excess heat (from various gas cooling steps) can be recovered for the production of useful thermal heat and/or cogeneration of power. The "Heat rec." box in Figure 5 represents heat recovery in the syngas production processes for HP and possibly LP steam production. The "Steam cycle" box in Figure 5 represents heat recovery steam cycles that are integrated with the biorefinery processes for the cogeneration of power and possibly useful thermal heat. Heat recovery targets for the integration of steam cycles are systematically estimated by assuming ideal process heat recovery and applying pinch analysis tools, as detailed in Section 3.2.2.

3.1.1.1 Conventional Fossil-Based Syngas Production (Base Case)

In the conventional fossil-based syngas production, NG and mixed off-gases are processed into syngas by partial oxidation with oxygen. The oxygen demand is currently supplied from a cryogenic air separation unit (ASU) that is located in another cluster plant. The ASU is assumed to be located within the system boundary to consider the power consumption for oxygen production.

A number of cleaning and conditioning steps are required for the raw syngas to comply with the required syngas specifications. In the final H_2/CO ratio adjustment step, a pure H_2-stream is obtained (due to a higher presence of H_2 in the syngas than required). The total H_2 demand in the downstream oxo synthesis is high, which requires additional H_2 import. After the final adjustment steps, tail gas is also obtained, which is fired in steam boilers that supply steam to the oxo synthesis plant.

Syngas production via partial oxidation of NG releases excess heat at high temperatures which can be recovered for HP steam production (indicated as "Heat rec." in Figure 5).

The LP steam demand of the case study oxo synthesis plant is currently produced in a boiler by firing purchased fuel gas from a neighbouring steam cracker plant. A boiler efficiency of 72% (higher heating value (HHV) basis) is assumed.

Note that the streams that indicate utilisation of biomass, RME, and tail gas split stream to the LP steam boiler and the "Steam cycle" box in Figure 5 do not concern the Base Case system.

3.1.1.2 Biomass Gasification-Based Syngas Production via SNG (BioSNG2Syngas)

In biomass gasification-based syngas production via the intermediate production of SNG (BioSNG2Syngas), the energy of the produced bio-SNG is set to match the current NG import. In the bio-SNG production process, lignocellulosic biomass is converted via thermal gasification to a raw syngas, which is cleaned and upgraded to a methane-rich gas. Bio-oil (RME) is employed in the tar removal step.

Two possible locations of the bio-SNG production are considered. The first option is to produce bio-SNG in a stand-alone plant and transport it via the NG grid to the oxo synthesis plant. The second option is to colocate the bio-SNG plant at the oxo synthesis plant site, which enables heat integration between the plants.

High-temperature excess heat in the bio-SNG production can be recovered in a steam cycle that cogenerates steam and power (indicated with “Steam cycle” in Figure 5). Depending on the location of the bio-SNG process, different heat recovery options can be considered. For example, in the case of bio-SNG that is produced in proximity of the oxo synthesis plant, back-pressure LP steam production can be considered, which reduces or completely eliminates the current fuel gas import to existing boilers. High-temperature excess heat in the downstream conventional syngas production is recovered for HP steam production (indicated with “Heat rec.” in Figure 5).

Note that the NG stream and the tail gas split stream to the LP steam boiler in Figure 5 do not concern the BioSNG2Syngas system.

3.1.1.3 Biomass Gasification-Based Syngas Production (Bio2Syngas)

For the Bio2Syngas case, the produced bio-syngas is set to match the requirements of the current syngas for downstream oxo synthesis in terms of energy flow rate, composition (H_2/CO specifications and purity), temperature, and pressure.

In the bio-syngas production process, lignocellulosic biomass is converted via thermal gasification to a raw syngas, which is cleaned and upgraded. As in the bio-SNG process, bio-oil (RME) is employed in the tar removal step. In contrast to the bio-SNG process, the methane concentration in the syngas is not desirable but is necessary to reform the undesired methane and various off-gases from the oxo synthesis plant. Thus, oxygen is required. To account for the power consumption for oxygen production, an ASU is considered to be located within the system boundary. Similar to the conventional syngas process, the final H_2/CO ratio adjustments of the syngas produces a pure H_2 side-stream and a tail gas, which affects the additional H_2 import and the LP steam production balance (represented by the tail gas split stream to the LP steam boiler in Figure 5).

High temperature excess heat in the bio-syngas production can be recovered for cogeneration of power and/or useful thermal heat. Depending on the heat recovery option, a condensing steam cycle network (indicated by “Steam cycle” in Figure 5) or heat recovery for the production of useful thermal heat (indicated by “Heat rec.” in Figure 5) are considered. Note that the HP steam demand of the oxo synthesis plant is set as a requirement. In the case of heat recovery for LP steam production, the current fuel gas import can be reduced or completely eliminated.

Note that the NG stream in Figure 5 does not concern the Bio2Syngas system.

3.1.2 The Oxo System

As shown in Figure 5, the Syngas system produces a spectrum of products that are considered fixed in the analysis. For the process economics analysis (**Paper II**), the performance indicator is defined as the difference of the total productions costs of the BioSNG2Syngas and the Bio2Syngas concepts compared with the Base Case, which is expressed per tonne of oxo product. The considered system boundary is expanded to include the oxo synthesis plant, as shown in the “Oxo system” in Figure 5. By applying this approach, the obtained economic evaluation can become more generalised. Future comparisons of other opportunities to switch to biomass-based production are also facilitated.

Ethylene, propylene, and oxygen comprise the feedstock in the oxo synthesis. The power consumption for oxygen production in an ASU and the power consumption in the oxo synthesis plant are considered. The final product of the Oxo system (denoted as the oxo product) is selected as the resulting primary aldehyde production (i.e., propionaldehyde and butyraldehyde).

3.1.3 The Expanded System

For the global GHG emission balance (**Paper II**), as discussed in Wetterlund et al. (2010), the considered system boundary is expanded to account for both onsite and offsite GHG emission effects that are associated with the production of oxo products, as shown in the “Expanded system” in Figure 5. This approach implies that well-to-gate emissions (i.e., associated with production and distribution to the plant battery limit) are considered. CO_2 uptake associated with photosynthesis during biomass growth is also included. The final use of the fossil- and biomass-based oxo products is identical. When comparing the changes in GHG emissions for the biomass-based concepts to the fossil Base Case, the nature of the end use does not affect the results, as discussed in Holmgren et al. (2014). The final use for the oxo products is not considered and is beyond the Expanded system boundary.

3.2 Energy Efficient Process Design

The process layout of the investigated syngas production concepts will influence the total process performance, which requires that energy efficiency be considered at the preliminary process design stage. The process layout of the investigated syngas production concepts (**Paper I**) was determined based on information obtained from the literature. The mass and energy balance of the selected process designs were generated using process simulation tools.

3.2.1 Process Layout

In the Base Case process layout, NG with mixed off-gases are processed into syngas by partial oxidation with oxygen. Noncatalytic partial oxidation (NC-POX) is a commercially available technology.

Biomass gasification has not been proven at a commercial scale. For the BioSNG2Syngas route, in which syngas is produced via intermediate bio-SNG production, the process design of the bio-SNG production is similar to the layout of the proof-of-concept demonstration plant GoBiGas phase 1 (refer to Section 2.1).

The two biomass conversion processes are based on the same gasification, tar removal, and sulphur removal technologies. As the direct Bio2Syngas route does not aim for a methane-rich gas, as in the case of the bio-SNG process, but for a syngas that fulfils the specifications for direct oxo synthesis, the process equipment downstream from the sulphur removal deviates from the bio-SNG process. As mentioned in Section 3.1.1.3, reforming of undesired methane and various off-gases from the oxo synthesis plant is necessary. Downstream of the reformer, the process layout of the direct bio-syngas route is similar to the Base Case route.

The selected process layouts are described in Section 4.1.2. and **Paper I**.

Mass and energy balance calculations were performed by establishing process simulation models of the investigated syngas production concepts (**Paper I**) based on information available in the literature. The commercial flowsheeting software Aspen Plus was employed (AspenTech, 2011). The Peng-Robinson equation of state with the Boston-

Mathias modifications (PR-BM) property method[3] was utilised as the investigated processes involve gas processing at high temperatures and pressures. The results were validated where possible with published data. For detailed modelling assumptions, data and relevant references, refer to **Paper I**.

In this study, pinch analysis tools are utilised for establishing targets for maximum heat recovery for the different syngas concepts, as discussed in Section 3.2.2. This approach implies that no assumptions about the possible layout of the heat exchanger network (HEN) are included in the process design. Stream heating and cooling requirements are identified and quantified as separate heaters and coolers, respectively.

3.2.2 Process Integration

The IEA definition of process integration is "s*ystematic 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 (addressed in **Paper I**) have been analyzed: (*i*) material integration of biorefinery products into conventionally fossil-based value chains at different entry points, e.g., the production of syngas via intermediate bio-SNG production or directly for downstream oxo synthesis and (*ii*) heat recovery targeting of thermal process streams in the investigated syngas production concepts using pinch analysis tools.

For geographical or technical reasons, unconstrained heat recovery cannot be achieved within the boundaries of the entire Syngas system, and appropriate subsystems must be considered (refer to **Paper I**). The subsystems include the conventional syngas production process, the bio-SNG production process, and the direct bio-syngas production process. Different heat recovery options are considered for the different concepts, as discussed in Section 3.1.1.

For the Base Case, the heat recovery target in the conventional syngas production process for HP steam production is estimated and set as a requirement for the biorefinery cases.

For the BioSNG2Syngas case, two different heat recovery options are considered depending on the location of the bio-SNG production process. First, in the stand-alone bio-SNG process, the high-temperature excess heat is assumed to be recovered in a heat recovery condensing steam cycle to maximise the electricity generation potential (denoted

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[3] Complemented with steam tables for water and steam processes.

as Case El). In this setup, the electricity import of the system is minimised; however, purchase of fuel gas for firing in a boiler for LP steam production is required. Second, in the colocation case, the high-temperature excess heat released from the bio-SNG process is assumed to drive a heat recovery back-pressure steam cycle for cogenerating electric power and LP steam, which is delivered to the downstream oxo synthesis plant (denoted as Case LP). In this setup, the current fuel gas import is reduced or completely eliminated. Compared with Case El, the system's electricity import is consequently increased.

For the Bio2Syngas case, two different heat recovery options are investigated. First, the electricity production is maximised by installing a condensing steam cycle network (Case El). Second, the opportunity for LP steam production by heat recovery in the bio-syngas process is investigated (Case LP).

Pinch analysis is a method that is based on the first and second law of thermodynamics for systematically estimating heat recovery targets of thermal systems. The concept was originally developed by Linnhoff's group at the University of Manchester's Institute of Science and Technology (UMIST), who produced the first user guide in the 1980s (Linnhoff et al., 1982). Updated descriptions of pinch analysis are provided in Smith (2005) and Kemp (2007).

Heat recovery targets can be estimated by analysing the thermal cascades of the process streams' heating and cooling requirements (i.e., without predefining a HEN design, as discussed in Section 3.2.1). Maximum heat recovery for all investigated syngas production processes is assumed. To prevent unrealistic heat transfer conditions among process streams, a minimum temperature difference (ΔT_{min}) for heat exchange is imposed. In this study, a ΔT_{min} value of 10 K is assumed. A process thermal cascade can be represented in the grand composite curve (GCC), which provides graphical insights into the required and available amount of heat and the temperature levels for the conditions of ideal heat recovery. To access the potential integration between two process parts (or two different processes), one GCC can be plotted against another GCC following the principles of split-GCC graphical analysis (Kemp, 2007).

In this study, split-GCC analysis is applied for estimating steam generation targets by representing the GCC of the steam production against the GCC of the process under investigation and by properly adjusting the steam mass flow rate to maximise the recovery of process excess heat. Similarly, power generation targets by steam turbines can also be estimated by including the GCC of the steam cycle network. For assumptions regarding the steam production and steam network, refer to **Paper I**. In the case of integration of a heat recovery steam network, the steam extractions are iteratively adjusted to match the heat demands of the background processes, which activate at least one pinch point between the GCC for the steam network and the GCC for the process.

3.3 Process Performance Evaluation

Performance indicators are defined to assess and compare different options to fully substitute the syngas in a conventional oxo synthesis plant with biomass-derived syngas. The investigated biorefinery options are compared based on their thermodynamic performance (energy and exergy efficiencies) (**Paper I**), global GHG emission balance (GHG emission reduction potential) (**Paper II**), and process economics (change in production cost compared with the Base Case) (**Paper II**).

3.3.1 Thermodynamic Performance

For systems that can be generally characterised as an energy conversion process (e.g., when a feedstock is also conventionally employed as a fuel or when heat and power are generated and/or consumed), the evaluation of the thermodynamic performance of the process is useful. Depending on the purpose of the analysis, thermodynamic performance can be defined using several approaches. As discussed in the evolving eBook *Systems Perspective on Biorefineries* by Lind et al. (2014), the definition of energy efficiency is especially difficult for multi-product systems.

In this study, two performance indicators are used to assess the thermodynamic material and energy utilisation efficiency of the investigated syngas concepts (**Paper I**): energy and exergy efficiency. Note that the Syngas system's products are fixed for all investigated syngas concepts in this analysis. In the energy performance indicator definition, 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.

3.3.1.1 Energy Efficiency

Energy efficiency can be defined in several ways (Lind et al., 2014; Haro et al., 2014). In this study, the energy efficiency (η_{en}) is defined as the ratio between the net useful energy products and the net required energy inputs according to eq. (1):

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

where $\dot{n}_p$ and $\dot{n}_f$ are the molar flows (kmol s^{-1}) and HV_p and HV_f, respectively, are the corresponding heating values (HHV basis) (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, i.e., a given energy stream is considered either as a product or a feed to the system.

3.3.1.2 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 to 1.01325 bar and 25 °C.

The exergy efficiency (η_{ex}) is defined as the ratio between the exergy content of the net useful products to the exergy content of the net required inputs, according to eq. (2):

$$\eta_{ex} = \frac{\sum_p \dot{n}_p \cdot e_p + \sum \dot{E}_{\dot{W}^-} + \sum \dot{E}_{\dot{Q}^-}}{\sum_f \dot{n}_f \cdot e_f + \sum \dot{E}_{\dot{W}^+} + \sum \dot{E}_{\dot{Q}^+}} \qquad (2)$$

where $\dot{n}_p$ and $\dot{n}_f$ are the molar flows (kmol s^{-1}) and e_p and e_f, respectively, are the corresponding exergy content (MJ $kmol^{-1}$) of the net products (index p) and net feeds (index f), respectively; $\dot{E}_{\dot{Q}^-}$ and $\dot{E}_{\dot{Q}^+}$ are the exergy content of the net useful thermal heat production and net useful thermal heat demand (MW), respectively; and $\dot{E}_{\dot{W}^-}$ and $\dot{E}_{\dot{W}^+}$ are the exergies of the net power production and net power demand (MW), respectively. Similar to the energy efficiency, the exergy efficiency is based on net flows (i.e., a given energy stream is considered either as a product or a feed to 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 variation is null or negligible against the remaining terms. Values and group contributions for standard chemical exergies of the components at the reference state (MJ per $kmol^{-1}$) are tabulated in Szargut et al. (1988). For biomass, the chemical exergy is estimated by its elemental composition and heating value, as described by Szargut et al. (1988).

3.3.2 Global Greenhouse Gas (GHG) Emissions

The environmental effect of a process can be quantified using several different criteria. The environmental performance indicator retained in this study is the GHG emissions reduction potentials per tonne of oxo product (assumed to be primary aldehydes, as discussed in Section 3.1.2) for producing oxo products from biomass-derived syngas compared with fossil-derived oxo products (**Paper II**).

The considered GHG emission sources are sources that cross the system boundary of the Expanded system (refer to Section 3.1.3), as shown in Figure 5. All emissions are considered to be CO_2 equivalents[4] ($CO_{2,eq}$). The GHG emission reduction potential (kg $CO_{2,eq}$ per tonne of oxo product) for the syngas origin switch in the production of oxo products is estimated according to eq. (3):

$$GHG\ Reduction\ Potential = \left[\left(\dot{E}_{NG} \cdot ghg_{NG,wtg+sg} + \dot{E}_{FG} \cdot ghg_{FG,wtg+comb} + \dot{E}_{H_2} \cdot ghg_{H_2,wtg+comb} + \dot{E}_{BIO} \cdot ghg_{BIO,upt-wtg-sg} + \dot{E}_{RME} \cdot ghg_{RME,upt-wtg-comb} - \dot{E}_{EL} \cdot ghg_{EL}\right) \cdot t\right] / \dot{m}_{oxo\ product} \qquad (3)$$

where $\dot{E}_i$ is the change in the energy/material flow i (MW), which includes avoided NG import (NG), avoided fuel gas import (FG), avoided H_2 import (H_2), biomass import (BIO), RME import (RME), and the change in net electricity import (EL); $ghg_{i,j}$ is the GHG emissions associated with the energy/material flow i of type j (kg $CO_{2,eq}$ MWh^{-1}), in which the material/energy flows (i) includes NG (NG), fuel gas (FG), H_2 (H_2), biomass (BIO), RME (RME), and electricity (EL) and the GHG emission types (j) include uptake (upt), well-to-gate (wtg), combustion ($comb$), and syngas production (sg); t is the operating time (h y^{-1}) and $\dot{m}_{oxo\ product}$ is the annual production of oxo products (t y^{-1}).

Note that the GHG emission sources from the olefins production and the oxo synthesis (refer to Figure 5) are fixed in the analysis (regardless of syngas origin), and consequently, the relative change compared with the Base Case is zero.

Regarding the changes of the site net electricity import, the electricity generation in a reference base-load grid power plant is assumed to be affected. In this study, the reference grid power plant from an European perspective is assumed to be a fossil fuel-fired condensing power plant (Sköldberg et al., 2006), which is represented by modern high-

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[4] Considering CO_2, methane, and N_2O in accordance with their respective global warming potential for a 100 year period (GWP_{100}) (GWP_{100} conversion factors: $CO_2 = 1$ $CH_4 = 25$, and $N_2O = 298$) (Forster et al., 2007).

efficient coal power plants (coal PP) with and without carbon capture and storage (CCS). For details about the effect of GHG emissions, refer to **Paper II**.

3.3.3 Process Economics

There are several methods for assessing the profitability or economic performance of investments, of which the best methods are based on cash flow projections over the project lifetime (Smith, 2005). Examples of metrics based on cumulative cash flows are the payback period (PBP), the return on investment (ROI), the net present value (NPV), and the discounted cash flow rate of return (DCFRR). The latter two metrics consider the time value of money and variations in cash flows over the project lifetime. The NPV is an adequate measure of profitability, whereas the DCFRR is an adequate measure of how efficiently the capital is used. The inputs to calculate the cumulative cash flows for an investment consist of fixed and variable costs and revenue (or avoided costs). In addition, assumptions regarding project lifetime and interest rate are required.

The objective of this study is to compare the option of retaining the existing conventional syngas production at a conventional oxo synthesis plant and switch from NG to bio-SNG with the option of scrapping the existing syngas production unit and investing in a new biomass-based syngas unit. As shown in Figure 5, several different material and energy inputs are required in the production of oxo products (assumed as resulting primary aldehydes). Establishing reasonable costs for feedstock, energy commodities, and sale prices of products are major challenges when conducting an economic assessment. In this study, we compare the change in specific production cost relative to the fossil route (Base Case). Fixed inputs are eliminated from the calculations and no sales prices of the product are necessary.

The economic performance indicator used in this study is the change in production cost ($\Delta C_{oxo\,product}$) for producing oxo products from biomass-derived syngas compared with fossil-derived oxo products (**Paper II**) on a per tonne oxo product basis. The change in the production cost of oxo products is based on the annual incremental capital investment, changes in the fixed and variable operating costs (in which the considered operating cash flows are the flows that cross the system boundary of the Oxo system, as shown in Figure 5) and estimated according to eq. (4):

$$\Delta C_{oxo\,product} = \left[a \cdot C_F + C_{O\&M} + C_{lb} + \left(\dot{E}_{BIO} \cdot p_{BIO} + \dot{E}_{EL} \cdot p_{EL} - \dot{E}_{NG} \cdot p_{NG} - \dot{E}_{FG} \cdot p_{FG} - \dot{E}_{H2} \cdot p_{H2}\right) \cdot t - \dot{m}_{CO_2} \cdot p_{CO_2}\right] / \dot{m}_{oxo\,product} \quad (4)$$

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), avoided H_2 import (H_2); $\dot{m}_{CO_2}$ is the avoided annual onsite fossil CO_2 emissions (t CO_2 y^{-1}); p_i is the price of the energy/material flow i (€ MWh^{-1}), which includes biomass (BIO), electricity (EL), NG (NG), fuel gas (FG), H_2 (H_2), onsite fossil CO_2 emissions (CO_2); t is the operating time (h y^{-1}) and $\dot{m}_{oxo\,product}$ is the annual production of oxo products (t 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 of estimating the capital investment using the factorial approach is ±30% (Smith, 2005).

The changes in fixed operating costs are estimated from 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 amount of man hours, respectively.

The changes in variable operating costs are estimated from the changes in material and energy flows and onsite fossil CO_2 emissions. Note that the ethylene and propylene import (refer to Figure 5) are fixed in the analysis (regardless of syngas origin) and consequently, the relative change to the Base Case is zero.

It is crucial to base the economic evaluation on realistic cost of 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 2030 (which is assumed to be a representative operating year for the considered investments). Prices for fossil fuels (i.e., NG 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[5] (denoted as WEO current policies) and the 450 ppm scenario[6] (denoted as WEO 450 ppm) (IEA, 2013).

Based on fossil fuel prices and assumed policy instruments, the price of biomass and electricity are projected using the methodology described in Axelsson and Harvey (2010)

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[5] Only policies enacted by mid-2013 are considered.

[6] The implementation of policies required to attain 50% probability to limit the long-term increase in average global temperature to 2°C is assumed.

and Axelsson and Pettersson (2014). In this analysis, the only policy instrument that is considered is the CO_2 charge. Note that few policy instruments have been developed, e.g., in the form of subsidies, for the chemical sector.

The H_2 price is estimated based on the hydrogen levelised costs reported by the US Department of Energy (US DOE) (Dillich et al., 2012). For detailed calculation assumptions, data, and relevant references, refer to **Paper II**.

4. RESULTS & DISCUSSION

This Chapter presents and discusses some of the key results from the appended papers. First, the process simulation results and the results of the energy targeting analysis of the different routes to syngas (**Paper I**) are presented. The different syngas routes are compared based on their thermodynamic performance (**Paper I**), global GHG emission balance, and process economics (**Paper II**).

4.1 Process Simulation Results

The process simulation results (input data, selected process layouts, and resulting mass and energy balance) presented in this Section are based on **Paper I**.

4.1.1 Process Simulation - Input Data

Data for the conventional fossil-based syngas production (Base Case) are listed in Table *2*. Data on the total supply to the plant (“Total”) are presented, and break-down details are presented for the syngas production (“Syngas”) and the oxo synthesis units (“Oxo”) (as parts of the Oxo system). Oxygen and electricity flows to the syngas production unit, which are presented in Table 2, are estimates based on the mass and energy balance calculations in **Paper I**.

The Base Case Syngas system was determined from the specified flows of NG and H_2 (refer to Table 2), off-gases (2.0 kt per year), and LP steam (20 MW) as input data. The produced syngas must satisfy the requirements for downstream oxo synthesis, i.e., H_2/CO ratio within the interval 1 to 1.1 (1.1 was assumed in this study) and a combined H_2+CO concentration that exceeded 99.4 mol%. The material and energy streams exchanged between the Syngas system and the oxo synthesis plant (i.e., syngas, H_2, tail gas, LP and HP steam, and off-gases) were specified accordingly.

The Base Case results determine the design specifications for the biorefinery cases. For detailed descriptions, refer to **Paper I**. The data for the NG and lignocellulosic biomass feedstock are listed in Table A1 and Table A2, respectively, in the Appendix.

Table 2. Data for the conventional fossil-based syngas production (Base Case). The values are reported as mass flow rate (energy flow rate) in kt per year (MW).

	NG	Ethylene	Propylene	H_2	Oxygen[a]	El.[b]	Oxo prod.[c]
Total	95 (175)	24 (42)	190 (322)	5.7 (28)	145 (8.1)	- (10)	364 (-)
Syngas	95 (175)	- (-)	- (-)	5.7 (28)	124 (6.9)	- (3.9)	- (-)
Oxo	- (-)	24 (42)	190 (322)	- (-)	21 (1.2)	- (6.1)	364 (-)

[a] The oxygen demand for syngas production was estimated, as reported in **Paper I**. The energy flows (in MW) for the oxygen flows correspond to the power consumption for production in an ASU and are added to the electricity demand of the system.

[b] The total electricity (El.) demand is based on reported average annual values (Perstorp Holding AB, 2010), and the electricity demand in 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 separately listed as the energy flow rate in the "oxygen-column".

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

4.1.2 Process Simulation – Process Layout

4.1.2.1 Conventional Fossil-Based Syngas Production (Base Case)

The process layout assumed for the conventional fossil-based syngas production (Base Case) is shown in Figure 6. Incoming NG and various off-gases are processed by partial oxidation with oxygen. The raw syngas undergoes a number of cleaning and conditioning steps to fulfil the specifications for downstream oxo synthesis. The high temperature raw syngas is cooled, passed through a fabric filter, and quenched with water to remove impurities such as soot particles. The soot-free syngas is cooled (and condensed water is separated) prior to the removal of CO_2 in a conventional amine absorption unit.

Due to the large concentration of H_2 in the syngas than required for downstream oxo synthesis, the H_2/CO ratio is adjusted using integrated membrane and PSA technology. Prior to the membranes, the syngas is cooled to condense water and other potential impurities prior to reheating to the temperature required in the separation unit. The CO-rich non-permeate stream is cleaned in activated carbon and zinc oxide beds. The H_2–rich permeate stream is cleaned using PSA technology, which results in a pure H_2 stream (used in downstream oxo synthesis) and a tail gas stream (used as fuel in a steam boiler).

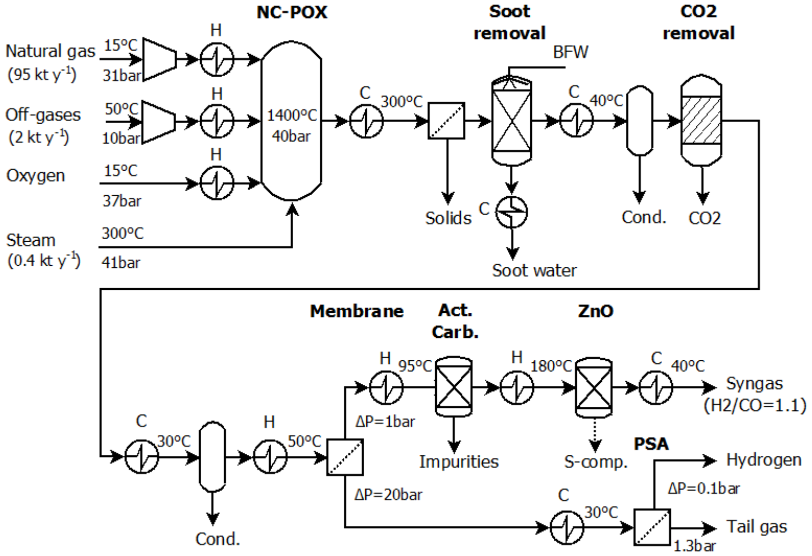

Figure 6. Process layout of the conventional fossil-based syngas production for downstream oxo synthesis (Base Case). The stream cooling (heat sources) requirements and heating (heat sinks) requirements are denoted by C and H, respectively.

4.1.2.2 Biomass-Based Syngas Production via SNG (BioSNG2Syngas)

The process layout of the bio-SNG process (BioSNG2Syngas) is shown in Figure 7. As described in Section 3.2.1, the bio-SNG design is similar to the GoBiGas phase 1 layout.

Incoming lignocellulosic biomass is initially dried in a low-temperature air dryer and subsequently gasified using indirect steam gasification technology. The obtained raw syngas undergoes a number of cleaning, conditioning, and synthesis steps to be upgraded to a methane-rich gas. The high-temperature raw syngas is cooled, passed through a fabric filter, and scrubbed with bio-oil (RME) to remove tar. The tar-free gas is compressed prior to acid gas removal (using conventional amine absorption technology).

Due to the reduced presence of H_2 in the syngas than required for optimal methane synthesis, the H_2/CO ratio is adjusted to 3 using partial shift technology. After the shifting, another similar amine wash is used to remove CO_2. The methanation synthesis occurs in three adiabatic reactors in series with intercooling and a recycle on the first reactor. Water is removed from the methane-rich gas by gas cooling followed by a temperature swing adsorption (TSA) unit using aluminium oxide as the adsorbing medium.

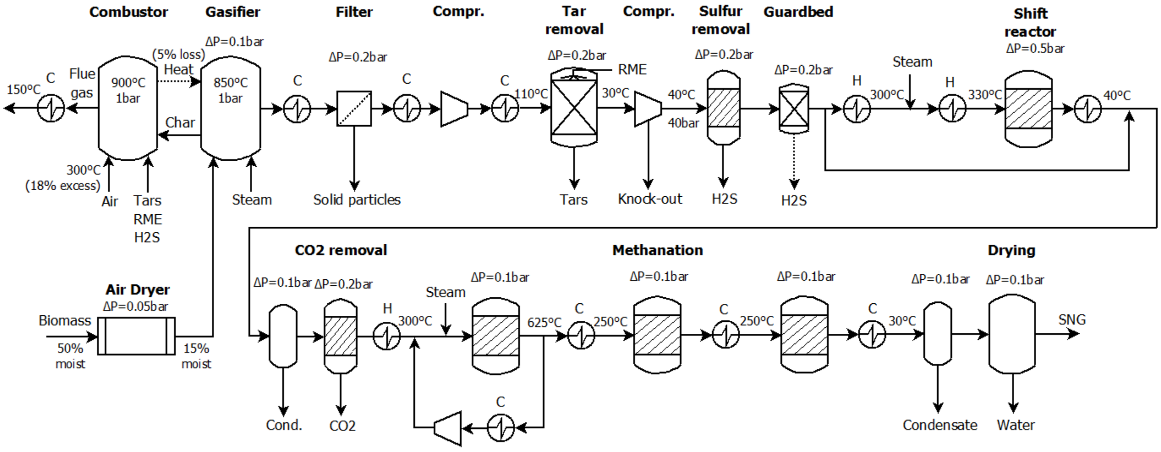

Figure 7. General process layout for biomass-based syngas production via SNG (BioSNG2Syngas). The stream cooling (heat sources) requirements and heating (heat sinks) requirements are denoted by C and H, respectively.

4.1.2.3 *Biomass-Based Syngas Production (Bio2Syngas)*

The process layout assumed for the bio-syngas process (Bio2Syngas) is depicted in Figure 8. As described in Section 3.2.1, the bio-syngas design is a combination of the bio-SNG and fossil syngas production routes.

The biomass drying, gasification, tar cleaning, and sulphur removal steps are similar to the steps in the bio-SNG process. The downstream gas conditioning steps differ. To fulfil the syngas purity specifications for downstream oxo synthesis, undesired methane and various off-gases available from the oxo synthesis plant are reformed in an ATR unit. The final upgrading steps are similar to the steps used in the fossil route (i.e., CO_2 removal, integrated membrane and PSA technology, and activated carbon and zinc oxide beds).

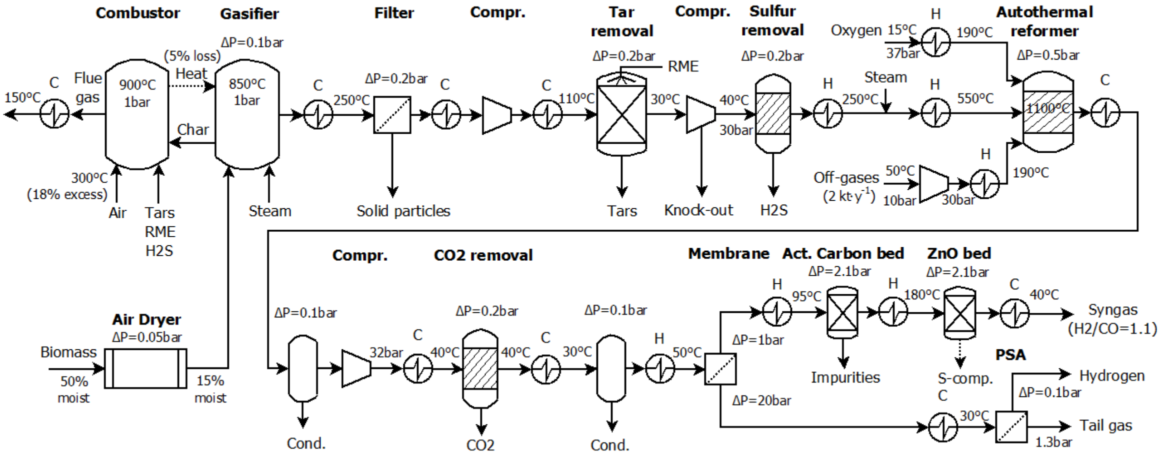

Figure 8. General process scheme for biomass-based syngas production (Bio2Syngas). The stream cooling (heat sources) requirements and heating (heat sinks) requirements are denoted by C and H, respectively.

4.1.3 Process Simulation – Mass and Energy Balances

Table 3 presents the calculated mass and energy balances for the investigated syngas production routes.

The results show that by processing 175 MW NG and 2.4 MW of off-gases and importing 28 MW H_2, the conventional syngas route (Base Case) delivers 115 MW of syngas, 57 MW of H_2, and 6.7 MW of tail gas to the oxo synthesis plant. To attain a temperature of approximately 1400°C in the NC-POX process, 124 kt per year of oxygen are required. To cover the oxo synthesis plant's net LP steam demand (20 MW), 27 MW of fuel gas must be imported. The electricity demand of the Base Case Syngas system is estimated at 11 MW.

For the route via intermediate bio-SNG production (BioSNG2Syngas), the results show that 262 MW of biomass is required to entirely substitute the NG feed (175 MW). In addition, 4.2 MW of RME is required for gas cleaning. The electricity demand of the bio-SNG process is estimated at 23 MW.

For the direct route to syngas (Bio2Syngas), the results show that 216 MW of biomass is required to satisfy the syngas requirements of the oxo plant (115 MW). In addition, 2.4 MW of off-gases is reformed and 3.5 MW of RME is consumed in the gas cleaning. The H_2 and tail gas production of the bio-syngas process are slightly increased compared with NG reforming (+2.5 MW and +0.5 MW, respectively). Thus, the H_2 import can be decreased by a corresponding amount. The extra tail gas can be utilised for other purposes, e.g., for LP steam production. In the gas conditioning and clean-up section, 55 kt per year of oxygen are required (corresponds to 40% of the oxygen demand in the NC-POX in the Base Case). The electricity demand in the bio-syngas process is estimated at 21 MW.

Table 3. Summary of the results for the Base Case, BioSNG2Syngas, and Bio2Syngas.[a]

		Base	**BioSNG2Syngas**		**Bio2Syngas**	
		Case	**Case El**	**Case LP**	**Case El**	**Case LP**
Input						
NG	MW (en)	175	0 (-175)	0 (-175)	0 (-175)	0 (-175)
	MW (ex)	165	0 (-165)	0 (-165)	0 (-165)	0 (-165)
Off-gases	MW (en)	2.4	2.4 (0)	2.4 (0)	2.4 (0)	2.4 (0)
	MW (ex)	2.3	2.3 (0)	2.3 (0)	2.3 (0)	2.3 (0)
Biomass	MW (en)	-	262 (+262)	262 (+262)	216 (+216)	216 (+216)
	MW (ex)	-	277 (+277)	277 (+277)	228 (+228)	228 (+228)
RME	MW (en)	-	4.2 (+4.2)	4.2 (+4.2)	3.5 (+3.5)	3.5 (+3.5)
	MW (ex)	-	4.2 (+4.2)	4.2 (+4.2)	3.5 (+3.5)	3.5 (+3.5)
Fuel gas	MW (en)	27	27 (0)	0 (-27)	27 (-0.4)	9.4 (-18)
	MW (ex)	26	26 (0)	0 (-26)	26 (-0.4)	8.9 (-17)
Power (net)	MW	11	11 (+0.2)	14 (+3.1)	10 (-0.8)	21 (+9.7)
Production						
Syngas	MW (en)	115	115 (0)	115 (0)	115 (0)	115 (0)
	MW (ex)	105	105 (0)	105 (0)	105 (0)	105 (0)
H_2 (net)	MW (en)	29	29 (0)	29 (0)	31 (+2.5)	31 (+2.5)
	MW (ex)	24	24 (0)	24 (0)	26 (+2.1)	26 (+2.1)
Tail gas (net)	MW (en)	6.7	6.7 (0)	6.7 (0)	6.7 (0)	6.7 (0)
	MW (ex)	5.8	5.8 (0)	5.8 (0)	5.8 (0)	5.8 (0)
HP steam	MW (en)	16	16 (0)	16 (0)	16 (0)	16(0)
	MW (ex)	6.8	6.8 (0)	6.8 (0)	6.8 (0)	6.8 (0)
LP steam	MW (en)	20	20 (0)	20 (0)	20 (0)	20 (0)

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

4.2 Energy Targeting Analysis

All investigated syngas production routes are associated with high-temperature excess heat, which can be recovered for the production of useful thermal heat or the cogeneration of heat and electric power by integrating a heat recovery steam cycle. This section reports the results from the energy targeting analysis of the investigated syngas concepts (**Paper I**). The energy targeting analysis results, i.e., heat recovery targets for the production of useful thermal heat or cogeneration of heat and power affect the electricity and fuel gas import (for steam production) of the integrated Syngas systems. The resulting mass and energy balance of the investigated Syngas systems are listed in Table *3*.

4.2.1 Conventional Fossil-Based Syngas Production (Base Case)

Figure 9 shows the GCC of the Base Case. The pinch analysis indicates large amounts of high-temperature excess heat. Using split-GCC analysis, i.e., representing the GCC of HP steam production (dashed line) against the GCC of the Base Case (solid line), the target for HP steam production can be estimated, as shown in Figure 9. The target for HP steam production in the Base Case is estimated at 16 MW.

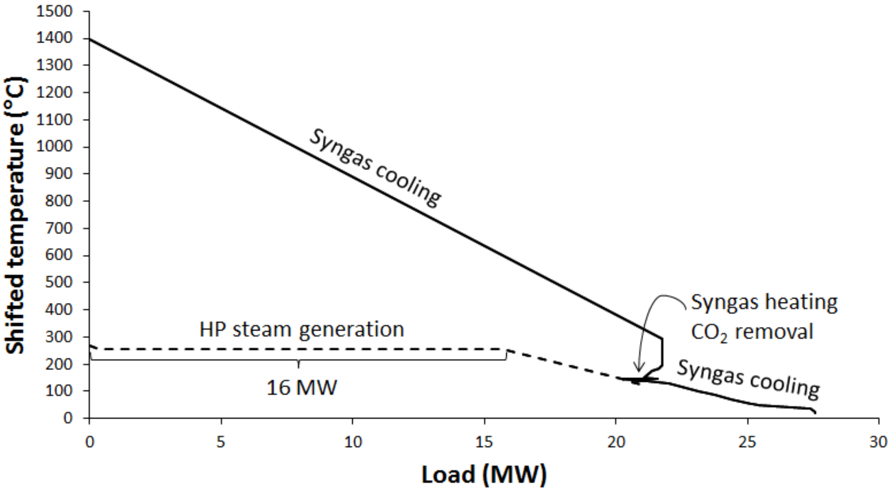

Figure 9. Split-GCC of the Base Case (solid line) and HP steam production (dashed line).

4.2.2 Biomass-Based Syngas Production via SNG (BioSNG2Syngas)

Figure 10 shows the GCC of the bio-SNG production process. The pinch analysis indicates large amounts of high-temperature excess heat (note that 45 MW of the 51 MW of the total heat available are available above 400°C) and a large heat pocket. By integrating a heat recovery steam cycle, the heat pocket and the high-temperature excess heat can be exploited for the cogeneration of heat and power. These opportunities are highlighted by the split-GCC analysis, i.e., matching the GCC of a condensing steam network (dashed line) against the GCC of the bio-SNG process (solid line), as shown in

Figure 10. The final use of the recovered process heat (Case El or Case LP) affects the electricity and fuel gas import to the syngas production unit.

For Case El, the maximum electricity production potential is estimated at 22 MW, as shown in Figure 10. Regarding its electricity demand (23 MW), the bio-SNG process can be considered close to self-sufficient with a small net electricity demand of 0.2 MW. As no extra LP steam generation via heat recovery is considered in Case El, the fuel gas import remains similar to the fuel gas import in the Base Case (27 MW).

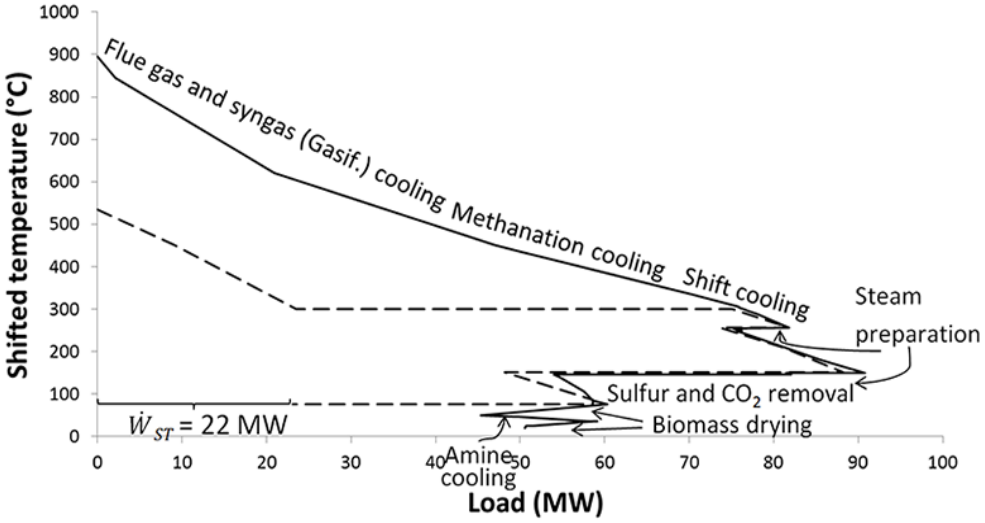

Figure 10. Split-GCC of the bio-SNG process (solid line) and a heat recovery condensing steam cycle (dashed line) (BioSNG2Syngas Case El).

For Case LP (refer to split-GCC in **Paper I**), the electricity generation potential is estimated at 19 MW (3.4 MW less compared with Case El). Considering the entire syngas production system (BioSNG2Syngas Case LP), the net electricity demand is increased by 3.1 MW compared with the Base Case. The current purchase of fuel gas for LP steam production is eliminated in this arrangement.

4.2.3 Biomass-Based Syngas Production (Bio2Syngas)

Figure 11 shows the GCC of the bio-syngas production process (including HP steam generation). The pinch analysis indicates high-temperature excess heat (13 MW available above 600°C) and a large heat pocket.

Similar to the bio-SNG process, a heat recovery steam cycle can be integrated to exploit the heat pocket and the high-temperature excess heat for combined heat and power production. The high-temperature excess heat can be alternatively recovered for the production of useful thermal heat (LP steam). To explore these opportunities, the concept of split-GCC analysis is employed. The final use of the recovered process heat (Case El or Case LP) affects the electricity and fuel gas import to the syngas production unit.

For Case El, the maximum electricity production potential is estimated at 11 MW, as shown in Figure 11. The net electricity demand of the Bio2Syngas Case El system is reduced by 0.8 MW compared with the Base Case. As no extra LP steam generation via heat recovery is considered in Case El, the fuel gas import remains similar to the fuel gas import in the Base Case (27 MW).

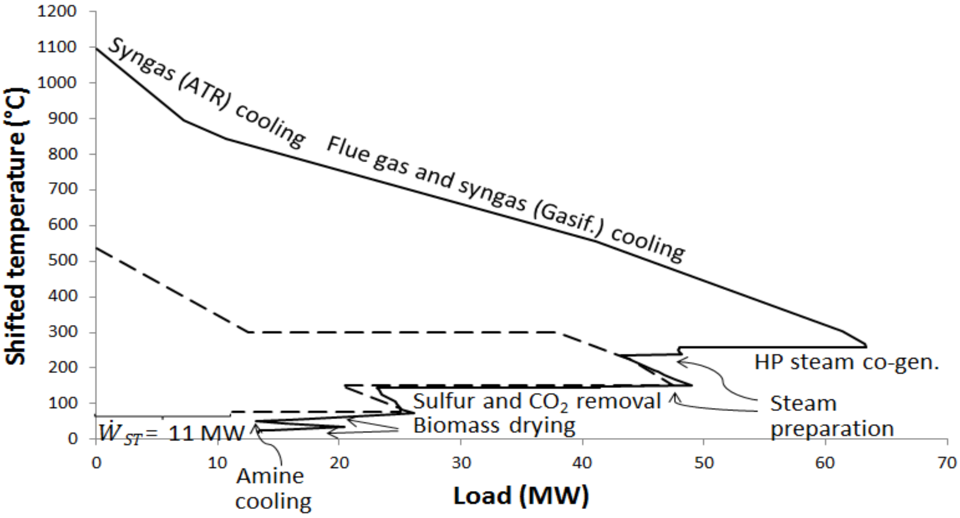

Figure 11. Split-GCC of the bio-syngas process including HP steam production (solid line) and a heat recovery condensing steam cycle (dashed line) (Bio2Syngas Case El).

For Case LP (refer to split-GCC in **Paper I**), the LP steam production potential is estimated at 13 MW (corresponds to 6 kg/s). The site's current purchase of fuel gas for LP steam production can be reduced (but not eliminated) by this arrangement; however, another 9.4 MW fuel gas still needs to be purchased. In the Bio2Syngas Case LP setup, the potential for electricity cogeneration is non-existent and the net electricity demand of the Bio2Syngas Case LP system is increased with 9.7 MW compared with the Base Case.

4.3 Process Performance Evaluation

This section presents and discusses the process performance evaluation results, i.e., the thermodynamic performance (energy and exergy efficiency) (**Paper I**), global GHG emissions (GHG emission reduction potential), and process economics (change in production cost) (**Paper II**). The main results are listed in Table 4.

4.3.1 Thermodynamic Performance

The calculated energy (η_{en}) efficiency and exergy (η_{ex}) efficiency for the investigated biomass-based syngas production concepts range from 60% to 75% and 46% to 57%, respectively. For comparison, the conventional fossil route (Base Case) achieves higher energy (86%) and exergy (72%) efficiency values as the thermochemical conversion of NG is significantly less energy-intensive than biomass conversion and less gas cleaning and conditioning is required. Table 4 shows a summary of the results.

Table 4. Summary of the process performance evaluation results for the investigated options.

		Base	BioSNG2Syngas		Bio2Syngas	
		Case	Case El	Case LP	Case El	Case LP
Performance indicators						
η_{en}	%	86	60	66	73	75
η_{ex}	%	72	46	49	55	57
GHG em. red.[a]	kg $CO_{2,eq}$ t^{-1}		775 / 778	860 / 897	854 / 844	753 / 870
$\Delta C_{oxo-product}$[b]	€ t^{-1}		114 / 217	90 / 192	-12 / 77	-26 / 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) achieves 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. This finding is due to the intrinsic conversion loss of the methanation and subsequent partial oxidation steps that are avoided in the direct route to bio-syngas. However, the heat recovery targets for combined heat and power production are reduced. The gain in avoided intrinsic conversion losses is more significant than the decrease in the combined heat and power production potential in the direct Bio2Syngas route (compared with BioSNG2Syngas).

For both investigated bio-syngas concepts, the option to (co)generate LP steam to eliminate or reduce the fuel gas import (Case LP) shows better performance compared with 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 onsite location (Case LP) are estimated at 5.2/3.6 (energy/exergy) efficiency points.

4.3.2 Global GHG Emissions

4.3.2.1 Global GHG Emissions - Input data

Data for changes in energy and material flows by switching the syngas origin compared with the Base Case (results from **Paper I**) are listed in parenthesis in Table 3. Care should be taken when applying eq. (3), e.g., the change in material/energy flow for NG is defined as “avoided NG import” and should be inserted as a positive value.

Utilisation-associated GHG emissions are listed in Table 5 and Table 6. The CO_2 uptake during biomass growth (*upt*) is based on the compositions used for lignocellulosic biomass and RME (refer to **Paper I**). The well-to-gate (*wtg*) and combustion (*comb*) emissions are based on Gode et al. (2011). The emissions from the syngas production (*sg*) are based on the simulation results obtained in **Paper I**.

The methodology for calculating the GHG emission effects for the different flows is detailed in **Paper II**. Avoided H_2 import is assumed to produce excess H_2 at the H_2 production site (primarily obtained as a by-product of naphtha cracking). The excess H_2 is fired in a boiler to prevent NG firing. As discussed in Section 3.3.2, changes to the site’s net electricity balance are assumed to affect electricity generation in a reference grid power plant, as shown in Table 6 for associated GHG emissions. For a detailed description, refer to **Paper I** and **Paper II**.

Table 5. Utilisation-associated GHG emissions in kg $CO_{2,eq}$ per MWh (HHV basis).

Flow type (i)	**NG**		**Biomass**	**RME**
Emission type (j)	*wtg+sg*	*wtg+comb*	*upt-wtg-sg*	*upt-wtg-comb*
GHG emissions ($ghg_{i,j}$)	50	227	103 / 135	-60

[a] The GHG emissions associated with biomass utilisation are reported as BioSNG2Syngas/Bio2Syngas. Note that the emission type of biomass (*upt-wtg-sg*) and the RME (*upt-wtg-comb*) indicate that positive and negative values correspond to a large carbon uptake and small carbon uptake, respectively, compared with the GHG emissions associated with well-to-gate and syngas production or combustion (i.e., increasing the GHG emission reduction potential and reducing the GHG emission reduction potential, respectively).

Table 6. GHG emissions in kg $CO_{2,eq}$ per MWh (electricity) with coal-fired grid power generation technologies (in 2030).

Technology	coal PP	coal PP with CCS
GHG emission[a] (ghg_{EL})	816	273

[a] Based on GHG emissions associated with coal utilisation (Gode et al., 2011; Uppenberg et al., 2001). A CO_2 capture efficiency of 88% is assumed for the CCS technology (Axelsson and Pettersson, 2014).

4.3.2.2 GHG emission reduction potentials

The calculated GHG emission reduction potentials for the biomass-based syngas production concepts relative to the Base Case range from 753 to 897 kg $CO_{2,eq}$ per tonne oxo product. The totals and the break-downs of the GHG emission reduction potentials are illustrated in Figure 12. The results are presented in Table 4.

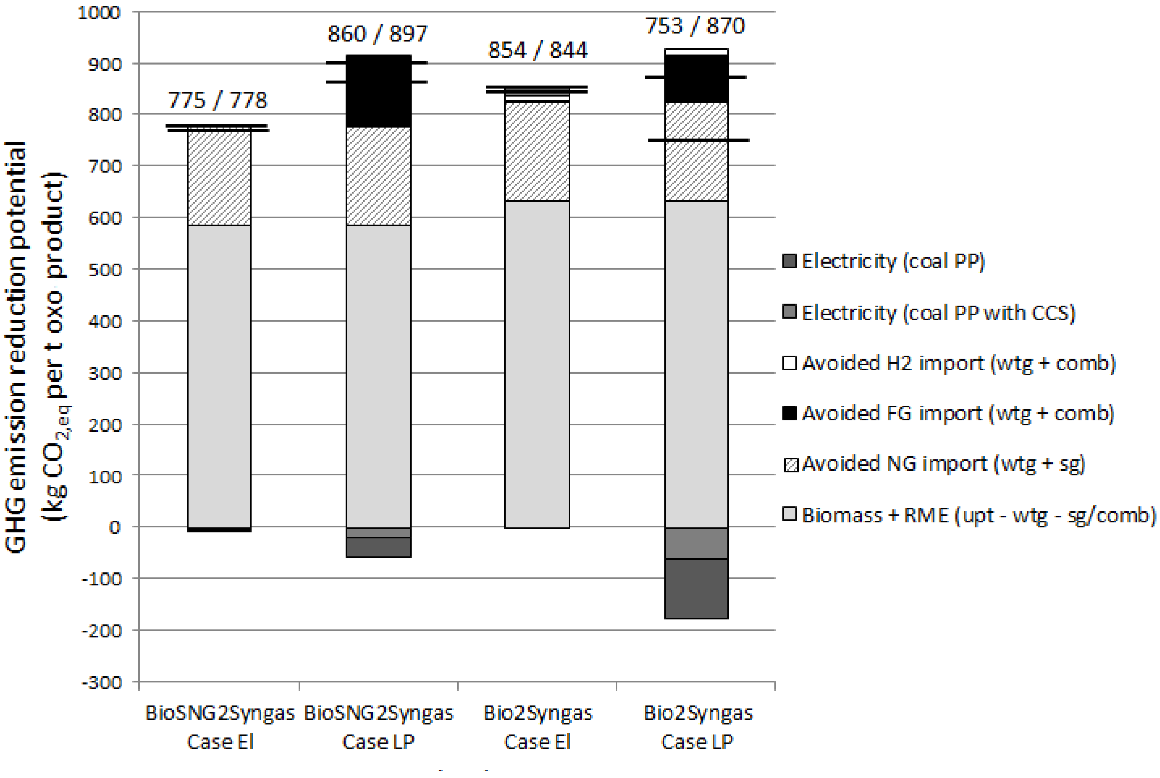

Figure 12. Break-down of the GHG emission reduction potentials (kg $CO_{2,eq}$ per tonne oxo product) for the investigated biomass-based concepts. The total GHG emission reduction potentials, in which the reference grid electricity generation technologies are coal PP/coal PP with CCS, are indicated. 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 coal PP with CCS and the coal PP emission contributions.

The BioSNG2Syngas Case LP concept achieves the highest GHG emission reduction potential (860/897 kg $CO_{2,eq}$ per tonne oxo product) (coal PP/coal PP with CCS). The subsequent ranking of the investigated cases varies according to the selected reference grid electricity generation technology. Bio2Syngas Case LP achieves the lowest GHG emission reduction potential and second-highest GHG emission reduction potential (753/870 kg $CO_{2,eq}$ per tonne oxo product) for high-emitting reference grid electricity generation technology and low-emitting reference grid electricity generation technology (coal PP/coal PP with CCS), respectively.

The Case LP heat recovery option achieves higher GHG emission reduction potentials compared with Case El, with the exception of Bio2Syngas with coal PP as the reference grid electricity generation technology. The GHG emission 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 emission reduction potentials for Case El show minimal dependence on the electricity balance (and the reference grid electricity generation technology).

Note that Bio2Syngas Case El shows a higher GHG emission reduction potential for the high emitting reference grid electricity generation technology (coal PP) compared with the low emitting reference grid electricity generation technology (coal PP with CCS) as (in contrast to the remaining investigated concepts) the net electricity import is slightly reduced compared with the Base Case.

In addition to the reduction effect from introducing renewable feedstock (accounts for 58% to 75%), the two main emission items that contribute to the GHG emission reduction potential are as follows:

- avoided NG as feedstock (accounts for 17% to 24%)
- avoided fuel gas firing for LP steam production (accounts for 0% to 15%)

Combined, they account for 83% to almost 100% of the total GHG emission consequences.

The GHG emission reduction potential contribution of introducing renewable feedstock is high for the direct Bio2Syngas compared with the BioSNG2Syngas concepts (as intrinsic conversion losses are minimised and less thermal input is required for the same substitution). During the production of syngas, approximately 59% and 68% of the CO_2 fixed during biomass growth is released to the atmosphere for the Bio2Syngas concept and BioSNG2Syngas concept, respectively. The remaining biogenic-carbon is “stored” in the final oxo product.

The GHG emission reduction potential effect of avoiding NG as feedstock is identical for all investigated biorefinery concepts.

The GHG emission reduction potential effect of avoiding fuel gas firing is dependent on whether LP steam is (co)generated in the applied heat recovery option (Case LP) or not generated in the applied heat recovery option (Case El). The Case LP heat recovery option can entirely eliminate or significantly reduce the fuel gas firing in the BioSNG2Syngas concept and Bio2Syngas concept, respectively.

4.3.3 Economic Evaluation

4.3.3.1 Economic Evaluation - Input Data

The general economic assumptions applied in the annual capital investment and fixed operating cost estimation are listed in Table 7.

Table 7. General economic assumptions.

Parameter	Value	Parameter	Value
Annuity factor (a)	0.1 y^{-1}	Man hours BioSNG2Syngas	212333 h y^{-1}
Operating hours (t)	8000 h y^{-1}	Man hours Bio2Syngas	133333 h y^{-1}
O&M costs	5% of the tot. cap. inv.	Labor costs	32 € h^{-1}

For the variable operating costs, data for changes in energy and material flows by switching syngas origin compared with the Base Case (results from **Paper I**) are listed in parenthesis in Table 3. Care should be taken when applying eq. (4), e.g., the change in the material/energy flow for NG is defined as “avoided NG import” and should be inserted as a positive value. The CO_2 emissions considered in the economic evaluation comprise the onsite fossil CO_2 emissions, as shown in Figure 5 and Table 8.

Table 8. Onsite fossil CO_2 emissions for the Base Case.

Onsite fossil CO_2 emissions	Value
Total[a]	84 kt y^{-1}
Syngas[b]	54 kt y^{-1}
Oxo[c]	30 kt y^{-1}

[a] Based on the average values reported for a conventional Oxo system (Perstorp Holding AB, 2010).

[b] Including CO_2 emissions from the syngas production (based on simulation results) (**Paper I**) and the LP steam boiler (based on usage related emissions) (Gode et al., 2011) in the Syngas system.

[c] Based on the carbon balance of the oxo synthesis plant, approximately 45% of the incoming carbon originates from syngas or tail gas is estimated (**Paper II**).

The projected prices for chemical feedstock, energy commodities, and CO_2 charge for the two WEO scenarios are summarised in Table 9. In the variable operating cost estimation, the cost for oxygen is assumed to be included in the electricity cost and the cost for RME and MEA are assumed to be included in the O&M costs.

Table 9. Projected prices for material and energy flows and CO_2 emission charge.

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
H_2 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.

4.3.3.2 Change in Production Cost of Oxo Products

The estimation of fixed costs (incremental capital investment and fixed operating costs) for the investigated biomass-based concepts compared with the Base Case is summarised in Table 10. The results show that annual fixed costs of approximately 70 M€ and 30 M€ are required to completely switch to biomass-derived syngas via intermediate bio-SNG production (BioSNG2Syngas) and directly (Bio2Syngas), respectively. The annual fixed costs can be reduced to approximately 50% by taking the direct route to syngas compared with the route via bio-SNG. For detailed equipment cost results, refer to the supplementary information to **Paper II**.

Table 10. Annual incremental capital investment (An. incr. cap. inv.) and fixed operating (op.) costs for the investigated biorefinery concepts relative to the Base Case (monetary value of 2012).

		BioSNG2Syngas		**Bio2Syngas**	
		Case El	**Case LP**	**Case El**	**Case LP**
Incr. cap. inv. (C_F)	M€	444	440	304	278
An. incr. cap. inv. ($a \cdot C_F$)	M€ y^{-1}	44	44	30	28
Change in O&M costs ($C_{O\&M}$)	M€ y^{-1}	22	22	1.3	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}	71	70	33	29

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

The calculated change in production cost of oxo products for the biomass-based syngas production concepts relative to the Base Case range from -12 to 217 € per tonne oxo product. The totals and the break-downs of the change in production cost of oxo products based on two possible future energy market scenarios—WEO current policies and WEO 450 ppm (IEA, 2013)—are illustrated in Figure 13. The results are presented in Table 4.

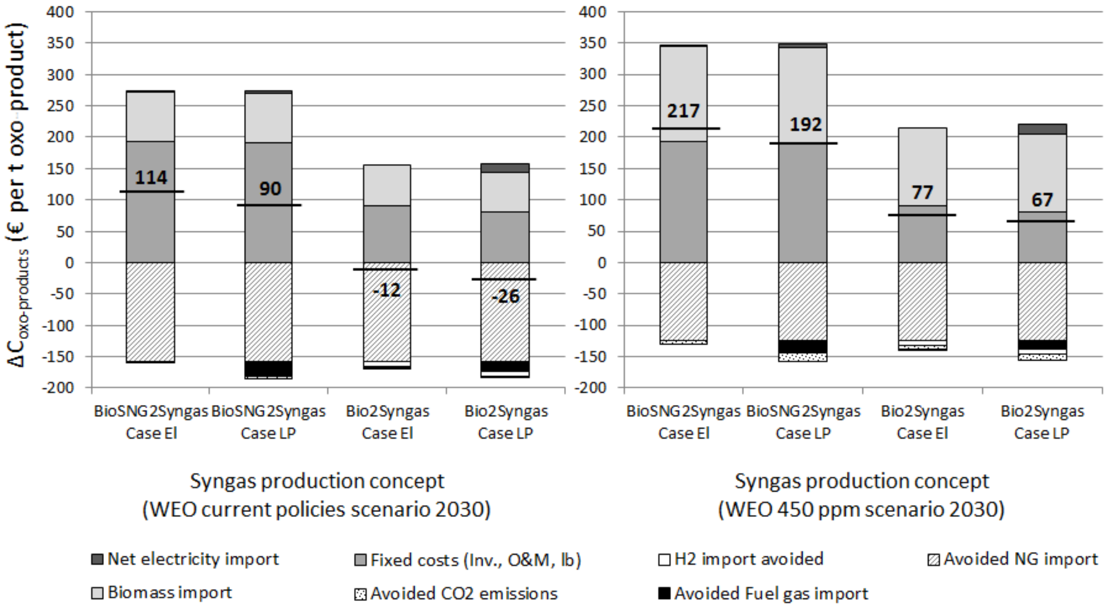

Figure 13. Break-down of the change in production cost of oxo products (€ per tonne oxo product) for the investigated biomass-based concepts based on prices projected from the WEO's current policies scenario (left) and the WEO's 450 ppm scenario (right). The total change in production costs are indicated with marks and absolute values.

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, see Figure ***13***. For prices based on the WEO current policies scenario, the Bio2Syngas routes achieves a negative change in production costs (-12/-26 € per tonne oxo product for Case El/Case LP), i.e., a lower production cost compared with the conventional fossil-based syngas route. Particularly interesting results are obtained with the heat recovery option to (co)produce LP steam (Case LP).

Producing oxo products from biomass-based syngas can be competitive with NG-based syngas under the current policies scenario. However, if significant changes are introduced to current policies (such as the implementation of the WEO 450 ppm scenario), biomass-based syngas will become less competitive for replacing fossil syngas in the production of oxo products. This situation is the consequence of an increased CO_2 charge, which is assumed to cause an increased willingness to pay for biomass and a reduced demand (and reduced price) for fossil fuels. In a carbon constrained world, however, other policy instruments that are not considered in this study can be expected impact the cost of materials and energy.

As shown in Figure 13, the items with the largest impact on the change in production costs are as follows:

- the fixed costs
- the avoided NG import
- the biomass import

These cost items represent approximately 90% or more of the total new expenditures and savings. The results indicate that the incremental capital investment and the change in feedstock costs have a much higher impact on the change in the production cost of oxo products compared with the variation in the cost of supporting energy flows (i.e., the net electricity import and the avoided fuel gas import) and due to energy and climate policies (CO_2 charge for onsite fossil CO_2 emissions) (with price projections based on two possible future scenarios).

The same amount of NG is saved in the investigated biorefinery concepts. The NG price has a large influence on the profitability, which will affect the opportunity and driving force of switching the syngas to biomass-based for the future production of oxo products. This finding is particularly interesting considering the rapid change in the NG market due to the recent shale-gas wave. The biomass price also exhibits a significant impact. The price of feedstock and the energy commodities in the energy systems market are closely connected.

With a ±30% price variation in the price of NG and biomass (compared with price projects based on the WEO current policies scenario), the change in the production cost for the Bio2Syngas Case LP concept varies by ±54 € per tonne oxo product and ±19 € per tonne oxo product, respectively (refer to **Paper II**). The results indicate that the price of NG has a larger impact on the change in production cost. As expected, the fossil route benefits from low NG prices, especially in combination with high biomass prices, whereas the biorefinery concepts become more competitive with high NG prices, particularly in combination with low biomass prices. In terms of price dependence, similar trends will be obtained for the remaining investigated biomass-based concepts; however, the absolute values will differ.

Due to uncertainties in the capital investment estimation (±30%), the change in production cost for BioSNG2Syngas Case El/Case LP and Bio2Syngas Case El/Case LP is assumed to range from approximately ±55/±54 and ±41/±37 per tonne of oxo product to ±38 € per tonne of oxo product, respectively, compared with currently reported estimations.

4.3.4 Summary of Key Results

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

In Figure 14, the change in production cost of oxo products (estimated by price projections based on the WEO current policies scenario) is plotted against the corresponding GHG emission reduction potential for the investigated biomass-based concepts. In this type of graph, the most competitive and promising concept is shown in the lower right corner and the least beneficial concept is shown in the upper left corner in Figure 14. Figure 14 is not intended as a rigorous optimisation tool. However, it can be used to form some general conclusions about the process performance from an economic and environmental perspective.

The Bio2Syngas Case LP concept demonstrates promising opportunities to perform well from an economics and GHG emissions reduction perspective, assuming coal PP with CCS as the reference grid electricity generation technology, as shown in Figure 14. The Bio2Syngas Case El concept, however, shows a similar performance and 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 emission reduction potential, in which a high-emitting reference electricity production (coal PP) is assumed.

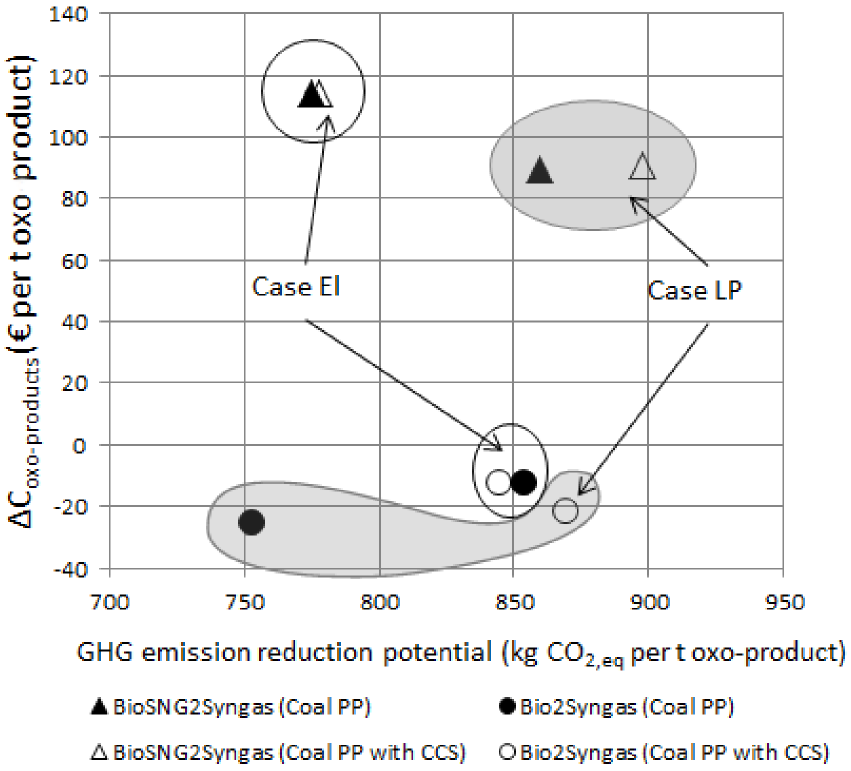

Figure 14. Change in production cost of oxo products (€ per tonne oxo product) based on prices projected from WEO's current policies scenario versus the corresponding GHG reduction potential (kg $CO_{2,eq}$ per tonne oxo product) for the investigated biomass-based concepts.

In this assessment, the CO_2 charge for fossil emissions is the only energy and climate policy that is considered. The results show that no economic incentive for switching to biomass-based syngas in the production of oxo products is achieved with an increase in CO_2 charge for onsite fossil emissions (i.e., price projections based on the WEO 450 ppm scenario, which generates an increased willingness to pay for biomass and reduced NG prices). To create stronger economic incentives and to reduce risks for the transition towards biomass-based chemicals production, alternate policies such as a reward for the “replaced fossil carbon” or “stored” biogenic carbon may be topics for further investigation.

5. CONCLUSIONS

This licentiate thesis is a summary of the progress accomplished during the first part of a PhD research project, which comprises **Paper I** and **Paper II**. The objective of the PhD project is to investigate and assess different opportunities for fossil-based production of chemicals to switch to biomass-based production, particularly via thermochemical gasification. Different entry options in the conventional process value chain are considered for the biomass-based conversion plant. A conventional oxo synthesis plant is used as a case study. Two different options to switch the syngas origin, which is currently produced from NG, are investigated: (*i*) complete replacement of the NG feedstock with bio-SNG (BioSNG2Syngas) and (*ii*) direct substitution with bio-syngas (Bio2Syngas). The conventional NG-based syngas production is used as a reference (Base Case).

The results of this work highlight the importance of adopting an appropriate systems perspective when defining system boundaries and performance indicators and comparing different transition pathways for the chemical industry. The importance of applying sound material and energy integration to enable this transition is also emphasised.

As expected, to completely substitute the syngas demand (115 MW) for downstream oxo synthesis (currently processing 175 MW NG), less lignocellulosic biomass is required by the direct route (Bio2Syngas) (216 MW) compared with the bio-SNG route (BioSNG2Syngas) (262 MW). However, the heat recovery potential for combined heat and power production is also lower. The Bio2Syngas concept achieves higher thermodynamic performance (maximum difference of 12 efficiency points) compared with the BioSNG2Syngas route. The gain in avoided intrinsic conversion losses is more significant than the decrease in combined heat and power production potential in the direct Bio2Syngas route (compared with BioSNG2Syngas).

The option to (co)generate LP steam to eliminate or reduce the fuel gas import (Case LP) achieves a higher thermodynamic performance compared with maximising the electricity production (Case El) for both investigated bio-syngas concepts. For the BioSNG2Syngas option, the thermodynamic efficiency penalties for remote location (Case El) compared with an onsite location (Case LP) are estimated at 5.2/3.6 (energy/exergy) efficiency points.

The route via bio-SNG in combination with LP steam production (BioSNG2Syngas Case LP) achieves the highest GHG emission reduction potential (860/897 kg $CO_{2,eq}$ per tonne oxo product) (coal PP/coal PP with CCS). Bio2Syngas Case LP achieves the lowest or second-highest GHG emission reduction potential for the high-emitting reference grid electricity generation technology (coal PP) and low-emitting reference grid electricity generation technology (coal PP with CCS), respectively. The heat recovery option for producing LP steam (Case LP) achieves higher GHG emission reduction potentials compared with the option of maximising the electricity production (Case El), with the exception of Bio2Syngas when coal PP is assumed as the reference grid electricity generation technology.

In addition to introducing renewable feedstock, the two main factors that determine the GHG emission reduction potential are avoidance of NG as feedstock and avoidance of fuel gas firing for LP steam production. They account for 83% to almost 100% of the total GHG emission consequences.

The direct production of biomass-derived syngas achieves a higher economic performance compared with the “chemical detour” via intermediate bio-SNG production. The results indicate that the production costs of biomass-based oxo products, which are lower than the conventional fossil-based route, can be potentially achieved for the direct syngas route (change in production cost of 12/26 € per tonne oxo product for Case El/Case LP) (for price projections based on the WEO current policies scenario). The results indicate that as long as current policies are not significantly modified, biomass-based syngas can be competitive with NG-based syngas for the production of oxo products. By increasing the CO_2 charge (as in the WEO 450 ppm scenario that causes an increased willingness to pay for biomass and reduced fossil fuel prices), no economic incentive for switching to biomass-based syngas in the production of oxo products 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. The creation of stronger economic incentives that promote a transition towards biomass-based chemicals production may be a topic for further investigation. For example, a reward for “replacing fossil carbon” may be a potential incentive.

The factors with the greatest impact on the change of production costs include the fixed costs, avoided NG import, and the biomass import. They account for approximately 90% or more of the total new expenditures and savings

The Bio2Syngas Case LP concept demonstrates promising opportunities to perform well from an economic and GHG emissions reduction perspective for a low-emitting reference grid electricity technology. The Bio2Syngas Case El concept shows a similar performance and minimal dependence on reference grid electricity production.

6. FUTURE STUDIES

This licentiate thesis is a summary of the progress accomplished during the first part of a PhD research project. The results form the basis of the direction and development of the project. A number of different aspects have been identified as interesting topics for further analysis. Considering the goal of developing efficient pathways to enable the chemical industry to participate in the transition to a bio-based economy, several different opportunities can be identified.

Similar to Figure 2 in Section 1.2.2, Figure 15 illustrates an overview of possible pathways for thermochemical gasification. However, in Figure 15, some of the pathways of particular interest for a transition of the chemical industry are highlighted. Recalling Figure 3, some of the feedstock, intermediates, and final products for a conventional oxo synthesis plant included NG, olefins, hydrogen, syngas, and butanol.

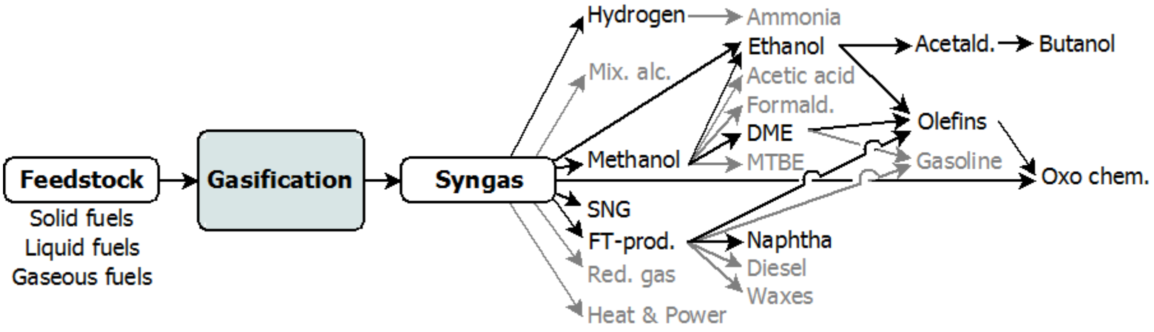

Figure 15. Overview of possible production routes for thermochemical gasification. Pathways of particular interest for a transition of the chemical industry are highlighted.

If the system boundary limit is expanded, olefins are conventionally produced via naphtha cracking. Therefore, the production of bio-naphtha for additional conversion to olefins may also be of interest for a transition by the chemical industry.

Among the pathways highlighted in Figure 15, the option to switch the NG-based syngas production for downstream oxo synthesis (via bio-SNG or directly with bio-syngas) has been assessed in this licentiate thesis. The next step in this PhD research project is to investigate the opportunities for switching the origin of the olefins-feedstock to biomass-based.

One of the aims of this project is to investigate different integration points for biomass-based conversion plants in conventional process value chains. Considering the case study oxo synthesis plant, the olefins are currently produced in a neighbouring conventional naphtha steam cracker plant. To switch the production of olefins from fossil-based to biomass-based, two interesting options can be identified: (*i*) to retain the existing steam cracker unit and switch the corresponding amount of naphtha feedstock by either importing or producing bio-naphtha onsite or (*ii*) to scrap the existing, or parts of it, steam cracker unit and directly produce biomass-derived olefins to comply with the specifications for downstream synthesis.

For the feedstock switch, the route via FT-naphtha and conventional cracking will be the primary focus. Although a topic of interest, alternative routes to bio-naphtha is not be the primary option in this study. Different locations of the biomass-conversion plant can be considered, such as stand-alone, colocation at the steam cracker plant (enables possible utilisation of existing equipment).

For the direct switch of olefins, the route via methanol and DME will be the primary focus. Similar locations of the biomass-conversion plant can be considered, i.e., stand-alone, colocation at the steam cracker plant (enables possible utilisation of existing equipment), or colocation at the oxo synthesis plant.

Among all routes to olefins, oxo synthesis is only one of many downstream conversion options. For options based on stand-alone and colocation at the steam cracker plant, other downstream conversions, such as polymerisation, may be options that warrant further investigation, depending on the composition of the olefin fractions (ethylene and propylene) for the different routes. The primary intention of this study is the use of a conventional oxo synthesis plant as a case study.

Another interesting research question is to assess the opportunity of a large and flexible biomass gasification unit for supplying syngas, olefins, and hydrogen to a conventional oxo synthesis plant. This option could be compared with three “smaller” biomass gasification units, each supplying one main product. An additional alternative to the total onsite switch could be to produce bio-SNG and bio-naphtha elsewhere and use the existing logistic infrastructure to directly transport these energy carriers to the oxo synthesis plant and via a naphtha cracker, respectively. Depending on the outcome of the assessment, a combination of a direct onsite switch and an indirect offsite switch can also be advantageous for further investigation. However, this research question will not be investigated in the second part of the PhD project.

An assessment approach that is similar to the approach applied in this licentiate thesis will be performed to compare the different pathways: definition of appropriate system boundaries, process design and simulation of the relevant process routes to establish mass and energy balances, identification of interesting integration issues, such as changes at existing sites in the case of substitution and energy targeting, and process performance evaluation that considers thermodynamic performance, global GHG emission balances, and process economics.

NOMENCLATURE AND ABBREVIATIONS

Abbreviations

ASU	air separation unit
ATR	autothermal reforming
Base Case	fossil-based syngas production system
BFB	bubbling fluidized bed
BioSNG2Syngas	biomass-based syngas production via bio-SNG system
Bio2Syngas	biomass-based syngas production system
bio-SNG	biomass-derived synthetic natural gas
Case El	heat recovery option with maximized electric power generation
Case LP	heat recovery option with low-pressure (LP) steam (co)generation
CCS	carbon capture and storage
CFB	circulating fluidized bed
CHP	combined heat and power
coal PP	coal power plant
coal PP with CCS	coal power plant with carbon capture and storage
$CO_{2,eq}$	CO_2 equivalents
DCFRR	discounted cash flow rate of return
DME	dimethyl ether
ECN	Energy Research Centre of the Netherlands
EU	European Union
FICFB	fast internally circulating fluidized bed
FT	Fischer Tropsch
GCC	grand composite curve
GHG	greenhouse gas
GoBiGas	the Gothenburg biomass gasification project
GWP_{100}	global warming potential for a 100 year period
HEN	heat exchanger network
HHV	higher heating value
HP	high pressure (steam)
IEA	International Energy Agency
LP	low pressure (steam)
NC-POX	non-catalytic partial oxidation
NG	natural gas
NPV	net present value
O&M	operation and maintenance

PET	polyethylene terephthalate
PLA	polylactic acid
PR-BM	Peng Robinson cubic equation of state with Boston-Mathias alpha function extension
PSA	pressure swing adsorption
RME	rapeseed methyl ester
SNG	synthetic natural gas
TSA	temperature swing adsorption
WEO	world energy outlook
WEO current policies	price projections based on the IEA's WEO current policies scenario
WEO 450 ppm	price projections based on the IEA's WEO current 450 ppm scenario
WGS	water-gas-shift

Symbols

a	annuity factor (y^{-1})
e	exergy content (MJ $kmol^{-1}$)
f	economic correction factor
ghg	GHG emissions (kg $CO_{2,eq}$ MWh^{-1})
$\dot{m}$	mass flow rate (t y^{-1})
$\dot{n}$	molar flow rate (kmol s^{-1})
p	price of energy/material flow (€ MWh^{-1}) or charge of CO_2 (€ t CO_2^{-1})
t	operating time (h y^{-1})
C	cost (€, M€ or M€ y^{-1})
$\dot{E}$	exergy content (MW) or change in energy/material flow (MW)
ghg	utilization-related GHG emissions (kg $CO_{2,eq}$ MWh^{-1})
HV	heating value (HHV basis) (MJ $kmol^{-1}$)
$\dot{Q}$	net useful thermal heat (MW)
$\dot{W}$	net electric power (MW)
$\Delta C_{oxo\ product}$	change in production cost of oxo products (€ t^{-1})
ΔT_{min}	minimum temperature difference
η_{en}	energy efficieny
η_{ex}	exergy efficiency

Subscripts

$comb$	combustion
f	net feeds
lb	labour
$oxo\ product$	oxo product
p	net production
sg	syngas production

upt	uptake
wtg	well-to-gate
BIO	biomass or biomass import
CO_2	onsite fossil CO_2
EL	electricity or change in net electricity import
F	incremental capital
FG	FG or avoided fuel gas import
H_2	H_2 or avoided H_2 import
$O\&M$	operation and maintenance
NG	NG or avoided NG import
RME	RME or RME import

Superscripts

$-$	net production
$+$	net demand

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APPENDIX

Table A1. Average NG composition (Swedegas, 2012) and corresponding heating values.

Composition (mol %)								Heating values (MJ kg^{-1})	
CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	CO_2	N_2	HHV	LHV
88.83	6.13	2.48	0.93	0.21	0.06	1.04	0.32	53.0	48.0

Table A2. Properties used for the lignocellulosic biomass (forest residues).[a]

Ultimate analysis (wt % df)[b]						
C	H	O	N	S	Cl	Ash
50.30	5.43	41.57	0.47	0.04	0.01	2.18
Proximate analysis (wt %)[b]				**Heating value (MJ kg^{-1})[c]**		
moisture content (ar)	volatile matter (df)	fixed carbon (df)	ash (df)	HHV (df)	LHV (df)	LHV (ar)
50	77.82	20	2.18	19.6	18.4	8.0

[a] Abbreviations: df, dry fuel; ar, as received.

[b] Adapted from Heyne and Harvey (2014).

[c] Estimated using the correlation reported in Sheng and Azevedo (2005).