



Syngas Production by Integrating Thermal Conversion Processes in an Existing Biorefinery

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Department of Applied Physics and Electronics
Licentiate Thesis
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Front: collage of i) oil painting of Domsjö pulp mill by Frans Michael Kempe, 1942, with permission from Örnsköldsvik Museum, ii) *Integrated biobased value chains*, Bio-based Industries Consortium

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To my baby, whomever you turn out to be.

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Sammanfattning

Användning av kol, olja och naturgas leder till förändringar i jordens klimat på grund av utsläpp av växthusgaser. Biomassa är den enda förnyelsebara kolkällan som kan omvandlas till drivmedel och kemikalier, marknader som idag helt domineras av traditionella petroleumprodukter. Bioraffinaderier för förädling av biomassa har stor potential att minska utsläppen av växthusgaser och ersätta fossila produkter. De flesta bioraffinaderier använder biologiska och/eller kemiska omvandlingsprocesser med flera restströmmar som lämpar sig som råvara för termisk omvandling och produktion av syntesgas. Vidareförädling av syntesgasen till bränslen och kemikalier kan öka andelen högvärdiga produkter från bioraffinaderiet.

I denna licentiatavhandling har termiska omvandlingsprocesser tillämpats och utvärderats för befintliga bioraffinaderikoncept. Två biproduktströmmar har undersökts som råvara till förgasning/reformering: hydrolysrest från en etanolanläggning och biogas från vattenrening. Dessutom har den termiska förbehandlingsmetoden torrefiering utvärderats med avseende på förbättrade bränsleegenskaper och integrationsaspekter. Slutligen har ett nytt process- och systemkoncept (Bio²Fuels) föreslagits och utvärderats som en alternativ väg för syntesgasframställning. Processen separerar biomassan i en väterik gas och en kolrik fast produkt och systemet har potentiellt en negativ koldioxidbalans.

Resultaten från detta arbete har visat att hydrolysresten är ett lämpligt förgasningsbränsle med avseende på syntesgasens sammansättning. Biogasen kan ytterligare reformeras till syntesgas genom kombinerad förgasning av biomassa och metanreformering med lovande resultat för temperaturer över 1000°C gällande reformeringsgrad och ökat H₂/CO-förhållande. Förbehandlingsmetoden torrefiering visade sig förbättra flera bränsleegenskaper och torrefierad biomassa är väl lämpad som råvara för entrained flow förgasning. Genom att integrera en torrefieringsanläggning med ett existerande bioraffinaderi kan lågvärdig restvärme effektivt utnyttjas för torkning av råvaran före torrefiering. Bio²Fuels-konceptet utvärderades och bedömdes och är intressant för vidare studier.

Tillämpning av termiska omvandlingsprocesser i ett befintligt bioraffinaderi för att förädla biproduktströmmar och lågvärdig biomassa (bark, GROT) har stor potential för energiintegrering, ökad produktionskapacitet samt för att begränsa klimatförändringar.

Nyckelord: bioraffinaderi, biobränsle, syntesgas, förgasning, torrefiering, metanreformering, H₂/CO förhållande, systemanalys, CO₂ negativitet

Abstract

The use of carbon from fossil-based resources result in changes in the earth's climate due to emissions of greenhouse gases. Biomass is the only renewable source of carbon that may be converted to transportation fuels and chemicals, markets now fully dominated by traditional oil supply. The biorefinery concept for upgrading and refinement of biomass feedstocks to value-added end-products has the potential to mitigate greenhouse gas emissions and replace fossil products. Most biorefineries use biochemical conversion processes and may have by-product streams suitable as feedstocks for thermal conversion and production of syngas. Further synthesis to value-added products from the syngas could increase the product output from the biorefinery.

The application of thermal conversion processes integrated into an existing biorefinery concept has been evaluated in this licentiate thesis work. Two by-product streams; hydrolysis (lignin) residue from an ethanol plant and biogas from wastewater treatment, have been investigated as gasification/reforming feedstocks. Also, the pre-treatment method torrefaction has been evaluated for improved gasification fuel characteristics and integration aspects. A new process and system concept (Bio²Fuels) with potential carbon negative benefits has been suggested and evaluated as an alternative route for syngas production by separating biomass into a hydrogen rich gas and a carbon rich char product.

The evaluation demonstrated that hydrolysis residue proved a suitable feedstock for gasification with respect to syngas composition. Biogas can be further reformed to syngas by combined biomass gasification and methane reforming, with promising results on CH₄ conversion rate and increased H₂/CO ratio at temperatures $\geq 1000^{\circ}\text{C}$. The pre-treatment method torrefaction was demonstrated to improve fuel qualities and may thus significantly facilitate entrained flow gasification of biomass residue streams. Also, integration of a torrefaction plant at a biorefinery site could make use of excess heat for drying the raw material before torrefaction. The Bio²Fuels concept was evaluated and found feasible for further studies.

The application of thermal conversion processes into an existing biorefinery, making use of by-products and biomass residues as feedstocks, has significant potential for energy integration, increased product output as well as for climate change mitigation.

Keywords: biorefinery, biofuels, syngas, gasification, torrefaction, methane reforming, H₂/CO ratio, system analysis, CO₂ negativity

List of Publications

This thesis is based on the following publications, referred to in the text by their corresponding roman numerals, I to V.

- I. Torrefaction and Gasification of Hydrolysis Residue**
Katarina Håkansson^a, Ingemar Olofsson, Kristoffer Persson^b and Anders Nordin
Conference proceedings, 16th European Biomass Conference and Exhibition (2008), Valencia, Spain

- II. Syngas Production by Combined Biomass Gasification and In-situ Methane Reforming**
Katarina Åberg, Linda Pommer and Anders Nordin
Manuscript

- III. Effects of Temperature and Residence Time on Torrefaction of Spruce Wood**
Martin Strandberg, Ingemar Olofsson, Linda Pommer, Susanne Wiklund-Lindström, Katarina Åberg and Anders Nordin
Manuscript

- IV. Process and System Integration Aspects of Biomass Torrefaction**
Katarina Håkansson^a, Anders Nordin, Martin Nordwaeger^c, Ingemar Olofsson and Martin Svanberg
Conference proceedings, 18th European Biomass Conference and Exhibition (2010), Lyon, France

- V. A Process and System Concept for Thermal Conversion of Biomass Potentially Facilitating BTL with Carbon Negativity**
Katarina Åberg, Linda Pommer and Anders Nordin
Manuscript

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^bNew family name: Kollberg

^cNew family name: Strandberg

1 Introduction

Population growth and improved standard of living result in continuously increased global primary energy consumption, making the supply of energy a critical issue for the world economy and environment. While fossil, carbon-based feedstocks remain the main source of energy, significant interest exists to replace fossil resources with sustainable renewable materials. Biomass, in particular with lignocellulosic origin, has a significant potential to reduce greenhouse gas emissions by sustainable production and use of efficient biomass conversion systems [1]. In addition, biomass is the only renewable source of carbon that may be converted to transportation fuels and chemicals, markets presently dominated by traditional oil supply. Thus, biomass is the only renewable option for replacement of oil as a refining feedstock.

The concept of a biorefinery for co-generation of energy, fuels, chemicals and other refined value-added products has gained interest over the last decade to both mitigate greenhouse gas emissions and replace fossil products [2]. As a limited resource, increased biomass use results in elevated prices at a competitive market, making efficient systems and full feedstock utilization important. Many of the existing pulp and paper industries already operate as partial biorefineries and may benefit from considerable expansion towards a full forest biorefinery with increased production of different renewable energy carriers and chemicals.

For most biorefinery concepts and studies, the typical focus is on biological and/or chemical conversion processes to decompose the biomass into chemical building blocks for further refinement or as end-products. By-product streams from the conversion processes are either sold or used as fuel for combustion.

Thermal conversion by gasification, decomposing the biomass into a syngas consisting of mainly carbon monoxide and hydrogen is another complementary strategy for chemicals and fuels production of residual or secondary streams. The syngas is subsequently synthesized to the desired end-products through several refinement steps. The combination of initial biological or chemical processing of the biomass for extraction of specific high-value products followed by thermal conversion of by-products and biomass residue streams for syngas production seem promising for maximum refinement to valuable end-products, as well as for economic and environmental performance.

The objective of this thesis work was to examine the integration of thermal conversion processes to an existing biorefinery site to enhance feedstock utilization and increase the output of value-added products by:

- 1) Identifying a few available process streams in an existing biorefinery and evaluate their potential as feedstocks for syngas production via gasification.
- 2) Evaluating the potential for optimizing the conversion of biomass to syngas by adding and integrating torrefaction to the gasification system and the biorefinery.
- 3) Evaluating another potentially interesting thermal conversion concept for syngas production, Bio²Fuels, facilitating a carbon negative system.

Thesis structure and delimitation.

The thesis is divided into two background sections on biorefineries and thermal conversion processes respectively, followed by a results and discussion section based on the appended publications. Experimental procedures and methods are fully described in the corresponding paper and only briefly mentioned in the specific result section. Lastly, the thesis conclusions and recommendations for future studies are presented.

This licentiate thesis does not address efficiency or economic aspects of integration of thermal conversion into a biorefinery but instead focuses on technical potential and general estimates on suitability for the specific concepts.

2 The Biorefinery Concept

The biorefinery concept is to upgrade and refine biomass feedstocks to value-added end-products using different conversion processes and integration of resources. The IEA define the term as “*biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy*” [3]. The definition could be expanded to specify that a biorefinery separate biomass resources into their chemical building blocks which can then be sold or further converted to value-added products (fuels, chemicals, fibers etc.), i.e. a sawmill is not by definition a biorefinery. Different technologies based on physical, chemical, biological and thermal conversion of biomass may be combined and preferably integrated in regard to feedstock, energy supply and waste treatment.

Most bio-based industries currently focus on a single production chain with potentially one or two by-product streams. In a biorefinery, polygeneration with a diverse product portfolio may provide financial security against price fluctuations in a particular product and make refining of smaller volume products or by-product streams economically viable alternatives. Further, process integration opportunities and collaboration with supply of utilities and feedstocks make the biorefinery concept appealing compared to single production chain systems.

Biorefinery research today is mostly focused on biological and chemical (biochemical) conversion technologies for extraction of valuable products from biomass. These processes are especially well suited for production of specific high-value products and chemicals, while syngas production by thermal and chemical (thermochemical) conversion is the most techno-economically favorable for large production volumes of bulk (petro-) chemicals and liquid fuels. As previously mentioned, the thermochemical pathway is potentially suitable as supplement to biochemical conversion. Residue streams, directly from the biomass or stemming from the biochemical processes, may be used as feedstocks for thermochemical conversion as the requirements on feedstock type and quality are often lower and less specific than for biochemical conversion.

The concept of exergy, i.e. the quality of a product/energy stream, should be carefully considered in a biorefinery for optimal use of the biomass feedstock. Heat (low exergy) is for instance almost always produced as a by-product and should thus not be the main product of the biorefinery, whereas processes for extracting the biomass fibers, high-value chemicals etc. (high exergy) may preferably be prioritized before production of high-bulk but less valuable product streams.

2.1 Pulp-based Biorefineries

In addition to entirely greenfield biorefinery concepts, supplementary biochemical or thermochemical processes can be added to existing biomass processing sites either as adjacent industries or integrated into the existing plant [4]. Existing pulp production facilities have been frequently suggested as logical sites for biorefinery application and have several prerequisites to become successful forest biorefineries, such as established biomass feedstock supply, existing infrastructure, economy of scale, and numerous by-product streams, several already utilized for energy purpose or refined to commercial products [5, 6]. By integrating additional conversion technologies at an existing plant, potential benefits for the pulp mill are 1) improved feedstock utilization, 2) new markets for bioenergy and bio-products with additional revenue and 3) protection of traditional product lines [4].

New pulp mill facilities emerging in tropical regions with lower manufacturing costs, declining newsprint use and dropping product price levels are just a few of the threats that traditional pulp mills face today. Expanding the product portfolio and increasing the biomass refinement is one approach for existing mills to remain profitable. Many current pulp mills may already be considered as rudimentary biorefineries with by-products utilized for internal energy supply and generation of few additional marketable products such as ethanol or tall oil. However, most of these are underdeveloped as a biorefinery in regard to full conversion of the biomass feedstock to value-added products.

2.2 The Domsjö Biorefinery - A Case Study

2.2.1 *Brief History and Overview*

The biorefinery site referred to in this thesis as the Domsjö Biorefinery is composed of several different companies established around what was once the Domsjö sulfite mill. The mill started operation in 1903 and was built adjacent to the existing sawmill, both part of the *Mo och Domsjö Aktiebolag* (MoDo AB), with an initial pulp production of 6000 ton/y which steadily expanded. In 1940, at a time where petroleum-based chemicals were scarce due to World War II, the sulfite ethanol plant was added to the mill site with an initial capacity of ~8.5 million liter of ethanol (95%). Additionally around 70 different chemical products were produced from the sulfite ethanol [7] making the site an early biorefinery, although the term had not yet been recognized. In the after war time, with oil yet again available at low cost, production were discontinued for many of the products.

Today the plant is owned and run by Domsjö Fabriker, part of the Indian group Aditya Birla, and has over the last decade fully developed from a traditional pulp mill into a biorefinery. The main products are specialty cellulose, lignin and bioethanol (Figure 2.1) from which a wide range of end-products can be produced. The specialty cellulose is the first step in producing viscose for fabrics and hygiene products, tablets for pharmaceutical application, paint and food thickeners, preservatives and more. The lignin can be used as concrete additive, binding agent in mineral and animal feed industries and as feedstock for thermal conversion. The produced bioethanol can be used as a fuel, a finished chemical product or as an intermediate for production of a wide range of other green chemicals.

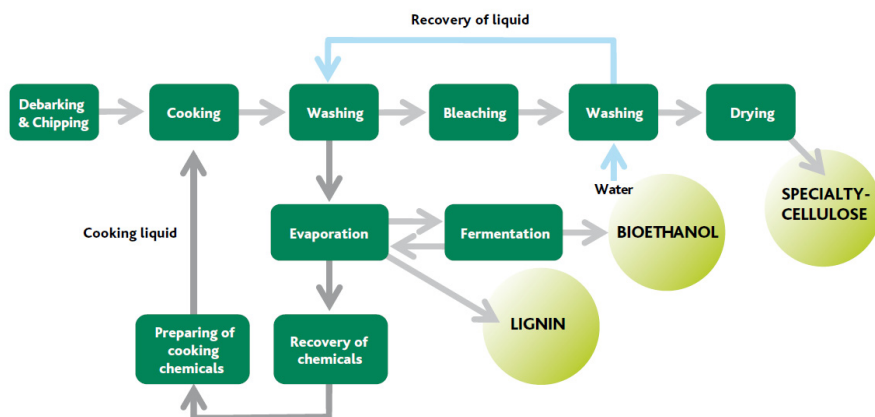


Figure 2.1: Flow chart for Domsjö Fabriker's current operation (source: Domsjö Fabriker).

Part of the biorefinery site in addition to Domsjö Fabriker are companies such as AkzoNobel (cellulose derivate), SEKAB (ethanol and derived products, lignin and biogas) and the local energy company Övik Energi (electricity, heat and steam). Also involved in the collaboration is the company Domsjö Fiber, co-owned by Domsjö Fabriker and Övik Energi for feedstock supply to several different facilities. The Domsjö biorefinery is one part of *The Biorefinery of the Future*, which combines industry and universities for biorefinery research and development in a platform coordinated by the cluster SP Processum, owned in part by the 21 member companies (40%) and SP Technical research institute (60%).

2.2.2 Ethanol Demonstration Plant

The company SEKAB imports, produces, refine and sell; ethanol and several of its chemical derivatives, lignin and biogas at the Domsjö biorefinery site and has evolved from the old sulfite ethanol plant into large supplier of ethanol and

derived chemicals. In the Biofuels and Chemicals plant acetaldehyde, ethyl acetate, ethanol (99%) and acetic acid is produced.

A demonstration plant for production of second generation cellulose-based ethanol is located in close proximity to SEKAB's production facility and the Domsjö Fabriker pulp mill and has been in operation since 2004. In 2013 the plant was renamed Biorefinery Demo Plant and SP Technical research institute took over the daily operation while the ownership remained with EPAB (co-owned by Umeå University, Luleå University of Technology and SEKAB). The plant has generated >40,000 operating hours, while performing research and development on the different process steps and a large variety of other areas such as raw materials, integration and control technology. The plant has a maximum input capacity of 2 ton D.S./day of wood chips producing approximately 400 l of lignocellulosic ethanol.

The technology employed in the demo plant consist of four main steps; 1) pre-treatment, 2) enzymatic hydrolysis converting cellulose to glucose (sugar), 3) fermentation of the sugars to ethanol and 4) distillation to increase the ethanol concentration to 90% (Figure 2.2).

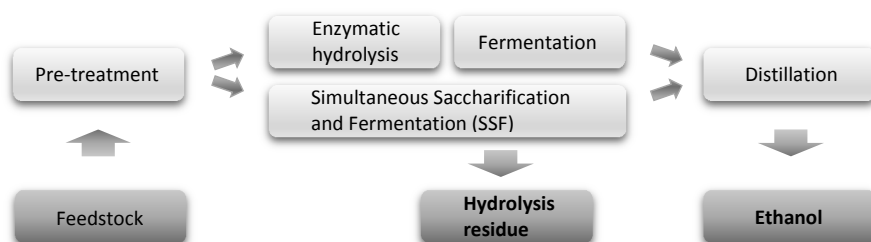


Figure 2.2: Schematic description for lignocellulosic ethanol production at the biorefinery demo plant.

In addition to ethanol, biogas and a solid residue is produced from the demo plant. Some dissolved substances, which can be used to produce biogas as an additional product (section 2.2.3), remain in the process water after filtration and distillation. The solid residue product containing mainly lignin but also un-hydrolyzed cellulose and water is filtered from the main process stream either before or after fermentation [8]. The hydrolysis (lignin) residue consists of 40-45% of the original feedstock [9] and should be utilized for the overall process to be economically viable.

2.2.3 Biogas Production

The Domsjö Fabriker bio treatment plant has been in operation since 1985 and produce biogas from the remaining organic matter in wastewater streams at the biorefinery site. The plant is the largest producer of biogas in Sweden with ~80 GWh annually produced and a CH₄ content of 85%. The bio treatment is a two-step process where the first step is anaerobic digestion producing biogas, followed by aerobic digestion from which sludge residue is recycled to the first step in order to preserve active microbes [10].



Figure 2.3: The Domsjö bio treatment plant (source: Domsjö Fabriker).

At the onset of this thesis project the biogas was used as combustion fuel for heat and electricity production during months of high heat demand, but flared during the summer and other low heat demand periods. According to the Swedish Energy Agency's report on production and use of biogas in Sweden 2012 [11], 10% of the produced biogas was not utilized and simply combusted in a gas flare. Unless available for combustion, the utilization of small produced gas streams where no integration potential with adjacent industry exist is often not economically feasible.

At present time, the biogas produced from the bio treatment plant is used as feedstock for drying lignin or in the adjacent combined heat and power plant operated by Övik Energi AB for production of heat and electricity. The internal gas requirement is approximately 30-50 GWh, leaving equal amount available for other uses without disturbing the lignin drying process. Although the addition of the lignin dryers have improved the utilization rate, and thereby the product value of the biogas, the chemical potential of such a high quality product may perhaps be further realized by other end-uses. Currently, an ongoing project managed by

SP Processum is evaluating the market interest for using the biogas as transportation fuel.

2.2.4 Black Liquor Gasification

In a conventional pulp mill, spent pulp cooking liquor, water and the lignin residue form a mixture called black liquor. The high water content is decreased through evaporation before the black liquor is burned in a recovery boiler for production of steam to be used internally or sold to external customers when applicable. The boiler also serves as a chemical recovery unit for the cooking chemicals that are recycled to the process.

Black Liquor Gasification (BLG) has been developed as an alternative to the recovery boiler. Instead of being used as combustion feedstock, the organic material is converted to syngas in the gasifier for further processing to valuable products while retaining the recovery system for the cooking chemicals. However, replacing a recovery boiler with BLG will change the energy balance of the plant and additional feedstock for internal steam supply is usually necessary.

At the onset of this thesis work, Domsjö Fabriker in collaboration with the gasifier supplier Chemrec planned the construction of a black liquor gasification unit at Domsjö with additional supply of steam being provided by Övik Energi via the adjacent combined heat and power plant. The Chemrec technology typically comprise of an oxygen blown, pressurized (32 bar) entrained flow gasifier (see section 3.2) operating at 950-1000°C [12]. For the Domsjö black liquor gasification demo project, a total of three gasifiers were included for redundancy reasons.

The planned black liquor gasification project in Domsjö was unfortunately discontinued in 2012 by Domsjö Fabriker and the new owners Aditya Birla. According to the CEO Lars Winter, the project did not suit the new owner's business plan for the Domsjö site [13]. When in operation, the plant would have produced 100,000 ton/year of the biofuels DME and methanol. Although, the project is no longer planned, it demonstrated that integration of thermo-chemical conversion processes into the biorefinery was considered highly viable and was supported by both investors and the Swedish Energy Agency.

3 Thermal Conversion Processes for Syngas Production

Syngas, a gaseous mixture of H_2 and CO and various less desired components such as CO_2 , H_2O and CH_4 , is an important intermediate in chemical synthesis that can be generated from a wide variety of feedstocks such as natural gas, coal, petroleum, biomass and organic waste. Synthesized products from syngas include a large variety of valuable chemical intermediates/end-products and transportation fuels such as ammonia, methanol, synthetic natural gas (SNG), dimethyl ether (DME) and Fischer-Tropsch (FT) diesel. The requisite composition of the syngas differs depending on end-product, particularly regarding the H_2/CO ratio and tolerance for impurities, though the latter is rarely allowed with low concentration limits. A H_2/CO ratio of 1.0 to 2.0 is generally required (Table 3.1) and if necessary, upgrading the syngas before synthesis to a higher ratio in a separate water gas shift (WGS) process is possible.

Table 3.1: List of common end-products from chemical synthesis of syngas and their requirements for H_2/CO ratio.

Product	H_2/CO	Product	H_2/CO
Methanol	~ 2	FT-diesel	2
Ammonia ^a	∞	Hydrogen ^b	∞
SNG	1.5-3	Alcohols	1-1.5
DME	1		

^a $CO + CO_2 < 20 \text{ ppmV}$, ^b $CO + CO_2 < 10-50 \text{ ppmV}$ [14]

The chemical synthesis processes are catalyst driven reactions and often mandate specific requirements on syngas purity in regard to trace elements to improve catalyst life-time. In general, catalysts are very sensitive to poisoning and in particular sulfur and chlorine compounds require complete removal. Also particles, tars, alkali metals and for some catalysts inert gases (nitrogen for SNG synthesis) cause catalyst deactivation [14]. Most catalysts operate at severe conditions with high pressure (100-250 bar for ammonia, 25-60 bar for FT-diesel) and temperatures of generally 200-400°C [14]. Generation of excess heat is common and efficient cooling systems are often necessary for operation. However, process integration benefits with processes requiring this heat load is possible.

3.1 Traditional Methane Reforming

Syngas manufacturing from natural gas correspond to the largest market share of the total volume of globally produced syngas. Commercial production is

dominated by steam reforming (1), followed by partial oxidation (2) and the newer technology of CO₂ reforming (3).



While feedstock prices for natural gas are comparatively low, the reforming systems are capital intensive in both investment and operation. Steam reforming [15] has a high conversion rate (>95%) but is operated at high temperature and pressure, serving high demands on resistant materials. Furthermore, the resulting H₂/CO ratio in the syngas is often too high for most applications. Partial oxidation, which may operate either with or without a catalyst [16-18], also require high process temperature and produce a syngas with the preferable H₂/CO ratio of 2. Unfortunately, without catalyst it experiences low conversion rate and the catalyst used is prone to deactivation and resulting short life span. The CO₂ reforming [19] is greatly affected by carbon deposit on the catalyst with resulting catalyst deactivation. Only partial oxidation may operate excluding catalyst meaning that for all other reforming processes a minimum of two catalytic synthesis processes are required before reaching the specific end-product.

3.2 Gasification

Syngas production from solid or liquid feedstocks is achieved by the thermal conversion process gasification. In contrast to combustion, where the purpose is to convert as much of the chemical energy as possible in the fuel to other forms of energy (heat and, by extension, mechanical or electrical energy), gasification retain chemical energy in the gas product by operating at insufficient oxygen levels for complete combustion (full oxidization) to occur. The partial oxidation is generally achieved by either introduction of oxygen (direct) or steam (indirect gasification).

The gasification process has been known for several centuries. It developed from the production of town gas by pyrolysis, initially produced from wood feedstock and then from coal as wood resources became sparse in populated areas. Today, coal remain the predominant feedstock for gasification and the building of large commercial plants has gained interest the last decade in response to increased oil and gas prices and local large coal reserves (China). There are a variety of technologies available and in use with the most common being moving bed gasifiers, fluidized bed gasifiers (FBG) and entrained flow gasifiers (EFG). They all have their strengths and weaknesses; moving bed gasifiers are

inexpensive but produce a lower quality syngas containing pyrolysis products (tars, soot, methane) whereas fluidized bed gasifiers have excellent heat and mass transfer due to good mixing of fuel and oxidant in the bed. However, the FBG is restricted to operation below the ash-softening temperature to avoid bed agglomeration and require more advanced systems. Entrained flow gasifiers have improved carbon conversion and operate at high temperature and short residence time, which demand small particle sizes ($<100\text{ }\mu\text{m}$) and large oxygen supply. EFG is a well-developed coal gasification technology with large commercial operation globally due to its ability to handle low-reactive coals and cost efficiently produce a clean, tar-free syngas. Outlet gas temperatures of $1250\text{--}1600^{\circ}\text{C}$ and elevated pressure of 20–80 bar are common operating conditions.

In the production of a clean syngas suitable for synthesis, the gasification is only one of several steps (Figure 3.1). The gasification process itself usually represents $<1/4$ of the total investment cost (depending on technology) for a conversion plant with a large part comprised of the gas cleaning and conditioning processes. Therefore, any improvements possible in the gasification process that removes one or more subsequent steps is often highly economically viable.

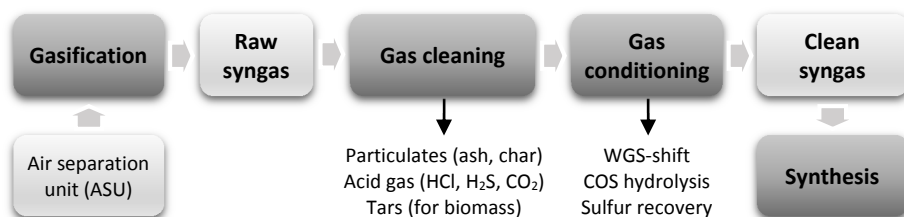


Figure 3.1: Schematic description of a gasification plant with examples of gas cleaning and conditioning processes [20].

For biomass gasification, the fluidized bed technology is most commonly used although entrained flow gasification has gained interest, particularly in combination with some form of thermal pre-treatment [21–24]. Biomass is often heterogeneous with high moisture content making fluidized bed gasification suitable in terms of feeding and stable operation, but the syngas produced is often polluted by pyrolysis products such as tars. As biomass is more reactive than coal, the lower temperature used in fluidized bed gasification is sufficient. However, the upper temperature limit due to the softening of the ash is decreased for biomass due to the more reactive ash components. Thus, operation above the ash-melting temperature for biomass in an entrained flow gasifier may not demand as high temperatures compared to coal, which combined with the increased reactivity for biomass make entrained flow operation potentially cost effective. However,

additional disadvantages restrict biomass as a suitable coal replacement and entrained flow gasification feedstock. It is hydrophilic, i.e. absorbs moisture, which makes slurry feed impossible and the biomass difficult to transport and store. Also, due to the fibrous structure of biomass, comparable high amounts of milling energy is required to produce sufficiently small particles, and the milled powder is often difficult to feed.

3.3 Torrefaction

Torrefaction has been recognized as a method to improve fuel characteristics for both gasification and combustion end-use as well as logistics and handling. The process is briefly described as a thermal pre-treatment method operated in inert atmosphere where biomass is heated to temperatures between 200°C and 350°C for 3 minutes up to 3 hours at atmospheric pressure. However, the most common operation range for torrefaction are a process temperature of 250-300°C and 5-30 min residence time. The process has two product streams; the refined solid product retaining most of the feedstock energy, i.e. the torrefied biomass, and the torrefaction gas containing released volatiles from the biomass feedstock. The torrefied solid product is closer to coal in characteristics compared to the untreated biomass with higher energy density and lower oxygen and hydrogen content (less volatiles). It is also more homogeneous, less fibrous [25], hydrophobic [26], demonstrated higher resistance against fungal attack [27] and reported as more brittle compared to raw biomass [28]. The improved characteristics make the biomass easier to transport, store and feed into an end-use process. As result, the combination of torrefaction pre-treatment of biomass and entrained flow gasification has been suggested and evaluated in several projects with promising results [22, 28-30]. Pre-treatment by torrefaction, specifically in combination with densification, increase the energy density of the biomass material with significant improvements on the supply chain economics and efficiency [31, 32].

The torrefaction gases contain a variety of organic compounds that could potentially be further valorized [33], but is most commonly considered as fuel for combustion to internally supply the torrefaction process with heat. Temperature and residence time are both positively correlated with volatilization, i.e. increased torrefaction severity, with lower mass and energy yields for the solid product. However, high torrefaction severity often demonstrates a more significant improvement for the above mentioned fuel characteristics and must be weighed against the lower mass and energy yields to identify optimal operation settings.

Torrefaction is typically preceded by a drying process to remove the remaining moisture in the biomass feed, preferably in a separate reactor in order not to unnecessarily dilute the torrefaction gases with steam. The drying process constitutes the largest energy demand of the combined drying and torrefaction system (Figure 3.2), approximately 6:1 depending on moisture content and torrefaction process settings.

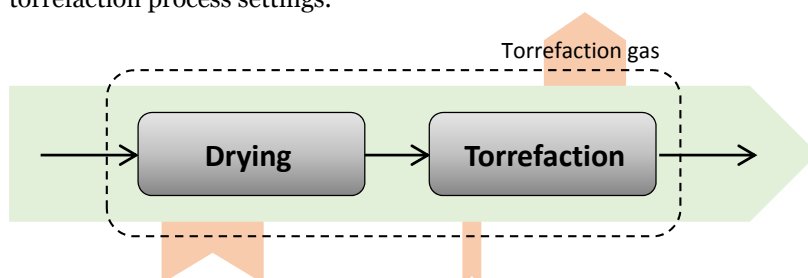


Figure 3.2: Schematic description of the drying and torrefaction energy system. Arrow width correspond to typical energy input or output.

The combined system may operate on an autothermal basis, i.e. the energy requirements for the processes equal the energy contained in the torrefaction gas. Whether autothermal operation is possible depend on the feed moisture content and the torrefaction severity, i.e. the energy content of the gas.

As the drying energy may be supplied by low value heat, torrefaction is well suited for integration in a biorefinery as a pre-treatment for gasification and synthesis. By torrefaction, low-quality biomass previously unsuitable as gasification feedstock may also be made available for syngas production. The torrefied material as refined solid energy carrier may also be an interesting commercial product from the plant.

3.4 Bio²Fuels

The Bio²Fuels process principally suggested in Paper V is a thermal conversion process that can be described as slow pyrolysis or high temperature torrefaction in a temperature range of 300-500°C. The main focus of the concept is to optimize the total process and system integration benefits by improving operation, combating several challenges for biomass conversion and ensuring a carbon negative system.

In the Bio²Fuels process, biomass is separated into two product streams; a hydrogen rich *gas* stream and a carbon rich *char* stream (Figure 3.3). By selecting suitable operation temperature, the ash-forming elements are retained in the solid product leaving a gas stream free of disruptive ash-related issues and suitable for

syngas production by gas reforming. The retained ash in the biochar may be neutralized in the co-firing step with the introduction of sulfur and mineral-rich coal ash. Another benefit is that the gas is more easily fed to a subsequent reactor compared to solid biomass.

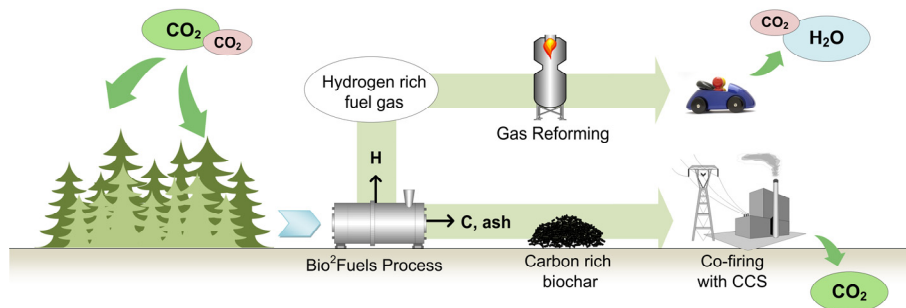


Figure 3.3: System overview of the Bio²Fuels concept.

The hydrogen and carbon separation serve several purposes:

- More hydrogen and less carbon available for syngas production result in a syngas with higher H_2/CO ratio, suitable for subsequent synthesis without additional adjustment process.
- Reduced amount of carbon in the production of transportation fuels equal less CO_2 released into the atmosphere when the fuel is combusted if hydrogen rich biofuels are used.
- If the biochar is potentially combusted in a large facility that utilizes carbon capture and storage (CCS), the overall system possesses an interesting transport driven carbon negativity. CCS is the common name for technologies dealing with the capture and storage of CO_2 instead of releasing it to the atmosphere. In combination with biomass feedstock, employment of CCS may result in negative emissions for the specific plant and supply system.

4 Summary of Results and Discussion

4.1 Case Study Implementation

The first section of the thesis objective aimed to explore integration of thermal conversion processes in an existing biorefinery by identifying available process streams and evaluate their potential as feedstocks for gasification. For the case study biorefinery in Domsjö, two process streams were evaluated; biogas from the bio treatment plant and hydrolysis residue from the ethanol biorefinery demo plant, both lacking in suitable application at the onset of this thesis work.

4.1.1 Hydrolysis Residue

The large amount of residue produced at an ethanol plant, referred to as hydrolysis residue or lignin residue, has previously been suggested as feedstock for thermal conversion by either combustion or gasification [34]. The use of gasification instead of combustion could improve the ethanol yield or just increase the overall product output of the biorefinery as well as improving plant efficiency. In Paper I, both torrefaction and gasification of the hydrolysis residue was evaluated and the gasification results are summarized in this section (for torrefaction of hydrolysis residue, see section 4.2).

Gasification of both torrefied and raw hydrolysis residue as well as a reference wood fuel was performed in a bench-scale fluidized bed gasifier and the syngas composition and total dust load was sampled and analyzed. The hydrolysis residue appeared to be a suitable feedstock for gasification with almost identical syngas composition and close to half total dust load compared to wood gasification. The syngas composition from gasification of the torrefied residue differed slightly compared to untreated hydrolysis residue, with higher CO₂ and lower CO and CH₄ concentrations and increased dust load. Further refinement of the hydrolysis residue stream by gasification may be a suitable path to increase the chemical yield of the ethanol plant.

4.1.2 Methane Reforming

The biogas from the bio treatment plant, pre-dominantly containing methane (85%), may be directly used as fuel for combustion but most likely require cleaning/upgrading for use as transportation fuel. For other end-products, the biogas could be utilized as an additional gasification feedstock.

As fully described in Paper II, the concept of co-gasification of a coal feedstock and CH_4 has been suggested as a method to reform unexploited CH_4 streams without having to apply expensive conventional reforming technologies or in attempt to increase the H_2/CO ratio in the syngas from coal gasification. In the gasification environment, the necessary reactants (O_2 , CO_2 , and H_2O) are all present and the presence of carbon and ash particles from the solid feedstock may provide a catalytic effect on the CH_4 reforming.

Co-gasification of locally generated biogas with biomass or black liquor appear promising in an integrated biorefinery with a gasification unit. Such a system has several potential advantages e.g. increasing the output of valuable products from the biorefinery, providing more cost efficient CH_4 reforming at less severe conditions and increasing the H_2/CO ratio of the syngas.

In Paper II, the combined reforming of methane and gasification of biomass was evaluated by means of 1) a parametric chemical equilibrium study for co-gasification of CH_4 with woody biomass and black liquor feedstocks and 2) bench-scale experiments of co-gasification of wood/peat pellets and CH_4 in a fluidized bed gasifier. For detailed description of parameters, experimental settings and procedure, refer to Paper II.

For both feedstocks and levels of methane addition according to the chemical equilibrium study; increased temperature, addition of steam and increased OER all result in higher CH_4 conversion rate while increased pressure reduce the overall CH_4 reforming. However, in an actual gasification environment chemical equilibrium is often not fully attained.

For the bench-scale experiments, the temperature was varied between 800°C and 1000°C in increments of 50°C . For each temperature setting, a reference run (Ref) with solely biomass gasification and an experimental run including the addition of methane ($+\text{CH}_4$) was performed and the syngas sampled and analyzed. Figure 4.1 illustrate the CH_4 reforming before and after addition of methane and the H_2/CO ratio, calculated from the syngas composition.

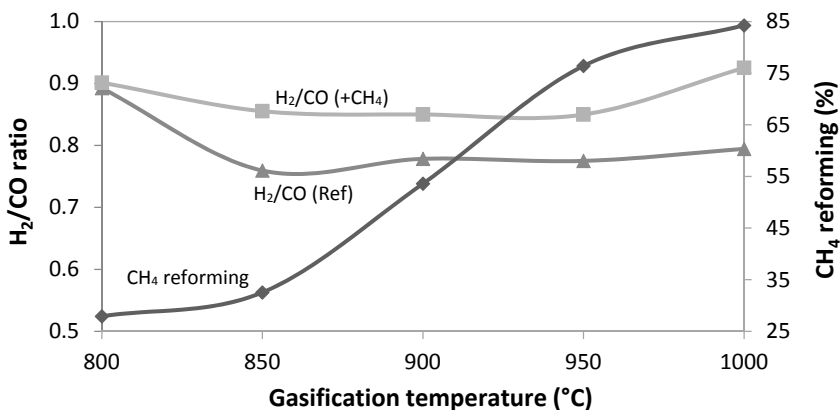


Figure 4.1: Methane reforming (right axis) during co-gasification of biomass and CH₄ and H₂/CO ratio (left axis) in the syngas before and after methane addition.

The results demonstrate that CH₄ reforming is highly temperature dependent due to the thermal instability of CH₄ and that the H₂/CO ratio significantly increases with addition of CH₄ to the gasifier. Evaluating the complete syngas composition (Figure 3 in Paper II) illustrate that the addition of CH₄ has a negative effect on the molar yields of both H₂ and CO at temperatures up to 850°C and 900°C respectively, while the yield of CO₂ and CH₄ increases. At the higher temperatures, the increased CH₄ conversion rate in addition to elevated yields of H₂ and CO demonstrate that more and more of the added methane has been reformed to syngas.

As the CH₄ reforming and the overall yields of H₂ and CO increase with temperature, high gasification temperature is suggested. In the work described in Paper II, a limit on maximum possible experimental bed temperature was necessary due to the applied gasification technology (fluidized bed).

4.2 Torrefaction

The second part the thesis objective was to evaluate the potential addition and integration of torrefaction to a biorefinery system with gasification for syngas production. The evaluation was made on the basis of torrefaction as a pre-treatment for gasification and its potential to optimize the total system in regard to cost and/or efficiency. Paper I, III and IV all investigate torrefaction to some extent for hydrolysis residue, Norway spruce and willow feedstocks respectively.

4.2.1 Experimental Evaluation

The torrefaction experiments on hydrolysis residue were carried out in a batch reactor according to a full factorial experimental design for three variables (torrefaction residence time, temperature and input temperature) with three center points (see Paper I). The reduction in milling energy consumption (calculated as required electrical energy divided by chemical energy in the sample) was experimentally evaluated and demonstrated a significant reduction in milling energy after torrefaction. The parametric analysis revealed that relative milling energy demand is negatively correlated with high torrefaction temperature and long residence time.

In Paper III, an extensive evaluation of the combined quantitative effect of torrefaction residence time and temperature was performed on a large amount of responses such as heating value, mass and energy yields, milling energy consumption and hydrophobicity. For a complete list of evaluated responses and corresponding results, consult Paper III.

A continuous torrefaction pilot plant was constructed, evaluated and optimized by the Umeå University torrefaction team to improve process control and measurement accuracy for both time and temperature compared to the batch process. For detailed description on pilot design and experimental methodology, see Paper III. For Norway spruce, the torrefaction temperature proved the most influential factor on the investigated responses with some interaction effects with time, whereas the residence time was the most influential factor on the responses for hydrolysis residue. The dissimilarity could be derived from the significant difference in feedstock preparation between the two feedstocks. Residence time and torrefaction temperature also demonstrated significant impact on the analyzed responses for Norway spruce and hydrolysis residue respectively. Long residence time equals a larger reactor with higher equipment cost, making the option of operating at short time and higher temperature attractive.

All experimental torrefaction work in this thesis demonstrated increased heating value and carbon content and decreased volatiles, oxygen and hydrogen content and milling energy consumption with torrefaction. Also, all listed product qualities are positively correlated with increased torrefaction severity (increased temperature and time). Paper III also evaluated hydrophobicity using two different methods, contact angle and equilibrium moisture content, both demonstrating a significant improvement by torrefaction. The contact angle measurement proved unsuitable for the coarse-surface wood chips and exposed no significant difference between the different torrefaction samples. The results

from equilibrium moisture content analysis demonstrated a decrease by more than 50% for torrefied spruce compared to the raw feedstock and the decrease was positively correlated with increasing torrefaction severity.

4.2.2 System and Integration Aspects

As described and extensively discussed in Paper IV, the entire supply chain and site-specific systems must be considered to fully explore the maximum energy/exergy and cost efficiency of biomass torrefaction. As previously described, the drying process requires most of the energy input in a torrefaction plant which can be supplied by low-value heat potentially available at the integration location. Paper IV discusses several potential integration sites operating as both potential importers and exporters of torrefied biomass. For a biorefinery with integrated gasification, large amount of excess heat would be available from different sources on-site, such as the chemical synthesis processes, making integration with torrefaction potentially suitable. While providing integration potential, on-site torrefaction does not benefit from improved logistics in the biomass supply chain. However, a large gasification unit will most likely require more feedstock than readily supplied by only one torrefaction unit. Imported torrefied biomass from stand-alone plants or plants integrated at other types of production sites may further supply the gasifier and benefit from the supply chain advantages by torrefaction.

An energy and mass balance for a torrefaction plant based on torrefaction data from experimental work on willow [22] was used to illustrate the influence of different levels of integration in Paper IV. The calculations demonstrate that integration design is important and that the thermal efficiency of the torrefaction plant can be increased by integration with adjacent industry.

4.3 Bio²Fuels

In accordance with the last section of the thesis objective, a thermal conversion process and system concept for syngas production facilitating carbon negativity was evaluated. In a biorefinery, the Bio²Fuels process presents an alternative route to syngas production with the char stream as an additional product output in the form of a solid energy carrier. If desired, the biochar could be used as feedstock at the biorefinery site with loss of the system benefits of carbon negativity as a consequence, unless CCS is employed at the biorefinery site.

As described in Paper V, the Bio²Fuels process and concept was proposed and evaluated based on several aspects:

- Assess the potential for hydrogen and carbon separation into gas and solid products based on previous work and the influence of such separation on the final H_2/CO ratio in the produced syngas.
- Discuss and evaluate the thermochemical driving forces for volatilization of ash-forming elements in biomass by use of chemical equilibrium calculations.
- Briefly assess the potential benefits in terms of CO_2 negativity for the overall system.

The yield of hydrogen and carbon distributed to the gas phase was calculated for the suitable pyrolysis literature data and unpublished torrefaction results for both spruce and wood residues (Figure 4.2). The results clearly demonstrate the separation of hydrogen and carbon into gas and solid stream, and that most of the feedstock hydrogen is volatilized. Both hydrogen and carbon volatilization increased with temperature.

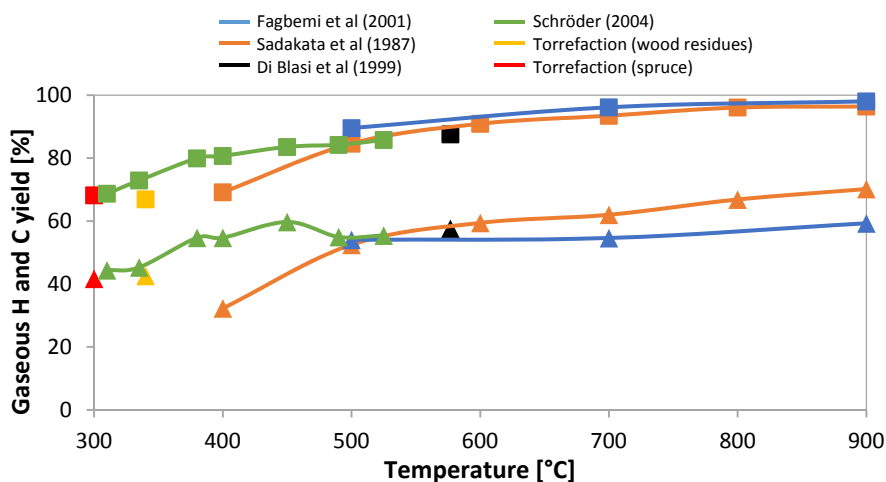


Figure 4.2: Distribution yields of C and H to gas phase as percentage of feedstock input on molar basis from literature and unpublished torrefaction data [35-38]. Square and triangle data points represents hydrogen and carbon respectively.

Based on literature data from the selected base case in Paper V (Fagbemi et al (2001) [35], pyrolysis at 500°C) gas reforming/gasification was emulated by performing chemical equilibrium calculations for varying pressure and OER, using the raw wood data and pyrolysis gas respectively. The calculated H_2/CO ratio was distinctively higher in the syngas calculated from gas reforming of pyrolysis gas compared to the syngas calculated from gasification of the untreated wood feedstock (Figure 4, Paper V).

The volatilization driving forces for the ash-forming elements were evaluated based on chemical equilibrium calculations for pyrolysis process settings and a temperature range of 300-900°C for a typical wood fuel. All ash-forming elements were predicted to be retained in the char except chlorine, potassium and sodium, but operating at a temperature below 500°C could potentially result in an alkali-free gas.

The carbon negativity potential of the overall Bio²Fuels system in relation to process temperature was evaluated by performing a simplified carbon balance for two of the previously published reports on experimental pyrolysis [35, 36]. The feedstock carbon was distributed to gas and solid products in accordance with the published data, and the carbon in the solid fraction assumed captured at an efficiency of 90%. All the volatilized carbon in the gas product was assumed to end up in the atmosphere as CO₂ regardless of process steps in between. The calculated CO₂ negativity potential was highest (61%) at the lowest pyrolysis temperature, further supporting low process temperature for the Bio²Fuels process.

5 Conclusions

The integration of thermal conversion processes with syngas production in a biorefinery could potentially increase the product output of the biorefinery site by utilizing by-product streams from existing processes as feedstocks.

- The hydrolysis residue proved to be a suitable feedstock for gasification with aspect to syngas composition and demonstrated similar positive behavior to the torrefaction pre-treatment as wood feedstock.
- Combined biomass or black liquor gasification and biogas reforming could be a suitable utilization of the chemical energy in the biogas at a biorefinery site. Furthermore, the increase in H_2/CO ratio improves the overall gasification plant cost efficiency by potentially eliminating the need for adjustment by WGS. However, high operation temperature is required and the process is potentially most suited in (low pressure) entrained flow gasification applications and with addition of steam.

The pre-treatment method torrefaction improve fuel qualities such as heating value, grindability and hydrophobicity and may facilitate operation of entrained flow gasification. Due to the inherent qualities of the process, integration of a torrefaction plant on the biorefinery site could make use of readily available excess heat from adjacent processes for the drying, improving the thermal efficiency of the plant.

The concept of the thermal conversion process and system Bio²Fuels was substantiated and initially supported by both theoretical calculations and previously published empirical data for pyrolysis:

- Bio²Fuels is potentially a suitable process preceding syngas production by gas reforming of an alkali-free and high hydrogen gas stream, increasing the H_2/CO ratio in the syngas.
- Application of carbon capture and storage with conversion of the carbon rich char could facilitate a carbon negative transportation system by use of Bio²Fuels.

6 Future Work

Suggestions for future work within this thesis topic include the evaluation of both efficiency and economic aspects of integrating the different thermal conversion processes in a biorefinery. Some interesting concepts for future evaluation that could be derived from this work are analysis of:

- The total biomass supply chain to a biorefinery including off-site torrefaction units for pre-treatment of gasification feedstocks.
- The energy integration of torrefaction and gasification at a biorefinery site with synthesis to chemicals or fuels.
- Techno-economic analysis of the Bio²Fuels system including the carbon balance.
- Experimental feasibility study of Bio²Fuels.

Further process evaluation is required for several of the included projects. For the co-processing of methane with biomass gasification, the addition of steam in combination with higher gasification temperature should be evaluated. The use of entrained flow gasification technology could facilitate a parametric experimental evaluation of the combined effect of temperature, steam, OER and pressure for process optimization to compare with the chemical equilibrium study performed in Paper II. Experimental evaluation of co-gasification of methane and black liquor could potentially demonstrate high conversion rates for CH₄ reforming.

The Bio²Fuels study included in this thesis should be considered as a pre-feasibility study for further experimental and system analysis. Both lab and pilot scale experiments are planned to validate the hydrogen and carbon separation and the ash volatilization characteristics. The role of water, both in the form of feedstock moisture and as an additive, would be interesting to evaluate as it could significantly further increase the H₂/CO ratio in the syngas.

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8 References

1. Chum, H., et al., *Bioenergy*. In *IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation*, O. Edenhofer, et al., Editors. 2011: Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
2. Cherubini, F., *The biorefinery concept: Using biomass instead of oil for producing energy and chemicals*. *Energy Conversion and Management*, 2010. **51**(7): p. 1412-1421.
3. IEA, *IEA bioenergy Task 42 on biorefineries: co-production of fuels, chemicals, power and materials from biomass*. 2008: In: Minutes of the third Task meeting, Copenhagen, Denmark, 25-26 March 2007.
4. Bajpai, P., *Biorefinery in the Pulp and Paper Industry*. 2013: Academic Press, Elsevier Inc.
5. Pettersson, K., M. Mahmoudkhani and A. von Schenck, *Opportunities for biorefineries in the pulping industry*. 2012. In: Sandén, B (Ed.), *Systems Perspectives on Biorefineries*, Chalmers University of Technology, Energy Area of Advance, Göteborg, Sweden.
Available at: <http://bit.ly/EvolvingEbook>.
6. Towers, M., et al., *Biorefinery opportunities for the Canadian pulp and paper industry*. *Pulp & Paper-Canada*, 2007. **108**(6): p. 26-29.
7. Mo och Domsjö, *Skogen ger: en bok om Mo och Domsjö aktiebolag*. 1946, Stockholm.
8. SEKAB Company Webpage. 2014-08-04]; Available from: <http://www.sekab.com/biorefinery/demo-plant>.
9. Öhman, M., C. Boman, and H. Hedman, *Residential combustion performance of pelletized hydrolysis residue from lignocellulosic ethanol production*. *Energy & Fuels*, 2006. **20**(3): p. 1298-1304.
10. Naturvårdsverket, *Biogas ur gödsel, avfall och restprodukter - Goda svenska exempel*. 2012. Rapport 6518
11. The Swedish Energy Agency, *Produktion och användning av biogas 2012*. 2013. ISSN 1654-7543
12. Ekbom, T., et al., *Technical and Commercial Feasibility Study of Black Liquor Gasification with Methanol/DME Production as Motor Fuels for Automotive Uses-BLGMF*. Report for Contract No. 4.1030/Z/01-087/2001, European Commission, 2003, Altener program, Stockholm, Sweden

13. *Domsjös miljardprojekt avblåst*, in *Örnsköldsviks Allehanda*. 2012: Örnsköldsvik.
14. Bridgwater, A.V., H. Hofbauer, and S. van Loo, eds. *Thermal Biomass Conversion*. 2009, CLP Press.
15. Rostrupnielsen, J.R., *PRODUCTION OF SYNTHESIS GAS*. Catalysis Today, 1993. **18**(4): p. 305-324.
16. Hickman, D.A. and L.D. Schmidt, *SYNTHESIS GAS-FORMATION BY DIRECT OXIDATION OF METHANE OVER PT MONOLITHS*. Journal of Catalysis, 1992. **138**(1): p. 267-282.
17. Mleczko, L. and T. Wurzel, *Experimental studies of catalytic partial oxidation of methane to synthesis gas in a bubbling-bed reactor*. Chemical Engineering Journal, 1997. **66**(3): p. 193-200.
18. Armor, J.N., *The multiple roles for catalysis in the production of H-2*. Applied Catalysis a-General, 1999. **176**(2): p. 159-176.
19. Qin, D. and J. Lapszewicz, *STUDY OF MIXED STEAM AND CO₂ REFORMING OF CH₄ TO SYNGAS ON MGO-SUPPORTED METALS*. Catalysis Today, 1994. **21**(2-3): p. 551-560.
20. Higman, C. and M. van der Burgt. *Gasification*, 2nd ed., Elsevier Science, Oxford, UK, 2008.
21. Weiland, F., et al., *Pressurized Oxygen Blown Entrained-Flow Gasification of Wood Powder*. Energy & Fuels, 2013. **27**(2): p. 932-941.
22. Prins, M.J., K.J. Ptasinski, and F.J.J.G. Janssen, *More efficient biomass gasification via torrefaction*. Energy, 2006. **31**(15): p. 3458-3470.
23. Henrich, E. and F. Weirich, *Pressurized entrained flow gasifiers for biomass*. Environmental Engineering Science, 2004. **21**(1): p. 53-64.
24. Swanson, R.M., et al., *Techno-economic analysis of biomass-to-liquids production based on gasification*. Fuel, 2010. **89**: p. S2-S10.
25. Arias, B., et al., *Influence of torrefaction on the grindability and reactivity of woody biomass*. Fuel Processing Technology, 2008. **89**(2): p. 169-175.
26. Hakkou, M., et al., *Investigation of wood wettability changes during heat treatment on the basis of chemical analysis*. Polymer Degradation and Stability, 2005. **89**(1): p. 1-5.

27. Hakkou, M., et al., *Investigations of the reasons for fungal durability of heat-treated beech wood*. Polymer Degradation and Stability, 2006. **91**(2): p. 393-397.
28. Bergman P.C.A., et al., Torrefaction for entrained-flow gasification of biomass. In: The 2nd world conference and technology exhibition on biomass for energy, industry and climate protection, 2004, Rome, Italy
29. Couhert, C., S. Salvador, and J.M. Commandre, *Impact of torrefaction on syngas production from wood*. Fuel, 2009. **88**(11): p. 2286-2290.
30. Weiland, F., et al., *Entrained flow gasification of torrefied wood residues*. Fuel Processing Technology, 2014. **125**: p. 51-58.
31. Svanberg, M., et al., *Analysing biomass torrefaction supply chain costs*. Bioresource Technology, 2013. **142**: p. 287-296.
32. Uslu, A., A.P.C. Faaij, and P.C.A. Bergman, *Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation*. Energy, 2008. **33**(8): p. 1206-1223.
33. Pommer, L., et al. *Review and Compilation of Existing and New Experimental Data on Torrefaction Gas Composition*. in *21st European Biomass Conference and Exhibition*. 2013. Copenhagen.
34. Ek, M., *The Status of Applied Lignin Research*. 2005, Processum Technology Park AB.
35. Fagbemi, L., L. Khezami, and R. Capart, *Pyrolysis products from different biomasses: application to the thermal cracking of tar*. Applied Energy, 2001. **69**(4): p. 293-306.
36. Sadakata, M., et al., *PRODUCTION OF FUEL GAS AND CHAR FROM WOOD, LIGNIN AND HOLOCELLULOSE BY CARBONIZATION*. Fuel, 1987. **66**(12): p. 1667-1671.
37. Di Blasi, C., et al., *Product distribution from pyrolysis of wood and agricultural residues*. Industrial & Engineering Chemistry Research, 1999. **38**(6): p. 2216-2224.
38. Schröder, E., *Experiments on the pyrolysis of large beechwood particles in fixed beds*. Journal of Analytical and Applied Pyrolysis, 2004. **71**(2): p. 669-694.