DOCTORAL THESIS

Systems Analysis of Chemicals
Production via Integrated Entrained Flow
Biomass Gasification

Quantification and improvement of
techno-economic performance

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Abstract

Lignocellulosic biomass gasification is a promising production pathway for green chemicals, which can support the development towards a more sustainable society where fossil fuels are replaced. To be able to compete with fossil fuels, a highly efficient production of biomass-based products is required in order to maximize overall process economics and to minimize negative environmental impact. Large production plants will likely be required to obtain favourable economy-of-scale effects and reasonable production cost. Entrained flow gasification (EFG) is a favourable technology due to its suitability for large-scale implementation and ability to produce a high quality syngas from various biomass feedstocks. In order to estimate overall energy efficiency and production costs for gasification-based biorefineries, it is important to be able to characterise the gasifiers’ performance. This in turn requires reliable estimations of the gasification process.

Integration of EFG-based biorefineries with existing pulp mills or other large-scale forest industries can be achieved by integration of material and/or energy flows, as well as by co-utilisation of process equipment. This could potentially induce both technical and economic added-values. At chemical pulp mills, an important feedstock for green chemical production may be the black liquor from the pulp production, since it provides an attractive combination of advantages. The black liquor availability is, however, directly correlated to the pulp production (i.e. the mill size) and the potential green chemical production volume via pure black liquor gasification (BLG) is therefore limited.

In this thesis, two systems are considered that expand on the BLG concept with the intent to increase the chemical production volume, since this could generate positive economy-of-scale effects and is a rather unexamined area. In addition to this, an EFG configuration entailing a lower availability related risk for the considered host pulp mill is also considered. The three considered integrated systems are: (i) co-gasification of biomass-based pyrolysis oil blended with black liquor for methanol production, (ii) parallel operation of BLG and solid biomass EFG for methanol or ammonia production, and (iii) replacing the bark boiler with solid biomass EFG for methanol or ammonia production. These system solutions establish a combination of material, energy and equipment integration.

The main aim of this thesis is to increase the knowledge of the characteristics of entrained flow biomass gasification systems and their opportunities for integration in existing industries for production of green chemicals (methanol and ammonia). An appropriate modelling framework that combines chemical modelling on a high level of detail with holistic industrial site modelling is designed and used to identify and quantify energetic and economic added-values for the integrated biorefineries. Mathematical process integration models based on Mixed Integer Linear Programming (MILP) of pulp mills are used to study integration of the biomass gasification systems with the mills. An iterative modelling approach is applied between the process integration model and the detailed biomass gasification models based on Aspen Plus or a Matlab-based thermodynamic equilibrium model. As a complement to the modelling framework, a multi-scale equivalent reactor network (ERN) solid biomass-based EFG model is developed to be able to identify and study influential parameters on the gasifiers’ performance in the Aspen Plus platform. This is approached by considering the effect of mass and heat transfer as well as chemical kinetics.

The results show that replacing a recovery or a bark boiler with EFG for green chemicals production improves the overall energy system efficiency and the economic performance,
compared to the original operation mode of the mill as well as compared to a stand-alone gasification plant. Significant economy-of-scale effects can be obtained from co-gasification of black liquor and pyrolysis oil. Co-gasification will add extra revenue per produced unit of methanol and reduces the production cost significantly compared to gasification of pure pyrolysis oil. In general, integrated EFG systems producing methanol sold to replace fossil gasoline are shown to constitute attractive investments if the product is exempted from taxes. Ammonia produced via EFG is per unit of produced chemical significantly more capital intense than the corresponding system producing methanol. The economic viability in the considered ammonia configurations is therefore found to be lower compared to methanol.

The ERN model is shown to be able to estimate key performance indicators such as carbon conversion, cold gas efficiency, syngas composition, etc. for a real gasification process, showing good agreement with experimental results obtained from a pilot scale gasifier. This simulation tool can in future work be implemented in more global models to study and use to improve the techno-economic performance of EFG-based biorefineries, by quantifying the influence of important operational parameters.

The main conclusion from this work is that production of green chemicals from biomass EFG integrated with a pulp mill is techno-economically advantageous compared to stand-alone alternatives. It is also concluded that the pulp mill size will be decisive for what integration route is the most favourable. Integration of an individual BLG plant with a pulp mill of maximum size would be the most economically beneficial alternative. However, the possibility to increase the green chemical production from a given black liquor volume improves the viability for integration in smaller mills. Increasing the production volume would therefore result in the highest efficiency and economic benefits given mill sizes up to 300 kADt/y. From a resource perspective, this would however lead to an increased demand for biomass import to the mill, and this expansion could be limited by the overall availability of biomass resources.

**Keywords:** Pulp mills, integration, biomass, gasification, green chemicals, methanol, ammonia.
Appended papers


Paper overview and contribution statement

In Paper I, an entrained flow biomass gasifier model is developed to estimate the performance of key performance indicators of a real gasifier.

Andersson was the lead author responsible for planning and developing the model. Andersson was also responsible for running the simulations and validating the model. The model was designed by cooperation among Andersson, Umeki, Kirtania and Furusjö. Validation data was supplied by Fredrik Weiland at SP ETC.

Paper II-III investigate potential technical and economic benefits deriving from the integration of biomass-based entrained flow gasification biorefineries in an existing Swedish pulp mill for production of methanol or ammonia.

Andersson was the lead author responsible for design and model development of the gasification-based biorefineries and process integration modelling framework/procedure. Anderson made all of the simulations and techno-economic evaluations of the stand-alone/integrated biorefineries concepts. Marklund supplied data related to the pressurized entrained flow technology in Paper II. The work was done under supervision of Lundgren who also co-authored the papers.

Paper IV-V investigates techno-economically the opportunity to increase the methanol production at Swedish pulp mills via co-gasification of pyrolysis oil blended with black liquor.

Andersson was the lead author responsible for the design and model development of the gasification-based biorefineries, pulp mill model and process integration modelling framework/procedure. Anderson made all of the simulations and techno-economic evaluations for the stand-alone/integrated biorefineries concepts. Furusjö performed the simulations of the gasifier. Landälv supplied information about the commercialization of the BLG technology. Wetterlund was responsible for the calculation related to the overall potential supported by data from Andersson. The work was done under supervision of Lundgren who also co-authored the papers.
Related work not included in this thesis


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Thanks,
Jim
Nomenclature

Abbreviations
Adt  Air dried ton
ASU  Air separation unit
BB   Bark boiler
BIGCC Biomass integrated gasification combined cycle
BLG  Black liquor gasification
CEPCI Chemical Engineering’s Plant Cost Index
CFD  Computational fluid dynamics
CGE  Cold gas efficiency
CHP  Combined heat and power
DME  Di-methyl ether
EF   Entrained flow
EFG  Entrained flow gasification
ERN  Equivalent reactor network
FBG  Fluidized-bed gasification
FT   Fischer-Tropsch
GHG  Greenhouse gas
GTCC Gas turbine combined cycle
HHV  Higher heating value
HP   High pressure
LHV  Lower heating value
LP   Low pressure
MeOH Methanol
MILP Mixed Integer Linear Programming
MIND Method for analysis of INDustrial energy systems
MON  Motor octane number
MP   Medium pressure
PEBG Pressurized entrained flow biomass gasification
PFR  Plug-flow reactor
RB   Recovery boiler
RON  Research octane number
SA   Stand-alone
SNG  Synthetic natural gas
WACC weighted average cost of capital
WGS  Water-gas shift
WSR  Well-stirred reactor
WTW  Well-to-wheels

Chemical symbols
CH$_3$OH Methanol
CH$_4$ Methane
CO  Carbon monoxide
CO$_2$ Carbon dioxide
H$_2$  Hydrogen
H$_2$O Water
H$_2$S  Hydrogen sulphide
N$_2$  Nitrogen
NH$_3$ Ammonia
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1. Introduction

This section gives an introduction to the role of biomass gasification in green chemicals production chains (i.e. biorefineries). Concepts and possible advantages of industrial integration of biorefineries are described, partly based on a literature review. The section ends by describing identified research needs that led to this thesis.

Biorefineries are identified as a potential solution that may help mitigate the threat of climate change and the seemingly boundless demand for energy, chemicals and materials. The global bioenergy supply is also expected to grow significantly in the medium term, from 45 EJ in the year 2005 to 80–140 EJ by 2050, including extensive use of agricultural and forest residues to mitigate adverse impacts on land use and food production (GEA 2012).

The primary overall goal in the concept of biorefineries is to obtain a diversified and integrated process technology mix, wherein a multiplicity of products is produced from a variety of biomass feedstocks (Kamm & Kamm 2004). The markets for bio-based products may be expected to grow in the near future due to at least four underlying trends:

- Economic deterioration for fossil-based products due to political pressure
- Growing need for energy supply security
- Increasing public pressure for environmental sustainability due to higher environmental awareness
- Introduction of new low-cost biotechnologies

These fundamental trends may trigger a vast interest in bio-based products and place them high on the strategic agenda of variety of industries. In forestry, for example, new economic opportunities will emerge from the rising demand for biomass. Moreover, in the chemicals industry, bio-based innovations will confer an advantage to firms who manage to find the right molecules and insert them into existing or new value chains. In the automotive, marine and aviation industries, firms are looking at biofuels as an important means to reduce the greenhouse gas (GHG) emissions, while utilities are making investments in the expansion of renewable combined heat and power (CHP) capacity, where bioenergy is a strong option.

The European as well as the North American forest industry is currently facing increasing challenges related to increased global competition. According to Hetemäki et al. (2014), the key for the forest industries in Northern Europe to stay competitive is by branding new and more high-value added products that promote a strong bioeconomy. Biomass gasification is considered as a key technology pathway for converting low-grade biomass resources, such as forest-based residues to high-value added end-products (e.g. biofuels or green chemicals) (Heyne et al. 2013). Lignocellulosic biomass gasification is also an efficient and feedstock flexible
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pathway for production of several advanced biofuels, such as di-methyl ether (DME) Fischer-Tropsch (FT) diesel or synthetic natural gas (SNG). Different potential production pathways of advanced biofuels from lignocellulosic biomass are illustrated in Figure 1. Integration of such a process for large-scale green chemicals production could be one solution to extend the product portfolio. The development of biorefineries and integration with existing industries is arguably one of the more important issues for an efficient utilization of woody biomass and in the transition towards a bio-based economy.

Figure 1. Alternative production pathways for advanced biofuels from lignocellulosic biomass.

By integration with existing industry structure, e.g., forest industries, refineries, chemical industry or other biofuel production facilities, economies of scale and increased resource efficiency can be achieved with subsequent lower costs. Numerous scientific papers concerning industrially integrated gasification-based biorefineries have recently been published.

Arvidsson et al. (2014) studied the integration of biomass gasification with a conventional oxo-synthesis plant to replace natural gas with biomass-based syngas. Process simulations were used to analyse the energy efficiency of the new processes under different integration scenarios. The study showed that the current natural gas demand (175 MW$_{\text{HHV}}$) in the oxo-synthesis plant could be replaced by a 216 MW$_{\text{HHV}}$ or a 262 MW$_{\text{HHV}}$ biomass gasification plant depending on the integration scenario. Heyne et al. (2012) also analysed integrated SNG production. Here energy efficient advantages are presented by utilizing the excess heat from an indirect gasification unit integrated with an existing power production plant. Isaksson et al. (2012) showed that integration of a biomass gasification process with a mechanical pulp is beneficial from the point of view of CO$_2$ emissions compared to stand-alone production. The considered end-products were power, methanol or FT-liquids. In a study by Holmgren et al. (2014) the GHG-emissions were assessed for biomass-based methanol produced via gasification. This study, as Isaksson et al. (2012), showed that integrated biorefineries offer a higher reduction potential of related
GHG-emissions than stand-alone biorefineries, here for a petrochemical cluster as the considered integration site.

Other potential sites evaluated for integration of biorefineries are oil refineries (Brau & Morandin 2014; Johansson et al. 2013) and steel plants (Lundgren et al. 2013). Brau & Morandin (2014) studied the integration of a biomass-based indirect as well as a direct fluidized-bed gasification unit to produce hydrogen in an existing oil refinery. Several integration configurations were evaluated and the results show that all configurations point to a potential for reducing emissions of CO₂. A biomass-to-hydrogen concept utilizing an indirect gasification unit showed to be slightly more preferable in terms of energy and exergy efficiency than a fluidized-bed. Lundgren et al. (2013) investigated from a techno-economic and environmental perspective (CO₂ reduction potential) the possibility for co-utilization of biomass-based syngas and off-gases from steelmaking to produce methanol. The results showed that off-gases could be more resourcefully used for methanol production, than the current export to a nearby CHP-plant. The investment in biomass-based gasification plant integrated in the steel plant could also be economically viable and environmentally beneficial.

A large part of the published studies in the field deals with biorefinery integration in chemical pulp industries, especially for techno-economic publications (Andersson et al. 2013). In chemical pulp mills, black liquor provides a good feedstock for gasification (Ekbom et al. 2003) and black liquor gasification (BLG) is associated with major synergetic benefits as infrastructures (i.e. feedstock logistics) as well as the knowledge and competence for biomass and chemical handling/processing are inherent. Previous studies have shown that upgrading the syngas to biofuels or chemicals from a BLG plant would improve the technical performance compared to the recovery boiler/back-pressure turbine system. The studies by Ekbom et al. (2003) and Ekbom et al. (2005), showed that methanol, DME or FT-liquids produced via BLG are efficient alternatives and investment in a BLG plant would be more profitable compared to investing in a new recovery boiler. Furthermore, Consonni et al. (2009) evaluated DME, FT-liquids and ethanol-rich mixed-alcohols from BLG-based biorefineries, where integration of an additional solid-based gasifier also was considered in some configurations. This study also supported the potential advantages gained by introducing a BLG process instead of new recovery boiler for the pulp and paper industry. Consonni et al. (2009) also showed that the specific investment costs (per produced unit of biofuel) of the considered integrated biorefinery concepts can compete with significantly larger coal-to-liquids plants. Further support for the profitability of the BLG concept can be found in Pettersson & Harvey (2012) and the potential for a BLG to DME route to reduce emissions of GHG given a carbon capture system. The performance of the BLG concept has also been thoroughly assessed in a comprehensive well-to-wheels (WTW)-analysis (Edwards et al. 2014). DME or synthetic diesel produced via BLG showed among the best WTW-performances in the study by Edwards et al. (2014). The BioDME-project is a successful example where the BLG concept including down-stream
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Syngas upgrading to bioDME has been demonstrated at demo-scale (3 MW_ste, BLG process) (Landälv et al. 2014).

One disadvantage with BLG is that the production capacity is limited to the availability of black liquor, as the quantity of black liquor at a pulp mill site is fixed by the pulp production rate. The limitations set by pulp mill production rate and subsequent black liquor availability therefore restrict the attractiveness for integration of biorefinery in many pulp mills. Replacing the recovery boiler with BLG also induce a high risk/complexity for the pulp mill availability, as it is part of the crucial chemical recovery cycle necessary to keep the pulp production in operation. In order to be competitive at prevailing macroeconomic conditions, biomass-based biorefineries with focus on production of biofuels or bio-based chemicals must aim to match the resource efficiency and scalability as close as possible to fossil-based industries. Zwart & van Ree (2009) estimated that the production cost of FT-liquids for different plant sizes and according to their calculations, the production cost will be almost halved when the primary biomass supply to the plant increases from 50 MW to a level with comparable size of an oil refinery (8.5 GW). Other studies have shown that competitive biofuel production plants should have a feedstock supply capacity of at least several hundred megawatts (e.g. Hamelinck & Faaij 2002; Kirkels & Verbong 2011; Wright & Brown 2007).

It cannot, however, be generally assumed that integration always constitutes added-values over stand-alone operation. Tunå et al. (2012), showed an example of this by evaluating several biorefinery concepts in terms of overall system efficiency (using electricity equivalents) and potentially avoided CO₂ emissions. Production of methanol, DME or FT-liquids from biomass-based entrained flow, fluidized-bed and indirect gasifiers was considered. The different biorefinery concepts were either operated in a stand-alone unit or integrated in a pulp and paper mill. Tunå et al. (2012) concludes that the improved energetic and GHG performance could not be gained for all the integrated biorefineries in comparison to a stand-alone operation. Further research concerning advanced integrated biomass gasification in pulp and paper industry is therefore motivated.

It is crucial to identify biorefinery concepts that would maximize the resource efficiency for production of bio-based products from the limited resources of biomass and potentially minimize the emissions of GHG. Identifying and evaluating new integrated solutions with a highly efficient production that can impose a low complexity and/or improve the plant operating flexibility and simultaneously progress, the scalability is therefore important and required. Although a large number of studies have been published regarding integrated biomass gasification using one single feedstock in combination with chemical pulp mills (e.g. Isaksson et al. 2014; McKeough & Kurkela 2008; Naqvi et al. 2010; Wetterlund et al. 2011), there are still a number of different process concepts unexamined. One single feedstock is generally considered as fuel to the gasifier. Limited or none attention has been given to adding other types of raw materials to the gasification process (i.e.
co-gasifying) or increasing the syngas production by other gasification units operating in parallel. Only a few publications were found that consider co-integration of dual gasification units (Consonni et al. 2009; Pettersson & Harvey 2012; Maunsbach et al. 2001) and no techno-economic publications were found for co-gasification of different non-fossil fuels.

In order to make reliable and robust techno-economic analyses of new biorefineries concepts, sophisticated process models are needed. Models should be able to both easily and with a good level of details represent the material and energy flows for an integrated green chemicals plant and simultaneously ensure that all boundary condition and constraints are met for the entire system (here referring to the integrated biorefinery with a pulp mill). Since no single modelling tool can account for these criteria, the development of a modelling framework and procedure was identified as a requirement. Modelling frameworks that combine different tools have previously been used within the field. Hackl (2013) used a framework methodology partly based on the Pinch analysis to study energy efficiency improvements in industrial facilities as well as integration opportunities for new processes based on renewable feedstocks in industrial clusters. Mardan (2012) combined discrete event simulation and energy systems optimization tools and Bengtsson et al. (2002); Nilsson & Sundén (1994) combined Pinch analysis and mathematical programming (MIND (Method for analysis of INDustrial energy systems)). The Pinch analysis is well suited for studies related to identify measures to achieve energy efficiency improvements of an existing industry or for design of energy efficient green-field installations. Other tools can however be more suitable for techno-economic assessment of integrated gasification-based biorefineries. Wetterlund (2012) used mathematical programming to evaluate different integrated biomass gasification systems in a pulp and paper mill. Here, the performance of the integrated gasification plants was represented via a black/grey-box approach using operational data translated from equally sized stand-alone gasification plants. An alternative to this is to explicitly simulate the considered gasification-based biorefineries via additional modelling tools and incorporate mathematical programming. This modelling procedure could be an approach to improve the accuracy in the performance estimations of new integrated biorefineries concepts.

Furthermore, to be able to maximize the performance of gasification-based biorefineries based on global parameters, such as overall energy efficiency and production cost, reliable estimations of the gasification performance can be useful. Suitable advanced gasifier models are therefore a way to increase the knowledge on how operating conditions influence (and potentially improve) the overall techno-economic performance of biorefineries. Modelling the gasifier based solely on equilibrium reactions, reliable estimations of the char conversion and the methane yield cannot be made, since these are kinetically limited (Carlsson, Marklund, et al. 2010; Dufour et al. 2009; Dupont et al. 2007; Jand et al. 2006; Weiland et al. 2015). To estimate the performance of a gasifier, the effect of chemical kinetics as well as heat and mass transfer should therefore be taken into account. Computational fluid
dynamics (CFD) could be used to consider these phenomena. From an engineering perspective, the high computational load would be disadvantageous if the gasifier operation is to be linked to the overall techno-economic performance of a biorefinery. The model should therefore be simple enough to be suitable for integration in more extensive biorefinery plant models for, e.g., techno-economic analyses. Such a simplified model of a solid-based entrained flow biomass gasifier that can account for the above-mentioned criteria is however not found in the literature.
2. **Aim and scope**
This section presents the aim and objectives of and defines the scope and limitations of this thesis.

2.1 **Aim and objectives**
This thesis comprises five papers (Papers I-V), where the main aim is to increase the knowledge of the characteristics of entrained flow biomass gasification systems and their opportunities for integration in existing industries for production of green chemicals. An appropriate modelling framework is designed to quantify key performance indicators for such systems. The framework is designed to be able to:

- Identify and quantify energetic and economic added-values for industrially integrated entrained flow biomass gasification systems compared to stand-alone units
- Identify operational as well as design measures to improve the techno-economic performance of such systems

Supporting the overall aim, specific objectives of the thesis work are to:

- Develop and validate a detailed process model of an entrained flow biomass gasification process that can estimate key performance indicators such as carbon conversion, cold gas efficiency, syngas composition and its influence on overall process economics
- Develop a complete system model of selected industrially integrated green chemicals production routes via biomass-based entrained flow gasification
- Analyse energetic and economic feasibility of the biorefinery cases based on the outputs of above mentioned system models

2.2 **Scope and limitations**
This thesis focuses on biomass-based entrained flow gasification (EFG) technologies integrated in chemical pulp mills. Both solid and liquid biomass feedstocks are considered. This includes feedstock sources from different types of forest-based residues from either forestry operation (e.g. branches, tops, stumps, here denoted as “forest residues”) or forest industry operation (black liquor which is a by-product from pulp making based largely on stem wood). Forest residues are selected as the primary feedstock because they are an underutilized biomass resource and have potential for substantial increase in outtake in many regions. Forest residues are thereby a major resource for production of the future bioenergies and biomaterials. Further, increased harvesting can be supported without increasing the competition with either the other forest-based industries or the food production.

Two different syngas derived end-products have been studied; methanol (MeOH or CH$_3$OH) and ammonia (NH$_3$). Methanol is a versatile chemical with a worldwide
Aim and scope

annual production capacity around 100 million metric ton (MI 2015). Most of the produced methanol is used as an intermediate chemical in the chemical industry, but methanol is also an excellent substitute to fossil transportation fuels. Studies show that engines specially designed for methanol fuels can even match the best efficiencies of diesel engines and have the same low particulate matter emissions as gasoline engines (Bromberg & Cheng 2010). The biomethanol production in this thesis is intended to be used as replacement of fossil transportation fuels. Biofuel policies have therefore been included in the economic evaluation.

The chemical industry is today heavily dependent on fossil feedstocks. Ammonia is a chemical that also could be produced via gasification of lignocellulosic biomass. Green ammonia, used for example as a fertilizer\(^1\) in forestry, could help increase the annual forest growth and thereby enable an increased outtake. Fossil GHG-emissions can simultaneously be reduced. The fertilizer production annually stands for 1.2% of the world’s total energy use, where the large share (87%) is directly coupled to ammonia production (IFA 2009). Green ammonia is in this thesis assumed to replace fossil derived ammonia, where the envisioned end-product is renewable solid fertilizers, after further downstream upgrading (the latter is however not taken into account in this work).

All system studies include a techno-economic evaluation with system boundaries surrounding both the host industry (i.e. the pulp mill) and green chemicals plants (i.e. biomass gasification plants including downstream synthesis). In order to limit the scope of this thesis, the environmental performance has been left out of the assessment for the selected biorefineries.

\(^1\) In Europe, ammonia is commonly further processed into solid fertilizers (Ahlgren 2009).
3. Biomass gasification and green chemical synthesis
This section gives an overview of biomass gasification, with special focus on the EFG technology. In addition, a description of syngas upgrading to green chemicals is included.

3.1 The gasification concept
The purpose with a gasification process is to transform and preserve the chemical energy within the fuel. Any carbonaceous-based feedstock can be converted to a usable synthesis gas (or syngas) with mainly carbon monoxide (CO) and hydrogen (H₂) as the primary components. The gas can be used directly in, e.g., a gas engine or a gas turbine for power and heat production or upgraded to high valued end-products (e.g. transportation fuels or chemicals). By definition gasification is a thermochemical process for converting a solid or a liquid carbonaceous fuel to a syngas under elevated temperatures.

The gas leaving the gasifier (often referred to as product gas or raw syngas) will also contain varying levels of CO₂, CH₄, H₂O, C₂-hydrocarbons and tars. The gas composition and quality depend on several parameters, such as type of reactor, fuel type, gasification agent, operating temperature and system pressure as the most influencing parameters. High reactor temperatures (> 1000 °C) will start to convert methane and higher hydrocarbon within the reactor and produce a raw syngas that mainly consists of carbon monoxide and hydrogen. Lower gasification temperatures will generate a gas with higher levels of different hydrocarbons (e.g. CH₄, tar), which can be further processed to syngas via catalytic or thermal cracking (Börjesson et al. 2013). Air is a low-cost gasifying agent, but it generates a low-value syngas with high concentration of nitrogen and it is commonly applied in combination with power and heat production. Using oxygen as a gasification agent, the ballast of nitrogen is avoided and the heating value of the raw syngas is increased compared to when using air. The downside is that separating oxygen via an air separation unit (ASU) is cost- and energy intensive. Steam is a third option that will generate a hydrogen rich syngas via the water-shift reaction.

The syngas can, as mentioned, be used for further upgrading into a range of different end-products. For example, hydrogen can react via a catalytic synthesis processes with nitrogen to form ammonia or with carbon monoxide to form methanol, DME etc.

3.1.1 Large-scale biomass gasification
A high syngas quality is required to catalytically upgrade syngas to green chemicals. The EFG and the Fluidized-bed gasification (FBG) technologies are the main reactor designs considered to be capable and viable for large-scale production of biomass-based products. The dual fluidized-bed (indirect gasification) technology is also
Biomass gasification and green chemical synthesis

considered to be capable of a larger production capacity, but not in the same range as the EFG and the FBG technology. Among the different biomass-based gasification designs, not one stands out as the primary alternative for gasification of lignocellulosic biomass because all of them have different advantages and disadvantages. As mentioned in Section 2.2, this work is limited to biomass-based EFG systems. Perhaps the major advantage with the EFG technology is the high quality and nearly tar-free generated syngas (see Table 1), which do not require complex downstream gas cleaning equipment. Another advantage with the EFG technology is the possibility to operate under pressurised condition, usually between 20-70 bar (Heyne et al. 2013).

In a top-fed entrained flow (EF) gasifier, the fuel and the gasification agent is co-currently fed into a heated reactor for partial combustion, as illustrated in Figure 2 (Börjesson et al. 2013; Heyne et al. 2013). Fuel, in the form of a solid, liquid, or slurry, is suspended (entrained) in the reactor only for a few seconds (Weiland 2015). High reactor temperatures and small particles/droplets are therefore required to achieve a high carbon conversion (Börjesson et al. 2013). Due to the ballast of nitrogen in air, oxygen is often required as gasification agent. The resulting high temperature is generally above the ash melting temperature, i.e. reactor is operated in the so-called slagging mode. The fuel ashes are then dispersed via the reactor wall and removed as a smelt from the gasifier (Weiland 2015). A challenge when gasifying untreated solid biomass in EF gasifier is the associated high energy requirement for reducing the fuel to particles of sufficiently small size. The power consumption for milling is estimated to be in the range of 1-8% of the thermal fuel load (Bergman et al. 2005; Eriksson et al. 2012; Esteban & Carrasco 2006; Svoboda et al. 2009) for particle diameters below 1 mm. Another challenge is to continuously feed fibrous material under pressurized conditions (Heyne et al. 2013). A pressurized entrained flow gasification (PEBG) pilot plant has been in operation at SP ETC in Piteå, Sweden, during the last years. Typical gas composition from wood powder gasification in the above mentioned PEBG plant is presented in Table 1 (Weiland 2015).
The EF technology capability to operate in a slagging mode enables use of fuels with high and reactive ash content to be gasified, making the technology rather fuel flexible (Weiland 2015). Black liquor is an example of fuel with a high and reactive ash content that can be gasified in EF reactors. Black liquor is a residue from Kraft pulp production, that contains spent cooking chemicals (alkali-based ashes) and unsolved organic (lignin residue and hemicellulose). Compared to the other fuels, black liquor can be gasified under relatively low reactor temperatures (approximately 1000 °C) and still yield a high syngas quality (tar-free) and a high carbon conversion rate, see Table 1. This is believed to occur due to the alkali metals catalytic effect, which is known to enhance normally slow gasification reactions (Huang et al. 2009; Kajita et al. 2010; Umeki et al. 2012). The spent cooking chemicals, which are the basis for the green liquor in the Kraft process, are removed as a smelt from the gasifier and recycled back to the pulp mill. A complete carbon conversion is therefore required to guarantee a smelt that is free from unconverted char. The high viscosity of black liquor is challenging to atomize to small droplets. The technical feasibility of a BLG concept has via the BioDME-project and the LTU Biosyngas Programme been demonstrated by accumulating a produced DME volume that exceeds 900 tons (Furusjö 2016).
Another biomass-derived fuel that can be gasified using the EF technology is pyrolysis oil. Biomass pyrolysis results in primary char, permanent gases, and condensable vapours (Scott et al. 1985). The vapours can be recovered as viscous liquids (i.e. pyrolysis oil) via condensation. The absence of catalytic alkali content in pyrolysis oil (and solid biomass) leads to that a higher gasification temperature compared to black liquor (>1200°C) is required, to achieve a high syngas quality, see Table 1. This has been demonstrated in the so-called Bioliq project (Dahmen et al. 2012) and in pilot scale experiment in SP ETC PEBG pilot (Leijenhorst et al. 2015). In the Bioliq concept, a pyrolysis slurry is gasified, while in the latter case, only the liquid pyrolysis oil is gasified. In a pyrolysis slurry (or just slurry) the residual char particles are mixed with the oil to increase the energy content. The residual char also contains the biomass’ ash forming elements and an EFG is required to operate in a slagging mode (Leijenhorst et al. 2015). For “pure” pyrolysis oil gasification, a non-slagging operation is possible due to the low ash content. This is generally less cost intensive compared to the slagging equivalent (Leijenhorst et al. 2015). Pressurizing and feeding both pyrolysis oil and black liquor is more practical and less expensive, compared to solid biomass.

**Table 1.** Gas composition (mol%) for different feedstock in EF gasifiers.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Wood powder</th>
<th>Pyrolysis oil</th>
<th>Black liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification agent</td>
<td>Oxygen</td>
<td>Oxygen</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Gasification temperature [°C]</td>
<td>1100-1600</td>
<td>1320</td>
<td>~1000</td>
</tr>
<tr>
<td>Gasification pressure [barg]</td>
<td>&lt;10</td>
<td>4</td>
<td>27</td>
</tr>
<tr>
<td>CO</td>
<td>41-47</td>
<td>46</td>
<td>29</td>
</tr>
<tr>
<td>H₂</td>
<td>22-29</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>CO₂</td>
<td>14-26</td>
<td>23</td>
<td>34</td>
</tr>
<tr>
<td>H₂O</td>
<td>Dry</td>
<td>Dry</td>
<td>Dry</td>
</tr>
<tr>
<td>N₂</td>
<td>6-9</td>
<td>N₂ free</td>
<td>N₂ free</td>
</tr>
<tr>
<td>CH₄</td>
<td>0-4</td>
<td>2</td>
<td>~1.4</td>
</tr>
<tr>
<td>Other</td>
<td>&lt;1</td>
<td>&gt;0.2</td>
<td>~2</td>
</tr>
<tr>
<td>Cold gas efficiency (CGE) (%)</td>
<td>57-76</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Methanol and ammonia production from syngas

3.2.1 Methanol from syngas

Methanol can be produced from many different feedstocks that are first converted into syngas. The majority of the syngas-based methanol is produced via steam reforming or partial oxidation of natural gas or naphtha. Production via coal or biomass gasification is a possible alternative but today less practiced. Methanol is produced via catalytic synthesis mainly from hydrogen and carbon monoxide. Catalytic methanol reactors usually operate at elevated pressure (50-100 bar) and temperatures (200-280 °C), using a copper oxide-zinc oxide-alumina catalyst. The presence of CO₂ in the syngas increases the formation of methanol significantly (Wender 1996). A small concentration of CO₂ is therefore required in the syngas to maximize activity and selectivity. The synthesis to methanol requires a molar ratio, defined as (H₂-CO₂)/(CO+CO₂), above 2 for maximum formation of methanol (Zinoviev et al. 2010). A water-gas shift (WGS) process is therefore required prior to the catalyst to raise the H₂-fraction in the biomass-based syngas (see Figure 3 and Table 1) by converting CO and steam to H₂ and CO₂. Removal of impurities, catalyst poisonous compounds and inert gases is very crucial for an efficient synthesis and a long catalyst lifetime. A cleaned and conditioned syngas is fed into a reactor vessel in presence of a catalyst producing methanol and small amounts of water vapour (from the reaction of CO₂ and H₂). The crude methanol is fed to a distillation plant for a two-step separation process to remove volatiles and water and higher alcohols respectively. The unreacted syngas is recirculated back to the methanol catalyst, where a fraction is withdrawn in order to avoid inert gas accumulation in the methanol synthesis loop (Spath & Dayton 2003).

**Methanol fact box**

- Methanol is the simplest of all alcohol molecules (CH₃OH)
- Heating value (LHV): 15.8 MJ/litre or 19.9 MJ/kg
- Octane number: RON 107 & MON of 92
- Almost 2/3 of the methanol used for producing formaldehyde, methyl tert-butyl ether (MTBE) and acetic acid
3.2.2 Ammonia from syngas

Ammonia (NH₃) can be produced by synthesis from nitrogen and hydrogen in the Haber-Bosch process, where the economic challenge is to produce the hydrogen. The main source for hydrogen was previously coal, but falling petroleum feedstock prices led to the use of mainly natural gas (Spath & Dayton 2003). Independent of the feedstock, a WGS process is used to maximize hydrogen content in the syngas. After conditioning and gas cleaning steps (see Figure 4) a pure hydrogen stream is mixed with nitrogen (fixed from the air) to achieve the 3:1 ratio between H₂ and N₂ desired for ammonia synthesis (Higman & van der Burgt 2008). The ammonia synthesis takes place over an iron promoted catalyst at elevated pressures (150-350 bar) at a minimum temperature of 430-480 °C (Spath & Dayton 2003). The exothermic ammonia reaction requires the cooling of the process, which, in combination with the operating conditions, enables high quality steam generation. A refrigeration system is used to separate the produced ammonia from the unreacted gases. The unreacted gases are recycled back to increase the ammonia production rate, yet part of the unreacted gases is purged to prevent accumulation of inert gas in the synthesis loop (Spath & Dayton 2003).
Figure 4. Main process steps for upgrading raw syngas to ammonia.
4. Overview of the studied system

This section describes the considered integrated EF gasification cases that include solid as well as liquid based-biomass feedstocks for methanol or ammonia production.

Chemical pulp mills use a recovery and a bark boiler to produce the required steam necessary for the pulp production. The recovery boiler is also necessary to recover the spent cooking chemicals in the black liquor. The integration approach to replacing either the bark or the recovery boiler with gasification-based biorefinery is evaluated in this thesis. Figure 5 illustrates how the considered production pathways affect the mill in the different integration scenarios, from Papers II-V.

![Diagram of a pulp mill with integrated biomass gasification pathways.](image)

**Figure 5.** Generic overview of a pulp mill with the integrated biomass gasification pathways. Coloured boxes specify which units/streams are active/affected in the different integration biorefineries. Hatched units indicate processes that are removed after integration. LP, MP and HP denotes low, medium and high pressure (steam), respectively.
Since the purpose of Paper I is to develop a gasifier model (see Section 5) and no techno-economic assessment are (yet) made considering that model, the system in Paper I is not further described here.

4.1 Integrated EFG for methanol and ammonia production

In Papers II-III, different possibilities for integrating EFG-systems aimed for production of MeOH and NH₃ in a semi-integrated pulp mill are technoeconomically evaluated. The gasifier systems are assumed to replace the recovery boiler or the bark boiler. The paper and pulp mill BillerudKorsnäs Karlsborg AB, located in the northern part of Sweden and is used as the host mill in the implemented case studies. The mill incorporates batch digestion, while for modelling purposes in this work, it is assumed that the digester operates continuously. Table 2 shows current key energy data of the mill.

<table>
<thead>
<tr>
<th>Table 2. Key energy data for the BillerudKorsnäs Karlsborg mill.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual production capacity</td>
</tr>
<tr>
<td>Black liquor</td>
</tr>
<tr>
<td>Electricity produced/purchased</td>
</tr>
<tr>
<td>Steam production for internal consumers</td>
</tr>
<tr>
<td>Biomass to bark boiler total consumption/purchased</td>
</tr>
<tr>
<td>Oil to recovery boiler</td>
</tr>
<tr>
<td>Tall oil to lime kiln</td>
</tr>
</tbody>
</table>

In all the integrated cases, the steam system of the gasification plant is assumed to be completely integrated with the steam system of the mill. The techno-economic evaluation is made as a comparison between an investment in a new boiler (recovery or bark boiler depending on case) or an investment in a green chemicals plant. Two different integration cases for each of the produced chemical commodities are considered and shortly described below:

- EFG-systems replacing the bark boiler (BB)

Falling bark originally used for firing the bark boiler is used together with a supplementary required amount of imported biomass as additional fuel to maintain the pulp mill’s steam balance. Excess off-gas (tail gas) from the synthesis is assumed to replace/reduce the oil demand in the lime kiln. A corresponding amount (MW) of tall oil is assumed to become available for the market. The cases are denoted MeOH-BB and NH₃-BB respectively.

- EFG replacing the recovery boiler (RB)

The recovery boiler is assumed to be replaced by a BLG. In these cases, integration of a solid EF biomass gasifier is also considered to be operated in parallel with the BLG. The gasifiers share the ASU, gas cleaning and synthesis plant to reach
Overview of the studied system

economy-of-scale effects. The capacity of BLG is determined by the available amount of black liquor (see Table 2). The capacity of the solid EF biomass gasifier is dimensioned to cover the marginal steam demand to maintain the steam balance of the mill. To limit the size of the system and the correlated biomass import the bark boiler is kept in operation. Here too, tail gas from the synthesis is assumed to be used as fuel in the lime kiln and thereby make tall oil available for export. The cases are denoted MeOH-RB and NH3-RB respectively.

As reference cases, non-integrated, stand-alone EF gasification plants for methanol and ammonia production respectively are used. In order to make the systems comparable, the thermal input to these reference plants is determined by the capacities of the solid biomass gasification plants that replace the bark boiler. The system boundaries in the reference cases are set to also include the operation of the original mill. Recovered surplus heat is assumed to be sold to a district heating network during the heating season (5000 h per year). The cases are denoted MeOH-SA and NH3-SA respectively.

Table 3 shows an overview of the studied cases.

<table>
<thead>
<tr>
<th>Case name</th>
<th>Paper nr.</th>
<th>Case description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH-SA</td>
<td>II</td>
<td>Business-as-usual mill and stand-alone (SA) gasification plant</td>
</tr>
<tr>
<td>NH3-SA</td>
<td>III</td>
<td>with the same thermal input as in MeOH-BB resp. NH3-BB</td>
</tr>
<tr>
<td>MeOH-BB</td>
<td>II</td>
<td>Bark boiler replaced by a solid biomass gasification plant</td>
</tr>
<tr>
<td>NH3-BB</td>
<td>III</td>
<td></td>
</tr>
<tr>
<td>MeOH-RB</td>
<td>II</td>
<td>Parallel operation of solid EFG and BLG that replaces the recovery boiler</td>
</tr>
<tr>
<td>NH3-RB</td>
<td>^</td>
<td>Complementary case for thesis.</td>
</tr>
</tbody>
</table>

Note that the case with ammonia produced from parallel operation of a BLG and an EFG unit is included as a complement in this thesis and is not included in Paper III.

4.2 Methanol via co-gasification of black liquor and pyrolysis oil

Papers IV-V techno-economically investigates the opportunity to increase methanol production at Swedish pulp mills by adding pyrolysis oil to the available black liquor and co-gasifying the blend. By blending, the operational flexibility of the gasification plant is also improved and this subsequently generates reduced redundancy in the gasifier train. Blends that contain up to 50% pyrolysis oil on wet mass basis are considered.

In Paper IV, the Rottneros Vallvik mill is the considered integration site for a BLG system fed with either the available black liquor or a blend with pyrolysis oil. The Vallvik mill is a Kraft pulp mill producing flash-dried bleached and unbleached pulp located on the east coast in the middle of Sweden. The current annual production is around 200 kADt. The mill is currently implementing a long-term program of
measures that by stepwise upgrades of the process equipment will make it possible to reach a production level of 270 kADt/y, which is consequently applied as the reference case for this study. In Table 4, average key data for the operation of the Vallvik mill is presented, valid for both the current and the planned future production capacities.

*Table 4. Annual average key operation data [kWh/ADt].*

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor – LHV dry basis (SF-LHV dry basis)</td>
<td>6473 (5548)</td>
</tr>
<tr>
<td>Mill power demand</td>
<td>863</td>
</tr>
<tr>
<td>Steam turbine power production</td>
<td>678</td>
</tr>
<tr>
<td>Mill steam demand</td>
<td>3084</td>
</tr>
<tr>
<td>Lime kiln fuel use</td>
<td>555</td>
</tr>
<tr>
<td>Falling bark available (65% DS)</td>
<td>894</td>
</tr>
</tbody>
</table>

^A Mill’s demand for medium and low pressure steam.  
^B Prior to the integration of a BLG plant, the falling bark is exported with a moisture content of 65%. After the integration of a BLG plant the falling bark is dried to a 35% moisture content and burnt to generate steam.

In the progress of upgrading the pulp production capacity of Vallvik, the existing recovery boiler will be rebuilt to support a higher pulping capacity. The upgrading process of the recovery boiler will however not be necessary for the integrated biorefinery cases. Methanol production is evaluated from three different feedstock blends in Paper IV: (i) from the available black liquor (Case RV-BLG 0); (ii) from a blend with 25% pyrolysis oil and 75% black liquor (Case RV-BLG 25), and (iii) from a fifty-fifty blend of pyrolysis oil and black liquor (Case RV-BLG 50). The blend contains the entire amount of available black liquor and the blend ratios are defined on a wet mass basis. The evaluation is carried out as comparison between an investment in a rebuilt recovery boiler and methanol production via the gasification alternatives.

In Paper V, a generic Swedish pulp mill is considered as a potential integration for the methanol production via co-gasification. The pulp mills annual pulp production capacities range from 200 to 600 kADt/y. The operation of the Swedish Rottneros Vallvik mill is selected as a basis to represent a generic mill. Based on the current operation, linear extrapolation is used to model five pulp mill sizes in between 200-600 kADt/y. Key operation data presented in Table 4 is therefore also applicable to the generic mills.

Six blend ratios ranging from 10 to 50% (Cases G-BLG 10-50)\(^2\) oil content are evaluated in Paper V. The main objective is to techno-economically evaluate different blends ratios for different pulp mill capacities (200-600 kADt/y) with

\(^2\) RV denotes that the Rottneros Vallvik mill is the considered host industry.  
\(^3\) G refers to that a generic mill being considered as host industry.
BLG-based methanol production as a case study. Two alternative reference methanol production configurations are used to evaluate the co-gasification cases: (i) Case G-BLG 0, with gasification of the available black liquor only, and (ii) Case G-100, with gasification of unblended pyrolysis oil in a stand-alone gasification plant, with a pyrolysis oil input corresponding to the pyrolysis oil input load of the fifty-fifty blend in Case G-BLG 50 (i.e. 11250 kWh pyrolysis oil per ADt). The co-gasification cases are also compared to a case that considers the combination of Case G-BLG 0 and Case G-100 as one configuration (Case G-BLG-0+100). This is done to determine potential technical and economic added-values with co-gasification compared to the unblended gasification alternatives. All integrated gasification systems (Cases G-BLG 0-50) are evaluated as a comparison between an investment in a new recovery boiler and methanol production via the gasification alternatives.

Figure 6 shows a schematic view of the different gasification plant configurations (in Papers IV-V) including the pulp mill. All cases consider an external oxygen supply, i.e. oxygen "bought over the fence".

Figure 6. Schematic flowsheet for the different methanol production cases. Plant areas and material/energy flows without any blend number mark are present in all configurations. The biomass intended for pulp making, pulp products, etc., is not shown since it is same in all cases.
5. Methodology

This section presents the methodologies used to quantify and evaluate techno-economic key performance indicators for the considered biomass gasification pathways.

5.1 Process modelling approach

The modelling framework is designed to be able to quantify key performance indicators for industrially integrated gasification systems and combines a chemical simulation tool (Aspen Plus or a Matlab-based thermodynamic equilibrium model - SIMGAS) with a process integration tool (reMIND) based on Mixed Integer Linear Programming (MILP). The process integration tool is used to avoid sub-optimization of the industrial energy system and to minimise the energy cost for the integrated system, given both technical and economic criteria. It is not possible, however, to easily describe all the processes in the conversion of biomass to green chemicals via gasification with a high level of detail using MILP. The framework therefore combines modelling tools to complement each other. A bottom-up modelling approach is adopted using the chemical simulation tools to ensure a higher level of details of the modelled sub-processes, i.e. the gasification-based green chemicals plants in Papers II-V. This strategy allows each of the units in the biomass gasification plant and its auxiliary upstream (oxygen plant, pre-treatment) and downstream (gas conditioning units and synthesis loop) process equipment to be represented by an individual sub-model and thereby connected via material and energy streams. Steam pressure levels are selected for the biorefineries to match the steam system in the considered host mills.

An iterative modelling approach, illustrated in Figure 7, between a simulated sub-process model and the process integration modelling tool is implemented to ensure that all boundary conditions and constraints are met. The resulting material and energy balances from the gasification plant model are translated to linear equations and supplied as inputs to the larger process integration model representing the pulp mill in reMIND.
The general integration approach in Papers II-V replaces either the recovery or the bark boiler and the most important modelling constraint is to keep the pulp production constant. In Papers II-III the capacity of the integrated biomass gasification system is adjusted to maintain the process steam balance of the mill. A solid biomass boiler is used to maintain the marginal steam of the mill for the integrated gasification cases in Papers IV-V. The iterative approach (see Figure 7) is also used to minimize any misrepresentation or errors due to translating of the gasification plant material and energy balance to linear equations. From the simulations in the process integration model, the required size of the integrated biorefinery can be approached. New simulations of the gasification plant performance can then be done with a more target (i.e. the required) thermal input. Refining the translation of the gasification plant’s material and energy balance to linear equations is then possible. The required size of biorefinery can thus via iterative modelling approach be reached and the range where the linear equation
represents the gasification plant’s performance can be minimized, to continuously improve the accuracy in the translation.

In addition, a more global approach can also be applied in order to avoid sub-optimization of the system if the entire pulp mill is included within the system boundary (see Figure 8). For stand-alone cases (present in Papers II, III and V) the resulting material and energy balance from the simulation tools are directly used as inputs for the techno-economic evaluation, see Figure 7.

Figure 8 illustrates the system boundaries for the different tools used in the modelling framework. In Paper I, the system boundary is narrower than in Papers II-V because the objective is to develop a tool that can be used to study the characteristics of a solid EF biomass gasifier.

Figure 8. System boundaries between modelling tools in Papers I-V. Note: The pathway ending with a green hatched line (parallel operation of a solid EF biomass gasifier and a BLG) is included in this thesis as a complement.
5.1.1 Aspen Plus

Aspen Plus is a graphic simulation tool designed for creating system models and running advanced process simulations (Aspen Technology Inc 2013). The Aspen Plus platform is, in this thesis, used for the development of a multi-scale equivalent reactor network (ERN) model over a solid EFG described in Paper I. ERNs have been previously implemented in commercial software like Aspen Plus for modelling EF coal gasifiers, generally giving good agreement with experimental data (Biagini et al. 2009; Dai et al. 2008; Monaghan et al. 2012; Monaghan & Ghoniem 2012). Simultaneously with a similar modelling approach has also been applied for biomass gasification representing an EF process in lab scale (Adeyemi & Janajreh 2015) and fluidized-bed processes (Nikoo & Mahinpey 2008; Mathieu & Dubuisson 2002).

The ERN model applies a multi-zonal approach, where the kinetically limited reactions and heat and mass transfer effects are implemented. The multi-zonal structure is divided in accordance with the major reaction stages (drying/pyrolysis, homogeneous reactions, char combustion and gasification) and the flow characteristics occurring in the reactor. Material and energy streams are connected to each reactor block, and represent the mass and heat flows in the reactor. A schematic view of the ERN modelling approach in Aspen Plus is illustrated in Figure 9. The ERN model also include multi-scale effect caused by the transport phenomena at particle scale both during heating/pyrolysis and char burnout is in combination with the effect of macroscopic gas flow including gas recirculation.

The simulation results are compared against the experimental data, which include carbon conversion, cold gas efficiency and syngas composition from the SP ETC (PEBG) pilot (see Section 3.1.1). Further details regarding the design and the development process of the ERN model as well as a description pilot plant is found in Paper I. The ERN model requires some so-called reactor-specific design parameters that are determined for each gasifier. The reactor-specific design parameters, recycling ratios, heat losses and zone/total volume(s), are therefore selected to correspond to the experimental estimation and measurements from the PEBG pilot in the validation process. The recycling ratio refers to the fraction of total mass flow that is enters the recirculation zone in comparison to flow rate leaving the gasification zone, see Figure 9.
Figure 9. Model approach for the kinetic-based ERN in Aspen plus (left) and corresponding conversions zones (right). The abbreviations WSR and PFR refer to a well-stirred reactor respectively a plug-flow reactor.

The biomass gasification plants in Papers II-III are also modelled in Aspen Plus for the solution of material and energy balances. The boundary of the biomass gasification plant system ranges from the incoming raw biomass to the outgoing final syngas-based product (i.e. methanol or ammonia), and includes the pretreatment, the gasifier(s), the gas conditioning and the synthesis loop, as illustrated in Figure 10. The dashed line is valid in the case where a BLG is co-integrated with the solid biomass EFG unit and operated in parallel. Syngas composition and yield from Aspen Plus model over the BLG are validated against data from the semi-industrial scale BLG plant presented in Carlsson, Wiinikka, et al. (2010).
Each of the blocks in Figure 10, is modelled using one or several of the built-in models. In those mass and energy balances, phase and chemical equilibrium and to some extent also reaction kinetics together with reliable physical properties, thermodynamic data and supplied operating conditions are used to simulate actual equipment behaviour. Note that a significantly higher level of details is applied in the ERN model in Paper I in comparison to Aspen Plus plant models in Papers II-III. Material, heat and/or work streams are used to connect the modelled units. A more detailed description of each sub-process and of their model in the Aspen Plus environment are found in Papers II-III.

5.1.2 Matlab-based thermodynamic equilibrium model - SIMGAS

SIMGAS is a thermodynamic model originally developed for gasification of black liquor using thermodynamic data from Lindberg (2007) for pure inorganic components and from Knacke et al. (1991) for the remaining species. SIMGAS is implemented in the Matlab platform and based on system Gibbs energy minimization under the assumption of ideal mixtures, but with empirical modifications for CH₄ and H₂S as further described in Carlsson, Marklund, et al. (2010). The tool uses an active-set method to solve the constrained non-linear minimization problem with the chemical composition of gas and smelt phases as independent variables.

The SIMGAS model is used to simulate both the BLG process and co-gasification of black liquor and pyrolysis oil in Papers IV-V. This relies on co-gasification of
pyrolysis oil blended with black liquor being able to achieve the same catalytic effect as for pure BLG. The study by Bach-Oller et al. (2015) supports that similar catalytic effects can be obtained even when the alkali content in a blend is lower than for pure black liquor, by experimentally studying single droplet swelling, devolatilization rate and char gasification rate. Preliminary analysis of pilot plant experiments using mixtures with up to 20% pyrolysis oil in black liquor confirms these results (Furusjö et al. 2015). A gasification process fed with a black liquor/pyrolysis oil blend or pure black liquor could therefore be operated using the same operating conditions (and the same model). The same process temperature (1000–1100°C) is used for the mixed feedstock. A further description of the co-gasification process can be found in Papers IV-V.

5.1.3 Process integration model using reMIND

The process integration models in this thesis are based on mathematical programming using the MIND method. The Java-based software tool reMIND supplies MIND with a graphical interface that enables the design of a network of nodes and branches to represent a given process application via MILP (Karlsson 2011). The MIND method was developed at the University of Linköping for modelling of industrial energy systems. reMIND has previously been used to represent a wide range of industries, such as the mining/steel industry (Larsson 2004; Sandberg et al. 2006), foundry industries (Söding et al. 2009; Thollander et al. 2009), pulp mills (Klugman et al. 2009; Ji et al. 2012; Svensson et al. 2008; Wetterlund 2012), as well as district heating networks (Vesterlund & Dahl 2015; Wetterlund & Söderström 2010).

Mathematical process integration models of two existing Swedish pulp mills are used for the system studies in which the gasifiers are integrated in the mill, i.e. the BillerudKorsnäs Karlsborg plant (Papers II-III) and the Rottneros Vallvik plant (Paper IV). The latter model is adjusted to represent a generic pulp mill in Paper V. Steam generating units and steam consumers in the mill are represented by an individual node where linear equations are used to express the materials and energy balances of that specific unit. The branches connect the steam generating units and steam consumers in the mill, by representing the internal network of material and energy flows.

The process integration model of the BillerudKorsnäs Karlsborg mill in Papers II-III is validated against business-as-usual operational data, while the Rottneros Vallvik plant model is designed in accordance with a scenario including an increased pulp production (270 kADt/y) in Paper IV. The development of the former model is described in detail by Ji et al. (2012). The operation of the Rottneros Vallvik mill is selected as a basis to represent a generic mill. Based on the current operation, linear extrapolation is used to model five generic pulp mill sizes in the range between 200 and 600 kADt/y in Paper V.
5.2 Evaluating gasification-based green chemical plants

5.2.1 System efficiency

Several available methods exist to calculate energy system efficiencies, where using mixed sources of energy carriers as outputs over inputs (i.e. MWh\textsubscript{out}/MWh\textsubscript{in} based on LHV or HHV) is very common. The following three methods are also often applied: (i) accounting for the exergy in the material and energy flows; (ii) using electricity equivalents; or (iii) converting all the mass and energy flow except the main product to its biomass equivalents (Andersson et al. 2013). Differently defined system boundaries are also frequently used for system efficiency calculations. Comparing system efficiencies of different production systems may therefore be problematic and sometimes highly misleading.

It can also be misleading trying to compare system efficiencies for different industrially integrated biorefineries also on equalised basis. This is because the potential efficiency improvement is often in direct correlation with how the industries exploited their resources prior to the integration. The resulting efficiencies are therefore very site-dependent. Efficiency calculations should instead be viewed as a measure of the potential improvement a specific industry could achieve with the integrated operation of a biorefinery concept versus the non-integrated operation of the same concept in a stand-alone configuration and business-as-usual operation of the industry.

The material and energy balances in Papers II-V are calculated on an incremental basis compared to the operation of the industry prior to the integration, i.e., marginal supply of biomass and other energy carriers needed to produce green chemical. This is an attempt to measure the potential improvement that a specific industry could gain by implementing a biomass gasification route. A general definition of how the marginal material and energy flows can be viewed is illustrated in Figure 11.

Only using mixed sources of energy carriers as outputs over inputs to evaluate system performance could provide an inadequate assessment of pathways, especially when low quality energies is ranked equal to high quality energies. In this thesis, electricity equivalents are used as it is a simple approach to better value the diverse level of energy qualities in the different flows (biomass, bark, hot water, steam, chemicals, etc.). All energy carriers (main end-product, biomass, etc.) are converted to electricity equivalents according to the efficiency ($\eta$) to Table 5.
Figure 11. General representation of the basis for calculating the marginal supply of biomass and other energy carriers needed to produce green chemicals.
Methodology

Table 5. Electricity generation efficiencies used for calculation of electricity equivalents (Tunå et al. 2012).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>η</th>
<th>Comment (Reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>46.2%</td>
<td>BIGCC (Stahl 2001)</td>
</tr>
<tr>
<td>Pyrolysis oil</td>
<td>50%</td>
<td>Assumed</td>
</tr>
<tr>
<td>Methanol</td>
<td>55.9%</td>
<td>GTCC (Basu et al. 2001)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>49.0%</td>
<td>Received by multiplying the methanol power generation efficiency with the ratio of the lower heating values between ammonia and methanol.</td>
</tr>
<tr>
<td>District heating</td>
<td>10.0%</td>
<td>Opcon power box (Opcon 2011)</td>
</tr>
<tr>
<td>LP steam 4.5 bar(a) 150°C</td>
<td>16.6%</td>
<td>Steam levels from KAM, calculated using 30°C condensing temperature, 25°C reference point, 72% η_{isentropic}</td>
</tr>
<tr>
<td>MP Steam 11 bar(a) 200°C</td>
<td>19.6%</td>
<td></td>
</tr>
<tr>
<td>IP Steam 26 bar(a) 275°C</td>
<td>22.6%</td>
<td></td>
</tr>
<tr>
<td>HP steam 81 bar(a) 490°C</td>
<td>27.2%</td>
<td>90% η_{mechanical} (Andersson et al. 2006)</td>
</tr>
</tbody>
</table>

The system efficiencies for all configurations are calculated based on the marginal energy supply (Q) to produce green chemicals and converted to electricity equivalents according to Eq 1:

$$\eta_{EL} = \frac{\eta_{\text{Green chem.}} \cdot Q_{\text{Green chem.}} + \eta_{\text{By-product}} \cdot \Delta Q_{\text{By-product}}}{\eta_{\text{Biomass}} \cdot \Delta Q_{\text{Biomass}} + \Delta Q_{\text{Power}} + \eta_{\text{Other}} \cdot \Delta Q_{\text{Other}}}$$  

Eq 1

The subscripts denote the different material and energy flows. Biomass for pulp making and the final pulp products are not accounted for in the resulting overall energy system efficiency calculations since they are equal in the case study and the reference case. In Papers IV-V pyrolysis oil and oxygen are assumed to be delivered to gate and bought over the fence, respectively. However, the energy losses in converting biomass to pyrolysis oil and the energy requirement for producing oxygen are included in the overall system efficiency evaluation to apply a more global approach.
5.2.2 Economic evaluation

The economic analysis is based on the assumption that the boiler being replaced by a biomass gasification system is approaching the end of its service life. The capital investment cost for the integrated gasification plant is therefore calculated on an incremental basis as a comparison toward a new investment in a boiler, except for the system considered in Paper IV. The recovery boiler in the considered pulp mill in Paper IV is expected to be operational for additional 20 years with planned upgrades (see Section 4.2). The investment cost for the gasification cases in Paper IV is therefore calculated on an incremental basis compared to a rebuilt recovery boiler. Any operational changes in the pulp mill caused by the integration of the gasification plant are included in the material and energy balance for that specific case.

The investment cost for equipment and assembly is calculated as the sum of the cost for the all process units (pre-treatment, gasifier, gas cleaning units, etc.). Chemical Engineering’s Plant Cost Index (CEPCI) is used to update the cost data of the investment of equipment and assembly (I) from the given reference year (x), to the considered value year (see Table 6) according to Eq 2:

$$I_{\text{Current year}} = I_x \cdot \left(\frac{\text{CEPCI}_{\text{Current year}}}{\text{CEPCI}_x}\right)$$  \text{Eq 2}

The specific investment for each unit is dependent on the actual capacity, reference size and the updated reference investment cost according to Eq 3:

$$I = I_{\text{ref}} \cdot \left(\frac{P}{P_{\text{ref}}}ight)^n \cdot F$$  \text{Eq 3}

where P denotes the size and the subscript (ref) refers to the investment cost and size of the reference equipment. F is the overall installation factor and n denotes the scale factor (usually between 0.65-0.7). The total investment cost for each biorefinery scenario is given by the cost of equipment and assembly plus associated indirect investment costs. Indirect costs cover cost for project administration and development, legal permits, engineering, interest during the construction, insurances, working capital etc. In Papers II-III the indirect costs are assumed to represent 42% of the total of the equipment and assembly cost. Whilst in Papers IV-V, investment related to equipment and assembly cost as well as indirect costs are scaled based on a 100 MW methanol BLG plant (Chemrec AB 2013) using Eq 3.

The calculated investment costs are used to analyse and compare the process economics of the different system configurations, either via a cash flow analysis.
Methodology

using the Internal Rate of Return (IRR) or by viewing the economic competitiveness of the production cost.

Table 6 summarises the feedstock costs and product prices used in Papers II-V. Papers II-V employs economic scenarios based on Swedish market conditions according to the value year in Table 6. Paper II is also evaluated under four different future energy market scenarios. The energy market scenarios are for the year 2030 with value year according to Table 6 and are developed by Axelsson & Harvey (2010); Axelsson et al. (2009). These scenarios make assessments regarding future fossil fuel price levels, CO₂ emissions charge and policy support for renewable energy production for a European energy market. In Paper V, the economic evaluation considers nth-plant estimates where the BLG and the pyrolysis oil production technologies are assumed to be commercialized. The biorefineries are therefore in Paper V considered to be deployed in the future (around year 2030), but evaluated using 2014 price levels.

Table 6. Feedstock costs and product prices in €/MWh (if not otherwise indicated).

<table>
<thead>
<tr>
<th></th>
<th>Paper II</th>
<th>Paper III</th>
<th>Paper IV</th>
<th>Paper V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value year</td>
<td>2011</td>
<td>2012</td>
<td>2013</td>
<td>2014</td>
</tr>
<tr>
<td>Current or Future scenario</td>
<td>Both</td>
<td>Current</td>
<td>Current</td>
<td>Future</td>
</tr>
<tr>
<td>Nr. of cost scenarios</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Biomass</td>
<td>22-61</td>
<td>22</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>Pyrolysis oil</td>
<td></td>
<td>35-95</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>Green chemicals</td>
<td>59-184</td>
<td>IRR⁴</td>
<td>118-178</td>
<td>IRR⁴</td>
</tr>
<tr>
<td>Policy support</td>
<td>20-68ᵇ</td>
<td>Tax</td>
<td>Tax</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>exempted ²</td>
<td>exempted ²</td>
<td></td>
</tr>
<tr>
<td>District heating</td>
<td>19-57</td>
<td>70</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>Power</td>
<td>66-100ᵈ</td>
<td>63</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>Oxygen (€/ton)</td>
<td>Internal ASU</td>
<td>Internal ASU</td>
<td>69</td>
<td>69</td>
</tr>
<tr>
<td>Lime kiln fuel</td>
<td></td>
<td>46</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Tall oil</td>
<td>35-58</td>
<td>74</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

² In Papers III and V, the required green chemical selling price is determined by imposing a given IRR. The required green chemical selling prices are compared to fossil selling prices of ammonia and gasoline/fossil methanol respectively.

ᵇ The range of policy support for biofuel production in the Energy market scenarios. For the current scenario, biofuel production is assumed to be exempted from CO₂ or energy taxes.

⁴ Methanol and ammonia are considered to be exempted from any related CO₂ or energy taxes.

ᵈ A renewable electricity support of 26 €/MWh and 6.9 €/MWh is present future and current market scenarios, respectively.

The resulting production cost of green chemicals is summarized in this thesis for the considered biorefinery cases based on the economic conditions in Table 6. The green chemical production costs include both costs and revenues from other
products (power, biomass, district heating, etc.). The annual capital cost is estimated by the annuity factor method. The interest rate for the calculation of the annuity factor is based on the weighted average cost of capital (WACC). An annuity factor of 11.8% is used for the presented production costs in this thesis. An example of financial parameters and economic conditions resulting in an annuity factor of 11.8% can be viewed in Paper III.
6. Results and discussion

This section presents and discusses selected results from the appended papers with some additional results as a complement. The section begins by presenting the main results regarding the ERN model (Paper I), followed by the results from the integration studies in Papers II-V. The section ends with a general discussion regarding the implications of the results presented.

6.1 Development and validation of an EFG model

Among the technologies included in Papers II-V, the solid EF biomass gasification step is the least commercially proven technology. The development of the multi-scale ERN gasifier model in Paper I aims at increasing the knowledge regarding the process performance under various conditions and linking global parameters to overall plant energy efficiency and production cost. The ERN model is therefore designed to be simple and suitable for implementation in wider gasification plant models, with which the impact that process parameters have on the overall plant techno-economic performance will be assessed in future work.

The recycling ratio is the mass proportion of the accumulated flow that is returned along the reactor wall from the exit of the reactor to the burner inlet. A recycling ratio is required to be determined before each simulation, which is a difficult parameter to quantify experimentally. The considered range of recycling ratio (between 65% and 85%) is based on CFD-based models of BLG (see, e.g. Carlsson, Marklund, et al. 2010; Marklund et al. 2005) with similar geometry of the reactors. In this range the outgoing syngas temperature and gas composition are affected significantly but not greatly, and only for lower oxygen to biomass ratios. Another crucial process parameter, the char conversion, is shown to be rather insensitive to the recycling ratio. A mass recycling ratio of 85% is used as it showed the best agreement between measured and simulated results over a wide range of operating conditions.

Figure 12 shows a point-to-point comparison between the model results and the experimental data from the PEBG pilot plant, regarding CGE and carbon conversion. Operating conditions (thermal load, particle size, etc.) and specific-reactor design parameters (heat losses, reactor volume) are selected to be as identical as possible for a fair comparison. The model proves to be able to predict both carbon conversion and CGE well depending on thermal load and lambda value as seen in Figure 12. It should be noted that although results are on the same position on the x-

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4 The BLG concept has been thoroughly evaluated and assessed via modelling/simulations work and experimentally demonstrated in demo-scale during the last decade (Carlsson, Wiinikka, et al. 2010; Landälv et al. 2014; Wiinikka et al. 2012). The other process parts, like an ASU, methanol synthesis unit, a WGS, etc., are already commercially available in large scale.
axis, different thermal loads as well as nitrogen flows are used. In Figure 12 an example is shown of an oxygen to wet biomass ratio of around 0.4 (corresponding to a lambda of 0.3), where the thermal load is 400 kW (light circles/squares) and 600 kW (dark circles/squares), respectively, and the nitrogen to oxygen flow ratios are different. Based on the results in Figure 12, there seems to be a small trade-off in the gasifier operating conditions between the highest CGE and the highest carbon conversion. The simulation results also showed that particle sizes up to 1.0 mm did not affect the outcome, which is in agreement with experimental observations from the operation of the PEBG pilot (Weiland et al. 2015).

Figure 12. Point-to-point comparison between the developed ERN model estimations and the PEBG pilot plant experimental (Exp.) data about CGE for hydrogen and carbon monoxide (top) and carbon conversion (bottom). The dark circles and squares represent a thermal load of 600 kW, whilst the light represents a 400 kW thermal load.
Results and discussion

6.2 Integration studies

6.2.1 Energy balances and performance
The first kind of integrated system configuration considered is when a solid EFG system replaces the bark boiler in the mill, i.e. red boxes in Figure 5. This configuration has an annual production capacity of approximately 1.2 TWh/y of ammonia (Case NH$_3$-BB) or 1.5 TWh/y per year of methanol (Case MeOH-BB). As a reference case, a stand-alone gasification plant of equal production capacity is evaluated, i.e. Cases NH$_3$-SA and MeOH-SA which are assumed to be situated nearby the mill but without exchanging energy or material flows with it. The required import demand of biomass and the production volume of green chemicals are presented in Figure 13, together with the resulting system efficiencies.

The bark boiler produces high pressure steam that is used for electricity generation, before the process steam is extracted from the turbine. Only medium and low pressure steam can however be recovered from the green chemicals gasification plants. The energy content of the steam from the green chemicals plant in the integrated cases is therefore lower in comparison to the stand-alone configuration when the bark boiler is in place. This will reduce the electricity production in the integrated scenarios.

As shown in Figure 13, integration improves the overall system efficiency compared to the corresponding stand-alone system, which is a general outcome throughout the evaluated gasification system in Papers II-V. The main reasons for higher system efficiency are that (i) the available surplus of biomass (bark) can be more effectively used and (ii) tall oil can be exported in the integrated scenarios. It should be pointed out that in the stand-alone case, a large part of the biomass is converted into heat for district heating, which from an electricity equivalent point-of-view has low value.

The process step required for an ammonia biorefinery allows for higher steam recovery per thermal input in comparison to the methanol alternative. The thermal input is therefore higher if methanol is selected versus ammonia. The resulting system efficiency is however higher with methanol as the end-product in comparison to ammonia, that is when the integrated or the stand-alone configurations are compared to each other. The main explanation of this is the higher power requirement per produced unit of green chemical in the ammonia pathway.
Figure 13. Import demand of biomass and production capacity of green chemicals (bars), and resulting incremental overall system efficiency calculated using electricity equivalents (dots).

The second integrated configuration builds on the BLG concept, but is designed to increase the chemical production by operating two gasifiers in parallel (cases MeOH-RB and NH3-RB). Figure 14 presents the thermal import of biomass and the production volume of green chemicals as well as the resulting system efficiencies for these cases. High thermal inputs are required in these biorefineries, since the replaced recovery boiler originally generated around 80% of the mills’ process steam. Another implication of replacing the recovery boiler is that nearly no high pressure steam is generated from the only remaining boiler (i.e. the bark boiler). The integrated configurations for both end-products therefore generate no power.

For the methanol pathway (case MeOH-RB), the overall system efficiency is improved to the same degree as when the bark boiler is replaced by a solid biomass gasifier for methanol production (case MeOH-BB), both in comparison to the stand-alone plant. The main explanation for the higher system efficiency in the integrated case MeOH-RB is the benefits related to gasifying the available black liquor. This also improves the system efficiency for case NH3-RB in comparison to the stand-alone case NH3-SA. However, when comparing the integrated ammonia pathways in Figure 13 and Figure 14, it is seen that ammonia production via parallel gasifiers cannot compete with case NH3-BB from the point of view of energy efficiency. This is due to the very high power demand, which penalizes the resulting overall system efficiency for case NH3-RB. Both cases required a significant power import, but the power input per produced unit of green chemical is higher in case NH3-RB in comparison to case MeOH-RB.
Results and discussion

Figure 14. Import demand of biomass and production capacity of green chemicals (bars), and resulting incremental overall system efficiency calculated using electricity equivalents (dots). Results for case MeOH-RB are from Paper II and case NH3-RB is provided as a complement in this thesis.

The third integrated configuration also builds on the BLG concept, but here pyrolysis oil blended with the available black liquor is co-gasified. The incremental supply of biomass and pyrolysis oil as well as the production of methanol is shown in Figure 15, for a 200 and 600 kADt/y pulp mill for five selected cases (from Paper V). The resulting system efficiencies are independent of pulp mill size, i.e. corresponding cases therefore obtain the same system efficiency for all pulp mill sizes considered in Papers IV-V.

The possibility to gasify the available black liquor is the main explanation of the higher system efficiency received for the integrated biorefineries compared to methanol produced gasification of pure pyrolysis oil, see Figure 15. By blending pyrolysis oil with black liquor, the inorganic content of the gasification feedstock decreases significantly and thereby also the thermal ballast in the system. As a result, the cold gas efficiency and the specific methanol output (per MW of input) are improved with increasing proportions of added pyrolysis oil. The higher methanol yield together with some other added-values, like lower import demand of lime kiln fuel and biomass to the boiler, improves the overall system efficiency for the co-gasification cases compared to methanol production via BLG, see Figure 15.

Pyrolysis oil is an intermediate feedstock and the energy requirement for producing pyrolysis oil should be included in order to globally assess the system efficiencies for these configurations. For instance, the production of pyrolysis oil integrated with
a CHP or pulp mill can reach efficiencies up to 85%-90% (McKeough et al. 2005). Given this production efficiency level of pyrolysis oil, approximately the same system efficiency (i.e., ~67%) is obtained for all co-gasification cases independent of the blend ratio including the pure BLG case. In the stand-alone pyrolysis oil to methanol scenario (Case G-100), the entire feedstock volume must be imported, which results in the lowest system efficiency. This is also independent whether the pyrolysis efficiency is included or not.

![Image](image.png)

**Figure 15.** Incremental material and energy supply for a 200 and a 600 kADt/y pulp mill from Paper V (bars) and resulting incremental overall system efficiency calculated using electricity equivalents (dots).

### 6.2.2 Economic results

Generally, green ammonia produced via the biomass gasification route is associated with a capital and power intensive process, primarily the synthesis loop and its operating conditions. A relatively high selling marginal is therefore needed to make the investment in an ammonia production plant economically feasible. Integrating the ammonia production in the pulp mill, instead of operating the stand-alone gasification plant, would however reduce the required selling marginal. The possibility to utilize available biomass when the bark boiler is removed and export tall oil results in improved overall system efficiency and thereby lowered energy requirements per ton of produced ammonia. This integrated ammonia route (case NH₃-BB) can lower the production cost by 12% compared to the non-integrated stand-alone alternative (case NH₃-SA), see **Figure 16**.

The improved scalability caused by the large production volume and the possibility of equipment co-utilization in case NH₃-RB lower the investment intensity compared to the other ammonia cases. These positive scale effects are, however, diminished by the lower overall system performance. As seen in **Figure 16**, the
ammonia production cost is therefore reduced in the same range in both integrated cases in comparison with case NH$_3$-SA.

![Graph: Fossil ammonia selling price and NH$_3$ production cost](image)

**Figure 16.** Production cost for the green ammonia production pathways and selling price for fossil ammonia.

The resulting production cost for the methanol pathways is displayed according to the different considered value years in Figure 17. Note that even if the same value year is considered, different cost scenarios (see Table 6) and economic assumptions are present among the resulting production costs in Figure 17. Comparisons should therefore only be made between cases evaluated with the same economic market conditions.

In both the integrated cases, MeOH-BB and MeOH-RB, the production cost is rather similar to case MeOH-SA, but a tendency towards a reduced cost (6-7%) is seen for the integrated configurations when evaluated in a current market scenario. However, the created scale effects with two gasifiers operated in parallel (case MeOH-RB) leads to a slightly higher IRR. The feasibility of methanol production via biomass gasification is however diminished when evaluated under the future market scenarios. Note that these future scenarios, used in Paper II, have significantly higher price levels than the other (static) price scenarios in Papers III-V. The economic benefits from integration are still very obvious, but in assessed future market scenarios with higher prices, especially for biomass, the viability of the co-integration solution is penalized due to its high biomass import demand. The lower investment intensity cannot compensate for the relatively high operational costs and the smaller integrated route with a solid biomass gasifier is therefore a better investment opportunity in this case. The general economic viability of any of these methanol cases is however low or non-existing under these future market scenarios.
As seen in Figure 17, the co-gasification cases are also evaluated both in a current scenario and a future market scenario. A big difference between Paper IV and Paper V is that a first-plant and an nth-plant investment cost estimate, respectively, are considered. For the current scenario (Paper IV) the uncertainty of a non-commercialized market pyrolysis oil price is represented by the large difference in production cost for cases RV-25 and 50. However, blending will improve the operational flexibility of the gasification plant that subsequently provides reduced redundancy in the gasifier train. This added-value, in combination with increased methanol yield per thermal input, makes co-gasification the wiser solution based on received IRR for pyrolysis oil prices up to 70 €/MWh in comparison to case RV-BLG 0.

![Figure 17. Production cost range for the different methanol production pathways.](image)

One advantage of BLG-based biorefineries is the investment credit given for the replacement of the recovery boiler that is approaching the end of its service life. Since the mill in Paper IV does not require a new recovery boiler, a full investment credit cannot be applied. A lower production cost (or higher IRR) could therefore be expected if the biorefineries cases in Paper IV were integrated in a similar sized mill and the recovery boiler is required to be replaced. A full investment credit is however applicable for the mill in Paper V.

Different sizes of the host mill (200-600 kADt/y) are considered when the co-gasification is evaluated for future value years in Paper V. The impact of the pulp mill size results in the production cost range in Figure 17 for cases G-BLG 0 to 50, as well as cases G-100 and G-BLG-0+100. The added-values for methanol produced either via BLG or co-gasification are obvious compared to the two reference
configurations. For larger pulp mills, the cost for pyrolysis oil import will slightly offset the added-values for the co-gasification configuration and pure BLG will result in the best economic solution. However, as seen in Figure 17, the production cost difference between G-BLG 0 and 50 is rather small (74 ±11€/MWh). This production cost span is valid for an annual methanol production capacity range in between 600 GWh/y for the smallest mill with pure BLG, to over 6.5 TWh/y for the largest mill size and co-gasification of a fifty-fifty blend.

6.2.3 Overall potential
Some of the large gasification configurations require a considerably large amount of biomass supply, i.e. large feedstock supply areas and significant demands on the supply chain. Although a higher harvesting of forest residues can be well supported, it is a limited resource. Both the case with parallel operation of two gasifiers and the larger co-gasification cases could be limited by both overall and local biomass availability. Furthermore, static based prices are considered in all energy market scenarios, while such large biorefineries would require buying out the entire local biomass market and thus influence the biomass price.

Among the considered configurations, pure BLG seems to require the lowest marginal biomass import per produced unit of green chemical. This system would thus from an overall biomass availability perspective allow for the highest production volume of green chemicals. Given the perspective of a region or country, the total production volume via pure BLG is restricted by the availability of mills suitable for integration purposes. By increasing the production of green chemicals via adding pyrolysis oil to the available black liquor, the feasibility for integrating in smaller mills is improved in comparison to pure BLG. Co-gasification could therefore increase the number of available mills suitable for integration, considering the perspective of the specific region or country as above. However, for configurations with very high demand of pyrolysis oil the probability that the whole required amount of oil could be produced with a high efficiency in integrated production facilities is lowered. This would reduce the system performance and increase the biomass demand per produced unit of green chemical, which circles back to the overall biomass availability perspective. Pre-treatment of the feedstock by pyrolysis (or torrefaction) prior to transportation could however improve the economics of the complete biomass logistics chain (Svanberg et al. 2013; Uslu et al. 2008; Zwart et al. 2006) and enable transportation from other regions.

6.3 Uncertainties and their implications
Simulating any real world system with computer models requires an accurate translation and simplification of the system’s characteristics. Nevertheless, no matter the level of detail of the model(s), uncertainties and discrepancies will be present. The modelling framework in this thesis has been designed to minimize the uncertainties by using detailed bottom-up models of the simulated gasification plant to give reliable material and energy balances. This is combined with the more
holistic process integration model that covers both the host mill and the considered integrated gasification pathway. This to ensure that all constraints are met and that the pulp production is unaffected and maintained. Nevertheless, some uncertainties are unavoidable due to input data and different assumptions. An assumption to take into account is that the performance of different pulp mill sizes is scaled using linear extrapolation in Paper V. This can be viewed as a conservative approach, but in general the specific steam consumption is expected to decrease with increasing pulp mill sizes. Furthermore, no energy efficiency scale-effect can be accounted for with the used gasification plant modelling. Another assumption related to the pulp mills performance is that the mill operation is considered to be continuous based on yearly average values, whereas the pulp production rate and the performance vary during the year. The steam consumption is for example rather dependent on the current season, especially in the Nordic countries where the outdoor temperature differs a lot during the year. Therefore, when conclusions are drawn, the uncertainties should be kept in mind. The small differences presented between methanol productions costs in the current scenario from Paper II could perhaps be reduced or even non-existing when considering possible uncertainties.

The largest uncertainty is for the used investment cost estimation, which is given with an accuracy of ±30%. However, it is important to weigh the sensitivity of investment cost variation by ±30% and the variation of other different process parameters (e.g. biomass price) into the impact on the techno-economic results. For instance, an increase of production capacity will result in a reduction of the investment intensity via economy-of-scale effects. The sensitivity against the investment cost uncertainties thus decreases with larger gasification plant sizes. The primary target for larger plants are thus to maintain a low cost for import of feedstocks and energies, as e.g. for the large co-gasification biorefineries in Paper V. An opposite trend occurs with decreasing plant sizes, where the investment is the most influential parameter on the process economics, as seen in Paper III for the smaller cases. This is also particularly the case when green chemicals are produced via BLG, since no primary feedstock is required to be imported for gasification process.

Another aspect to consider is the relative price margin between imported commodities and exported products as well as the specific selling price of the main product, which is very decisive for the economic viability. Here a certain degree of speculation and assumption is required, especially for future market conditions. Questions like: "what will the green chemicals compete against, i.e. what determines the market price of that product?", "what is the availability and the price level for biomass products?", "will there be any policy support on biomass products?" are impossible to answer, especially over a long term for a volatile market and uncertain political conditions. The results and conclusions can therefore only be said to be valid for the considered conditions and system boundaries applied in the techno-economic evaluation. Complementing with sensitivity analyses is therefore very useful to increase the knowledge regarding how the studied system responds to
Results and discussion

possible changes in conditions. Influential operating and economic parameters can thus be identified, to characterise favourable as well as unfavourable economic conditions and frameworks for the different gasification-based biorefinery pathways.
7. Conclusions

The main aim of the thesis is to increase the knowledge of the characteristics of biomass-based EFG systems and their opportunities for integration in existing industries for production of green chemicals. The two most produced chemicals globally, methanol and ammonia, are chosen as end-products.

In general, production of green chemicals via biomass-based EFG integrated in a pulp mill where a recovery or a bark boiler is replaced shows that advantages over stand-alone alternatives can be obtained in the form of improved system efficiency and economic viability. The main conclusions are that integration of biorefinery concepts with chemical pulp mills (i) offers better utilization of limited biomass resources for a more efficient green chemicals production, and (ii) limits the specific investment cost per produced unit of green chemicals and promotes cost-efficient production towards green chemicals.

The following more specific conclusions are also presented based on the work in this thesis:

- The developed ERN model has shown good agreement with experimental data and may be used to analyse how different operation parameters influence the system performance and overall economics of a biorefinery plant based on solid biomass gasification.

- The modelling framework developed is shown to be helpful in identifying and quantifying the energetic and economic performance of the different configurations. It can be applied to assess additional industrial integration sites as well as other biorefinery concepts as those considered in this work.

- Co-gasification of biomass-based pyrolysis oil and black liquor provides a great possibility to efficiently increase the green chemical production capacity for a given black liquor volume. Adding pyrolysis oil can improve the system efficiency for methanol produced via BLG. The pyrolysis oil production route is however an important factor to achieve high production efficiency for biorefineries based on co-gasification. Blending also induce better operational flexibility and reduce redundancy compared to BLG.

- Co-gasification will add extra revenue per produced unit of methanol and reduce the production cost significantly compared to gasification of pure pyrolysis oil.

- Integrating a solid biomass EFG or co-integrating a solid biomass EFG unit and a BLG unit are two alternatives that would improve the efficiency of methanol or ammonia in comparison to stand-alone gasification.
Conclusions

- Methanol produced via integrated biorefineries concepts, considering solid biomass EFG, parallel operated solid biomass EFG and BLG, or co-gasification of black liquor/pyrolysis oil, could compete with today’s fossil gasoline and be attractive investment opportunities, if the product is exempted from taxes. The highest efficiencies and the most attractive investments (based on received IRR) are reached for methanol produced via co-gasification of black liquor/pyrolysis oil, or when co-integrating a solid biomass EFG unit and a BLG unit.

- The biorefinery with two parallel gasifiers co-integrated, requires a significant import of biomass and the positive scale-effects are diminished in case of high biomass prices.

- Both integrated and stand-alone ammonia production via EFG are shown to be significantly more capital intensive than methanol per produced unit of green chemical. The production profitability for the ammonia configurations is therefore diminished in comparison to methanol production.

- Pulp mill size will be decisive in determining which integration route is the most favourable. Integration of an individual BLG would be the most economically beneficial considering pulp mills larger than 300 kADt/y. The possibility to increase the green chemical production via co-gasification improves the viability for integration in smaller mills.

- Co-gasification can reduce the specific investment cost for green chemical production. This effect is more pronounced for integration with smaller pulp mills.

- Co-gasification thus increases the number of suitable pulp mills for integration and decreases the number of mills required to produce a given amount of green chemicals. Factoring in the technical and organizational complexity and high investment associated with integration of biorefineries, a few large co-gasification plants could be strategic and advantageous over several smaller BLG plants to produce a given amount of green chemicals.
8. Recommendations for future work

Based on the work carried out in this thesis suggestions for future work are given on three system levels. First, the syngas methane content is the most difficult to estimate because there is a lack of accurate kinetic parameters for steam methane reforming. The methane decomposition could be better described by the ERN model if experimental studies could provide new kinetic data for biomass-based methane-steam reforming in the temperature range of 1000 °C and 1500 °C. Furthermore, the ERN model is limited to gasification of untreated raw biomasses. Interesting suggestions to make the model more versatile are to include the chemical and physical phenomena related to larger biomass particles (> 1 mm) and/or to account for powder coated by different additives to increase catalytic activities of char reactions.

Secondly, the intended purpose of the development work for the ERN model is to increase the knowledge of and potentially improve the techno-economic performance of the EFG technology. The ERN model should therefore be implemented in biorefineries models with similar system boundaries as in Papers II-V, to provide information on potential system energetic and process economic improvements for entire gasification plants dependent on the operating conditions of the EFG technology.

Finally, the results in this thesis show that the possibility to increase the green chemical production from a given black liquor volume may generate advantages concerning economies-of-scale as well as overall efficiencies. This would however also entail very large biomass requirements at a given production site. In this thesis a static biomass price model has been applied for the techno-economic evaluation. Markets for forest biomass are however generally of a relatively regional/local nature and increased demand from one or a few large new demand points may greatly affect the price situation in the region. In order to study the potential for increased use of forest biomass in the short to medium term, a geographically explicit dynamic market perspective, considering supply as well as demand aspects, is thus motivated when evaluating technologies that can be expected to put significant stress on the biomass supply chain. It is also necessary to complement the assessment of the selected biorefineries in this work with evaluations of their environmental performance.
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Paper I

Multi-scale reactor network simulation of an entrained flow biomass gasifier – Model description and validation
Multi-scale reactor network simulation of an entrained flow biomass gasifier – model description and validation

(Manuscript)

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Abstract
This paper describes the development of a multi-scale equivalent reactor network model for pressurized entrained flow biomass gasification (PEBG) to quantify the effect of operational parameters on the gasification process, including carbon conversion, cold gas efficiency and syngas methane content. The model, implemented in the commercial software Aspen Plus, includes chemical kinetics as well as heat and mass transfer. A characteristic aspect of the model is the multi-scale effect caused by the combination of transport phenomena at particle scale during heating, pyrolysis and char burnout with the effect of macroscopic gas flow including gas recirculation.

A validation using experimental data from a pilot scale PEBG process showed that the model can estimate carbon conversion, concentrations of main syngas components and cold gas efficiency accurately over a wide range of oxygen-to-biomass ratios and reactor loads. Syngas methane content was most difficult to estimate accurately due to unavailability of accurate kinetic parameters for steam methane reforming.

Keywords: Entrained flow biomass gasification, Reactor network modelling,
Abbreviations and nomenclature

Abbreviations
- CFD: Computational fluid dynamics
- CGE: Cold gas efficiency
- d.a.f.: Dry ash free
- EF: Entrained flow
- ERN: Equivalent reactor network
- PEBG: Pressurized entrained flow biomass gasification
- PFR: Plug-flow reactor
- WSR: Well-stirred reactor

Nomenclature
- $C$: Gas concentration (mol/m$^3$)
- $C_s$: Gas concentration at the char particle surface (mol/m$^3$)
- $d$: Diameter (m)
- $D_{A,m}$: Bulk molecular diffusivity in gas mixtures (m$^2$ s$^{-1}$)
- $D_{A,K}$: Knudsen diffusivity (m$^2$ s$^{-1}$)
- $D_e$: Effective diffusivity (m$^2$ s$^{-1}$)
- $E_a$: Activation energy (kJ mol$^{-1}$)
- $k_o$: Pre-exponential factor (-)
- $k_d$: Mass transfer coefficient (m s$^{-1}$)
- $k''''$: Rate constant with respect to char volume ($(m^3$–gas)$^n$ (kmol)$^{-n}$ (m$^3$–char)$^{1-n}$ s$^{-1}$))
- $n$: Reaction order (-)
- $p$: Pressure (bar)
- $q$: Depletion flux (kgm$^{-2}$s$^{-1}$)
- $R$: Ideal gas constant (kJ kmol$^{-1}$ K$^{-1}$)
- $T$: Temperature (K)
- $x$: Char conversion (-)

Greek letters
- $\epsilon$: Char porosity (-)
- $\eta$: Effectiveness factor (-)
- $\Phi$: Thiele modulus (-)
- $\psi$: Initial pore structure parameter (-)
- $\tau$: Pore tortuosity (-)

Subscripts
- $A$: Gas component
- $ext$: External
- $int$: Internal
- $p$: Particle
- $s$: At the char particle surface
- $\infty$: Ambient (partial pressure) of gas specie
1. Introduction

Gasification of lignocellulosic biomass, such as forest residues, provides the opportunity to produce sustainable, carbon dioxide-neutral fuels and chemicals without competing with food production or the forest industry. Oxygen-blown pressurized entrained flow biomass gasification (PEBG) is an attractive option due to the possibility to achieve a syngas that is well suited for upgrading to fuels and chemicals, due to low levels of unwanted components, such as nitrogen, methane and tars [1–3]. Pressurized entrained flow (EF) gasification can be implemented on a large scale as shown by the large commercial coal gasification plants offered by numerous suppliers.

EF gasifiers are typically operated auto-thermally at high temperatures and short residence times. The composition of the syngas obtained from a gasifier and the efficiency of the gasification process depend on several parameters, such as type of pre-treatment, fuel composition (including moisture content), gasification agent, temperature, operating pressure, gasifier design, etc. [4]. Small particles are beneficial to obtain an acceptable conversion [1,3,5] but biomass is known to be more difficult to disintegrate than for example coal; energy consumption for production of 0.2-1.0 mm particles from wood has been reported to be approximately 10-80 kWd/MWu [6–9]. Relatively large milling energy consumption shows that particle size can be an important factor in the overall optimisation of a gasification-based biofuels plant. Accepting larger particles in EF gasifiers can be beneficial for the reduction of milling energy, but gasification efficiency (e.g. carbon conversion and cold gas efficiency (CGE)) can decrease due to the change in both fuel conversion and particulate flow [10]. This is because large fuel particles have lower apparent reactivity and shorter residence time than smaller particles. Hence, reliable estimations of gasification process performance under various conditions and particle sizes are important to optimise a gasification-based biofuels plant and to make good estimates of global parameters such as overall energy efficiency and production cost.

To predict the performance of a gasifier, several techniques can be applied such as equilibrium-based calculations and computational fluid dynamics (CFD). Equilibrium models can be useful to model EF biomass gasifiers but cannot account for the kinetically limited reactions and heat and mass transfer effects. Since char gasification and steam reforming of methane are kinetically limited [11], equilibrium models cannot estimate carbon conversion and methane production well [3,11–14]. On the other hand, a CFD modelling approach can be applied to EF biomass gasification to account for heat and mass transfer, e.g. turbulence along with chemical kinetics [15,16]. The possibility to implement complex models for various physical and chemical phenomena makes CFD an excellent tool to optimize the detailed design and operation conditions such as burner geometry. However, high computational load of CFD models is a disadvantage for engineering purposes. It is especially unrealistic to apply CFD for the optimization of the overall biofuel plant by implementing in-process simulation.

An approach between equilibrium and the CFD model is multi-scale equivalent reactor network (ERN). It can provide greater flexibility to model each sub-process seperately and it will use remarkably less computational effort. ERNs have previously been implemented in commercial software like Aspen Plus for modelling EF coal gasifiers, generally giving good agreement with experimental data [17–20]. Similar work for gasification of various types of biomass includes modelling of an EF process in lab scale [21] and fluidised bed processes [22,23]. To the best of our knowledge no comprehensive ERN of pressurized oxygen blown EF biomass gasification has been developed. There are several important differences between coal and biomass that need to be considered when developing an ERN for EF biomass
gasification. In addition to the difference in particle size discussed above and the differences in solid fuel conversion kinetics, it is important to consider the reactions related to the formation and decomposition of tar and soot to properly describe the gasification process because of the higher volatile fraction of biomass.

The main aim of this paper is to develop and validate an ERN-based model for EF biomass gasification to identify and study influential parameters on the performance of gasifiers. The ERN model was aimed to be simple enough to be suitable for integration in more extensive biorefinery plant models, e.g. for techno-economic analyses. The ERN model considers chemical kinetics for char gasification and gas phase reactions as well as the effect of heat and mass transfer inside fuel particles and boundary layers surrounding them. The developed ERN model was compared to the experimental results obtained from a pilot scale gasifier.
2. Experimental

The PEBG pilot plant at SP ETC in Piteå, Sweden [24–27] was used as a reference in the validation process of the developed ERN model. A brief description of the experimental setup is provided below.

2.1 General Description of the PEBG Pilot Plant

A schematic overview of the PEBG gasifier is shown in Figure 1. The gasifier operates on pulverized fuels. It is equipped with a refractory lined reactor to allow temperatures in the range of 1100-1600 °C. The pilot plant is designed for a maximum thermal load of 1.0 MW and an operational pressure up to 10 bar. The pulverized fuel is pressurized in the two lock hoppers using an inert gas (N₂ or CO₂) before being mechanically fed to the burner. The burner is located at the top of the reactor and oxygen (O₂) is added through a separate register surrounding the fuel inlet. The generated syngas is cooled by water sprays and a bubbling quench downstream of the reactor. The heat losses from the reactor have been estimated to be in the range of 15-25 kW for thermal loads in the range of 200-600 kW [3].

Figure 1. Schematic overview of the pilot gasification plant.
2.2 Experimental conditions and measurements

A commercial stem wood pellet fuel, produced from pine and spruce sawdust, was used in the gasification experiments. The fuel analysis is presented in Table 1. Gasification experiments were performed with pulverized fuel, prepared using a hammer mill (MAFA EU-4B) with 0.75 mm sieve size. The characteristic size distribution numbers, \(d_{50}\) and \(d_{90}\), corresponding to the mass median particle size under which 50% and 90% of the distribution lies, were approximately 130 and 240 µm, respectively.

The gasification experiments, used for comparison with the ERN model, were performed at a constant pressure of 7 bar(a). Several different operation conditions of the gasifier were tested according to an experimental design, where the fuel load (kW) and oxygen-to-wet biomass ratio were varied according to Table 2. A more detailed description of the experiments can be found in [3].

### Table 1. Biomass properties for the fuel used in the experiments.

<table>
<thead>
<tr>
<th>Ultimate analysis (wt% dry)</th>
<th>Proximate analysis (wt% as received)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>51.3</td>
</tr>
<tr>
<td>H</td>
<td>6.4</td>
</tr>
<tr>
<td>N</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>S</td>
<td>0.02</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>41.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Moisture content</th>
<th>Ash content</th>
<th>Fixed C</th>
<th>Volatile</th>
<th>77.9</th>
</tr>
</thead>
</table>

| LHV (dry basis)    | 19.5 MJ/kg       |

Process temperatures were measured by ceramic encapsulated type-S thermocouples at different locations inside the gasification reactor: three vertical positions and three azimuthal angles at mid height. The thermocouple tips were inserted approximately 20 mm from the reactor wall into the gas environment. During operation, a trace flow of He was added to the reactor in order to be used as a tracer for estimating the resulting syngas mass flow. A slip stream of the pressurized syngas was extracted for micro gas chromatography to monitor the volume fractions of He, H\(_2\), N\(_2\), CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_2\), C\(_2\)H\(_4\) and C\(_2\)H\(_6\). From the gas analysis and the fuel feeding rate, the yields of individual syngas components were calculated, as mol/kg of dry and ash free (d.a.f.) biomass. Furthermore, the CGE, defined as the ratio between the chemical energy in the cooled syngas and the energy input from the corresponding fuel, was calculated based on the lower heating values (LHV). The carbon conversion in this work was defined as the proportion of carbon atoms from the fuel that ends up as gaseous species in the syngas, i.e., CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_2\), C\(_2\)H\(_4\) and C\(_2\)H\(_6\).

### Table 2. Experimental operating conditions.

<table>
<thead>
<tr>
<th>Thermal load (kW)</th>
<th>Fuel feeding rate (kg/h)</th>
<th>Oxygen flow (kg/h)</th>
<th>Nitrogen flow (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>81</td>
<td>47</td>
<td>11</td>
</tr>
<tr>
<td>400</td>
<td>80</td>
<td>39</td>
<td>12</td>
</tr>
<tr>
<td>400</td>
<td>80</td>
<td>33</td>
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<tr>
<td>400</td>
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<td>600</td>
<td>121</td>
<td>71</td>
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<td>120</td>
<td>58</td>
<td>14</td>
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<tr>
<td>600</td>
<td>120</td>
<td>50</td>
<td>31</td>
</tr>
<tr>
<td>600</td>
<td>120</td>
<td>41</td>
<td>19</td>
</tr>
</tbody>
</table>
3. Gasifier model

The Aspen Plus software was used as a platform in the development of a model representation of an EF biomass gasifier. Aspen Plus is a modelling tool used for creating system models and running advanced process simulations [28]. Operating conditions and reactor-specific design parameters (e.g., heat losses, rector volume, etc.) were selected so that the model can be compared against the experimental data from the SP ETC PEBG pilot (see Section 2) for validation purposes. An ERN approach was used to describe the processes occurring from the burner inlet to the syngas exit (i.e., entrance of the quenching section). The reactor block (here referred to as zones) structure is organized to represent the major reaction stages (drying/pyrolysis, homogeneous reactions, char combustion and gasification) and flow characteristics occurring in the reactor. The zones are connected via energy and material streams. Figure 2 illustrates a schematic view of the ERN and how the zones are connected.

For a one-stage co-current EF gasifier the peak temperature occurs in the flame zone just below the fuel inlet. The pyrolysis products and/or syngas recirculated along the walls of the gasifier instantly react with the oxygen added through the burner. The exothermic combustion reactions provide heat for the drying and pyrolysis of the fuel particles in the flame zone.

![Figure 2. Model approach for the kinetic-based ERN in Aspen plus (left) and corresponding allocation of the zones in the reactor (right).]
3.1 Reactor network description

All zones were represented by one or more existing conventional units in Aspen Plus, where FORTRAN subroutines were used to treat the complex reaction scheme for pyrolysis (within the pyrolysis zone) as well as combustion and gasification in the flame, gasification and recirculation zones. The sum of the volumes of the individual zones is equal to the total reactor volume of the reactor in the PEBG pilot plant. A detailed description of each reactor block and its implementation in Aspen Plus can be found below.

3.1.1 Pyrolysis zone

This zone represents drying and pyrolysis of the biomass particles fed to the gasifier. It was assumed that the drying and pyrolysis completed instantaneously when a fuel particle enters the reactor. The moisture is evaporated according to the defined proximate value for the biomass feed. In this stage, ash is also released according to ash and sulphur content of the ultimate analysis of biomass. The ash content is assumed to be Ca in the form of CaO. Half of the sulphur remains as solid sulphur while the other half reacts with H₂ to forms H₂S. These components are thereafter treated as inert in the downstream zones.

To account for the difference in heating rate for different particle sizes, the pyrolysis process was modelled according to the ordinary heat transfer model, without the consideration of internal heat transfer, together with a multi-step kinetic model described in [29]. The pyrolysis model uses the ultimate analysis of C, H and O to describe the biomass as a mixture of cellulose, hemicellulose and lignin. Lignin has a complicated structure and is further described by the mixture of three model components rich in C, H and O [29]. Each biomass component was assumed to react independently, and the reaction schemes and kinetics were used together with the particle size and process temperature to estimate the yield of char, gravimetric tar and light gases, as follows:

\[
\text{Biomass} \rightarrow a_1\text{Char} + a_2\text{C}_{x}\text{H}_{y}\text{O}_{z} + a_3\text{H}_2 + a_4\text{CO} + a_5\text{CO}_2 + a_6\text{H}_4 + a_7\text{H}_2\text{O} \quad \text{Eq 1}
\]

Char was assumed to be pure solid carbon, and the particle size of char \(d_s\) was assumed to be reduced by 20% compared to incoming particle size for biomass [30]. The composition and yield of gravimetric tar \((\text{CH}_2\text{O})\) was determined by solving the material balance from the yields of the other products. The pyrolysis process was considered to be completed before exiting this zone. A secondary tar cracking step was implemented during pyrolysis, which is not kinetically controlled, where the gravimetric tar \((\text{C}_6\text{H}_{12}\text{O})\) was converted to phenol \((\text{C}_6\text{H}_6\text{O})\), \(\text{CH}_4\), \(\text{H}_2\) and \(\text{CO}\), as supported by [31,32].

In essence, the processes occurring in the pyrolysis zone are endothermic. As illustrated in Figure 2, heat for drying and pyrolysis is supplied from the stream leaving the flame zone. This process configuration is further described in Section 3.1.2. The outgoing temperature from the pyrolysis zone is set as 600 °C, which is when pyrolysis ends for most biomass types according to experimental data [31]. Since the processes considered in the pyrolysis zone occur at very short time scale in comparison with the other conversion processes in the reactor, the zone volume was ignored, i.e., the volume for the pyrolysis zone was set to zero.

3.1.2 Flame zone

A well-stirred reactor (WSR) was used to represent the flame in the gasifier. The combustion and gasification reactions in the flame zone were implemented using FORTRAN subroutines containing the calculation methods described in sections 3.2-3.3. The WSR assumes a perfect
mixing between the pyrolysis products, gasification agent and the recycled raw syngas as illustrated by the schematics in Figure 2. Since the WSR is a zero-dimensional model, the resulting block temperature will be uniform and will represent the average flame (or peak) temperature. If the flame zone is viewed as a cylinder, the average flame temperature is thus present over the whole length of this zone.

In a real gasifier, heat losses occur both by radiation from the flame and convective heat transfer at the reactor wall. However, heat losses by radiation dominate and for the sake of simplicity it was assumed that all the heat loss occurs in the flame zone via radiation as implemented using a heat stream from the flame zone, see Figure 2.

The exothermic reactions taking place in the flame zone are, as mentioned previously, providing the required energy for the drying and pyrolysis processes. The solution to transfer heat to the pyrolysis zone from the stream leaving the flame zone, as illustrated in Figure 2, was selected to give a distinctive difference between the flame zone temperature and gasification temperature in the gasification and recirculation zones. This is closer to the reality than the uniform temperature distribution between all zones (excluding the pyrolysis zone) which can be obtained by instead connecting the energy transfer stream from the flame zone. Since reaction kinetics is a nonlinear function of reaction temperature, it is reasonable to attempt to reproduce the temperature distribution of an actual gasifier, including the peak temperature in the flame zone.

3.1.3 Gasification and recirculation zones

The gasification and recirculation zones (see Figure 2) represent the reduction zone below the flame zone and the recycling flow along the walls of the reactor, respectively. As mentioned above, all heat losses were assumed to come from the flame, which entails that the gasification and recirculation plug-flow reactors (PFR) are treated as adiabatic processes. CFD-based models of black liquor gasification [12,33] showed that a large part of gas including unreacted char particles was recycled within the reactor. Due to the similar geometry of the reactors, an analogy can be made with the gasification process studied in this work. To the best of the authors’ knowledge the mass recycling ratio has not been explicitly quantified, but it is estimated to be well above 60% from the CFD results. Here, a recycling stream and a PFR were included to represent the gas transport along the reactor wall back to the flame zone. The impact of the magnitude of recycling was evaluated within this work.

3.2 Homogeneous reactions

Homogeneous reactions and their rates are summarized in Table 3. In the gas phase reaction, it was problematic to find reliable kinetic parameters for non-catalytic methane steam reforming due to the unavailability of relevant literature data. In this case, kinetic parameters used for coal gasification [34,35] with the consideration of the reverse reaction were used. The reaction sub-models were implemented to describe the processes in flame, gasification, and recirculation zones together with char gasification with H₂O and CO₂ (see section 3.3) via user-defined FORTRAN subroutines.
<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reaction rate $[\text{mol/m}^3\text{s}]$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$</td>
<td>$8.83 \times 10^5 \exp\left(-\frac{9.976 \times 10^4}{R \cdot T}\right) \text{C}_{\text{H}_2\text{O}}$</td>
<td>[34] via [35]</td>
</tr>
<tr>
<td>$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$</td>
<td>$3.09 \times 10^4 \exp\left(-\frac{9.976 \times 10^4}{R \cdot T}\right) \text{C}_{\text{CO}_2}$</td>
<td>[34] via [35]</td>
</tr>
<tr>
<td>$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$</td>
<td>$3.55 \times 10^{11} \exp\left(-\frac{9.304 \times 10^5}{R \cdot T}\right) \text{C}_{\text{CH}<em>4}\text{C}</em>{\text{O}_2}$</td>
<td>[34] via [35]</td>
</tr>
<tr>
<td>$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$</td>
<td>$2.5 \times 10^5 \exp\left(-\frac{1.38 \times 10^5}{R \cdot T}\right) \left(\text{C}\text{CO}\text{C}<em>{\text{H}<em>2\text{O}} - \frac{\text{C}</em>{\text{CO}}\text{C}</em>{\text{H}<em>2}}{\text{K}</em>{\text{eq}}}\right)$</td>
<td>$K_{\text{eq}} = 2.67 \times 10^{-2} \exp\left(-\frac{3941}{T}\right)$</td>
</tr>
<tr>
<td>$\text{CH}_4\text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$</td>
<td>$3.12 \times 10^2 \exp\left(-\frac{15094}{T}\right) \left(\text{C}<em>{\text{CH}<em>4} - \frac{\text{C}</em>{\text{CO}}\text{C}</em>{\text{H}<em>2}}{K</em>{\text{eq}}\text{C}_{\text{H}_2\text{O}}}\right)$</td>
<td>$K_{\text{eq}} = \exp(33.1371 - 25014.0499/T)$</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}<em>6 \rightarrow 0.5\text{C}</em>{10}\text{H}_6 + \text{CO} + \text{H}_2$</td>
<td>$1.0 \times 10^7 \exp\left(-\frac{1.0 \times 10^5}{R \cdot T}\right) \text{C}_{\text{C}_6\text{H}_6\text{O}}$</td>
<td>[32]</td>
</tr>
<tr>
<td>$\text{C}_{10}\text{H}<em>6 \rightarrow 10\text{C}</em>{\text{C}_1}\text{C}_2 + 4\text{H}_2$</td>
<td>$7.0 \times 10^{14} \exp\left(-\frac{3.6 \times 10^5}{R \cdot T}\right) \text{C}_{\text{C}_1\text{C}<em>2}\text{C}</em>{\text{C}_1\text{H}_6}$</td>
<td>[38]</td>
</tr>
<tr>
<td>$\text{C}_{\text{char}} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$</td>
<td>$3.0 \times 10^{14} \exp\left(-\frac{3.1 \times 10^5}{R \cdot T}\right) \text{C}_{\text{H}_2\text{O}}$</td>
<td>[38]</td>
</tr>
<tr>
<td>$\text{C}_{\text{char}} + \text{CO}_2 \rightarrow 2\text{CO}$</td>
<td>$3.47 \times 10^9 \exp\left(-\frac{2.81 \times 10^8}{R \cdot T}\right) \text{C}_{\text{CO}_2}$</td>
<td>Scaled from [38–40]</td>
</tr>
</tbody>
</table>

### 3.3 Char gasification

The multi-scale ERN approach was used to adequately describe the rate limiting char reduction process by considering the effects of particle size, transport phenomena and chemical kinetics [4]. The char gasification reaction rates ($r_{\text{char}}$) were described using the internal ($\eta_{\text{int}}$) and external ($\eta_{\text{ext}}$) effectiveness factor together with intrinsic reaction rate ($r_{\text{int}}$) as shown in Eq 2 [41,42].

$$r_{\text{char}} = \eta_{\text{ext}} \cdot \eta_{\text{int}} \cdot r_{\text{int}}$$  \hspace{1cm} \text{Eq 2}

As shown in Eq 3, the intrinsic reaction rate was calculated as the product of Arrhenius expression with power law model and the function describing the change in reactive surface area, $f(x)$.

$$r_{\text{int}} = f(x) \cdot k_0 n \cdot \exp\left(-\frac{E_a}{R \cdot T}\right)$$  \hspace{1cm} \text{Eq 3}

$k_0$, $E_a$ and $n$ denote the pre-exponential factor, activation energy and reaction order for H$_2$O and CO$_2$ as listed in Table 4. The random pore model, Eq 4, describes the change in reactive surface area at any char conversion ($x$) using the parameter $\psi$ to describe the initial pore structure [43].

$$f(x) = (1 - x)\sqrt{1 - \psi \ln(1 - x)}$$  \hspace{1cm} \text{Eq 4}
The value for the structural parameter for (ψ) was chosen to be 10 according to the experimental observations [39,40]. A high value of this structure parameter, as considered, means that there is less probability of pore overlap at the initial stage. Therefore, the surface area would increase as the pores grow at the beginning of the reactions.

The effectiveness factor is defined as the ratio between observed rate and rate in absence of diffusion [44]. The internal effectiveness factor (η-int) takes into account the effect of intra-particle mass diffusion on overall reaction rate according to particle size, internal pore structure, intrinsic reaction rate, and the shape of char particles (sphere in this study). It is expressed using the Thiele modulus (Φ).

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The Thiele modulus for nth-order surface reaction in sphere particles is defined as:

\[
\Phi = \frac{d_e}{3} \sqrt{\frac{(n+1)k^{n'}c_A^{-1}}{D_A}}
\]

Here, \(C_A\) is the gas concentration at the char particle surface and \(k^{n'}\) is the rate constant with respect to char volume. \(D_e\) is the effective diffusivity estimated from the char porosity (\(\epsilon\)), the char pore tortuosity (\(\tau\)), the bulk diffusivity in gas mixtures (\(D_{A,m}\)) and the Knudsen diffusivity (\(D_{A,K}\)) as follows.

\[
D_A = \frac{\epsilon/\tau}{D_{A,m} + \frac{1}{D_{A,K}}}
\]

The char porosity was set to 0.5 [44]. The char tortuosity describes the ratio between the actual lengths a molecule travels inside a pore in comparison to the corresponding straight line to/from the char surface. A char tortuosity value of 4 was used, which is a reasonable assumption in the absence of experimental data [44]. The calculation of the effective diffusivity is described in detail by Tanaka et al. [41].

The external effectiveness factor considers the effect of gas transport in the boundary layer, defined as the ratio of partial pressure of the gas species at the char particle surface (\(P_s\)) and the partial pressure of the same gas species (\(P_{\infty}\)) in ambient surrounding of the particle [42].

\[
\eta_{ext,A} = \frac{p_{sA}}{p_{\infty}}
\]
\( P_s \) can be calculated using the ambient partial pressure, the mass transfer coefficient (\( k_d \)) and the depletion flux (\( q \)) for the same gas species.

\[
p_{s,A} = p_{\infty,A} - \frac{q_A}{k_{d,A}}
\]  

Eq 9
4. Results and discussion

4.1 Validation of the simulation model and sensitivity to the design parameters

For validation of the developed model, simulation was carried out at operating conditions similar to the conditions (fuel type, biomass and oxygen feed, pressure) used during the experiments. The reactor-specific design parameters such as heat losses and total volume is based on experimental and given measurements of the PEBG pilot. Other required design parameters such as zone volumes and recycling ratios were selected corresponding to camera observations of the PEBG pilot scale reactor [24] and CFD simulations for black liquor gasification in a reactor with similar geometry [12,33]. Around 90% of the reactor volume was divided between the flame zone and the main gasification zone. Thus, only a small reactor volume (10%) was reserved for the recirculation zone where gas and entrained particles flowed back into the flame region. This limits the reactions occurring in the recirculation zone.

The simulated results were compared with operational data (see Table 2) for two thermal fuel loads (around 400 kW and 600 kW), where the biomass was milled by the hammer mill with 0.75 mm sieve. Sensitivity studies showed that the simulation results are not affected by particle sizes up to 1.0 mm. This is in agreement with experimental observation from the operation of PEBG pilot [3]. Simulation results with one representative particle size (250 µm) can therefore be used to represent the entire particle size distribution for this case since 90% of the biomass fuel particles were smaller than 240 µm. The heat losses from the reactor wall to the surroundings were assumed to be constant, due to rather constant reactor wall temperature during experiments for different fuel feeding rates. The proportion of the heat losses against thermal load was therefore more significant for lower thermal loads. The heat losses were assumed to increase from 4% to 6% of the thermal input of biomass when fuel load was decreased from 600 kW to 400 kW.

The recycling ratio, i.e., flow entering the recirculation zone as a fraction of the total flow rate leaving the gasification zone, was investigated in the interval 65% to 85%. As shown in Figure 3, the char conversion in the reactor was rather insensitive to the recycling ratio, and only small differences were noticed at lower oxygen to biomass mass ratio. The mass ratio between oxygen and wet biomass was used on the x-axis in the different figures instead of lambda. This was used to facilitate a simpler interpretation of the results in comparison to using lambda, where the existence of oxygen in the fuel also has to be taken into account.
The recycling ratio did, however, influence the calculated temperatures in the different zones of the reactor (Figure 4) and to some extent the major gas composition (see Figure A1 in Supplementary materials). At the examined conditions, the flame zone was always at under-stoichiometric conditions. Small recycling ratios result in low mass flow and locally high oxygen to fuel equivalence ratio in flame zone. This results in a higher conversion in the flame zone (see Figure A2 in Supplementary materials) and subsequently a higher temperature in flame zone, as shown in Figure 4. On the other hand, the outgoing temperature from the gasification zone was reduced at lower recycling ratios, at least at low oxygen to biomass ratios. This was because the sensible heat associated with the flow between the flame and the gasification zones decreased for smaller recycling ratios. Since the amount of heat required to be transferred to pyrolysis zone is constant, relative impact of this heat transfer (from the stream leaving the flame zone) became significant, hence giving a lower resulting temperature in the gasification zone. With increasing oxygen supply the flame temperature compensates for the lower mass flow and the outgoing temperature became insensitive to the considered recycling ratios. In general, it is observed that increasing the recycling ratio leads to a more even temperature in the gasifier, but still with a distinctive difference between the flame temperature and outgoing syngas temperature, see Figure 4.
Figure 4. Resulting simulated temperature in the reactor depending on recycling ratio (RR) and experimentally measured (exp.) temperature close to the reactor outlet.

An 85% mass recycling ratio was selected as a general value as the results showed closest agreement with measured temperature and syngas composition within the examined operating conditions. As shown in Figure 5, the model was able to estimate major gas yields with good agreement to measured values within the examined oxygen to biomass ratios. The major difference between experimental and model data appeared for hydrogen at the lower end of the oxygen supply ratio range. Carbon conversion and CGE were also well estimated by the ERN model as shown in Figure 6.

Model results in Figure 5 and Figure 6 match the experimental data point-to-point, including the nitrogen fraction and thermal load (see Table 2). In the pilot plant, variation of the thermal load influences the length of the flame, where a prolonged flame was observed with increasing thermal loads [45]. Different volumes of the flame and gasification zone respectively could therefore be motivated. Furthermore, the recycling ratio depends on a number of factors, including different thermal loads, oxygen and nitrogen mass flows. However, quantifying these zone volumes and the recycling ratio with good accuracy requires CFD simulation, which is excluded for the purpose of this model due to the high computational load as discussed above. Hence, these parameters (recycling ratio and zone volume) were kept constant for the results presented in Figure 5 and Figure 6 to avoid using design parameters as fitting parameters.
Figure 5. Yield of major syngas composition depending on the oxygen to biomass ratio for a 400 kW thermal load (top) and a 600 kW thermal load (bottom). D.a.f. refers to dry ash free.
4.2 Methane reforming

In a gasifier, methane is consumed by two main reactions – partial oxidation and steam reforming. Partial oxidation takes place in the flame zone and steam reforming primarily in the gasification zone. As methane steam reforming controls the final yield and molar fraction of methane in the syngas, it is necessary to know whether the reaction is in equilibrium or under kinetic control. It has been discussed in detail in the EF coal gasification literature that methane steam reforming is likely to be in equilibrium at a very high temperature (>1400 °C) [46]. On the other hand, in most studies of methane steam reforming the reaction is regarded to be chemically frozen at lower temperatures (<1000 °C), where fluidized bed biomass gasification is mostly operated [11]. Since typical operation temperature of EF gasification of biomass is in the range of 1000 °C to 1500 °C, steam reforming of methane can be thought to be in the transient regime (kinetically controlled regime). Unfortunately, the literature about non-catalytic steam reforming of methane at this temperature range is scarce, and it is difficult to find appropriate kinetic parameters. Moreover, it is difficult to get an accurate estimate of the temperature of the gasification zone. In this study, the molar fraction and the yield of methane were estimated by the kinetic constants available in the literature [34], instead of using the common approach to apply empirical correlations. The reverse reaction was also considered to achieve a better accuracy. It can be observed from Figure 7 that the simulated methane composition does not accurately describe the experimental values. The methane yield was lower compared to the estimation at high oxygen to biomass ratio (i.e., at higher...
temperatures). In fact, the methane concentration was almost zero at 1400 °C for the measured values (exp.) in Figure 7.

This can be explained by the fact that the depletion of methane was very sensitive to the temperature in the current range, i.e., 1000–1400 °C. According to Jess [47], reactions for methane decomposition accelerated at the temperatures above 1200 °C and the methane yield decreased by 70% with 0.5 s of residence time when the temperature was raised from 1100 °C to 1400 °C. From Figure 7, it is evident that this sharp decrease in methane composition is not well estimated by the kinetic parameters used in this study for methane steam reforming. However, accounting for the uncertainty of the kinetic parameters and gasification temperature, the methane yield from simulation results was considered to be acceptable since it was in the same range as that of the experiments. This deviation in methane concentration in this study was also too low to affect the compositions of H₂ and CO significantly. Nevertheless, further research on methane reforming during EF gasification of biomass is necessary, since the simulation and experiments showed different sensitivity to the operating conditions.

**Figure 7.** Modelled and experimental (exp.) yields of CH₄ as a function of the oxygen to wet biomass ratio (top) and the outgoing syngas temperature from the reactor (bottom).
5. Conclusions

A multi-scale equivalent reactor network (ERN) model was developed for a pressurized entrained flow biomass gasifier. The structure used for the ERN model in the Aspen Plus platform in combination with the short execution time (a few seconds on an ordinary laptop computer) enables future studies, where the model can be implemented in models with a larger scope, e.g. for the purpose of making techno-economic studies of biomass gasification-based chemicals production.

The ERN model successfully simulated a PEBG process by estimating key performance indicators such as carbon conversion, cold gas efficiency and syngas composition over a wide range of oxygen/fuel ratios. This was confirmed by the comparison with experimental measurements from a pilot scale EF gasifier.

The main discrepancies were observed while estimating the amount of methane in syngas, which leads to the conclusion that more accurate kinetic data for steam methane reforming in conditions relevant for EF biomass gasification (i.e., 1000-1400 °C) would be very useful to improve model performance. This can be done either through experimental studies or by numerical simulation with detailed kinetic model and consecutive mechanism reductions.

Simulation results are not affected by particle sizes up to 1.0 mm in agreement with experimental observation from the operation of PEBG pilot [3]. However, application of the model to larger biomass particles will most likely require improvements, for example through changes in the size of each reaction zone and the recirculation rates of char particles due to changes in inertia and drag forces. In addition, it may be necessary to consider the size of drying and pyrolysis zone, which is currently considered as zero.
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Supplementary materials

Figure A1. Yield of major syngas composition depending on the oxygen to wet biomass mass ratio and mass recycling ratio as indicated by the percentage value and experimental (exp.) yield of major syngas components.

Figure A2. Char conversion in the flame zone depending on the oxygen to biomass ratio and mass recycling ratio as indicated by the percentage value.
Paper II

Methanol production via pressurized entrained flow biomass gasification - Techno-economic comparison of integrated vs. stand-alone production
Methanol production via pressurized entrained flow biomass gasification – Techno-economic comparison of integrated vs. stand-alone production

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The main objective with this work was to investigate techno-economically the opportunity for integrated gasification-based biomass-to-methanol production in an existing chemical pulp and paper mill. Three different system configurations using the pressurized entrained flow biomass gasification (PEBG) technology were studied, one stand-alone plant, one where the bark boiler in the mill was replaced by a PEBG unit and one with a co-integration of a black liquor gasifier operated in parallel with a PEBG unit. The cases were analysed in terms of overall energy efficiency (calculated as electricity-equivalents) and process economics. The economics was assessed under the current as well as possible future energy market conditions. An economic policy support was found to be necessary to make the methanol production competitive under all market scenarios. In a future energy market, integrating a PEBG unit to replace the bark boiler was the most beneficial case from an economic point of view. In this case the methanol production cost was reduced in the range of 11–18 € per MWh compared to the stand-alone case. The overall plant efficiency increased approximately 7%-units compared to the original operation of the mill and the non-integrated stand-alone case. In the case with co-integration of the two parallel gasifiers, an equal increase of the system efficiency was achieved, but the economic benefit was not as apparent. Under similar conditions as the current market and when methanol was sold to replace fossil gasoline, co-integration of the two parallel gasifiers was the best alternative based on received IRR.

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1. Introduction

An increased share and a sustainable use of renewable energy are necessary both in the stationary and in the transportation sectors to reduce emissions of greenhouse gases [1,2]. Increasing the efficiency of the vehicle is the most cost-effective way to reduce greenhouse gas emissions in the transportation sector [3], but it is also important to replace fossil automotive fuels with non-fossil alternatives, i.e.
biofuels. The latter is particularly important in those countries where internal combustion engines will still be needed due to cold climates [1], e.g. the countries of Scandinavia.

In Sweden, a long term targets have been set to make the Swedish vehicle fleet independent of fossil fuels in the year 2030. In the year 2050, Sweden should not contribute with any net emissions of greenhouse gases to the atmosphere [3]. Currently, Sweden has a general energy tax put on most fuels based on their energy contents. In addition, the country has a carbon tax, which is proportional to the fuel carbon content. In order to promote an increased share of biofuels for transportation, such fuels are subject to a full tax exemption.

In the year 2006, a tax on new motor vehicles was introduced. The tax has a one fixed part and one variable based on the specific emissions of CO₂ [4]. From year 2009, the system supports purchases of environment-friendly cars through a tax exemption throughout the first five years after the purchase. This incentive has recently been strengthened with the introduction of an extra subsidy for cars that emits less than 50 g of CO₂ per km. Sweden also requires fuelling stations with an annual selling volume exceeding 1000 m³ to offer a renewable fuel (e.g. the pump law) [4].

Biomass based methanol is one good alternative to replace fossil petrol in conventional spark engines, only requiring moderate changes in the vehicles and the fuel distribution infrastructure [5]. In 2007, the annual global methanol production rose to 40 million tons [5], where the largest share is connected to the production of pulp and paper limiting the application of biomass and bioenergy. In 2007, the annual global methanol production rose to 40 million tons [5], where the largest share is connected to the production of pulp and paper limiting the usage of methanol for motor fuel production will be black liquor from pulp production. Previous studies (i.e. Refs. [7–9]) have shown that an investment in black liquor gasification (BLG) is advantageous regarding efficiency and economic performance compared to a new recovery boiler investment for pulp mills. However, the availability of black liquor is limited and it is also strongly connected to the production of pulp and paper limiting the maximum amount of fuel production. Another opportunity, besides black liquor gasification, is direct gasification of forest residues. This alternative is mainly limited by the overall availability of biomass and it can work with low-grade biomass, e.g. logging residues and stumps. This alternative could become particularly attractive if combined with BLG since both upstream (oxygen plant) and downstream process equipment (catalytic conversion into motor fuels) can be co-utilized improving the economies of scale.

A large number of studies exist regarding techno-economic evaluations of motor fuel production systems using biomass based gasification technologies [8–18]. Integration of biomass gasifiers in existing industries has been analysed in Refs. [7,8,17,18]. Wetterlund et al. [18] showed important advantages regarding economic performance and energy efficiency when integrating a biomass circulating fluidized bed (CFB) gasifier for production of bio-DME (dimethyl-ether) in a pulp and paper mill compared to a stand-alone production unit. Consolani et al. [7] showed that solid biomass and BLG technologies integrated in a pulp and paper mill for both motor fuel production (DME, Fischer–Tropsch liquids or ethanol-rich mixed-alcohols) and power production would result in good investment opportunities and provide environmental benefits. However, benefits from integrating gasification processes in pulp and paper mills may diminish depending on final products as well as gasification technology [17]. Moreover, integrating a gasification based process in an existing industry may involve an increased operational risk. If for example a BLG plant is deployed, the plant availability must be higher than the host mill to ensure that the spent cooking chemicals (the green liquor) can be recovered, in order to make the overall process efficient and economically feasible.

The entrained flow gasification (EFG) concept is well-known from direct coal gasification and thoroughly presented in the literature, e.g. by Higman et al. [19]. The main advantages of using this concept in coal-based applications are the flexibility in firing a wide variety of coal feedstocks, and the production of a clean, tar-free product gas. However, the main drawbacks (from an energy point of view) are the relatively high oxygen consumption and the need for a finely ground feedstock. EFG reactors usually operate at pressures between 20 and 70 bar and temperatures in the range of 1200–1800 °C, depending on the type of fuel and application. The pressurized entrained flow biomass gasification (PEBG) concept is described in general in Ref. [20] and in more detail in Ref. [21]. In order to obtain an optimal gasification process of the fuel particles, it is important to apply suitable burner design, reactor shape and fuel powder characteristics. The favourable result, which is strived for at these conditions, is a syngas with very low tar content. For synthetic fuel applications (i.e. production of fuels and chemicals from syngas) the requirements on syngas purification are very high. If not, the catalysts used in the synthesis of the fuel product will be deactivated prematurely, which in turn will be costly. Basically, all components other than H₂ and CO need to be removed below ppm levels. The exception is CO₂, which for some reactions is even used at a small concentration like the synthesis for methanol. In some catalytic systems, inerts such as N₂ and CH₄ will accumulate and will therefore have to be
removed/limited. Condensable hydrocarbons in the syngas also need to be removed.

Considering operating conditions for synthesis applica-
tions, increasing the operating pressure of the gasifier de-
creases the production costs the most. This is due to the high
pressures used in conventional synthesis processes down-
stream the gasification plant and the energy penalty resulting
from the need to raise the syngas pressure. Therefore, the
operating pressures are generally in the range 30–80 bar.
Furthermore, depending on operating temperature, the
introduction of additional steam as gasification agent gener-
ally has negative effects on production costs in the considered
gasification facility [22]. However, for cases including syn-
thesis gas upgrading and whenever the input fuel has prop-
erties enhancing soot formation and resulting in unfavourably
low H₂ content (e.g. very low moisture content), addition of
steam may still be beneficial overall.

The main aim of this paper was to techno-economically
investigate the opportunity to integrate a PEBG process into
an existing pulp and paper mill, Billerud Karlsborg in Sweden.
The objectives were to find possible and measurable added
values with integrated system solutions compared to stand-
one units. This was done by calculating the biomass to
methanol efficiency and the overall system efficiency of the
plant for each of the cases (non-integrated and integrated
systems). Furthermore, the process economics were eval-
uated by calculation of the methanol production costs and a
cash flow analysis. The analysis was performed for one stand-
one case and two integrated methanol productions cases, all
including a PEBG unit for methanol production.

2. Material and method

A process integration (PI) model was used to study integration
of biomass based methanol production using the PEBG tech-
nology in an existing pulp and paper mill. The modelling was
conducted with a bottom-up approach, which allows for a
higher detailed level of the modelled sub-processes (i.e. gasi-
fication plant) to be integrated with the larger global system
(i.e. pulp and paper mill). Each unit in the biomass gasification
plant (i.e. from raw biomass pre-treatment to final methanol
output) can thereby be represented by an individual sub-
model and connected via material and energy streams. The
whole pulp and paper mill was used as a system boundary to
avoid sub-optimization of the energy system.

The gasifier, the gas conditioning and synthesis were
modelled in the commercial software Aspen Plus for material
and energy balance calculations. The outputs served as inputs
for the PI studies, where the pulp and paper mill model based
on the reMIND methodology was used. The most important
modelling constraint was a maintained pulp production. The
PI model was not used for any optimization or minimization.
The iterations between the models was done in order to make
sure that the steam balance of the mill was kept after
replacing the existing boilers with the gasifiers and the
downstream gas processing and synthesis. An iterative
modelling approach (see Fig. 1) between the two models was
therefore adopted to ensure that all constraints of the pulp
and paper mill, as well as for the gasification plant, were met.

The mass and energy balance results from the Aspen model-
ling of the stand-alone system were directly used as inputs for
the techno-economic evaluation.

This was done in order to assess potential energetic and
economic benefits gained by replacing a boiler at the mill with
a PEBG unit for methanol production. The economic analysis,
see Section 3, was carried out using four different future en-
ergymarket scenarios and a scenario representing today’s
market. Due to that the modelling approach was applied on a
specific mill, the results cannot be considered as general.
However, the modelling approach and the evaluation
methods are.

2.1. The process integration model

The PI model was based on mathematical programming using
mixed integer linear programming (MILP) through the Java-
based software tool reMIND [23]. The model structure is
composed by a network of nodes and branches, each node
contains linear equations to express the materials and energy
balances of each steam generating units and steam con-
sumers in the mill. The branches connect the steam gener-
ating units and steam consumers in the mill, by representing
the internal network of material and energy flows. The
network thereby creates an energy system. The model of the
existing mill configuration has been validated against opera-
tional data. The model development and validation are
further described in Ref. [24].

2.2. Modelling of the biomass gasification system

To obtain high carbon conversion rates, good syngas quality
and steady operation in the reactor, pre-treatment of the
incoming biomass is required. The biomass feedstock was
dried in an indirectly heated rotary dryer to the desired water
content and ground into sufficiently small particles. In the
model, the incoming biomass was specified according to the
ultimate and proximate analysis. The specific power con-
sumption of the dryer was set at 15 kWh/wet tonne [11]. The
incoming biomass was assumed to be dried to a water content
of 8 wt%.

The energy consumption for size reducing untreated
woody biomass (moisture content up to 15 wt%) has been
investigated by Bergman et al. [25]. Based on the LHV, 1–3% of
the thermal input was required for power consumption for
size reducing to an average particle size between 0.6 and

![Fig. 1 - Workflow approach for the integrated system solutions studies.](image-url)
0.8 mm. In the modelling, 3% of the thermal input was assumed.

The PEBG was the considered technology for gasification of solid biomass fuels, where the reactor was top-fed with the fuel (wood powder) co-currently with the gasifying agent (pure oxygen). The gasifier unit was modelled in a detailed manner treating the major reaction steps in the gasifier separately (drying, pyrolysis, combustion and gasification). The zones were internally connected by material and heat streams. All zones were represented by conventional Aspen Plus blocks, except for the pyrolysis zone, where an external calculator was included in the model. This approach can increase the dependencies among various parameters and the outcome from the gasifier [26], e.g. the formation of different ash compounds can be connected and linked to the ash content in the incoming biomass.

The temperature of the syngas leaving the reactor was assumed to be 1200 °C after which the gas was partially quenched to 500 °C. The gasification pressure was set at 30 bar(a) in all the modelling cases.

The black liquor gasifier was modelled using the same approach as described for the PEBG and the results were validated against gas composition data presented in Ref. [27]. The largest difference between gasification of solid biomass fuels and BLG was the ash content. Typical black liquor contains 19.4 wt% sodium and 5 wt% sulphur [27]. These two components react together and with other constituents in the black liquor to form NaOH, Na₂S, Na₂CO₃, Na₂SO₄ and H₂S. The sodium compounds were separated from the syngas in the quench as a melt, which was the basis for the green liquor. 36% of the incoming sulphur was assumed to react with hydrogen forming H₂S [28] and will leave the reactor in gas phase.

An air separation unit (ASU) was used to supply pure oxygen to the gasifier(s). The power demand for a cryogenic air separation unit producing oxygen with 99.6 mol% purity consumes 1.0 MW/(kg-O₂/s) [10].

2.3. Modelling of the gas cleaning, conditioning and methanol synthesis

For the downstream catalyst, a hydrogen to carbon monoxide ratio slightly above 2 in the syngas favours the methanol generation [17]. The actual H₂/CO ratio of the gas leaving the gasifier was typically around 0.55 [21] and needs therefore to be increased prior to the methanol synthesis. A sulphur tolerant water gas shift (WGS) reactor adjusts the ratio to the desired one by converting CO and steam (30 bar) to H₂ and CO₂.

An acid gas removal (AGR) unit was placed before the synthesis loop, to remove the sulphur contaminations as well as CO₂, NH₃ and HCl. The AGR unit uses cooled methanol to remove separated unwanted impurities and gas species, similar to the Rectisol™ process [10]. In the case when the black liquor gasifier operates in parallel to the PEBG, the sulphur content was much higher in the syngas. The sulphur rich stream from the AGR process was then sent to a Claus sulphur recovery unit, where elemental sulphur was recovered [9].

The pressure of the shifted and cleaned syngas was raised to the operating pressure of the catalyst (106 bar with a Δp of 8 bar [13]) by a multistage compressor. The low conversion rate in the catalyst requires recycling of the gas. A fraction (~5%) of the recycled gas was withdrawn in order to prevent accumulation of inert gas in the methanol synthesis loop. These fractions of gases (off-gases) can be combusted in an off-gas boiler for heat production. Before recycling the gas, methanol, water and some carbon dioxide were separated for further purification. More than 98% of the methanol was recovered in the distillation column. The heat needed for distillation was generated by 4 bar steam condensation. Steam was raised in the methanol synthesis both by maintaining a constant exit temperature of 260 °C out from the catalyst and by cooling the outgoing gas prior to the methanol separation.

A simplified description of the complete methanol production process is shown in Fig. 2. The dashed line is valid when a black liquor gasifier is operated in parallel to the PEBG.

3. System description and evaluation

The Billerud Karlsborg AB pulp mill, located in the northern part of Sweden, was used as case basis. This is a partly integrated mill which incorporates batch digestion but was considered be continuous for modelling purpose. The maximum production capacity of the mill is 890 air dried tonnes of Kraft pulp per day and 460 tonnes of paper per day. The mill can principally be divided into two main processes: the fibre line and the chemical recovery process cycle. The fibre processing line includes the pathways for the dissolved cellulosic fibres and extends from the digester (where the pulp cooking occurs) to the pulp bleaching/paper making section of the mill, see Fig. 3.

The integrated chemical recovery cycle is a necessary part of the mill in order to make the overall process economically feasible and environmentally sound. Here, the black liquor, a by-product formed in the pulping process, is an important part that is concentrated in a multi-effect evaporation plant and burned in a so called recovery boiler where combustion of the organic material part provides heat and electricity to the

![Simplified flow sheet for the methanol production plant.](image-url)
mill and the inorganic part is partly regenerated to cooking chemicals. The final recovery of these chemicals to NaOH and Na₂S is made in the causticizing plant (i.e. lime kiln). Another (secondary) by-product, extracted from the black liquor evaporators, is rosin soap, which is further processed into tall oil that can be used as an internal fuel in the lime kiln.

A biomass fired bark boiler is also necessary to produce the marginal demand of process steam. If the supply of internally available biomass is not enough, oil and/or purchased biomass are used (depending on the current fuel market price). The high pressure steam produced in the recovery boiler and the bark boiler is expanded in a steam turbine producing electricity and process steam (10 and 4 bar) for internal use. A small amount of 30 bar steam is also extracted from the turbine for the purpose of soot-blowing in the recovery boiler. Table 1 shows the key energy data of the considered mill, in business-as-usual operation.

3.1. Case description

A schematic overview of the three considered cases, a non-integrated stand-alone gasification unit and two integrated gasification systems are shown in Fig. 4. The two integrated cases include the integration of a PEBG in a pulp and paper mill, one with a co-integration of a BLG operated in parallel with the PEBG. In all cases, methanol was the main final product.

3.1.1. Case A – stand-alone gasifier

In Case A, the PEBG was operated as a stand-alone gasification plant. To be able to compare the different cases, the size of the stand-alone plant was determined by Case B (see chapter 3.1.2), meaning that the thermal input of the biomass was the same as in that case. The system boundaries in Case A also

---

Table 1 – Current key energy data of the reference mill (MW).

<table>
<thead>
<tr>
<th>Energy Type</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity produced/purchased</td>
<td>35/16</td>
</tr>
<tr>
<td>Steam production for internal consumers</td>
<td>208</td>
</tr>
<tr>
<td>Biomass to bark boiler total consumption/purchased</td>
<td>51/7</td>
</tr>
<tr>
<td>Oil to recovery boiler</td>
<td>5</td>
</tr>
<tr>
<td>Tall oil to lime kiln</td>
<td>17</td>
</tr>
</tbody>
</table>

---

**Fig. 3** – Schematic overview of the conventional fibre line and chemical looping at Billerud Karlsborg mill.

**Fig. 4** – Schematic description of the studied cases.
include the original operation of the mill in combination with the stand-alone gasification plant to serve as reference case, as illustrated in Fig. 4. In this case no investments in boilers were considered.

Heat was primarily recovered for steam generation to satisfy the internal demand, with the assumption that the recovered surplus heat could be sold to a local district heating network during the heating season.

3.1.2. Case B – integrated biomass gasifier for methanol production in a pulp and paper mill

In this case, the PEBG replaces the bark boiler in the pulp and paper mill. The most important constraint was, as previously mentioned, a maintained pulp production. The gasification plant was therefore dimensioned to deliver the same amount of medium pressure and low pressure steam as the existing bark boiler did. It was furthermore assumed that the steam system of the gasification plant was completely integrated with the steam system of the mill with one common steam turbine. It was also assumed that the bark originally used in the bark boiler could be milled and used as a fuel in the gasifier, with purchased biomass as additional fuel if required. The excess off-gas (tail gas) from the methanol synthesis loop was assumed to replace/reduce the large oil demand in the lime kiln. The surplus tall oil can be sold on the market.

3.1.3. Case C – integrated biomass gasifier in parallel operation with black liquor gasifier

In Case C, the recovery boiler was replaced by a black liquor gasifier operating in parallel with the PEBG. The two gasifiers share an air separation unit (ASU), gas cleaning and methanol synthesis as an attempt to reach economy-of-scale effects. Also here, the most important modelling constraint translates to a maintained process steam balance of the mill. Since the black liquor gasifier is a by product from the pulp production, the available volume is limited. The size of the PEBG unit was therefore dimensioned to maintain the process steam balance of the mill, when operated in parallel with the black liquor gasifier. The bark boiler was not removed in this case to limit the size of the PEBG unit and the correlated biomass import. According to Ekbom et al. [9], gasification of black liquor results in a major part of the sulphur content will be converted into H₂S. A weaker green liquor will thereby be produced compared to when the black liquor was combusted in a recovery boiler. In the recovery boiler, the sulphur was recovered as Na₂S and dissolved in water to be hydrolysed to NaHS and NaOH. Ekbom et al. [9], assume that the lower content of Na₂O in the green liquor can be compensated by increasing the causticization by 25%, i.e. increasing fuel consumption by 25% in the lime kiln. The excess off-gas from the methanol synthesis loop was assumed to replace/reduce the tall oil demand in the lime kiln. The surplus tall oil can be sold on the market.

3.2. Overall energy system efficiency

Two different efficiencies of the gasification plants were calculated; the biomass-to-methanol efficiency and the overall energy system efficiency. The biomass-to-methanol efficiency was calculated as the annual methanol energy output divided by the annual biomass energy use.

For the calculation of overall energy system efficiency, electricity was calculated on an incremental basis compared to the operation of the pulp mill prior to the integration, i.e. required marginal supply of biomass and other energy carriers needed to produce methanol. This was done to analyse the effects on the overall energy system and determine the best system alternative for methanol production (i.e. integrated or non-integrated). Case B and Case C were compared to the original operation of the mill and the stand-alone plant (Case A) according to the system boundaries that are defined by the dashed lines in Fig. 4. Biomass used directly for the pulp making and the final pulp products were not included in the calculation of the overall energy system efficiencies.

3.3. Economic calculations and sensitivity analysis

In the economic calculations, it was assumed that investment in a new bark and a new recovery boiler was required in Case B and Case C, respectively. The investment cost for a new boiler was converted to an annual capital cost by assuming an economic lifetime of 20 years and an interest rate of 10%, corresponding to an annuity factor of 0.12. Annual operation and maintenance (O&M) cost for the pulp and paper mill was taken from the "Mill stand-alone case" presented in Wetterlund et al. [18]. Costs for wages, insurance for employees and chemical, water and ash disposal were assumed to be included in the annual O&M cost. The investment costs for the bark and the recovery boiler was used for the incremental production cost calculations in Cases B–C, as the difference between the investment in a new boiler and the investment in an integrated gasification plant for methanol production. The capital cost and operating costs for a new boiler were therefore accounted as a reduced cost for the integrated cases. The energy balances for Cases B–C also include any operational changes in the paper and pulp mill caused by the integration of the gasification plant. Investment cost references for the bark boiler and the recovery boiler are presented in Table 3. The annual O&M cost for Cases A–C was taken from the BIGDME-biorefinery case published in Ref. [18]. It was assumed that the cost can be scaled after the thermal input of biomass and black liquor to the gasifiers for all cases. In Case A, the residual heat was assumed to be sold as district heating.

<table>
<thead>
<tr>
<th>Energy carrier</th>
<th>Power generation efficiency</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>46.7%</td>
<td>Biomass integrated gasification combined cycle</td>
<td>[17]</td>
</tr>
<tr>
<td>Methanol</td>
<td>55.9%</td>
<td>Gas turbine combined cycle</td>
<td>[17]</td>
</tr>
<tr>
<td>Tall oil</td>
<td>55.9%</td>
<td>Assumed the same as methanol</td>
<td></td>
</tr>
<tr>
<td>District heating</td>
<td>10%</td>
<td>Opcon power box</td>
<td>[17]</td>
</tr>
</tbody>
</table>
during 5000 h per year. It should be noted that the sulphur recovered in the Claus recovery unit was neither included in the efficiency calculations nor the methanol production cost estimations.

Price levels and exchange rates for year 2011 (9.03 SEK/EUR and 6.5 SEK/US$) were used for monetary conversions. The annual operation time of the gasifiers and the pulp mill was set at 8000 h. The investment cost was calculated as the sum of the specific investment costs for the major units of the plant (gasifier, WGS, ASU, etc.). The investment costs for each unit were calculated according to the actual capacity, reference size and reference investment cost according to (1):

\[
IC = IC_{ref} \cdot \left( \frac{P}{P_{ref}} \right)^n \cdot F
\]

where IC and P denote the investment cost and size, respectively. The subscript (ref) refers to the investment cost and size of the reference plant. F is the overall installation factor and n denotes the scale factor. The calculated total investment of a plant is generally an uncertain value, and according to Hamelinck et al. [14] the uncertainty may be as much as ±30% of the total investment. The reference investment cost was converted into the price level of 2011, by multiplying the ratio between the Chemical Engineering's Plant Cost Index (CEPCI) of the year 2011 and CEPCI in the year the reference investments were made. Reference size and cost for the major units in the plant are summarized in Table 3.

The economic result is strongly dependent on the price formation on raw materials and future charges for CO2-emissions. Therefore, the cases were evaluated under four different future energy market scenarios (see Table 4). The energy market scenarios for the year 2030 were developed by Axelsson et al. [30,31], where assessments were made regarding future fossil fuel price level, CO2 emissions charge and policy support for renewable energy production for an European energy market. The biomass price was set according the high-volume users’ willingness to pay for biomass, which in these scenarios was coal power plant co-firing biomass [18]. Consequently, coal and CO2 charges determine the price for biomass. In scenario 1, the methanol price was set to the current selling price level (January, 2012) [32]. For each future scenario, the methanol prices were scaled in the same way as DME was scaled in Wetterlund et al. [18], where the price for biofuel was set after the fossil fuel price so that the pump cost was the equivalent on energy basis. A biofuel policy support was implemented via assuming that stand-alone large-scale biofuel production plants have equal willingness to pay for biomass as a coal power plant, e.g. here the methanol produced via biomass gasification.

### Table 3 – Reference investment cost in MEuro.

<table>
<thead>
<tr>
<th>Cost reference</th>
<th>Size unit</th>
<th>Reference size</th>
<th>Cost 2011 (MEuro)</th>
<th>Scale factor*</th>
<th>Overall installation factor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery boiler</td>
<td>Tons BL/day</td>
<td>3420</td>
<td>136</td>
<td>0.7</td>
<td>1.10</td>
<td>[9]</td>
</tr>
<tr>
<td>Bark boiler</td>
<td>MWth</td>
<td>46</td>
<td>24</td>
<td>0.7</td>
<td>1.00</td>
<td>[18]</td>
</tr>
<tr>
<td>Pre-treatment</td>
<td>Wet tons/h</td>
<td>34</td>
<td>9</td>
<td>0.79</td>
<td>2.00</td>
<td>[13]</td>
</tr>
<tr>
<td>Air separation unit</td>
<td>Tons O2/day</td>
<td>1001</td>
<td>47</td>
<td>0.85</td>
<td>1.30</td>
<td>[13]</td>
</tr>
<tr>
<td>BLG gasification unit and cooling unit</td>
<td>Tons BL/day</td>
<td>3420</td>
<td>92</td>
<td>0.7</td>
<td>1.10</td>
<td>[9]</td>
</tr>
<tr>
<td>Biomass gasification unit</td>
<td>kg/h</td>
<td>220</td>
<td>0.3</td>
<td>0.75</td>
<td>1.86</td>
<td>[29]</td>
</tr>
<tr>
<td>Gas cleaning unit (prewash, CO-shift, CO2-sep)</td>
<td>kg’s dry syngas flow</td>
<td>37</td>
<td>38</td>
<td>0.7</td>
<td>1.10</td>
<td>[9]</td>
</tr>
<tr>
<td>Claus sulphur plant*</td>
<td>Tons BL/day</td>
<td>3420</td>
<td>10</td>
<td>0.7</td>
<td>1.10</td>
<td>[9]</td>
</tr>
<tr>
<td>Methanol synthesis unit (incl. compressor &amp; storage)</td>
<td>Tons MeOH/day</td>
<td>1183</td>
<td>65</td>
<td>0.7</td>
<td>1.10</td>
<td>[9]</td>
</tr>
<tr>
<td>Off-gas boiler</td>
<td>MWth</td>
<td>355</td>
<td>42</td>
<td>1.0</td>
<td>1.49</td>
<td>[10]</td>
</tr>
<tr>
<td>District heating HEX</td>
<td>MWth</td>
<td>355</td>
<td>42</td>
<td>1.0</td>
<td>1.49</td>
<td>[10]</td>
</tr>
<tr>
<td>Balance of plant</td>
<td>2% of the total investment cost</td>
<td>42% of the total investment cost</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* A scale factor of 0.7 was assumed for investments if not specified in the reference.
* The same amount of sulphur was assumed to be recovered in the Claus unit per tonne black liquor as in Ref. [9].
* Same percentage of the total investment cost, as in Ref. [9] was assumed.
* Includes costs for interest during construction (10%), working capital (10%), project administration and development (7%), engineering (5%), start-up cost (5%), royalties, legal permits and insurance (5%).

### Table 4 – Energy market scenarios [30,31].

<table>
<thead>
<tr>
<th>Scenario</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Today scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel price level</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>CO2 charge</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Prices and policy instruments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood fuel</td>
<td>EUR/MWh</td>
<td>32</td>
<td>58</td>
<td>35</td>
<td>61</td>
</tr>
<tr>
<td>Electricity</td>
<td>EUR/MWh</td>
<td>69</td>
<td>92</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>Heavy fuel oil (incl. CO2 charge)</td>
<td>EUR/MWh</td>
<td>46</td>
<td>68</td>
<td>91</td>
<td>46</td>
</tr>
<tr>
<td>Tall oil (selling price)</td>
<td>EUR/MWh</td>
<td>35</td>
<td>58</td>
<td>58</td>
<td>35</td>
</tr>
<tr>
<td>Methanol (selling price)*</td>
<td>EUR/MWh</td>
<td>59</td>
<td>79</td>
<td>113</td>
<td>184</td>
</tr>
<tr>
<td>CO2 charge</td>
<td>EUR/CO2</td>
<td>36</td>
<td>111</td>
<td>111</td>
<td>36</td>
</tr>
<tr>
<td>Renewable energy policy support</td>
<td>EUR/MWh</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Biofuel policy support</td>
<td>EUR/MWh</td>
<td>36</td>
<td>68</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td>District heating</td>
<td>EUR/MWh</td>
<td>19</td>
<td>50</td>
<td>27</td>
<td>57</td>
</tr>
</tbody>
</table>

* In the today scenario, the methanol selling price was converted from the current selling price 1.67 Euro/litre of fossil gasoline. The fossil gasoline price includes production, distribution, energy tax, CO2-tax and VAT.
Biomass is often associated with one of the largest annual costs and a low biomass price (compared to the biomass prices in the future scenarios) can therefore create more favourable conditions for methanol production. As a complement to the future market scenarios the economic feasibility of the cases was also analysed in a "today scenario" (see Table 4), where methanol was sold to replace fossil gasoline with an estimated distribution cost of 0.222 Euro/litre per gasoline equivalent. In the today scenario, methanol was fully exempted from taxes in an approach to mimic the current Swedish biofuel policy support. The biomass price, electricity price, the renewable electricity support as well as the district heating selling price was based on the Swedish energy market [33–35], while the other parameters were assumed to be the same as in scenario 1.

If the income from the biofuel policy support in the future energy market scenarios was added to the methanol selling price (i.e. included as revenue in the production cost calculation) the revenues from each unit of methanol sold increase by 22–86% depending on scenario. The total revenues for production of a renewable motor fuel (here methanol) are therefore very influenced by the level of biofuel policy support for the future energy market scenarios. The biofuels policy support in these future energy market scenarios should be viewed as an incentive to initially aid biofuels to become competitive to fossil fuels. However, after a biofuel market is developed and commercialized, the policy support is supposed to gradually be phased out. Thus, biofuels should in the end be able to compete without any support. The production cost was therefore calculated including the given support according to each scenario as well as without any support at all.

The different energy market scenarios and the annual capital cost were used to calculate the production cost for Cases A–C and compare the potential economic marginal against the methanol selling price. Cases with net positive economic marginal were also evaluated in a cash flow analysis to determine the internal rate of return (IRR). In the IRR analysis, the production was assumed to be at 25% of the full capacity during the first year and increase with 25%-units annually until the start-up period ends. The investment cost was assumed to be paid during a three year construction period.

A sensitivity analysis was carried out, where identified parameters with potentially high influence on the methanol production cost were investigated. The studied parameters are:

- **Surplus tall oil sales.** Not all off-gas may be suitable for utilization in the lime kiln and the possibility that exist no surplus tall oil will be available for market sales. Therefore, the economic influence on the sale of surplus tall oil was investigated.
- **The capital cost** is a critical and uncertain parameter for the process economics. In the analysis the annual capital cost was assumed to change ±30%. This can be viewed as a fluctuation in the capital investment cost but also as a changed return on equity, i.e. a varied annuity factor that consequently translate to a changed interest rate and/or assumed economic lifetime.
- **The influence of the O&M cost** was studied by varying it in the range of ±30%.
- **Three operational plant parameters** were investigated with potentially vital influence on the process economics. The influences of a separate change in methanol production by ±10%, electricity consumption in the gasification plant by ±30% or annual operation time ±8%, were analysed.

A price change for an individual commodity was not investigated because the used scenarios were designed by interdependent parameters.

### 4. Results and discussion

Three different system configurations using PEBG technology to produce methanol were studied, one stand-alone plant (Case A) and two integrated into a pulp and paper mill (Cases B–C). The resulting material and energy flows for the cases are presented in Fig. 5. A biomass-to-methanol efficiency was calculated at 55% in Cases A and B, while Case C shows a slightly lower efficiency, 53%. The overall energy system efficiency (calculated as electricity-equivalents) of the studied cases was estimated by the incoming and outgoing energy flows over the systems’ boundaries represented by dashed boxes in Fig. 5. The results show that the system configurations according to the original operation of the mill and the non-integrated Case A reached an overall system efficiency of 50%. By integrating a PEBG unit and replacing the bark boiler (Case B), the overall system efficiency increases to 57%. With the integrated gasifier capacities chosen in this study, the net steam production supplied to the mill was more or less only sufficient to cover the steam demand of the different subprocesses of the mill. In the case where the PEBG unit was operated in parallel with BLG (Case C), hardly any high pressure steam was expanded in the steam turbine. The electricity production would therefore decrease from 35 MW (Case A) to only 4 MW for Case C. Such a significant change in operating conditions would probably require a new steam turbine. An investment in a new turbine was not considered in the current analysis and Case C was thereby noted for a zero electricity production. However, by removing the recovery boiler in favour of integrating PEBG in parallel operation with BLG (Case C) the overall system efficiency also increased to 57%.

Table 5 shows the resulting overall energy and material balances of the different cases. The energy balances for Cases B and C also include required operational changes in the pulp and paper mill due to the integration of the gasification plant. Table 5 also shows the specific investment cost of the major units as well as the O&M costs for each case. In all cases, the investment costs for pre-treatment, air separation unit and gasifier(s) represent the major part of the investment cost for equipment (56–66%). Case C showed the lowest specific investment of approximately 1.6 MEuro/MWh methanol produced. In Cases A and B, the specific investments were around 2.0 MEuro/MWh of methanol and 1.8 MEuro/MWh of methanol produced, respectively. At the pulp and paper mill necessary biomass handling infrastructure is in place, which may reduce the investment cost for an integrated methanol production plant. This was especially true for Case B, where the capacity of the plant (338 MW) should not impose very large changes for the incoming biomass handling.
infrastructure. These benefits were not addressed in the economic evaluation.

The resulting production cost for Cases A–C depended on the energy market scenarios 1–4 as well as the today scenario is presented in Fig. 6. The methanol production cost includes costs and revenues from other products (electricity, heat, tall oil, etc.) and the annual capital cost. In Fig. 6, the methanol production cost is also presented when the biofuel policy support also was included as revenue.

In the today scenario a biofuel policy support was implemented via tax exempting renewable motor fuel production (here methanol), because the methanol was assumed to replace fossil gasoline. All cases showed a considerably lower production cost compared to selling price in the today scenario and thereby an opportunity for a good production profitability. Note that the production costs in the today scenario also include a distribution cost of 0.222 Euro/litre. Nevertheless, if the methanol export was not tax exempted, the production costs were unable to compete with fossil gasoline (not presented in Fig. 6).

In the today scenario a biofuel policy support was also evident when the gasification systems were evaluated in the four future energy market scenarios, where none of the system configurations could be competitive with the methanol selling price without the support, see Fig. 6. At a low fossil fuel price level and high CO2 charge (scenario 2) the biofuel policy support was the highest (68 Euro/MWh), but the economic benefits gained via integration cannot reduce the production cost to compete with the methanol selling price. Note that this biofuel policy support level roughly correlates to the tax exemption benefits methanol receives in the today scenario.

For all the other considered scenarios, more favourable economic benefits with integration compared to stand-alone operation were obtained when the biofuel support was included. In scenario 3, the fossil price was high but the CO2 charge was low, which makes the biomass price relatively cheap and compared to the production cost of methanol Case B showed the largest economic net marginal in this scenario, see Fig. 6. Case C showed breakeven production cost compared to the methanol selling price in the scenarios where the CO2 charges were low (scenarios 1 and 3), because of the relative low biomass prices. In the scenarios with relative high biomass prices (scenarios 2 and 4), high import of biomass will be penalized and this explains the negative marginal’s received for Case C in these scenarios. Overall, the effect of the zero net electricity production in Case C was also a main
explanation in these economic results together with the low biomass-to-methanol efficiency. This points out that the full integration case configuration (Case C) was far from optimal from an economic point of view and an adjusted configuration would most probably end up in more favourable economic results. The stand-alone unit (Case A) showed a negative marginal in each scenario.

The result of the cash flow analysis is presented in Fig. 7 for cases with a net positive economic marginal (see Fig. 6). As illustrated in Fig. 7, an IRR below 10% was achieved in Case B, at three of the future energy market scenarios. At current conditions, the economy-of-scale effects were apparent and the parallel operation of a biomass and black liquor gasifier (Case C) seems to be the most attractive alternative when considering the IRR. Still, Cases A and B showed attractive production profitability.

Table 5 – Overall annual energy and material balances and capital investment costs.

<table>
<thead>
<tr>
<th>Plant production</th>
<th>Comment</th>
<th>Unit</th>
<th>Ref</th>
<th>P&amp;P</th>
<th>Case A</th>
<th>Case B</th>
<th>Case C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass input capacity/black liquor</td>
<td>As received, 40% moisture</td>
<td>MW</td>
<td>511</td>
<td>338</td>
<td>338</td>
<td>816 (199)</td>
<td></td>
</tr>
<tr>
<td>Biomass, annual input</td>
<td>As received, 40% moisture</td>
<td>tonnes</td>
<td>121,864</td>
<td>840,622</td>
<td>840,622</td>
<td>2,029,430</td>
<td></td>
</tr>
<tr>
<td>Power consumed</td>
<td></td>
<td>tonnes/year</td>
<td>50</td>
<td>41</td>
<td>91</td>
<td>161</td>
<td></td>
</tr>
<tr>
<td>Ash disposal</td>
<td>2% of dry biomass</td>
<td>tonnes/year</td>
<td>12,609</td>
<td>12,609</td>
<td>30,441</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td>MW</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td>MW</td>
<td>187</td>
<td>187</td>
<td>539</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol, annual output</td>
<td></td>
<td>tonnes</td>
<td>270,080</td>
<td>270,080</td>
<td>779,713</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tall oil</td>
<td></td>
<td>MW</td>
<td>17</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tall oil, annual output</td>
<td></td>
<td>GWh/year</td>
<td>136</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power produced</td>
<td></td>
<td>MW</td>
<td>95</td>
<td>29</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat/steam produced</td>
<td></td>
<td>GWh/year</td>
<td>55</td>
<td>55</td>
<td>30</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>Heat, annual output (during 5000 h annually)</td>
<td></td>
<td>GWh/year</td>
<td>275</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital investment cost</td>
<td></td>
<td>Unit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-treatment</td>
<td>MEuro</td>
<td>37</td>
<td>37</td>
<td>99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air separation unit</td>
<td>MEuro</td>
<td>43</td>
<td>43</td>
<td>109</td>
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<tr>
<td>BLG gasification unit and cooling unit</td>
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<td>72</td>
<td></td>
<td></td>
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<tr>
<td>Biomass gasification unit and cooling unit</td>
<td>MEuro</td>
<td>65</td>
<td>65</td>
<td>127</td>
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<td>Gas cleaning unit (pre-wash, CO-shift, CO2-sep)</td>
<td>MEuro</td>
<td>33</td>
<td>33</td>
<td>70</td>
<td></td>
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<td>Sulphur handling (Claus plant)</td>
<td>MEuro</td>
<td>7</td>
<td></td>
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<tr>
<td>Methanol synthesis unit (incl. compressor &amp; storage)</td>
<td>MEuro</td>
<td>57</td>
<td>57</td>
<td>119</td>
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<tr>
<td>Off-gas boiler</td>
<td>MEuro</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>District heating HEX</td>
<td>MEuro</td>
<td>10</td>
<td></td>
<td></td>
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<td>Balance of the plant</td>
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<td>5</td>
<td>12</td>
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<tr>
<td>Recovery boiler</td>
<td>MEuro</td>
<td>106</td>
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<td>Bark boiler</td>
<td>MEuro</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Equipment and assembly</td>
<td>MEuro</td>
<td>24/106</td>
<td>260</td>
<td>240</td>
<td>615</td>
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<tr>
<td>Indirect cost (42% of equipment and assembly)</td>
<td>MEuro</td>
<td>10/44</td>
<td>109</td>
<td>101</td>
<td>258</td>
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<tr>
<td>Total investment cost</td>
<td>MEuro</td>
<td>35/150</td>
<td>369</td>
<td>341</td>
<td>874</td>
<td></td>
<td></td>
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<tr>
<td>O&amp;M</td>
<td>MEuro/year</td>
<td>7</td>
<td>27</td>
<td>24</td>
<td>82</td>
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<tr>
<td>Capital costs</td>
<td>MEuro/year</td>
<td>4/18</td>
<td>44</td>
<td>40</td>
<td>103</td>
<td></td>
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</tr>
</tbody>
</table>

* Refers to business-as-usual operation of the pulp and paper mill. All residual heat was used internally.
* Total biomass use in the bark boiler.
* In Case C, 51 MW of biomass was supplied to the bark boiler. The total biomass use was 864 MW (PEBG and bark boiler) plus 199 MW of black liquor in the BLG.
* In Case C, the lime kiln fuel demand was assumed to increase by 25%. To satisfy the increased demand, 22 MW off-gases must be supplied from the gasification plant. 17 MW of surplus tall oil will be available for market sales.
* A significant decrease in internal electricity production occurs with the assumed gasifier capacities. Neither the electricity production nor an investment for a new turbine was included.
* Investment was valid for 4 parallel biomass gasifier units, each with a third of the needed capacity, for enable maintenance of one unit while operating at full capacity in the other three units.
* Costs for wages, insurance for employees and chemical, water and ash disposal.
* An annuity factor of 0.12, corresponding to an economic lifetime of 20 years and a 10% interest rate, was used.
* The capital cost and O&M cost for a new boiler were accounted as a reduced cost for the integrated cases in the economic evaluation.

Fig. 8 shows the methanol production cost as a result of the sensitivity analysis. The costs and revenues of other products (electricity, heat, tall oil, etc.), were also here included in the production cost calculation. The methanol yield has a large influence on the production cost. A 10% change in the yield results in a production cost increase/decrease by 9–11% in all scenarios. Slightly smaller influences were observed for the production cost when the O&M cost changes within the same range. A large uncertainty is the investment costs. An investment cost change of 30% results in a methanol production cost change in the range of 4–8%, depending on case and scenario. The production cost can therefore be viewed as relatively insensitive to large capital cost fluctuation. This was particularly evident for Case C (see Fig. 8) due to the low specific investment cost. If no tall oil was liberated and sold (i.e. the off-gases not used to replace the tall oil in the lime
the changes were small in Case C. The methanol production cost in Case B increased more than in Case C, with the highest production cost increase noticed in scenario 3 (when no surplus tall oil was available for sale).

None of the assumed plant improvements in Fig. 8 (increased methanol production, decreased O&M or investments cost, etc.) can by themselves lower the production cost to the same degree as the biofuel policy support did (Fig. 6). Thus, it is obvious that initial economic policy support will be required to make methanol production via PEBG economically feasible.

5. Conclusions

The main aim of this study was to perform a techno-economic evaluation of methanol production via the PEBG process integrated into an existing pulp and paper mill. Three different system configurations using PEBG technology were studied, one stand-alone plant (Case A) and two integrated into a pulp and paper mill (Cases B–C).

Replacing the bark boiler in a pulp and paper mill in favour of PEBG for methanol production (Case B) increases the overall plant efficiency by 7%-units (calculated as electrical equivalents) compared to the original operation of the mill operating together with the non-integrated PEBG concept (Case A). However, substantial increases in the imports of biomass feedstock and electricity were needed in order to fulfil the steam demand of the mill. Methanol produced via parallel operation of a solid biomass gasifier and a black liquor gasifier, Case C, received the same overall plant efficiency as Case B (57%). The positive effects from the high internal use of
resources (black liquor and biomass) in this case therefore compensate for the zero electricity production. However, the effect of the zero net electricity production in Case C becomes evident in the economic results and was one of the main reasons why Case C consistently has a higher methanol production cost than Case B in all scenarios. For all the cases, it was obvious that a biofuel policy support was needed in order to make production of biomethanol economically competitive for the considered process concepts. In comparison to the stand-alone plant (Case A) the methanol production cost was lowered in the range of 11–18 Euro/MWh for the integrated Case B and Case C.

Under similar conditions as today, attractive investment opportunities were shown for all cases if the methanol was exempted from taxes and sold to replace fossil gasoline. The economies-of-scale was apparent and the parallel operation of a biomass and a black liquor gasifier (Case C) seems to be the most alternative attractive when considering the internal rate of return.

The production profitability of methanol production via biomass gasification was however diminished when evaluated under future energy market scenarios, where price assessments were made based on the fossil fuel price level, CO2 emissions charge and biofuel policy support for a European energy market. The relative high biomass prices in a future market penalized the viability of Case C due to its high biomass import demand. The positive economy-of-scale effects cannot compensate for the relative high operational costs and the smaller integrated route with a PEBG unit (Case B) was therefore here a better investment opportunity.

Acknowledgements

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Paper III

Techno-economic analysis of ammonia production via integrated biomass gasification
Techno-economic analysis of ammonia production via integrated biomass gasification

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HIGHLIGHTS

- Techno-economic results regarding biomass-based ammonia production systems.
- Integration of an ammonia production process in a pulp and paper mill.
- Integrated ammonia production gains higher system efficiency than stand-alone production.
- The economics of an integrated production system is improved compared to stand-alone production.

ABSTRACT

Ammonia (NH₃) can be produced by synthesis of nitrogen and hydrogen in the Haber–Bosch process, where the economic challenge is the hydrogen production. Currently, substantial amounts of greenhouse gases are emitted from the ammonia industry since the hydrogen production is almost exclusively based on fossil feedstocks. Hydrogen produced via gasification of lignocellulosic biomass is a more environmentally friendly alternative, but the economic performance is critical. The main objective of this work was to perform a techno-economic evaluation of ammonia production via integrated biomass gasification in an existing pulp and paper mill. The results were compared with a stand-alone production case to find potential technical and economic benefits deriving from the integration. The biomass gasifier and the subsequent NH₃ production were modelled using the commercial software Aspen Plus. A process integration model based on Mixed Integer Linear Programming (MILP) was used to analyze the effects on the overall energy system of the pulp mill. Important modelling constraints were to maintain the pulp production and the steam balance of the mill. The results showed that the process economics and energy performance are favourable for the integrated case compared to stand-alone production. The main conclusion was however that a rather high NH₃ selling price is required to make both production cases economically feasible.

1. Introduction

The fertilizer sector annually stands for 1.2% of the world’s total energy use, where the bulk (87%) is directly coupled to ammonia (NH₃) production [1]. NH₃ is one of the most produced inorganic chemicals worldwide, with a total global production of 109 Mt in 2009 [1] and the global production capacity is forecasted to increase to nearly 239 Mt by 2020 [1]. NH₃ can be produced via synthesis of nitrogen and hydrogen in the Haber–Bosch process, where the economic challenge is the hydrogen production. Currently, substantial amounts of greenhouse gases are emitted from the NH₃ industry since the hydrogen production is almost exclusively based on fossil feedstocks. The main hydrogen source was previously gasification of coal, but falling petroleum prices shifted the production to steam reforming of natural gas [3]. A more environmentally friendly option would be to produce the hydrogen via thermal conversion of lignocellulosic biomass.

Existing ammonia plants usually have very large production capacities, typically exceeding 1500 tons of ammonia per day. To be competitive, it is likely that similar production capacities will be required for biomass based ammonia plants. Such a production level would approximately require in the order of 2000 tons of dry biomass per day, which puts high demands on biomass logistics and handling. The production capacity in practice will however be constrained by the available biomass supply and gasifier scales [2].

Gilbert et al. [2] have made a review of different biomass gasifiers in order to find the best suited technology for ammonia production. In that study, a Fast Internal Circulating Fluidised Bed gasifier
(FICFB) with CO₂ removal was selected due to its generation of a hydrogen rich syngas. This gasification technology is currently demonstrated in the scale of 8-10 MW [3,4]. Up-scaling to a production capacity exceeding 100 MW will be a great challenge and probably not economically feasible without transition to a pressurized concept. One issue is that the FICFB technology is more difficult to pressurize than direct gasifiers [5]. Therefore, a pressurized entrained flow biomass gasifier (PEBG) has been chosen in this study as this technology also produces a high quality and hydrogen rich syngas, but has a much better scale-up potential than FICFB gasifiers.

Integrating biomass gasification processes for large-scale chemical production in existing industries may result in several technical, energy-related as well as economic benefits, e.g. [6–8]. A large number of studies regarding integrated chemical production in pulp and paper mills have recently been published [9–12]. One reason why this industry is of such a great interest is the already existing biomass supply infrastructure, which provides large logistical and feedstock handling advantages. Furthermore, the industry is facing increasing energy prices and stronger competition on raw materials [13], which makes it important to find additional streams of revenues to their existing production.

The main aim of this work was therefore to perform a techno-economic evaluation of NH₃ synthesis, as it is produced by the reaction (1), in an integrated PEBG based ammonia production process. The main objectives were to:

- Investigate if this production concept is economically feasible at current market conditions.
- Find a solution for the trade-off between capital and operating costs.
- Find measurable technical and economic added values for integrated biomass based ammonia production compared to stand-alone units.

2. Material and method

A process integration (PI) model was used to evaluate the integration of gasification based NH₃ production in an existing pulp and paper mill. The most important modelling constraint was to maintain the pulp production and consequently the process steam balance. A detailed Aspen Plus process model was used to model energy and material balances of the complete biomass gasification system including the NH₃ synthesis. An iterative modelling approach between the two models was adopted to ensure that all constraints of the pulp and paper mill as well as for the gasification plant were met. The resulting material and energy balances were used to analyze the different system configurations in terms of overall energy efficiency and process economics.

2.1. The process integration model

The process integration model was based on mathematical programming on Mixed Integer Linear Programming (MILP). The model is composed of branches and nodes, where each node represents process units and energy/material flows, respectively. The different nodes are connected depending on the input and output to/from each process unit. Each node contains linear equations to express the energy and mass balance required in the process unit. Thus an entire energy system is created. The model of the existing mill configuration was validated against operational data. The model development and validation are further described in [14].

2.2. Modelling of the biomass gasification system

The gasifier model was based on the PEBG technology and created in Aspen Plus. Entrained flow gasifiers usually operate in a temperature range of 1200–1800 °C and at pressures in range of 20–70 bar [15]. These operating conditions yields a nearly tar and methane free syngas. The fuel was fed into a heated reactor co-currently with a gasifying agent, in this case pure oxygen (O₂), for partial combustion of the fuel [15,16]. The O₂ was produced using a cryogenic air separation unit (ASU) with an estimated power demand of 1.0 MW, per kg-O₂, assuming a 99.6 mol% O₂ purity [17].

The short residence time for the entrained fuel in the reactor requires particle sizes smaller than 0.5 mm, in order to facilitate high carbon conversion rates [16]. The water content and the particle size of the fuel must therefore be reduced before it is supplied to the reactor.

The fuel drying and the grinding were modelled as black-boxes. The biomass was specified according to the ultimate and proximate analysis of the fuel. The dryer was modelled as an indirectly heated rotary dryer, with a specific power consumption of 15 kWh per wet ton of biomass [18] and the water content of the biomass was assumed to be reduced from 40% to 8%. According to [19], in between 2% and 3% of the thermal input of the biomass (based on LHV) is estimated to be required in terms of specific electricity consumption for the grinding to 0.5 mm particle diameters. In this study, 3% was assumed. The biomass powder was assumed to be pressurized using screw feeders, which require an inert gas as an separation unit (ASU).

The gasification process was modelled in detail by treating the dominant reaction steps in the gasifier separately, i.e. drying, pyrolysis, combustion and gasification. The pyrolysis step was modelled using empirical relationships by an approach developed and described in [23]. Furthermore, equilibrium restrictions were
implemented to prevent underestimations of the methane and tar contents of the outgoing syngas. This approach provides a more accurate simulation of a pressurized entrained flow reactor [24]. A gasification pressure level of 30 bar (a) was assumed in the model. The temperature of the raw syngas leaving the reactor before entering the quench was assumed to be 1200 °C. In the quench, the gas was cooled to 500 °C after passing water jets and bubbling through a water reservoir. After the quench, the residual heat was recovered for steam generation.

2.3. Modelling of the gas cleaning, conditioning and ammonia synthesis

The optimal H₂:N₂ molar ratio is 3 for NH₃ synthesis [22] and to increase the hydrogen concentration of the syngas, a water gas shift (WGS) reactor was used. An acid gas removal (AGR) unit was placed after the shift reactor in order to remove any acid gas contaminations and CO₂. The AGR unit used cooled methanol as a physical solvent to remove unwanted impurities and gas species and is similar to the Rectisol® process [17].

As a final purification step, a liquid N₂ wash was used. The N₂ wash was located downstream the AGR unit and use the already cooled gas stream (below ~50 °C). Methanol and the remaining traces of CO₂ in the syngas must be removed before the N₂ wash to avoid freezing problems in the cold box heat exchanger [22].

The main task for the N₂ wash is to remove the remaining CO content, because it acts as a poison for the NH₃ catalyst [22]. Pressurized N₂ and syngas were cooled against the product streams (outgoing syngas and off-gases). As a result, the N₂ was liquefied and then fed to the top of the wash column. The cooled syngas entered at the bottom of the column, where inert gases such as CH₄ and argon will condensate from the syngas whilst the liquefied N₂ removes the CO. An additional nitrogen stream was mixed with the outgoing syngas to reach the desired H₂:N₂ ratio of 3 [22].

The syngas was pressurized to the operating pressure of the NH₃ catalyst (180 bar) before entering the synthesis loop. The NH₃ synthesis took place over an iron promoted catalyst [21], modelled using a Gibbs reactor with an outgoing gas temperature of 440 °C. Typically the conversion efficiency is of the order of 20–30% per pass, and recycling of the unreacted gases is therefore necessary to increase the NH₃ production yield [25]. The NH₃ reaction is exothermic, meaning that cooling of the outgoing gases can generate high quality steam [21]. The produced NH₃ is separated from the unreacted gases by condensation in a refrigeration system. Part of the recycled gas must be purged to avoid inter gas accumulation in the synthesis loop [21]. To compensate for the pressure drop over the catalyst, the recycled gas was recompressed to 180 bar before mixing with the incoming syngas.

A simplified description of the complete ammonia production process is shown in Fig. 1.

3. Case descriptions

The Billerud Karlsborg AB pulp mill, located in the northern part of Sweden, was used as case basis. The mill consists of two major processing lines: the fibre line and the chemicals recovery loop.

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![Fig. 1. Schematic model of the gasification based ammonia production plant.](image-url)
The fibre processing line extends from the digester to the outgoing pulp and paper, see Fig. 2.

In the processing line, cooking chemicals (white liquor) and heat are used to dissolve the binding agent in wood (lignin) in order to release the cellulose fibres needed as raw material for the pulp and paper. The black liquor (BL) is a by-product from pulp making and contains spent cooking chemicals and organic matter. The recovery of these chemicals is necessary to make the process economically feasible and to create a closed chemical recovery cycle. The solid content of the BL is concentrated in multi-effect evaporators before being burned in a recovery boiler (RB). The combustion of organics provides energy to produce high pressure (HP) steam and to carry out the reduction reactions to recover cooking chemicals. Sodium hydroxide (NaOH) and sodium sulphide (Na2S) are the main component in the white liquor solution, generated by passing the recovered cooking chemicals through the causticizing plant. In process of concentrating the BL, rosin soap is precipitated. The rosin soap is further processed into tall oil and used as fuel in the lime kiln. Furthermore, it was assumed that off-gases from the synthesis loop together with tail gas from the N2 wash could substitute the tall oil used in the lime kiln. The surplus tall oil can be sold on the market as an alternative to heavy fuel oil.

3.1. Overall energy system analysis

The energy system efficiency was calculated using electricity equivalents. All energy carriers were converted to their corresponding electricity equivalents according to the efficiency of the best-available technologies known to the authors, see Table 1. The material and energy balance for Case A was calculated on an incremental basis compared to the operation of the pulp mill prior to the integration, i.e., required marginal supply of biomass and other energy carriers needed to produce NH3. Case A was compared to the original operation of the mill and the stand-alone gasification plant (BAU/S-A) to analyze the effects on the overall energy system and to determine the best alternative for producing NH3 from biomass gasification (i.e., non-integrated or integrated).

The biomass dedicated for pulp making and the final pulp products were not accounted for when the overall energy system efficiency were calculated as that supply is equal in both cases. The internal by-product bark becomes available from the debarking process of the pulp wood. Bark is an unwanted biomass sort in the cooking process due to its high ash content and other contaminations. The bark was therefore not accounted for as pulp making biomass. The system boundaries used for the overall system efficiency calculations is illustrated by the dashed boxes in Fig. 3.

3.2. Economic calculations and sensitivity analysis

In the economic calculations, the incremental investment, calculated as the difference between the investment in a new bark boiler and the investment in an integrated gasification plant for NH3 production, was used in Case A. This implies that the bark

Table 1

<table>
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<tr>
<th>Energy carrier</th>
<th>Power generation efficiency (%)</th>
<th>Comment</th>
<th>Refs.</th>
</tr>
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<tr>
<td>Biomass</td>
<td>46.2</td>
<td>BIGCC</td>
<td>[9]</td>
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<tr>
<td>Methanol</td>
<td>55.9</td>
<td>Gas turbine combined cycle</td>
<td>[9]</td>
</tr>
<tr>
<td>Tall oil</td>
<td>55.9</td>
<td>Assumed the same as methanol</td>
<td>[9]</td>
</tr>
<tr>
<td>Hot water, 95 °C</td>
<td>10</td>
<td>Open power box</td>
<td>[9]</td>
</tr>
<tr>
<td>NH3</td>
<td>49</td>
<td>Converted by multiplying the methanol power generation efficiency with the ratio of the lower heating values between ammonia and methanol</td>
<td>[9]</td>
</tr>
</tbody>
</table>

![Fig. 2. Conventional fibre line and chemical looping.](image-url)
boiler of the mill is old and needs to be replaced in any case. The energy balances for Case A include the operational changes in the paper and pulp mill caused by the integration of the gasification plant. Cost and revenues associated with the original operation of bark boiler was included in the reference case, where the cost of operation and maintenance was taken from the "Mill stand-alone case" presented in [12].

Natural gas is the currently the main feedstock for NH₃ production [22], meaning that the price of natural gas is a determining factor of the NH₃ market price. Other factors, presumably the biomass price, would control the NH₃ market price if the production was primarily based on biomass. Therefore, an estimation of the required NH₃ selling price that would make biomass based NH₃ production an attractive investment opportunity was made. The NH₃ selling price was calculated via cash flow analysis at three levels of internal rate of returns (IRR). These required selling prices were also compared to the present average market selling price for fossil NH₃ ([514 €/ton][26]). In the cash flow analysis, a plant start-up period was considered, where the NH₃ production was 25% of the maximum capacity during year one and thereafter increased by 25%-points per year until the maximum production capacity was reached. The investment cost was assumed to be paid during a year in which the reference investments were made. The method for calculating the capital investment cost has an estimated uncertainty in the range of ±30% [31]. The required ammonia selling price to receive 15% IRR, was therefore also investigated for a ±30% change of the gasification plant investment cost. The weighted average cost of capital (WACC) was used as interest rate for the calculation of the annuity factor. The WACC was calculated using the financial parameters specified in Table 3. The annuity factor method was only used to calculate the NH₃ production cost. The required ammonia selling price to receive 15% IRR, was calculated using a biomass cost in the range of 11–44 €/MW h (i.e. 50% decrease up to a 100% increase of the reference value). The method for calculating the capital investment cost has an estimated uncertainty in the range of ±30% [31]. The required ammonia selling price to receive 15% IRR, was therefore also investigated for a ±30% change of the gasification plant investment cost.

4. Results and discussion

Two different system configurations using PEBG technology to produce NH₃ were studied, one stand-alone plant (S-A) and one integrated into a pulp and paper mill (Case A). The resulting material and energy flows for the cases are presented in Fig. 3. The overall energy system efficiency (calculated as electricity-equivalents) was estimated using the system boundaries represented by dashed boxes in Fig. 3. The stand-alone plant (S-A) has the same NH₃

**Fig. 3.** Resulting energy and material balances. The system boundary includes the P&P plant and the stand-alone gasification unit (left side) and the complete integrated biomass gasification plant (right side). Biomass for pulp making and the final pulp products (green arrows) are the same for both cases and are neither accounted for in the efficiency calculations (see dry tons = AD/t). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
production capacity and annual demand for biomass and electricity as the gasification plant in Case A.

An overall energy system efficiency of 44% (calculated as electricity equivalents) was reached for the non-integrated stand-alone production case (S-A), also accounting for the operation of the mill (BAU). This result also includes the delivery of nearly 188 GW h of heat per year to the district heating system from the NH₃ plant. In Case A, two additional product streams, NH₃ and tall oil, were added to total mill production. However, one consequence was an increased supply of external biomass to the mill by 50%. Other consequences were decreased electricity production due lower production of HP steam, at the same time as the electricity consumption was almost doubled compared to the reference case. The reasons were mainly that the available internal efficiency was increased by 10%-units compared to the reference case. The calculations showed, however, that the overall system efficiency was increased by 10%-units compared to the reference case.

The calculated capital investment costs and production costs are presented in Table 4. The gasification train accounts for 18% of the total cost for equipment and assembly. In both cases, a train of four gasifier units were assumed to be required to ensure the high annual operational load (8000 h), where each unit has a capacity of one third of the maximum. A major part (43–44%) of the total investment of equipment and assembly was connected to the NH₃ synthesis unit. The remaining part of the investment cost was more or less equally spread between the fuel pre-treatment unit (12%), the syngas cleaning and conditioning (12%) and the ASU (10–11%).

The economic benefit of integrating the ammonia production compared to the stand-alone case showed to be small as the total production cost (shown in Table 4) was almost equal for both cases. This was mainly due to the significantly higher electricity cost in Case A. The production cost difference of 65 €/t NH₃ can be explained by the avoided costs for the investment in and operation of a new bark boiler.

A NH₃ selling price in the range of 581–882 €/t will be required for the stand-alone plant to receive an IRR between 10% and 20%. Case A consistently required a lower selling price (509–774 €/t of ammonia) for the same IRR. The difference was reduced when a lower return on the invested capital was assumed. The production cost (excluding the cost of capital) for both cases accounted for 34–54% of the ammonia selling price. A selling marginal in the range of 48–66% is therefore required to obtain an IRR of 10–20%. Calculat-

Table 2 Investment estimates for the major process units.

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<th>Cost reference [Ref.]</th>
<th>Size unit</th>
<th>Ref. size</th>
<th>Mt 2012</th>
<th>Scale factor</th>
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<td>Bark boiler [12]</td>
<td>MW₄₀</td>
<td>46</td>
<td>25</td>
<td>0.7</td>
</tr>
<tr>
<td>Pre-treatment [27]</td>
<td>Wet Ch</td>
<td>33.5</td>
<td>19</td>
<td>0.5</td>
</tr>
<tr>
<td>Air separation unit [27]</td>
<td>Ω₈0/day</td>
<td>1000</td>
<td>48</td>
<td>0.09</td>
</tr>
<tr>
<td>PSEG unit [28]</td>
<td>MW₄₀</td>
<td>0.22</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Gas cleaning [29]</td>
<td>Dry gas feed kg/s</td>
<td>37</td>
<td>43</td>
<td>0.7</td>
</tr>
<tr>
<td>Synthesis plant [30]</td>
<td>TPD NH₃</td>
<td>1800</td>
<td>123</td>
<td>0.7</td>
</tr>
<tr>
<td>Off-gas boiler [17]</td>
<td>MW₄₀</td>
<td>355</td>
<td>67</td>
<td>1.0</td>
</tr>
<tr>
<td>District heating HEX [17]</td>
<td>MW</td>
<td>355</td>
<td>67</td>
<td>1.0</td>
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</table>

* The reference cost is presented after the conversion to the 2012s price level. Additionally, the overall installation factor (I) is included in the reference capital investment.

Table 3 Financial parameters for the value year 2012.

<table>
<thead>
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<th>Financial parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Bank interest</td>
<td>8%</td>
</tr>
<tr>
<td>Equity share of investment</td>
<td>30%</td>
</tr>
<tr>
<td>Debt share of investment</td>
<td>70%</td>
</tr>
<tr>
<td>Return on equity</td>
<td>15%</td>
</tr>
<tr>
<td>Annuity factor</td>
<td>11.8%</td>
</tr>
<tr>
<td>Project economic lifetime</td>
<td>20 years</td>
</tr>
<tr>
<td>Annual operating hours</td>
<td>8000 h</td>
</tr>
<tr>
<td>Annual operating hours, district heating</td>
<td>5000 h</td>
</tr>
</tbody>
</table>

Table 4 Estimates for capital investment costs (Mt) and production costs (€/t per year).

<table>
<thead>
<tr>
<th>Financial parameter</th>
<th>BAU</th>
<th>S-A</th>
<th>Case A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment and assembly</td>
<td>25</td>
<td>100</td>
<td>289</td>
</tr>
<tr>
<td>Indirect costs</td>
<td>11</td>
<td>125</td>
<td>121</td>
</tr>
<tr>
<td>Total investment cost</td>
<td>36</td>
<td>425</td>
<td>410</td>
</tr>
<tr>
<td>Total incremental cost</td>
<td>425</td>
<td>374</td>
<td></td>
</tr>
<tr>
<td>Production costs in Mt per year¹</td>
<td>13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass¹</td>
<td>1.3</td>
<td>43.5</td>
<td>35.6</td>
</tr>
<tr>
<td>Power¹</td>
<td>7.8</td>
<td>19.7</td>
<td>30.2</td>
</tr>
<tr>
<td>O&amp;M²</td>
<td>1.6</td>
<td>17.8</td>
<td>17.4</td>
</tr>
<tr>
<td>Tall oil³</td>
<td>–10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>District heating⁴</td>
<td>–13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other costs</td>
<td>3.2</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Subtotal costs (incl. capital)</td>
<td>13.9</td>
<td>68.7</td>
<td>71.9</td>
</tr>
<tr>
<td>Annual capital costs</td>
<td>4.2</td>
<td>50.3</td>
<td>48.5</td>
</tr>
<tr>
<td>Total production cost</td>
<td>18.1</td>
<td>119.0</td>
<td>122.4</td>
</tr>
<tr>
<td>Incremental production cost</td>
<td>119.0</td>
<td>104.5</td>
<td></td>
</tr>
<tr>
<td>Production cost (€/t NH₃)</td>
<td>523</td>
<td>458</td>
<td></td>
</tr>
</tbody>
</table>

* A negative sign represents revenue.

¹ Includes: operations for chemicals, water treatment, insurance, licenses assumed to be 1% of the equipment and assembly. Maintenance, 3% of the equipment and assembly and worker salaries, 6 Mt for S-A and Case A.
² O&M for the NH₃ production was calculated to 188 GW h annually for the S-A case.
³ Ash handling costs was estimated to 57 €/t. In addition, cost for heavy fuel oil in BAU was included.

Fig. 4. Required selling price for ammonia for an IRR of 15% when the investment cost and biomass price is varied.
ing with the current average selling price of fossil NH₃ (514 €/ton, [20]) an IRR just above 10% was possible to achieve for the integrated system solution, while the stand-alone case reached an IRR of 7%.

This example, valid for a 15%-IRR, shows that a 30% higher capital cost would increase the required selling price to the same extent as a 95% increase of the biomass price for Case A and a 75% increase for case S-A would thus. The capital cost influences the economic profitability in a higher degree than the biomass price.

5. Conclusions

The main objective of this work was to perform a techno-economic evaluation of ammonia production via integrated biomass gasification in an existing pulp and paper mill. The results showed that the overall energy system efficiency was increased by 10%-units (calculated on an electricity equivalence basis) for the integrated system compared to the original operation of the mill in parallel with the operation of a stand-alone ammonia production plant. The economic assessment showed that a higher NH₃ selling price than the current market price was required for the concept to be economically feasible. The integrated case required a selling price in the range of 509–774 €/ton to receive an IRR between 10% and 20%. For the stand-alone production plant, an even higher selling price was required. For such IRR-levels, the selling marginal accounted for 48–66% of the NH₃ selling price. Approximately 45% of the total investment cost was directly connected to the investment of the NH₃ synthesis loop, indicating that the production capacities of the studied system configurations (228,000 t/y NH₃ plant) were too small to be viable. Larger production plant capacities would most probably be needed to reach economic feasibility at current NH₃ market price. Lower production costs or higher costs for fossil based alternatives would be required to make biomass-based NH₃ production economically viable.

Acknowledgements

The authors greatly acknowledge the financial contribution from the Nordic Top Research Initiative via the NORD-SYNGAS Project. The authors would also like to thank Bio4Energy, a strategic research environment appointed by the Swedish government, for supporting this work.

References

[17] Lundgren J, Danielsson R, Stenlund P, Vardund M. Economic assessment of ammonia production via integrated biomass gasification in an existing pulp and paper mill. The results showed that the overall energy system efficiency was increased by 10%-units (calculated on an electricity equivalence basis) for the integrated system compared to the original operation of the mill in parallel with the operation of a stand-alone ammonia production plant. The economic assessment showed that a higher NH₃ selling price than the current market price was required for the concept to be economically feasible. The integrated case required a selling price in the range of 509–774 €/ton to receive an IRR between 10% and 20%. For the stand-alone production plant, an even higher selling price was required. For such IRR-levels, the selling marginal accounted for 48–66% of the NH₃ selling price. Approximately 45% of the total investment cost was directly connected to the investment of the NH₃ synthesis loop, indicating that the production capacities of the studied system configurations (228,000 t/y NH₃ plant) were too small to be viable. Larger production plant capacities would most probably be needed to reach economic feasibility at current NH₃ market price. Lower production costs or higher costs for fossil based alternatives would be required to make biomass-based NH₃ production economically viable.

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Paper IV

Co-gasification of pyrolysis oil and black liquor for methanol production
Co-gasification of pyrolysis oil and black liquor for methanol production

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Keywords: Black liquor, Pyrolysis oil, Co-gasification, Methanol, Pulp mill

Abstract

One alternative to reduce the motor fuel production cost and improve the operational flexibility of a black liquor gasification (BLG) plant is to add pyrolysis oil to the black liquor feed and co-gasify the blend. The objective of this study was to investigate techno-economically the possibility to increase methanol production at a pulp mill via co-gasification of pyrolysis oil and black liquor. Gasifying a blend consisting of 50% pyrolysis oil and 50% black liquor on a wet mass basis increases the methanol production by more than 250%, compared to gasifying the available black liquor only. Co-gasification would add extra revenues per produced unit of methanol (IRR > 15%) compared to methanol from unblended BLG (IRR 13%) and be an attractive investment opportunity when the price for pyrolysis oil is less than 70 €/MW h. The economic evaluation was based on a first plant estimate with no investment credit for the recovery boiler and a methanol product value volumetric equivalent to conventional ethanol, both these conditions will not apply when the technology has been fully commercialized.

1. Introduction

Production of renewable motor fuels and chemicals is important in the development toward a more sustainable society where fossil fuels are replaced. To be able to compete with fossil resources, efficient production of biomass based products is necessary to maximize overall process economics and to minimize negative environmental impact. In order to obtain reasonable production costs, large biorefinery plants will likely be required to yield favorable economy-of-scale effects [29]. Integrating large scale biofuel production processes in existing forest industries provides large feedstock handling and logistical advantages [1]. Gasification of black liquor can for example be applied in chemical pulp mills and has been successfully demonstrated in a 3 MW pilot plant in Piteå in Sweden [8,19,37]. Compared to combustion of black liquor in a recovery boiler, black liquor gasification combined with motor fuel production show advantages regarding economic performance and energy efficiency. The available volume of black liquor is however limited and strongly connected to the pulp production, which limits the potential motor fuel production. Furthermore a high availability of the gasification plant is required to ensure that crucial cooking chemicals in the black liquor are returned to the pulp mill. One way to increase the production of motor fuel as well as the operational flexibility of the black liquor gasifier is to add biomass based pyrolysis oil to the black liquor feed and co-gasify the blend.

Pyrolysis oil can be produced from various types of biomass such as straw, wood and wood waste, through a variety of technologies. Pyrolysis of biomass yields primary char, permanent gases, and condensable vapors [28]. The vapors can be recovered as viscous liquids via condensation. A fast pyrolysis (rapid heating) process results in a product that mainly consists of liquid bio-olfs, i.e. pyrolysis oil [27,28]. Pyrolysis oil can be used in a number of applications, including co-firing with fossil fuels in power plants [5]. There is great interest in using pyrolysis technology for...
production of green chemicals and fuels [10,11]. One possible route is to gasify pyrolysis oil to a syngas that can be used as raw material for various petrochemical processes [10,11,21]. Research has shown that a high gasification temperature or a catalytic bed is required to produce a syngas with high quality [33,34]. Without a catalytic material, gasification of pyrolysis oil requires substantially higher temperatures compared to gasification of black liquor to obtain a similar gas quality and carbon conversion. This is at least partly due to the lack of catalytically active alkali metals in pyrolysis oil. Alkali metals are known to catalyze gasification reactions [15,16,32] and this is believed to be an important explanation of the very high carbon conversion obtained for gasification of black liquor at relatively low global temperature of approximately 1000°C. By blending pyrolysis oil with black liquor it is possible to obtain catalytic effects in the co-gasification process [2]. The energy content in biomass based pyrolysis oil is almost twice as high as the black liquor energy content. A fifty-fifty blend (by mass) would therefore roughly triple the energy input to the gasification plant. This would result in increased production volumes and the economy-of-scale effects in the downstream gas conditioning and synthesis which may lower the production cost.

Catalysis of pyrolysis and gasification reactions from sodium salts is known to increase the reactivity of black liquor and black liquor char substantially [22,30,36]. Recent experimental work with pyrolysis oil and black liquor blend shows the feasibility in the concept of co-gasification. It has been shown that mixtures containing up to 30 wt% pyrolysis oil and 70 wt% black liquor have a reactivity similar to pure black liquor [2]. This indicates that pyrolysis and black liquor blend can be co-gasified in a black liquor gasifier without major operational changes, e.g., using the same gasification temperature. Pilot scale pyrolysis oil/black liquor co-gasification experiments validate against experimental data from the pilot plant and co-gasification of black liquor and pyrolysis oil are very similar. They studied single droplet swelling, devolatilization rate and char gasification rate experimentally without finding any significant differences. This indicates that a similar catalytic effect from black liquor sodium content can be realized in the co-gasification process, although the alkali content of the mixed feedstock was lower. Hence, simulations of the co-gasification process were carried out using a thermodynamic model developed for BLG using the same process temperature (1000–1100 °C) but including the new mixed feedstock composition and heating value.

The thermodynamic simulation model uses thermodynamic data from Lindberg [21] for pure inorganic components and from Knacke et al. [18] for the remaining species. Based on flows of feedstock and required reactor temperature, the model calculates oxygen flow to the reactor and syngas composition. Empirical modifications, based on operating experience from the 3 MWth BLG pilot plant in Piteå Sweden [8,26,37], were used for CH4 and H2/S/COS concentrations in the gas, since these were not well described by thermodynamic equilibrium. The model has been validated against experimental data from the pilot plant and compared to CFD modelling of the process [7].

The gasification technology considered is the Chemrec pressurized oxygen-blown entrained flow black liquor gasification/gasifier (BLG) technology. The study of Bach Oller et al. [2] shows that the BLG process and co-gasification of black liquor and pyrolysis oil are very similar. They studied single droplet swelling, devolatilization rate and char gasification rate experimentally without finding any significant differences. This indicates that a similar catalytic effect from black liquor sodium content can be realized in the co-gasification process, although the alkali content of the mixed feedstock was lower. Hence, simulations of the co-gasification process were carried out using a thermodynamic model developed for BLG using the same process temperature (1000–1100 °C) but including the new mixed feedstock composition and heating value.

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### Table 1

<table>
<thead>
<tr>
<th>Black liquor</th>
<th>Pyrolysis oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry substance (DS) (wt%)</td>
<td>73.2%</td>
</tr>
<tr>
<td>LHV MJ/kg (dry)</td>
<td>12.13</td>
</tr>
<tr>
<td>C (kg/kg dry)</td>
<td>5.52%</td>
</tr>
<tr>
<td>H (kg/kg dry)</td>
<td>32.50%</td>
</tr>
<tr>
<td>O (kg/kg dry)</td>
<td>3.40%</td>
</tr>
<tr>
<td>N (kg/kg dry)</td>
<td>0.08%</td>
</tr>
<tr>
<td>Na (kg/kg dry)</td>
<td>0.21%</td>
</tr>
<tr>
<td>K (kg/kg dry)</td>
<td>2.18%</td>
</tr>
<tr>
<td>Cl (kg/kg dry)</td>
<td>35.96%</td>
</tr>
</tbody>
</table>

* Model composition for pulp mill using the Kraft pulping process.

**From BTG Biomass Technology Group BV [6].

---

**Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGR</td>
<td>acid gas removal</td>
</tr>
<tr>
<td>ASU</td>
<td>air separation unit</td>
</tr>
<tr>
<td>BFP</td>
<td>biofuel plant</td>
</tr>
<tr>
<td>BLG</td>
<td>black liquor gasification/gasifier</td>
</tr>
<tr>
<td>CGE</td>
<td>cold gas efficiency</td>
</tr>
<tr>
<td>EFC</td>
<td>Elemental Chlorine Free bleached pulp</td>
</tr>
<tr>
<td>HP</td>
<td>high pressure</td>
</tr>
<tr>
<td>IRR</td>
<td>internal rate of return</td>
</tr>
<tr>
<td>LP</td>
<td>low pressure</td>
</tr>
<tr>
<td>MLP</td>
<td>Mixed Integer Linear Programming</td>
</tr>
<tr>
<td>MP</td>
<td>medium pressure</td>
</tr>
<tr>
<td>UKP</td>
<td>Unbleached Kraft pulp</td>
</tr>
</tbody>
</table>

---

The main aim of this study was to investigate techno-economically the possibility to increase methanol production from black liquor gasification/gasifier (BLG) technology. The study of Bach Oller et al. [2] shows that the BLG process and co-gasification of black liquor and pyrolysis oil are very similar. They studied single droplet swelling, devolatilization rate and char gasification rate experimentally without finding any significant differences. This indicates that a similar catalytic effect from black liquor sodium content can be realized in the co-gasification process, although the alkali content of the mixed feedstock was lower. Hence, simulations of the co-gasification process were carried out using a thermodynamic model developed for BLG using the same process temperature (1000–1100 °C) but including the new mixed feedstock composition and heating value.
heating values and chemical compositions of black liquor and pyrolysis oil used in the modeling. The same total mass flow of black liquor, corresponding to the full pulp mill production, was used in all cases but the number of gasification units (BLG:s) in parallel were determined on the pyrolysis oil addition, due to the limited gasifier size (see Section 2.4).

2.2. Biofuels plant modeling

The material and energy flows in the integrated biofuel plant (BFP) were represented by a model using Mixed Integer Linear Programming (MILP) through the Java-based software tool reMIND [17]. The model is structured by a network of nodes and branches, as schematically illustrated in Fig. 1. Each node contains linear equations to express the material and energy balances of each steam and power consuming/generating unit (e.g. BLG, methanol synthesis, boiler, etc.) in the BFP. The branches connect the units by representing the internal network of material and energy flows. The same setup of downstream syngas units were considered in all cases, but with operational changes and adjustments for the different feedstocks. The MILP methodology was used to apply a more global approach by also including the whole pulp mill within the system boundaries, see Fig. 1. The modeling strategy guarantees an unaffected pulp production when the BFP is integrated, done by ensuring that sufficient amount of steam was available for the pulp making by adjusting the biomass supply to the boiler (see Fig. 1).

From the BLG simulation (see Section 2.1), the resulting syngas composition, mass flow, specific oxygen consumption and steam generation from the gas-cooling unit were linearized as a function of the blend ratio. The syngas composition and the mass flow were used to model the processes downstream the BLG:s and eventually the methanol yield. Utility requirements for the water gas shift (WGS) reactor and the acid gas removal (AGR) units were scaled according to the syngas flow and the flow of gas species required to be removed, respectively. The methanol flow was used for the other units. The power and steam flows of each BFP unit, expect for the BLG:s, were scaled (i.e. linearized) and validated according to the performance of a reference black liquor gasification based BFP that produces 100 MW methanol [9]. The pulp mill’s power and steam balances were represented by equations based on historical mill process data and equipment supplier balances valid for the increased pulp production capacity (see Table 2). The available falling bark at the pulp mill prior the integration with the biorefinery was exported with a moisture content of 65%. After the integration, purchased biomass was co-fired with the dried bark.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Important key energy data for the pulp mill representing a yearly average production with a recovery boiler.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor</td>
<td>1500 ton DS/d</td>
</tr>
<tr>
<td>– LHV (on dry basis)</td>
<td>210 MW</td>
</tr>
<tr>
<td>– SF-LHV (on dry basis)</td>
<td>180 MW</td>
</tr>
<tr>
<td>Mill power demand</td>
<td>28 MW</td>
</tr>
<tr>
<td>Steam turbine power production</td>
<td>22 MW</td>
</tr>
<tr>
<td>Lime kiln fuel</td>
<td>18 MW</td>
</tr>
<tr>
<td>Bark available for export (65% DS)</td>
<td>29 MW</td>
</tr>
</tbody>
</table>

* The energy content of the falling bark is based on 35% moisture content. The actual moisture content before drying is 65%.

![Fig. 1. MILP model design of the material and energy flows in the integrated BFP including the pulp mill within the system boundary (dashed box). ‘AGE’ = acid gas enrichment and WLA = white liquor adsorption.](image-url)
failing bark (moisture content 35%) to maintain the steam balance. Heat for drying the bark was accounted for in the material and energy balance.

Integration of a BLG plant is associated with an increased lime kiln fuel demand due to somewhat different green liquor composition, which was accounted for in the analysis. According to Ekbom et al. [12], the changed composition of the green liquor can be compensated for by increasing the causticization by 25%, i.e. increasing the lime kiln fuel demand. The purge gas (off-gases) from the synthesis loop in the BFP is a valuable fuel that can be used as supplement to the lime kiln fuel. The lime kiln fuel import demand can therefore potentially be lower after the integration depending on the amount of available purge gas from the BFP.

2.3. System evaluation and economics

The Rottneros Vallvik mill produces two pulp products, ECF (Elemental Chlorine Free bleached pulp) and UOP (Unbleached Kraft pulp). During the UKP production the flow rate and energy content of the black liquor is lower than for the ECF. On a yearly basis the black liquor energy content is roughly reduced by 3% compared to a maximum continuous ECF production. The operation of the mill is therefore affected by the UKP production; these changes were however not explicitly addressed in the evaluation. The plant operation was tuned to match the yearly operation average of the Rottneros Vallvik mill during 348 days with a 90% availability compensated for lower black liquor energy content during the UKP production. This corresponds to a black liquor availability of 180 MW sulfur free heating value (SF-LHV) or 1500 tDS/h during 7517 t. The same overall capacity utilization for the BFP plant (90% of scheduled operation time) was used for all cases.

The overall system efficiency was calculated by using the pulp mill including the BFP as system boundaries, according to the dashed box in Fig. 1. The production of pyrolysis oil was assumed to be delivered to the gate (i.e. not an integrated production unit(s) within the mill). However, the effect on the system efficiency was also investigated when the losses in pyrolysis oil production were included, by accounting a biomass to oil system efficiency in the range of 67–90% [25]. The overall system efficiencies for all cases were calculated based on the marginal energy supply compared to the pulp mill with an upgraded recovery boiler including the BFP plant as system boundaries, according to the UKP production. This corresponds to a black liquor availability of 180 MW sulfur free heating value (SF-LHV) or 1500 tDS/h during 7517 t. The same overall capacity utilization for the BFP plant (90% of scheduled operation time) was used for all cases.

The incremental investment cost was calculated for all gasification units. The investment costs for the other units were determined according the following relation:

\[
C = C_{ref} \left( \frac{S}{S_{ref}} \right)^{0.65}
\]

C and S refer to the investment cost and the scaling size of each unit, respectively. The subscript (ref) denotes the investment cost and size of the reference units. Cost information was supplied by Chemrec AB [9], for a 100 MW methanol BLG plant. The used scale parameters for the different units are listed in Table 4.

In Table 4, cost and selling price for the different commodities and products are listed for a base cost scenario. The methanol selling price was used for determining the internal rate of return (IRR) in a cash flow analysis. The methanol product value used (see Table 5) in the calculations was based on a volumetric equivalence to ethanol. A volumetric valuation was considered relevant for a recovery boiler and methanol production via the gasification alternatives. The investment costs for the BFP pathways were scaled using a 0.65 scaling exponent for all units, except for the gasification units. The gasification unit of the BFP plant uses a multi-train arrangement. The maximum capacity for each individual gasifier was based on what was commercially offered by Chemrec for black liquor gasification (approximately 70 MWth feed). It should be noted that the Chemrec technology is in its commercialization phase and the assumed gasifier capacity is based on scale up design work from the pilot plant currently in operation to the size selected for the first commercial size plant. Entrained flow gasifiers operated on coal and oil are today considerably larger, 500–1000 MWth, and therefore the duplication of trains in the 70 MWth size is a very conservative approach when calculating the large scale up covered by this paper. The capacity 70 MWth was determined by a combination of gas residence time and inorganic smelt load on critical components [9]. Due to the lower inorganic content of black liquor/pyrolysis oil mixtures it was assumed that the capacity can increase by 20% compared to operation on pure black liquor with the same unit cost. This means that the maximum capacity used for each gasifier train was 85 MWth feed. The investment costs for the other units were determined according to the following relation:

\[
C = C_{ref} \left( \frac{S}{S_{ref}} \right)^{0.65}
\]

Table 4: Scale parameters used for investment cost calculation in Eq. 1.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Scale parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sour shift (WS)</td>
<td>Dry gas flow</td>
</tr>
<tr>
<td>Acid gas removal (AGR)</td>
<td>CO₂ flow</td>
</tr>
<tr>
<td>MeOH synthesis and distillation</td>
<td>MeOH flow</td>
</tr>
<tr>
<td>MeOH hydrogenation (MHC)</td>
<td>Same for all</td>
</tr>
<tr>
<td>White liquor adsorption (WLA)</td>
<td>Same for all</td>
</tr>
<tr>
<td>MeOH synthesis and distillation</td>
<td>Same for all</td>
</tr>
<tr>
<td>Balance of the plants</td>
<td>MeOH flow</td>
</tr>
<tr>
<td>Air flow</td>
<td>Same for all</td>
</tr>
<tr>
<td>Fire stack with safety zone</td>
<td>MeOH flow</td>
</tr>
</tbody>
</table>

Table 5: Feedstock costs and product prices [9].

<table>
<thead>
<tr>
<th>Commodities and products</th>
<th>Comment</th>
<th>Cost</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass fuel cost</td>
<td>2.94 MW h/ton (40% moisture)</td>
<td>28 €/MW h</td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>57 €/MW h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrolysis oil cost</td>
<td>4.27 MW h/ton (25% moisture)</td>
<td>70 €/MW h</td>
<td></td>
</tr>
<tr>
<td>Oxygen cost</td>
<td>69 €/ton</td>
<td>46 €/MW h</td>
<td></td>
</tr>
<tr>
<td>Lime kiln fuel</td>
<td>148 €/MW h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
first plant estimate as the methanol was assumed to be used as a gasoline blend component on the Swedish market according 3% by volume methanol addition allowed by the EU gasoline standard (by CEN) EN 228 and gasoline is sold on a volume basis. An ethanol price of 645 €/m³ was used, which is based on the 2013-H1 average ($\text{€}$ Rotterdam T2 Feb). Due to the novelty of the technology, the analysis considers a three year construction time and a conservative ramp up compared to corresponding data for a commercially mature technology. During the first production year it was assumed that only 60% of the maximum methanol production capacity was achieved. The second year and third year, were assumed to give 80% and 95% of the nominal capacity respectively. Full production was not reached until the fourth year. The lowest production cost for pyrolysis oil were found in Mark et al. [24] and Braimakis et al. [4], where pyrolysis oil was reported to be produced at a cost around $35 \text{€}/\text{MW} \cdot \text{h}$ in a large scale production facility (roughly 2000 t/d). A single facility with this capacity was not yet commercially available and the production cost could instead be used as an indication of the potential cost for pyrolysis oil production in the future. Furthermore, these pyrolysis oil prices were based on a 13–15 €/MWh biomass price range. Braimakis et al. [4] also estimated that the pyrolysis oil cost would increase with $5–10 \text{€}/\text{MW} \cdot \text{h}$ if the production capacity was reduced four times (i.e. roughly 500 t/d). According to Benjaminsson et al. [3], a 30 MW pyrolysis oil plant integrated in combined heat and power plants can produce pyrolysis oil at a cost in the range of 50–66 €/MWh. The corresponding range for 60 MW oil production integrated in pulp mills was 43–48 €/MWh. The production cost was valid for wood-chips with a 62% biomass-to-oil thermal efficiency, on a wet LHV basis. Benjaminsson et al. [3], also estimated that a 15 MW decentralised stand-alone pyrolysis oil plant can produce pyrolysis oil at a cost of 62 €/MWh. Pyrolysis of forest residues may yield a lower efficiency, around 50%. This increases the production cost to 77 €/MWh. [3]. The reported pyrolysis oil price range (43–77) in Benjaminsson et al. [3] was based on a 23 €/MWh biomass price. Benjaminsson et al. [3] also assess the transportation cost for pyrolysis oil to be 2.3 €/MWh in a 100 km radius with trucks or a 500 km radius with trains.

A reasonable average pyrolysis oil price was therefore assessed to be around 70 €/MWh for first generation production, including the cost for transportation and a 20% profit margin. This was based on the above reported production costs for different smaller production alternatives for pyrolysis oil (integrated and stand-alone) and different types and qualities of biomass feedstocks used for the production. A sensitivity analysis was also carried out to view the influence on the BFP from a 35-55 €/MWh variation of the pyrolysis oil price and a ±20% variation of the methanol selling price. This translates to methanol selling price range of 118–178 €/MWh. Please note that the lowest methanol price (118 €/MWh) was just slightly higher than a selling price for a methanol equivalent on an energy basis to the current selling price of ethanol (645 €/m³). It should also be noted that a pyrolysis oil price down to 35 €/MWh is not expected to be obtained in a near future or at least not with biomass prices over 20 €/MWh. Furthermore, the 70 €/MWh pyrolysis oil price used a base for the economic evaluation was viewed as generous and the price range above this value was significantly higher than projected future commercial scale production costs for pyrolysis oil from lingo-cellulosic raw materials.

2.4. Description of the case study

Today the Rottneros Vallvik Kraft pulp mill has plans to increase the pulp production capacity. To raise the pulp production, debottlenecking investments are required in the recovery boiler, the causticizing/lime kiln, pulp dryer and steam turbine. Investments in upgrading the capacity of the evaporation and auxiliary systems have already been made. The single largest investment for increasing the capacity of the mill, would be to rebuild the recovery boiler to support the higher pulp capacity (estimated to 35 MW). This investment would be avoided in all methanol production cases, because the gasification units replace the recovery boiler. Another 11 MW in mill upgrading investments were also avoided for the BFP pathways, since they were to be replaced by other investments included in the BFP scope.

Three methanol production levels were considered (i) Case BLG, a reference methanol production level, where only the available black liquor (2049 ton/d) was gasified for methanol production, (ii) Case 25, a medium methanol production capacity, where a blend of 25% pyrolysis oil (683 ton/d) and 75% black liquor (2049 ton/d) of the total wet feedstock mass flow was gasified and (iii) Case 50, where a fifty-fifty blend of pyrolysis oil (2049 ton/d) and black liquor (2049 ton/d) was gasified for a high methanol production level.

A BLP plant is normally designed with a redundant gasifier train to ensure the high availability required to support the mill with black liquor processing capacity. For the BLP reference case this requires a 4 × 33% design of the gasification unit capacity. When a second feedstock was introduced by mixing pyrolysis oil with the black liquor from the pulp mill, improved operational flexibility was obtained for the BLP plant. The redundant gasifier was no longer essential to ensure black liquor processing capacity, since the full black liquor flow can be processed even with one gasifier train shut-down for maintenance by decreasing the fraction of pyrolysis oil feed. Based on the mass and energy flows and previously mentioned crucial design parameters (Section 2.2), this corresponds to gasification unit trains with capacities of 4 ± 25% and 7 ± 14% in Case 25 and Case 50, respectively. The removal of the redundant gasifier will lead to temporarily lower capacity when gasifier maintenance is carried out but this can be compensated by the higher capacity utilization obtained by mixing a larger fraction of pyrolysis oil into black liquor when the pulp mill is running at reduced capacity. Note that, for the co-gasification cases (Case 25 and 50) it would be possible and probably wise to compensate for the lower black liquor energy content during the UKP production by increasing the consumption of pyrolysis oil so that the full capacity of the downstream units can be used, although this has not been considered in this study.

3. Results and discussion

Blending biomass based pyrolysis oil with a fixed amount of black liquor increases the total energy input considerably, due to the increased total feedstock flow and the higher heating value of the pyrolysis oil. Gasifying a 50/50 blend more than triples the sulfur-free heat input to the gasifier for a given black liquor flow. The simulations show that the cold gas efficiency (CGE) increases with the proportion of pyrolysis oil added to the blend, as shown in Fig. 2. CGE increases from almost 70% to 80% when going from pure back liquor to a blend with 50% pyrolysis oil. The incremental efficiency of the added pyrolysis oil, using black liquor gasification as a reference, was 80–85%. This high number was due to the lower temperature enabled by the catalytic effect from the black liquor sodium.

The reason for the higher efficiency compared to unblended black liquor gasification was primarily that the inorganic content of the gasification feedstock decreases significantly, which decreases the thermal ballast of the system. SF-LHV was used for presentation of the CGE results since the sulfur in the black liquor was returned in reduced form to the mill (as sodium sulfide in
green liquor). Hence, the heating value of the sulfur species was not useful. It should be noted that increased CGE was associated with a decreased low pressure (LP) steam production from the gas cooling unit from approximately 0.28 to 0.20 ton steam/MWth feed.

Changed synthesis gas composition and decreased specific oxygen consumption were associated with the higher efficiency obtained at higher pyrolysis oil fraction in the blends. The oxygen consumption decreases from 49 to 31 kg O₂/kg LHV synthesis gas when changing from pure black liquor feedstock to a 50/50 blend. A higher CGE leads to that the carbon dioxide content in the synthesis gas from the gasification unit decreases from 28 mol% to 18 mol% while the CO concentration increases from 30 mol% to 42 mol%, see Fig. 3. The hydrogen concentration changes only marginally. More medium pressure (MP) steam per ton of syngas was therefore required to shift the syngas to the desired H₂:CO-ratio suitable for methanol synthesis for the co-gasification cases. In all cases, the BFP has a deficit of MP steam while a surplus of LP steam. The mill was therefore required to supply MP steam to the BFP while surplus LP steam was returned to the pulp making processes. A higher CGE reduces the potential heat recovery per ton of syngas generated. The amount of LP steam delivered to the mill was reduced to half, per ton of methanol, for Case 50 compared to Case BLG but in absolute numbers there was an increased flow of LP steam to the pulp mill.

The utility requirement for an Acid Gas Removal (AGR) unit is primary steam and power. The demand was mainly controlled by the quantities of gas species that were required to be removed (mainly CO₂ and to some extend H₂S and COS). As seen in Fig. 3, after the shift process the carbon dioxide content in the syngas was declining with increasing pyrolysis oil content in the blend. Less steam and power were therefore required in the AGR per ton of syngas for higher blend ratios. This partly compensates for the increased MP steam use in the WGS. The fifty-fifty blend requires 20% higher MP steam import from the mill per ton of methanol compared to Case BLG.

The co-gasification routes seem to be advantageous with respect to energy efficiency compared to an unblended black liquor gasification route. The incremental methanol production capacity for Case 25 and Case 50 yields an overall system efficiency of 71% (calculated as electrical equivalents) which was 4%-units higher than for Case BLG. This was because, as seen in Fig. 4, gasifying a 25/75 blend (Case 25) would almost double the methanol production and a fifty-fifty blend (Case 50) increases the methanol production capacity more than 250% compared to Case BLG. For increasing blend ratios the total amount of high pressure steam generated in the boiler was reduced, since a larger share of the LP steam demand of the mill was delivered from the BFP. Thereby the import of external biomass can be reduced. However, a decreased production of HP (high pressure) steam, in
combination with an increased extraction of MP from the turbine to satisfy the BFP's steam demand, decreases the power production. However, the required power import was, calculated per ton of methanol, declining for increasing pyrolysis oil to black liquor blend ratios. Furthermore, the import demand of lime kiln fuel was also reduced in the co-gasification cases. The reduced demand of lime kiln fuel was accounted for as an export in the system efficiency calculations. In the original operation of the mill 29 MW of bark was available for export. However, for the gasification cases the bark was used internally in all cases, and as seen in Fig. 4, this was accounted for on the import-side. For the entire methanol production volumes in Case 25 and Case 50, the average system efficiencies were 1%-unit and 2%-units higher compared to the Case BLG (see Fig. 5). The energy balances for all cases include required operational changes in the pulp mill due to the integration of the gasification plant. If also the losses during pyrolysis of the biomass to pyrolysis oil were accounted for in the overall system efficiencies, Case BLG will receive the highest overall system efficiency (Fig. 5). However, when pyrolysis oil was produced with an efficiency of 90% the co-gasification cases yielded system efficiencies only around 1%-unit lower than Case BLG.

When the BLG to motor fuels concept was invented and patented in 2001, e.g. US Patent 7,294,225 [20], the concept was to be implemented when a mill needed to substitute the recovery boiler due to end of service life. The patent proposes that this is done utilizing BLG rather than a new recovery boiler. In the last couple of years Chemrec has worked on the implementation of the first full sized installation of a gasification based concept. One of the sites for this has been the Vallvik mill. These first of its kind replacement of recovery boiler technology is characterized by that there is no credit for the avoided recovery boiler re-investment due to that the recovery boiler is used as redundant recovery capacity during the BLG start-up phase. The credit to the investment for the avoided investment would be in the order of 150–200 M€ [12], which of course will change the economics presented in this paper dramatically.

This work thus uses a first plant investment cost estimate and does not consider an investment credit for a full recovery replacement, which results in a comparably high methanol production cost. The investment cost for the gasification unit is expected to decrease as experience gathers and gasifier trains increases in capacity.

The total investment cost together with the production is presented in Table 6. Only aggregated investment cost was shown due to commercial confidentiality. For Case 25, the investment cost for the incremental production capacity was 945 k€/MWMeOH. The
The total investment in Case 50 (€39 M) yields the highest IRR and seems to be the better investment opportunity when the cost for pyrolysis oil was below 75 €/MW h for a 148 €/MW h methanol selling price. The added-values from co-gasification in Case 50 start to diminish when the cost for pyrolysis oil exceeds 75 €/MW h (Fig. 6) compared to Case BLG. Case 25 was less sensitive to the pyrolysis oil cost and would return a better IRR than Case BLG for a pyrolysis oil cost up to 80 €/MW h. In fact, with Case BLG as reference, the incremental 85 MW of methanol produced in Case 25 consistently yields a higher IRR, irrespective of the cost of pyrolysis oil and methanol selling price, compared to the incremental methanol volumes in Case 50. This was because the reference production level yields a constant IRR and the contribution to the attained IRR for incremental production in Case 50 contributes more to the average IRR (Fig. 6) than Case 25. For the low methanol selling price only Case 50 would be a good investment (i.e. IRR above 15%) and this demands a pyrolysis oil prices around or below 40 €/MW h. Higher pyrolysis oil prices would make all case unprofitable and even return negative IRR results, see Fig. 6. However, this methanol selling price was equivalent to the selling price of conventional first-generation ethanol on an energy basis. It would be more relevant to have an energy equivalent selling price between second-generation ethanol and methanol, when second-generation ethanol (i.e. lignocellulosic biomass-based ethanol) is available on the market. The selling price of second-generation ethanol will therefore be dependent on the biomass price and could be expected to be higher than in this level.

For the high methanol selling price (178 €/MW h), Case 50 yields the highest IRR and seems to be the better investment opportunity when the cost for pyrolysis oil was below 80 €/MW h. The added-values from co-gasification in Case 50 start to diminish when the cost for pyrolysis oil exceeds 80 €/MW h (Fig. 6) compared to Case BLG. Case 25 was less sensitive to the pyrolysis oil cost and would return a better IRR than Case BLG (IRR 18%) for a pyrolysis oil cost up to 95 €/MW h.

4. Conclusions

By adding pyrolysis oil to the black liquor feed and co-gasifying the blend, the production volumes of methanol increased up to

![Fig. 6. IRR for the incremental investment compared to an upgraded recovery boiler dependent on pyrolysis oil (PO) price and methanol selling price. The methanol is assumed to be tax exempted.](image)
The potential techno-economic improvements gained from blending pyrolysis oil with black liquor are strongly connected to the blend ratio, the pyrolysis oil price, and future techno-economic studies that consider more blend ratios are required in order to gain a better knowledge of the optimal pyrolysis oil addition dependent on different pyrolysis oil price scenarios. A fifty-fifty blend was assumed to be the technical limit for a blend that still could achieve the required catalytic effects. More experimental work is required to further verify the concept of co-gasification and target the optimal (technical) oil addition. Laboratory scale and pilot plant experiments are planned to further confirm the technical feasibility and quantify the performance of the co-gasification technology. The economics of the concept would become considerably improved if the investments took into account relevant plant economics and that the gasifier trains will be larger and thus fewer for a given amount of black liquor and pyrolysis oil feedstock.

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References


25% of the incremental methanol volumes produced from the added pyrolysis oil yields 45% points higher system efficiency (calculated as electrical equivalents) than the methanol produced from the available black liquor (67%). According to published data, first generation pyrolysis oil can be bought to a cost around 70 €/MWh. Co-gasifying 28 ton/h respectively 85 ton/h of pyrolysis oil with black liquor (85 ton/h) would thereof increase the IRR with roughly 2%-units in comparison to methanol produced via available black liquor (IRR 13%).

5. Future work

Laboratory scale and pilot plant experiments are planned to further confirm the technical feasibility and quantify the performance of the co-gasification technology. The economics of the concept would become considerably improved if the investments took into account relevant plant economics and that the gasifier trains will be larger and thus fewer for a given amount of black liquor and pyrolysis oil feedstock.

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References

Paper V

Co-gasification of black liquor and pyrolysis oil: Evaluation of blend ratios and methanol production capacities
Co-gasification of black liquor and pyrolysis oil: Evaluation of blend ratios and methanol production capacities

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**A B S T R A C T**

The main aim of this study is to investigate integrated methanol production via co-gasification of black liquor (BL) and pyrolysis oil (PO), at Swedish pulp mills. The objectives are to evaluate technoeconomically different blends ratios for different pulp mill capacities. Furthermore, the future methanol production potential in Sweden and overall system consequences of large-scale implementation of PO/BL co-gasification are also assessed.

It is concluded that gasification of pure BL and PO/BL blends up to 50% results in significantly lower production costs than what can be achieved by gasification of unblended PO. Co-gasification with 20–50% oil addition would be the most advantageous solution based on IRR for integrated biofuel plants in small pulp mills (200 kADt/y), whilst pure black liquor gasification (BLG) will be the most advantageous alternative for larger pulp mills. For pulp mill sizes between 300 and 600 kADt/y, it is also concluded that a feasible methanol production can be achieved at a methanol market price below 100\(\text{€}/\text{MW h}\), for production capacities ranging between 0.9 and 1.6 TW h/y for pure BLG, and between 1.2 and 6.5 TW h/y for PO/BL co-gasification. This study also shows that by introducing PO/BL co-gasification, fewer pulp mills would need to be converted to biofuel plants than with pure BLG, to meet a certain biofuel demand for a region. Due to the technical as well as organizational complexity of the integration this may prove beneficial, and could also potentially lower the total investment requirement to meet the total biofuel demand in the system. The main conclusion is that PO/BL co-gasification is a technically and economically attractive production route for production biomethanol.

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1. Introduction

A review of new concepts of biomass gasification concluded that biomass gasification is a key technology that offers high flexibility and efficiency, but also that new knowledge and more efficient and cost-competitive industrial applications are required [1]. The production costs of final products via gasification are strongly dependent on the capacity of the production plants and large capacities are required to obtain beneficial economies-of-scales. Large capacities also increase the required feedstock supply area and put significant demands on the supply chain. Pre-treatment of the feedstock by pyrolysis or torrefaction prior to transportation could potentially improve the economies of the complete biomass logistics chain (i.e. transportation, storage and handling) [2–5].

Heidenreich and Foscolo [1] addressed two different ways to combine gasification and pyrolysis. In the first approach, pyrolysis and gasification are combined directly in a two or three stage gasification process. In the second approach, the pyrolysis and gasification are carried out at different geographical locations. In this concept, pyrolysis is used to concentrate biomass into an oil-char slurry at decentralized small pyrolysis plants for transport of the intermediary products to a centralized large gasification plant. An example of the latter is the bioliq process developed by the Karlsruhe Institute of Technology (KIT) in which low-grade lignocellulosic biomasses, such as straw or forest residues, are utilised [6,7].

Bach-Oller et al. [11], have shown that the BLG process and gasification is a key technology that offers high flexibility and efficiency, but also that new knowledge and more efficient and cost-competitive industrial applications are required [1]. The production costs of final products via gasification are strongly dependent on the capacity of the production plants and large capacities are required to obtain beneficial economies-of-scales. Large capacities also increase the required feedstock supply area and put significant demands on the supply chain. Pre-treatment of the feedstock by pyrolysis or torrefaction prior to transportation could potentially improve the economies of the complete biomass logistics chain (i.e. transportation, storage and handling) [2–5].

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A third innovative approach, not addressed in [1], is catalytic co-gasification of a blend of pyrolysis oil (PO) and black liquor (BL). Black liquor gasification (BLG) is a technology which is well proven in pilot scale, with an accumulated operating time exceeding 25,000 h (of which more than 8000 h with downstream biofuel production) in a 3 MW\(_\text{e}\) pilot plant located in Piteå, Sweden [8–10]. The catalytic effect of the alkali metals in the BL (originating in the spent pulping chemicals) allows for a high carbon conversion at lower global temperatures (~1000 °C). Bach-Oller et al. [11] have shown that the BLG process and...
The operation of the Swedish Rottneros Vallvik mill was selected as a basis to represent a generic mill. The Vallvik mill produces flash-fired bleached and unbleached kraft pulp, and represents a small to medium sized Swedish pulp mill. Pulp mill steam consumption depends on a number of factors, but in general the specific steam consumption could be expected to decrease with increasing production capacity. Here, however, a conservative approach is applied. Based on the current operation of 200 kAdt/y (air dried ton pulp), linear extrapolation is thus used to model five pulp mill sizes in the range from 200 to 600 kAdt/y. Key operation data of the pulp mill is summarised in Table 1.

A fifty-fifty PO/BL blend ratio on mass basis is considered as the maximum addition, where the alkali content in the blending can still provide sufficient catalytic effects based on experience of pilot plant sulphite thick liquor gasification [15,16]. Six different co-gasification cases for PO addition are therefore considered, in the range of 10–50% (Cases 10–50) of the available volume of BL on a wet mass basis, corresponding to 2630 kg (73.2% dry matter) BL per ADt. This corresponds to a PO addition in the range of 1250–11,250 kW h/ADt on energy basis to the available BL (5548 kW h/ADt). The considered PO has an LHV of 5.92 MW h/ton dry matter and a density of 1170 kg/m³. The BL density is 1400 kg/m³ at the gasifier feed temperature of 140 °C.

The co-gasification cases are compared to three alternative system configurations for methanol production: (i) Case 0, via gasification of the available BL only, (ii) Case 100, via gasification of pure PO in a stand-alone gasification plant, with a PO supply corresponding to the PO input of a fifty–fifty PO/BL blend (i.e., 11,250 kW h/ADt), and (iii) Case REF, which is a combination of Case 0 and Case 100 to quantify potential technical and economic added-values with co-gasification compared to the unblended alternatives.

2.1.1. Gasification plant modelling

The simulations of the gasification process were carried out using a thermodynamic model (SIMGAS) developed for simulating gasification of BL [11]. SIMGAS is implemented in the Matlab platform and is based on system Gibbs energy minimization under the assumption of ideal mixtures but with empirical modifications for CH₄ and H₂S formation as presented in [17]. The tool uses an active-set method to solve the constrained non-linear minimization problem with the chemical composition of gas and smelt phases as independent variables. The model is configured to represent realistic gasifier sizes and heat losses for a commercial implementation of a BLG and a BL/PO co-gasification process. In the simulation, the reactor temperature is fixed at 1000 °C for both BLG and the co-gasification process based on similar reactivity [11]. The specific oxygen consumption is calculated by solving the reactor energy balance at this temperature. Further simulations and model assumptions for Cases 0–50 are described in detail in [14,17].

Due to the absence of catalytic alkali content and a different reactor design, pure PO gasification is simulated using other assumptions regarding reactor temperature and heat losses. An estimated reactor temperature of 1300 °C is used for pure PO gasification, based on information about the Karslohe Institute of Technology biolig plant published before plant start-up [6,7], which also agrees with the pilot scale experiment carried out at the SP Energy Technology Center, in Piteå Sweden [18]. The biolig...
The integrated and the stand-alone configurations are modelled using Mixed Integer Linear Programming (MILP) through the Java-based software tool reMIND [20]. The performance and the utility requirement for the downstream units for all cases are scaled and validated according to a reference BLG plant that produces 100 MW methanol [21] and adjusted to the operation of the gasifier for the different blends (i.e. 0–100% PO).

The pulp mill’s power and steam balance are represented by a linear model as described above. In order to be able to meet the steam demand of the mill for the integrated gasification cases, the old recovery boiler is assumed to be converted to be able to combust solid biomass fuels. The primary modelling constraint for the integrated cases is to ensure that a sufficient amount of steam (low and medium pressure) is available for the pulp making, which is done by adjusting the biomass (forest residues) supply to the boiler. In Case 100, an off-gas boiler is used to generate steam to satisfy the internal demand of the gasification plant. No power generation is therefore considered in Case 100. The boiler is fuelled with the purged off-gases from the methanol synthesis loop. In the integrated cases, surplus off-gases are instead assumed to be used as a supply to the pulp mill to lower the import demand of lime kiln fuel. Further details regarding the scaling parameters, modelling approach and how the mill is affected by an integrated BL/PO gasification plant, can be found in [14].

Fig. 1 shows a schematic view of the different gasification plant configurations (Cases 0–100) including the pulp mill. All cases consider an external oxygen supply, i.e. oxygen is “bought over the fence”.

2.1.2. Process configuration

Gasification of pure BL, as well as co-gasification of PO/BL blends, uses a multi-train arrangement where the maximum capacity of each individual gasifier is assumed to be 200 MWth based on estimates for mature technology [21]. The individual reactors are sized between 70 and 200 MWth, depending on case and pulp mill size. A redundant gasification unit is required for Cases 0–10, to ensure that the spent cooking chemicals can be recovered also with one reactor down for maintenance. For the higher blend cases, the reactors are sized to be able to gasify the entire BL volume with one reactor down for maintenance and temporary reduced or removed addition of PO. The capacity of the reactors is for some cases therefore slightly increased, i.e. a small redundant capacity is required. For the configuration where only PO is gasified (Case 100), a 300 MWth is assumed to be the maximum for one gasification unit.

The BLG technology is currently in its commercialization phase and the gasifier capacities considered here (70–200 MWth) are based on a reasonable scale-up potential for one unit in a near future. The potential for a larger reactor size for a pure PO reactor is due to its high resemblance in operation to current coal and oil entrained flow gasifiers, which are today operated with 500–1000 MWth loads.

2.2. System efficiency assessment

The overall system efficiencies for all cases are calculated based on the marginal energy supply compared to operation of the pulp mill with a recovery boiler, including the utility requirements (power) for the air separation unit (ASU). Electrical equivalents are used as a measure of the overall system efficiency. The energy carriers (methanol, biomass, etc.) are converted to their electricity equivalents according to the efficiency (η) of the best-available technologies known to the authors. The efficiencies are shown in Table 2. Biomass used directly for the pulp making is not included in the calculation of the overall energy system efficiencies. The system boundary used is illustrated by the (large) dashed box in Fig. 1.

PO and oxygen are assumed to be delivered to the gate and over-the-fence respectively, but the energy requirements for producing PO and oxygen are included in the overall system efficiency evaluation to apply a more global approach. The material and energy streams flowing across the system boundaries (Fig. 1) are thus only the listed energy carriers in Table 2 and power. The system efficiency is evaluated excluding as well as including losses in the PO production. The former is done by converting delivered PO to power by the efficiency value (50%) in Table 2, whilst the latter is accounted for by a PO production system efficiency range in between 67% and 90% [23]. The lower efficiency value represents
Plant Cost Index (CEPCI). A new recovery boiler (250 M investment costs for each unit in the gasification plant cannot be used to scale the avoided investment cost associated with integration of the BLG concept instead.

PO production in a decentralized stand-alone facility where the surplus heat is unused. The higher efficiency represents a PO production process fully integrated with a CHP plant, which is connected to a district heating network (>100 MW heat). The PO production efficiency range is expressed using electricity equivalents. The power requirements for an ASU is set to 1.65 MJ/kg O\textsubscript{2} [24].

2.3. Economic assessment

The economic evaluation considers 2014 price levels and nth-plant estimates where the BLG as well as the PO production technologies are assumed to be commercialized and relatively mature. The investment cost for an individual reactor is therefore assumed to be 20% lower than today. All other technologies are commercially available today and are therefore assumed not to be subject to any price developments.

The purpose behind the patented BLG to biofuels concept is to replace a recovery boiler nearing the end of its service life [25]. The marginal investment between a BLG based biofuels plant and a new recovery boiler system is the additional investment required by the mill to expand its product palette with, for example, a syngas derived biofuel. If the mill is required to replace the recovery boiler system, investment credits to BLG plant investment can be given for the avoided cost for a new recovery boiler system. The incremental investment cost is therefore used in the economic evaluation of all relevant cases.

The investment costs are scaled according to a BLG plant production of 100 MW methanol supplied by Chemrec [21] and also used in the previous study [14]. Chemrec [21] received a specific investment cost for each process unit from real commercial licensed suppliers/vendors. The capital investment for all units is rescaled via Eq. (1), where C denotes the capital investment cost and S the scaling parameter. The used scale parameters for the different units are listed in Table 3. Due to commercial confidentiality, the specific investment costs for each unit in the gasification plant cannot be published.

Capital investment costs have been updated to the price level of the considered value year (2014) using Chemical Engineering’s Plant Cost Index (CEPCI). A new recovery boiler (250 M) including a steam turbine, with a capacity of 2500 t BL dry solids per day is used to scale the avoided investment cost associated with integration of the BLG concept instead.

\[ C = C_0 \left( \frac{S}{S_0} \right)^{0.35} \]  

In the economic analysis a two year construction time is assumed, and also that the plants reach 95% of maximum methanol production capacity during the first year and 100% during the subsequent years. The plant availability is assumed to be 95% (8322 h/y) which corresponds to a BL availability of 5548 kW h per ADt (dry basis SF-LHV).

### Table 2

<table>
<thead>
<tr>
<th>Energy carrier</th>
<th>Power generation efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>46.2</td>
<td>[21]</td>
</tr>
<tr>
<td>Methanol</td>
<td>55.9</td>
<td>[21]</td>
</tr>
<tr>
<td>LPG</td>
<td>57.6 (Assumed the same as for SNG [22])</td>
<td></td>
</tr>
<tr>
<td>PO (25% moisture content)</td>
<td>50.0 (Assumed)</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- By using excess off-gases in the lime kiln, the import demand of lime kiln fuel can potentially be reduced. The imported lime kiln is assumed to be LPG.
- Additional equipment and assembly:
- Capital investment costs have been updated to the price level of the considered value year (2014) using Chemical Engineering’s Plant Cost Index (CEPCI). A new recovery boiler (250 M) including a steam turbine, with a capacity of 2500 t BL dry solids per day is used to scale the avoided investment cost associated with integration of the BLG concept instead.

### Table 3

<table>
<thead>
<tr>
<th>Unit</th>
<th>Case</th>
<th>Scale parameter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biofuel plant</td>
<td>Cases</td>
<td>Thermal load of individual reactor</td>
</tr>
<tr>
<td>Gasification reactor</td>
<td>All cases</td>
<td>Thermal load of individual reactor</td>
</tr>
<tr>
<td>Sour shift (WSG)</td>
<td>All cases</td>
<td>Dry gas flow</td>
</tr>
<tr>
<td>Acid gas removal (AGR)</td>
<td>All cases</td>
<td>CO\textsubscript{2} flow</td>
</tr>
<tr>
<td>MeOH synthesis and distillation</td>
<td>All cases</td>
<td>MeOH flow</td>
</tr>
<tr>
<td>Acid gas enrichment (AGE)</td>
<td>Cases 0–50</td>
<td>Same for all</td>
</tr>
<tr>
<td>MeOH storage</td>
<td>Cases 0–50</td>
<td>MeOH flow</td>
</tr>
<tr>
<td>Balance of plant (BOP)</td>
<td>All cases</td>
<td>MeOH flow</td>
</tr>
<tr>
<td>Thermal oxidizer</td>
<td>Cases 0–50</td>
<td>Same for all</td>
</tr>
<tr>
<td>flare stack with safety zone</td>
<td>All cases</td>
<td>MeOH flow</td>
</tr>
<tr>
<td>Off-gas boiler and heat exchangers</td>
<td>Case 100</td>
<td>Off-gas thermal load</td>
</tr>
<tr>
<td>Additional equipment and assembly</td>
<td>Cost</td>
<td>MeOH flow</td>
</tr>
<tr>
<td>Recovery boiler and turbine rebuild</td>
<td>Cases 0–50</td>
<td>BL flow</td>
</tr>
<tr>
<td>Recovery boiler fuel</td>
<td>Cases 0–50</td>
<td>BL flow</td>
</tr>
<tr>
<td>Mill scope costs</td>
<td>Cases 0–50</td>
<td>Pulp mill capacity</td>
</tr>
</tbody>
</table>

**Notes:**
- Total capital cost for the gasification train is calculated by cost of the individual reactor multiplied by number of reactor required in the train.
- The balance of the plant cost for Case 100 is assumed to be 20% lower than them in Cases 0–50.
- Investment cost is taken from [24].
- Includes civil costs for roads, buildings of the process area and pipe bridge.
- The old recovery boiler is rebuilt to solid biomass fuel.
- New recovery boiler system with a steam turbine, based on the cost for the Iggesund mill in Sweden [26,27].
- Additional mill cost for a BLG plant recovery system includes cost for upgrade of white liquor plant, white liquor total oxidizer, evaporator modification, super-concentrator, back/biomass dryer and raw water mechanical filters.

The required methanol selling price at the pump, including cost for distribution, is determined by a 20% IRR for all gasification cases and pulp mill sizes. In Table 4, costs for the different commodities, products and operations are listed. The cost for producing PO is dependent on several factors, such as type of biomass, pyrolysis technology, and plant location [23,28,29]. However, one of the most important factors is obviously the price for biomass, which can represent more than 50% of the PO price [28]. This study considers low-value forest residues both as fuel for the rebuilt recovery boiler in the mill, and as feedstock for the PO production.

### Table 4

<table>
<thead>
<tr>
<th>Commodity types and operating costs [21]</th>
<th>Operating costs</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass price (t/MW h)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>PO (t/MW h)</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Oxygen (t/ton)</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>Lime kiln fuel (t/MW h)</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Methanol distribution cost (t/MW h)</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>Operation and maintenance (€/M3/year)</td>
<td>4% of biofuel plant investment</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- The PO price (including three months storage capacity and cost for transport) is based on reported costs for PO production from forestry residues recastulated for a 20 t/MW h biomass price [28]. PO is assumed to be delivered with a fifty-fifty distribution from oil production that is either integrated with a CHP plant or decentralized and stand-alone.
- Operation and maintenance costs include salaries as well as general material, spare parts, including gasifier ceramic lining and catalysts.
• Market price for biomass with ±30%, which also subsequently influences the PO cost by ±20%.
• Import power price with ±30%, which also entails an assumed ±20% oxygen price variation.
• Investment costs with ±30%. This is applied on the total investment cost for an implementation of a BLG-based biofuels plant and a new recovery boiler, i.e., the marginal investment cost is subjected to a ±30% variation.
• An annual operation availability reduction to 85% (7446 h).

3. Results and discussion

3.1. Energy balances and efficiency

By co-gasifying a blend of biomass based PO with a fixed amount of BL, the increased total feedstock flow and the higher heating value of the PO (4.27 MW h/ton at 25% water content) can significantly increase the total energy input. As a result, going from pure BL to a blend with 50% PO the SF-LHV cold gas efficiency will increase from almost 70–80%. This corresponds to an incremental efficiency of the added PO, using BLG as a reference, of 80–85%. The specific methanol yield increases around 9% per MW of input. For pure PO gasification, the cold gas efficiency is 77% on an SF-LHV basis with the assumptions used in this study. In all cases, the biofuel plant (excluding the pulp mill) has a deficit of medium pressure steam and a surplus of low pressure steam. The mill therefore supplies medium pressure steam to the gasification plant whilst surplus low pressure steam is returned to the pulp making processes. A higher cold gas efficiency, associated with higher PO blending fraction, decreases the specific steam production from the gas cooling unit and hence the specific surplus of low pressure steam. The (absolute) import demand of biomass to the rebuilt recovery boiler decreases, however, with increasing PO fraction, since the total amount of steam generated is increased due to the increased biofuel production capacity for a specific mill size.

The resulting incremental material and energy balances (system boundary as illustrated in Fig. 1) compared to the pulp mill prior to the integration are summarised in Table 5, independent of the size of the pulp mill. Note that Case 100 is a stand-alone configuration but with a thermal input of PO matching the PO input in Case 50, according to the specific mill size.

Overall system efficiencies of the incremental material and energy balances presented in Table 5 are shown in Fig. 2, calculated on the basis of the required marginal supply of biomass, PO and other energy carriers needed to produce methanol. The utility requirements for the ASU are included, which is an expansion of the system compared to Fig. 1, in order to apply a more global approach. The co-gasification routes seem to be advantageous with respect to energy efficiency compared to methanol produced from a stand-alone PO gasification plant, alone (Case 100) as well as in combination with gasification of BL (Case REF). The main reason for the lower system efficiencies (Fig. 2) in the stand-alone Case 100, is that the possibility to gasify the available BL is missing, and instead the entire feedstock volume must be imported. Correspondingly, the low system efficiency of gasifying pure PO also reduces the system efficiency for the combined Case REF, where Case 0 and Case 100 are viewed as one system.

If PO can be produced with an efficiency of 90%, the same system efficiency is obtained for all co-gasification cases independent of the PO/BL blend ratio, as for the pure BLG case (Case 0). A 90% overall pyrolysing efficiency is only reachable if the PO production plant is integrated with an external heat sink, for example a CHP plant or a pulp mill [23]. The potential oil yield from integrated pyrolysing plants situated within an efficient transport distance to the biorefinery therefore depends on the location. For the system configurations with a very high import demand of PO it may not be reasonable to assume that the whole amount of PO can be produced with a 90% overall system efficiency. If the cumulative overall pyrolysing efficiency is below 85%, the system efficiency of co-gasification cannot compete with that of pure BLG (Case 0).

Even though the import demand of biomass to the rebuilt recovery boiler decreases with increased PO fraction, the total demand for additional biomass (in this study assumed to be low-grade forest residues) naturally increases with higher PO blending fractions. Fig. 3 shows the relative amounts of supplementary biomass required for the studied cases per unit of produced methanol. As the figure shows, the biomass demand ranges from 1.3 MW h per produced MW h of methanol for pure BLG (Case 0), to 1.5–1.9 MW h for the 50/50 case, depending on the overall pyrolysing efficiency. With stand-alone PO gasification (Case 100), up to 2.5 MW h biomass would be required for each produced MW h of methanol.

3.2. Economic results

Fig. 4 presents the required selling price for methanol at the pump to give a 20% IRR for all cases, depending on mill size (left) and methanol production capacity (right). It is very clear that BLG (Case 0) and co-gasification (Cases 10–50) result in much lower production costs than cases involving gasification of unblended PO (Case 100, Case REF). This agrees with results from a smaller study with partially other assumptions [14]. The major reasons for the deviations between this study and the previous one is that this study aims at quantifying performance for a mature technology for both PO production and co-gasification, which lies further into the future compared to the first plant estimates used previously [14].

As illustrated in Fig. 4 (left), the differences in required methanol selling price for a 20% IRR between methanol produced via BLG and co-gasification with blends containing up to 50% oil are never

| Table 5 Incremental material and energy balances for the gasification cases [10^3 kW h/A]

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Case 0</th>
<th>Case 10</th>
<th>Case 20</th>
<th>Case 25</th>
<th>Case 30</th>
<th>Case 40</th>
<th>Case 50</th>
<th>Case 100</th>
<th>Case REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO</td>
<td>0</td>
<td>125</td>
<td>281</td>
<td>375</td>
<td>482</td>
<td>750</td>
<td>1125</td>
<td>1125</td>
<td>1125</td>
</tr>
<tr>
<td>Power</td>
<td>79</td>
<td>92</td>
<td>108</td>
<td>118</td>
<td>129</td>
<td>157</td>
<td>196</td>
<td>196</td>
<td>196</td>
</tr>
<tr>
<td>Biomass</td>
<td>295</td>
<td>291</td>
<td>287</td>
<td>285</td>
<td>282</td>
<td>275</td>
<td>264</td>
<td>0</td>
<td>205</td>
</tr>
<tr>
<td>Bark</td>
<td>89</td>
<td>89</td>
<td>89</td>
<td>89</td>
<td>89</td>
<td>89</td>
<td>89</td>
<td>0</td>
<td>89</td>
</tr>
<tr>
<td>Outputs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>300</td>
<td>388</td>
<td>497</td>
<td>563</td>
<td>638</td>
<td>825</td>
<td>1087</td>
<td>684</td>
<td>984</td>
</tr>
<tr>
<td>Lime kiln fuel</td>
<td>5</td>
<td>11</td>
<td>18</td>
<td>22</td>
<td>27</td>
<td>39</td>
<td>57</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

- a Incl. reduced power production and power for ASU.
- b Prior to the integration of a BLG plant, the falling bark is exported. After the integration of a BLG plant the falling bark is used in the steam boiler. Hence the numbers represent decreased back export.
- c The off-gases are used as lime kiln fuel in the pulp mill. The reduced demand for imported lime kiln (assumed to be LPG) fuel is accounted for as an export product in the system efficiency calculations.
higher than 10 €/MW h or 9 € cent per litre petrol equivalent, for a specific pulp mill size. However, if required methanol selling prices are studied as a function of methanol production capacity, as shown in Fig. 4 (right), the differences in required selling prices are larger. It can be concluded that for a certain methanol production capacity, it is advantageous to integrate the biofuel plant with an as large a pulp mill as possible (large pulp mills correspond to positions to the right on each line representing cases); a 300 MW methanol capacity can for example be accomplished via blending of 20–50% PO in the available BL, and would require a methanol selling price of 85–100 €/MW h for a 20% IRR depending on pulp mill size. It is profitable to use as much BL as possible due to the high efficiency with which energy from BL is replaced by solid biomass in the rebuilt recovery boiler.

When looking at a specific mill size (Fig. 4, left), co-gasifying a blend with 20–50 wt% of PO would slightly improve the process economics compared to pure BLG (Case 0) for the smallest considered pulp mill (200 kADt/y). For a 300 kADt/y, no significant differences are observed in the required methanol selling price for Cases 0–50, which means that 0.9–1.2 TW h/y of methanol can be produced at this mill size with the same return on the capital. For pulp mills larger than 300 kADt/y, production costs are lower for Case 0 than for the co-gasification Cases 10–50, which is explained by decreased economies-of-scale due to the fact that the biofuels production capacity is already fairly large for Case 0 for these pulp mill sizes.

The specific marginal investments, visualized in Fig. 5, explain some of the trends in production costs described above. The specific investment costs for cases with higher PO fractions are generally lower for a specific mill size (Fig. 5, left), which is mostly due to economies-of-scale associated with larger methanol production capacities. The reason why the specific investment cost for a specific methanol production capacity does not follow the same trend is that the investment credit for the avoided recovery boiler investment is constant for a specific mill size. As an example, Case 0 for a 500 kADt/y mill and Case 20 for a 300 kADt/y mill have the same methanol production capacity but the specific investment cost is 10% higher for the latter due to a larger recovery boiler investment credit for the large mill.

The specific scale-effects with increasing methanol production volumes are more distinguished for Case 0. The lower specific investment cost for Cases 20–50 is due to the increased methanol yield (from improved efficiency) and reduced redundancy requirements. The specific investment curve for Case 10 is distinguished from the other co-gasification cases’ because this configuration requires, as Case 0, a redundant gasification unit.

For all mill sizes, PO supply makes operational costs more important for production costs with increasing PO blending fraction. The most important reasons for the poorer economic performance of Cases 100 and REF are the lower efficiency of stand-alone PO gasification, the higher operational costs from PO consumption and the higher investment costs (Fig. 5). The higher specific investment cost for Case 100 is mainly due to the lack of recovery boiler investment credit. However, a number of investments related to pulp mill integration that are necessary in Cases 0–50 are avoided in Case 100 (see Table 3).
Case REF, which considers Case 0 and Case 100 in combination, can almost match the methanol production capacity (up to 6 TW h per year) from the co-gasification cases. However, the overall system efficiency (Fig. 2) and overall process economics (Fig. 4) would be significantly decreased in comparison with the co-gasification cases. The most important reasons are the high specific investment costs, caused by decreased economies-of-scale due to the two separate plants that in combination have the desired capacity, and the lower efficiency for the stand-alone PO gasification plant.

This study predicts required methanol selling prices in the range of 80–90 €/MW h for single plant methanol production capacities between approximately 200 and 800 MW, corresponding to 1.6–6.5 TW h annually per plant. The petrol price in Sweden is currently approximately 75 €/MW h without taxes and 140 €/MW h including carbon and energy taxes (but no VAT), both in methanol energy equivalents. The selling price for fossil methanol in Europe is currently below 70 €/MW h but if fossil methanol is sold as a transportation fuel in Sweden additional taxes would be applied in a similar manner as for petrol. Hence, the required selling prices are only slightly above the fossil alternatives without taxes. If taxes are applied to fossil fuels but not to second generation biofuels, which is the current situation in Sweden, the required selling prices for bio-methanol are approximately 40–50 €/MW h below fossil alternatives. The future of biofuels taxation in Sweden is, however, highly uncertain.

A more relevant comparison than fossil fuels can be future production costs for alternative second generation biofuels of which
cellulosic ethanol is arguably the most important. A relevant recent study based on European conditions [31] has estimated the future production cost for cellulosic ethanol to €130/MWh, i.e. significantly over the required selling prices in this study. It can be noted that first generation fuel ethanol prices have varied between approximately 60 and 120 €/MWh during the last three years (Rotterdam T2 price). (Rotterdam T2 price).

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3.2. Sensitivity analysis

A sensitivity analysis of the effect of important parameters on the required methanol selling price is presented in Fig. 6. The y-axis in Fig. 6 shows the relative (absolute) change in required methanol price for a 20% IRR, with the results in Fig. 4 as basis. The co-gasification cases (Cases 10–20 and Cases 30–40) excluded from the figure follow the same trend as Cases 0, 25 and 50.

The impact of a ±30% biomass price and a PO cost ±20% (white box) has a significant effect on all cases. The influence increases with higher PO/BL blend ratios as well as with larger plant sizes, reaching up to ±12% for Cases 50 and 100. This trend is explained by the extra amount of additional biomass required per produced unit of methanol for increasing PO blend fractions, as shown in Fig. 3.

When varying the investment cost by ±30%, the highest impact is found to be ±15% for the smallest considered methanol production capacity (200 kADt/y pulp mill, Case 0). The impact of the investment cost decreases for cases using more PO feedstock, since PO supply costs have a more significant impact than capital costs for these cases, as noted above. The primary target for the higher blend ratio cases and plant sizes is thus to maintain a low cost for importing (or producing) PO.

Changing the power price (±30%) and connected to this presumably also the oxygen price (±20%), shows an increasing impact with decreasing blend ratio, as does reducing the plant availability. These two parametric variations influence the required methanol selling price with opposite trends with respect to plant size. Note that the impact from changed power and oxygen prices is more influential than the biomass price for pure BLG (i.e. Case 0).

3.3. Overall potential in Sweden

In order to investigate overall system consequences of co-gasification of BL and PO, the potential in Sweden is investigated based on the current pulp production and recovery boiler capacities and age structure. Fig. 7 shows the recovery boilers currently in operation at Swedish kraft pulp mills. It is assumed that pulp mills with recovery boilers older than 25 years can be of interest for investments in BLG, with or without co-gasification of PO. In order to reach reasonable economies-of-scale effects, the smallest boilers (<800 ton DS/day) are excluded from the analysis. For comparison, the case mill considered here (Rotsneros Vallvik) has a capacity of 1300 ton DS/day at a pulp production rate of 1.2 Mton/year, with a payback time of 7–8 years for PO/BL gasification.

From a resource perspective, PO/BL gasification would however induce an increase in the amount of additional forest residues required to produce the same amount of biofuel, from 16 to 20 TW h annually, assuming a fifty–fifty distribution of PO produced in integrated facilities and in stand-alone plants. This can be related to estimations of potentials for increased outtake of forest residues, which range from 33 to 41 TW h in the short term, to around 60 TW h in a long term perspective (30–50 years) [31]. The estimated future potentials give an indication that an increased outtake sufficient to cover BL based biofuel production, with or without co-gasification of PO, could be supported.

4. Conclusions

The main objective of this study has been to evaluate methanol production via co-gasification of pyrolysis oil and black liquor for different blends ratios and for different pulp mill capacities, as well as to assess overall system aspects of large-scale implementation of PO/BL gasification.

It is concluded that for a 20% IRR, required methanol selling prices below 100 €/MWh can be reached for single plant methanol production capacities between 200 and 800 MW. This is cost competitive to estimated future production costs for lignocellulosic ethanol, and can, depending on future taxation policy, also be competitive to fossil fuels. BLG and PO/BL co-gasification would require significantly lower methanol selling prices to be economically feasible, compared to gasification of unblended PO. It is also
concluded that the pulp mill size has a considerable impact on the economic results, and for an individual biofuel plant integration with the largest possible pulp mill would be economically beneficial. For a given mill size, the required methanol price for a 20% IRR never ditters more than 110–120 k$/MWh for methanol produced via BLG and co-gasification.

With the exception of the two smallest considered pulp mill sizes, 100–200 kADt/y, the required methanol price for PO/BL co-gasification is 20–50% lower than for PO/BL gasification. However, for smaller mill sizes, the cost for the added amount of PO offsets the positive scale-effects compared to BLG. Further, since the same recovery boiler investment credit is given for a specific mill size irrespective of methanol production capacity, the scale-effects of increasing methanol production volumes are more pronounced for BLG than for PO/BL co-gasification.

Regarding efficiencies, the results show that by adding PO to the BI the overall system efficiency (calculated as electrical equivalents) can be increased by four percentage points, compared to producing methanol from only the available BL. However, the case of pure BLG yields the highest overall system efficiency (67%), unless PO can be produced at a system efficiency exceeding 85%, which would require a significant share of the utilised PO being produced in production facilities integrated with major heat sinks, e.g. CHP plants.

A major advantage of PO/BL co-gasification is the possibility to efficiently increase the potential biofuel production from a given available volume of BL. For pulp mills producing 200–600 kADt/y, a potential methanol production volume from pure BLG of 0.6–1.8 TW h/y can be reached, whilst the corresponding range for PO/BL co-gasification is 0.8–6.5 TW h/y. The number of mills possible to convert to gasification, with recovery boilers near the end of their service life is of course restricted. Due to the complexity of the integration, from a technical as well as an organizational viewpoint, it may be beneficial to use several large co-gasification plants instead of several smaller pure BLG plants, to produce a given amount of methanol or other biofuels. This could potentially also lower the total investment requirement from a regional or national point of view, to meet a certain demand for biofuels. As the system as a whole would require 4–45% of additional biomass per produced unit of methanol, depending on blend ratio and production efficiency, it is important to also consider the PO production route. If PO can be produced in plants integrated with e.g. CHP plants, PO/BL co-gasification can be a very efficient way to upgrade low-value biomass, such as forest residues, to high-value products and fuels.

References
